

MEASUREMENT OF pH FOR FIELD STUDIES IN KARST AREAS

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The determination of pH in karst waters is important for evaluating such chemical processes as cave growth, speleothem deposition, and overall water chemistry. Relatively small errors in pH readings can result in significant misinterpretations of the chemical processes taking place. For example, a pH error of 0.5 units would produce a correlative error in SIcalcite of 0.5. To ensure accuracy, pH must be measured in the field, but the conditions in karst settings make this hard to accomplish, and there is minimal published guidance available. Actions that help to improve data quality include: use of a good meter/electrode (accurate to 2 decimal places), careful preparation before field activities, cautious transport of instruments, frequent calibration, measurement in a beaker (not the water body), and allowance of time for equilibration. Instruments that allow measurement of very small samples, samples in wells, or continuous monitoring are available, but are more expensive and usually not as accurate.

INTRODUCTION

Water chemistry is an important factor controlling the growth of caves, the deposition of speleothems, and the suitability for healthy biota. Because of this, chemical studies are frequently conducted in karst areas. The measurement of hydrogen ion activity (commonly expressed as pH, the negative log of the activity) is an important component of such field investigations. pH is used to compare the acidity of different waters, to calculate CO₂ partial pressures, to determine the saturation state of the water with respect to calcite or other minerals, and for other geochemical modeling (see chapter 7, White, 1988 for review, examples, and discussion of these items). pH must be measured in the field, because changes during transport and storage of water samples will cause it to vary considerably. This sort of instability has also been recognized for other parameters (Baedeker and Cozzarelli, 1992). Laboratory-measured pH of natural waters is, therefore, not generally suitable for accurate geochemical calculations. The acquisition of field pH data in karst settings, however, is challenging due to the conditions encountered (remoteness, harsh transport, pervasive mud and water, etc.). Such difficulties are not addressed in the guidance literature or standards regarding the measurement of pH (American Society for Testing and Materials, 1990, Clesceri *et al.*, 1999).

Over the course of various projects, and with suggestions from other karst geochemists, we have considered many of the challenges of accurate pH measurement. We have also developed strategies to accomplish this goal. In the present paper we examine the importance of pH measurement to cave and karst studies, explain some of the special concerns, and make suggestions (based on our experience) about how to collect accurate pH values in these settings. This is done in the hope that the information presented may be useful to other researchers.

We do not address the theories of pH or its measurement, which are available elsewhere (e.g. Langmuir, 1997; Bates, 1973).

IMPORTANCE OF ACCURATE pH MEASUREMENT

There are many reasons (some mentioned above) why the accurate measurement of pH in karst terranes is important. As an illustration of this, we demonstrate the effect of possible errors in pH measurement on the calculation of calcite saturation index (SIcalcite), an important derived parameter, for several natural water samples. SI is given by the equation

$$SI_c = \log \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_c} = \log \frac{\gamma_{Ca^{2+}} [Ca^{2+}] \gamma_{HCO_3^-} [HCO_3^-] K_2}{10^{-pH} K_c}$$

where a is the activity of the given aqueous species, and K_{calcite} is the (temperature-dependent) equilibrium constant for the dissolution of that mineral (White, 1988). The expression on the far right is the one most often used, because it employs the commonly measured pH, Ca, and alkalinity parameters. In that expression the values in brackets are molar concentrations of the species, K_2 is the calculated activity coefficient for the species, and γ is the 2nd dissociation constant for carbonic acid.

A saturation index of less than zero indicates that the particular water is capable of dissolving calcite, hence can enlarge a cave. A saturation index greater than zero shows that calcite can be precipitated and that speleothems may grow. For purposes of illustration, we used analyses of three water samples taken from Scott Hollow Cave, West Virginia (Table 1). These waters are representative of those found in temperate karst regions throughout the world.

Laboratory data (major ions) along with field parameters (pH, conductance, temperature) for the samples were entered

Table 1. Geochemical parameters for three water samples from Scott Hollow Cave, West Virginia (Davis, 1999)

Location Sample Date	Craigs Creek		John's Flowstone
	2/21/1998	5/17/1998	2/21/1998
Temp (°C)	10.7	12.3	11.1
pH	7.78	7.41	7.8
Conductivity	303	361	294
TDS	196.9	191.1	191.1
SI _{Calcite}	0.099	-0.144	0.096
Cl	4.1	3.8	2.2
HCO ₃	162.0	206.8	150.4
NO ₃	11.0	11.8	9.7
PO ₄	0.15	nd	0.09
SO ₄	10.9	10.6	11.1
Ca	55.0	55.0	55.0
F	0.10	0.10	nd
K	0.8	1.5	0.4
Mg	4.5	5.0	4.2
Na	1.3	1.5	1.1
Si	35	35	35

Note: Values given in mg/L except pH and SI (std units) and conductivity (microsiemens). nd = not detected.

into the computer program WATEQ4F (Ball & Nordstrom, 1991) for calculation of SI. The results are shown in Figure 1. The symbols on the lines show the original values of SI as calculated for each sample, along with sample pH (actual pH of each of the three samples varied from 7.18 to 7.78, but was

normalized to zero to aid visual comparison in this graph). The lines have a constant slope (a consequence of the algebraic relationship between pH and SI) but are offset. The position of the original data points shows that sample 1 was just oversaturated, and sample 2 and 3 were undersaturated to differing degrees. For any error in pH of 0.1 units, an error of 0.1 SI units is generated. It can be seen in the figure that, in natural waters, such errors can easily make the difference between considering the system to be under- or oversaturated with respect to calcite. This in turn could lead to misinterpretation of the processes going on within the cave.

SELECTION OF A pH DETERMINATION METHOD

A review of any major scientific supply catalog shows that there are numerous instruments and supplies available for determining pH. Instruments may also be rented from environmental suppliers. Table 2 summarizes the features of several typical methods/instruments.

The least expensive methods employ titration and/or colorimetry. The materials required for these methods are also compact and robust, but unfortunately do not provide the precision needed for quantitative geochemical analysis. For this reason, electrometric methods (meters) are most commonly employed in karst geochemical studies. Some meters have a built-in electrode, but most use an external replaceable one which is purchased separately. Factors that come into consideration in selecting a meter/electrode include: cost, size, weight, sturdiness, accuracy, and precision.

Table 2. Comparison of pH determination methods.

Method	Make/ Model	Precision/ Resolution	Accuracy (+/-)	Analytical Range	Cost (US\$)	Temp. Range (°C)	Supplier
Colorimetric pH Test Strips ^a	pHydrion Comparator ^b	1	1	0 to 13	14	n/a	Thomas Scientific
	Colorphast Store Set	0.5	0.5	0 to 14	128	n/a	Cole-Parmer
Field Titration/ Color Wheel ^a	Hach Color Disc/ Bromthymol Blue	0.1	0.1	5.5 to 8.5	98	n/a	Dynamic Aqua-Supply
Electrometric (pH meters) ^c	LaMotte PockeTestor 2 ^d	0.1	0.1	0 to 14	89	0 to 50	Thomas Scientific
	Cardy Twin ^{d,e}	0.01	0.1	2 to 12	238	5 to 40	Cole-Parmer
	Hanna Checker ^f	0.01	0.2	0 to 14	35	0 to 50	Thomas Scientific
	Corning 307 ^f	0.01	0.01	0 to 14	187	0 to 50	Thomas Scientific
	Hanna HI-9024 ^g	0.01	0.01	0 to 14	349	0 to 100	Thomas Scientific
	Accumet AP62 ^g	0.01	0.01	-1.99 to 19.99	620	-5 to 100	Fisher Scientific
	Orion 525A ^h	0.001	0.002	-2 to 19.999	1389	-5 to 105	Fisher Scientific
Corning 455 ^h	0.001	0.001	-2 to 19.999	2688	-30 to 130	Fisher Scientific	

Note: The cost of electrodes for the pH meters can be an additional \$65 to \$450. The cost of pH buffers can add an additional \$20 to \$100.

^a May be more variable depending on the quality of the operator's color match assessment.

^b Includes comparator and test papers.

^c Variability may be seen in accuracy and precision values depending on the type and make of the electrodes that are used

^d Pocket model with non replaceable probe.

^e Able to measure samples as small as 150 µL.

^f Stick model with replaceable probes.

^g Portable models.

^h Bench model.

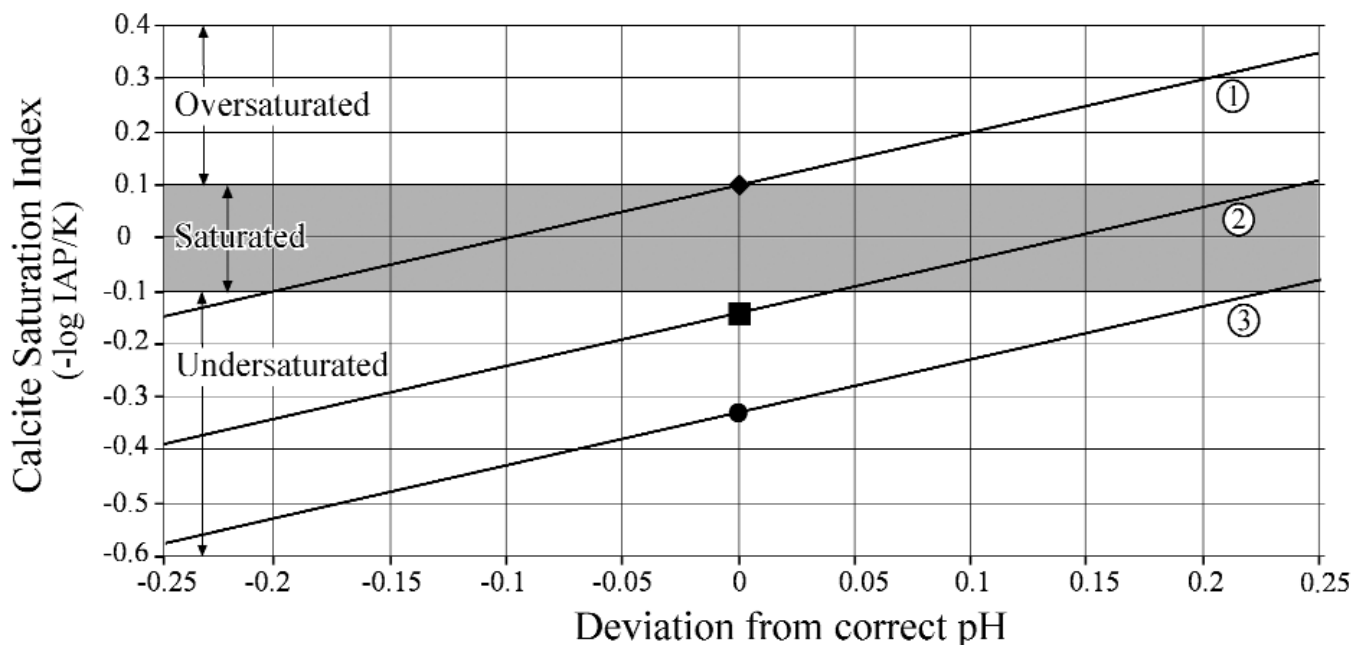


Figure 1. Fluctuations in the saturation index of calcite (SI_{calcite}) as a function of pH variation. The samples were collected from Scott Hollow Cave in West Virginia (Davis 1999) and showed a pH range from 7.18 to 7.78. For ease of visual comparison, measured pH was normalized to zero for this plot. A relative pH of zero indicates measured pH values as obtained in the field. Sample 1 was collected from Craig's Creek on February 21, 1998. Sample 2 was collected on May 17, 1998 from Craig's Creek, and Sample 3 was collected from John's Flowstone on February 21, 1998. This graph illustrates how small variations in measured field pH could result in misinterpretation regarding the degree of saturation of calcite in any particular sample.

There are many meters on the market, with varying sizes and features (Table 2). There is a rough correlation between accuracy and cost. For most geochemical studies, a meter with accuracy on the order of 0.01 pH units is desirable. More expensive models may offer additional features such as 3-point calibration, storage of measurements, download capabilities, etc. While these may be sought-after for specific applications, they are not crucial.

Features that are most essential are

1. Automatic temperature compensation. pH is highly temperature dependent, and it is essential that a correction be made either manually or automatically. This dependence is apparent on charts provided with the buffer solutions. As an example, pH "7" buffer has a value of 7.06 at 10 degrees C, and a pH of 6.99 at 30 degrees C.
2. Minimum 2 point auto calibration with slope and offset. Meters/electrodes require calibration to assure accuracy. Some of the less expensive models use only 1 point calibration.
3. Automatic buffer recognition, with temperature compensation. The values of pH buffer solutions vary with temperature, and this must be accounted for during calibration. A meter that includes the tables of the various buffer values is advantageous.
4. Compact, water-resistant, and robust meter design. The nature of karst environments dictates that the instrument

should be compact and easy to carry, while at the same time able to withstand rough handling. Waterproofing is ideal, but such meters are less common. Water resistance is useful for brief, accidental water contact.

5. Combination electrodes with a plastic (resin) body. Glass body electrodes have some good characteristics, but are too easily broken in the field. For this reason plastic body electrodes are recommended. A combination electrode includes both the reference and measurement electrode in one piece, minimizing weight and the number of cables needed. The electrode should include some sort of tip protector (bulb shield) for use while measuring and for transport. Note that electrodes have a limited life, whether being used or stored on the shelf. While in service and carefully maintained, a 1- to 2-year life may be expected. Do not order a replacement until it is needed.

FIELD MEASUREMENTS

Our discussion emphasizes the most common conditions for pH measurement in karst studies, manual collection of data at cave or surface streams, or springs. Determination of pH is usually accomplished at the same time as measurement of other field parameters (such as conductance and dissolved oxygen), and the collection of water samples. pH measurement

Table 3. List of suggested materials for field measurement of pH in karst investigations. Electrode filling solution may be needed for certain electrodes. For many electrodes, pH 7 buffer may be temporarily used in place of electrode storage solution. The manufacturer can provide information on this.

Meter and spare batteries
Electrode, with bulb protectors
Temperature probe
Two 100 mL HDPE beakers
100 mL LDPE wash bottle
Deionized water, volume as required
Fresh pH buffers, in 60 mL wide mouth HDPE bottles
Lint free wipes
Field notebook & pencils
Lightweight padded case to hold meter, etc.
Copy of instruction manual
Laminated instruction sheet
Electrode storage solution ^a
Electrode filling solution ^a

^a Optional items.

can regularly be accomplished in 15 minutes or so, although electrode equilibration may take longer in waters with low total dissolved solids (TDS).

PREPARATION

To assure that the best quality data are collected, preparation should be made before arriving in the field. Table 3 lists the suggested instruments and supplies for undertaking pH measurements. It is critical that any person who will be making the measurements becomes familiar with the process by reading the owner's manual and conducting trial measurements in the lab just beforehand. This also serves as a check that the instrument is working. A photocopy of the manual (perhaps photoreduced) should be brought into the field in case questions arise. If a condensed instruction sheet can be laminated, it is also very useful.

The meter, electrodes, and buffers should be packed in a padded container for protection. Water-proof hardshell cases such as those made by Pelican™ may be desirable, but are a bit heavy. A lightly padded soft case such as that shown in Figure 2 may be sufficient. If waterproofing is required for transit, a kayaker's "dry bag" may be employed. Electrodes can be destroyed by subzero temperatures. If there is a chance of freezing, then precautions must be taken during transport. This can be done by carrying the electrode within a cooler, or in an inside coat pocket. The bulb of the electrode should always be protected and kept immersed in electrode storage solution. If the bulb dries out or is scratched, the electrode may be rendered unusable.



Figure 2. Example of a kit for field pH measurement in karst settings.

MEASUREMENT PROCEDURE

Care should be taken to keep the equipment clean. If there is a level place near the water source, a cloth may be placed down to work on, or work may be done in the carrying case. A 2-point calibration (according to manufacturer instructions) should be conducted. Buffers should be chosen to bracket the expected pH of the sample. Most karst waters are in the pH 7 to 8 range, although some karst streams contaminated with mine drainage may be as low as 3.3 (Sasowsky & White, 1993, Webb & Sasowsky, 1994). The automatic temperature compensation (ATC) probe must also be placed in the buffer. The electrode and ATC probe should be rinsed with de-ionized water and shaken dry between using different buffers, and the glass bulb at the end of the electrode should be protected to avoid any chance of scratching. Some workers immerse the closed bottles of buffer in the water body being sampled so that the buffers will be at the same temperature as the water being measured. This is not a practice that we have followed, because the ATC probe and meter software are designed to compensate for this, and several informal field comparisons that we have made have not generated any difference in readings. Calibration is time-consuming, so some researchers calibrate only once at the beginning of a day, and use this for the remainder. In our experience, this usually provides good

Table 4. Summary of salient procedures for accurate pH measurement in karst settings.

Do	Do Not
Measure pH in the field	Use old electrodes
Use a good quality meter & electrode that are accurate to 2 decimal places	Use old buffer solutions
Allow readings to stabilize	Allow electrode to freeze
Calibrate meter frequently	Measure in moving water
Measure to 2 decimal places and record temperatures	Let the electrode bulb dry out

results. However, the highest data reliability will be obtained by calibration at each measurement location.

When calibration is complete, a sample of the water should be collected in a plastic beaker, and the electrode and ATC probe (rinsed with DI water) placed in the beaker. Use of a beaker is vital for two reasons. First, an accurate reading is not possible in moving water, due to generation of a streaming potential. Second, it is usually difficult to safely hold an electrode in a natural water body. It is also useful to have a second beaker available for temporarily holding the electrode.

Once the electrode is placed in the sample, the meter will usually give a pH reading within one minute, but this should not be considered accurate (even if the display gives a "locked" value). The electrode and probe should remain in the sample water for 5 minutes or so, until the meter readings stabilize. This allows the electrode to come into thermal and ionic equilibrium with the water being measured. After the value has stabilized, a fresh sample should be collected, and measurement should be made again. If there is still drift during measurement, an additional fresh sample should be collected until the reading has stabilized. Drift during pH measurement of karst waters is common, and is caused by three factors: degassing of CO₂, thermal disequilibrium between electrodes and water, and the relatively low ionic strength of the solution (response time for many pH electrodes is inversely proportional to the ionic strength). It is important to be patient, because drift on the order of 0.50 pH units is not unusual. Other tasks, such as collection of samples for elemental analysis, may be done while waiting. Final measurement should always be made on a fresh sample, because of potential ambient effects (warming, degassing, etc.).

When the final measurement has been made, it is recorded in the field book along with the water temperature. The meter is then turned off, and the electrode is packaged to keep safe and moistened.

MEASUREMENT IN SPECIAL INSTANCES

The majority of karst water samples are collected from streams and springs, and pH may be effectively measured using the procedures and equipment listed above. There are, however, several special instances which arise in karst studies, where different approaches and instruments may be needed. These include dripwater sampling, measurement of pH in wells, and situations where continuous monitoring is required.

The primary difficulty with dripwater sampling is lack of adequate sample size for usual measurement methods. Whereas in a cave stream a 100 mL sample can be collected instantaneously, a dripping stalactite might require over 24 hours to provide such volume. This delay would make it impossible to accurately measure pH using standard instrumentation, because the sample would not be fresh when measurement occurred. Using a specially designed, small-volume, pH instrument can circumvent this. Once such unit is the "Cardy" model (Cole-Parmer) which requires only 0.1 mL of sample. An unfortunate limitation is that it is only accurate to 0.1 pH unit.

Measurement of pH in well waters can be conducted either by bringing a sample to the surface and measuring as described in the previous section, or by using an instrument that measures *in situ*. Samples can be brought out of the well using a bailer or a pump. Continual slow pumping will probably provide the most representative sample. If depth-specific samples are desired, a Kemmerer sample vessel (or similar) may be employed. In each case some disturbance of the water chemistry may occur. *In situ* measurement can be made by using a pH electrode with long cable (hard to find), or by deploying a continuous monitoring device with a data logger. The latter option is discussed below.

In situations where a detailed, long term record of pH is needed, it may be desirable to install a continuous monitoring device/remote probe. These automated instruments have mainly seen use for flooding and storm pulse studies, where such detail is required. If there is a malfunction, data may be lost. This can be caused by electrical problems, electrode drift, or biofouling. The systems offer the benefit of multiple, closely-spaced readings, but drawbacks such as expense, lower accuracy, and maintenance make their use limited. One such device is the Yellow Springs Instruments (YSI, Inc.) 6 Series, which measures many different parameters. It has a resolution of 0.01 pH units, but an accuracy of only 0.2.

CONCLUSIONS

pH is a critical value to measure accurately, because H⁺ participates in many geologically important reactions. Since pH is a logarithmic scale, small changes in measured values correspond to large changes in hydrogen ion activity. pH must be measured in the field. The approaches we present are based upon our experience, and can be used in addition to informa-

tion available from manufacturers and other published sources. Table 4 summarizes the most critical points. Accurate determination requires forethought and careful field work, especially given the challenges of karst environments.

ACKNOWLEDGEMENTS

We thank William B. White for introducing Ira Sasowsky to the use of geochemistry for the solution of geologic problems. We acknowledge the help of the following individuals and organizations: Katie McKibben (Ohio EPA NWDO); Annabelle Foos and Rebecca Bixby (University of Akron). Heather Raymond, Carol Wicks, and an anonymous reviewer provided thoughtful comments. The research for this publication was financed in part through a grant from the Ohio Environmental Protection Agency and the United States Environmental Protection Agency, under the provisions of Section 319(h) of the Clean Water Act (01(h)EPA-11). The use of trade names is for example only and does not reflect the endorsement of the authors or any associated agencies.

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