Soiless Root Substrate pH Measurement Technique for Titration

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Abstract. Measurement of substrate pH entails procurement of the substrate solution and measurement of the solution pH. Acid–base reactions are completed at the time of testing. Determination of substrate pH during development of a titration curve is more complex because it involves initially the reaction of a base with the substrate. Five factors that can influence the resulting pH values were investigated in this study and include amount of water added to substrate, method to procure substrate solution for pH determination, chemical form of base used, time allowed for acid–base reaction and the addition of CaSO_4 . Substrate in this study consisted of 3 sphagnum peatmoss : 1 perlite (by volume) amended with wetting agent. Dolomitic limestone ($6 \text{ g} \cdot \text{L}^{-1}$ substrate) was added to substrate for the water amount and solution procurement method experiments. Except for the water amount experiment, deionized water was added by weight to achieve 95% container capacity. Dishes were incubated at 20°C for specified times. To identify the minimal level of water necessary to ensure complete contact between base and substrate for neutralization, additions equivalent to 95%, 100%, 120%, and 150% container capacity were tested. The 95% level proved adequate. The saturated media extraction and pour-through bulk solution displacement methods for pH determination resulted in higher pH measurements in the incubated substrate than the squeeze bulk solution displacement method. This indicated that the former two methods diluted the soil solution. The squeeze method was deemed most effective. NaOH resulted in higher pH endpoints than $\text{Ca}(\text{OH})_2$. This was apparently due to a higher affinity of Ca^{2+} for peatmoss exchange sites. Since Ca^{2+} is the predominant cation associated with liming materials for soiless substrates, $\text{Ca}(\text{OH})_2$ is more appropriate for titration. From the tested incubation times of 0, 2, 4, 8, 24, 48, and 96 hours, the duration of 24 hours was found to be adequate to allow complete reaction of base with substrate acidity. The best procedure for determining pH in a substrate titration situation included a water level of 95% container capacity, $\text{Ca}(\text{OH})_2$ base, an incubation time of 24 hours and the squeeze solution displacement method. The additional CaSO_4 was not necessary. Chemical names used: calcium sulfate (CaSO_4), sodium hydroxide (NaOH), calcium hydroxide [$\text{Ca}(\text{OH})_2$], calcium ion (Ca^{2+}).

A titration curve relating substrate solution pH to milliequivalents of base applied is a useful tool for comparing the neutralization requirements of various substrates or substrate components and neutralization capacities of different liming materials. The relationship between substrate solution pH and milliequivalents of base added to a soiless root substrate for the development of a titration curve is dependent on several factors. These include amount of water added to substrate, type of base used for titration, substrate solution procurement method, time allowed for acid–base reaction and the addition of calcium sulfate (CaSO_4).

The ratio of water to soil in the test suspension has the effect of increasing pH as the water

amount increases (Thomas, 1996). However, in soil suspensions, this is not a 1:1 effect. For instance, increasing the water content by 10 times does not result in an increase in pH of one unit. Rather, pH will increase by 0.4 units (Davis, 1943). The pH value is a measure of hydrogen ion (H^+) activity in a solution. The addition of water dilutes the concentration of H^+ . However, in soil suspensions, additional water also increases the dissociation of H^+ from substrate particles (Thomas, 1996). An additional concern of special importance for studies in which substrate, base, and water are incubated is the possible creation of anaerobic conditions which can impact substrate solution pH. Thus, while it is important to provide sufficient water to bring base into contact with the hydrogen ions (H^+) on the substrate exchange sites, anaerobic conditions caused by excess water must be avoided.

Various methods are used to extract or displace substrate solutions for measurement of pH. Those methods that entail the addition of water above the level of container capacity can result in elevated pH values (Reddy, 2001) due to the dilution effect previously mentioned. Those methods that use shaking or stirring result in lowering pH measurements. This

lowering effect is caused by mixing carbon dioxide (CO_2) from the air with the water in the solution, producing carbonic acid. The CO_2 effect can be highly significant, especially in substrates containing calcium carbonate (CaCO_3) (Thomas, 1996).

There are three similar procedures frequently used by the horticulture industry for extracting or displacing substrate solutions. The saturated media extract (SME) method (Warnke and Krauskopf, 1983) involves adding water to the substrate until it is just glistening on the surface. After reaching equilibrium, the solution is squeezed through cheesecloth. While the amount of water added is a subjective decision, the SME method provides fairly stable and reproducible pH measurements. In the pour-through (PT) method, the substrate solution is removed from the substrate for testing by displacement, rather than extraction. (Faber and Nelson, 1984). In this method, an amount of water moderately less than that held in a containerized substrate is poured over the substrate surface one hour after a fertilization or irrigation event, thus displacing the substrate solution which is collected as it leaches from the bottom of the container (Wright, 1986). The squeeze (SQ) method (Scoggins et al., 2001) involves simply squeezing the solution out of the substrate sample through cheesecloth. The PT and SQ methods provide an unaltered, displaced solution sample for testing. The SME extraction method does alter the solution to some extent by adding more water than exists at container capacity. Thus, the resulting pH is higher than in unaltered soil solutions and nutrient levels are lower.

Measured pH levels can also vary significantly depending on the type of base used to titrate substrate acidity. This effect is due, in part, to the strength of the base. Strong bases dissociate completely and quickly, whereas weak bases require more time to react completely. Additionally, the valency of the associated basic cations dictates differences in affinity for binding (exchange) sites on the substrate. Sodium (Na^+), being monovalent, does not have as great an affinity for exchange sites as does calcium (Ca^{2+}). Therefore, the number of H^+ dissociated from the substrate will be greater (causing lower pH) when Ca^{2+} is the exchanging cation than when Na^+ is used.

In incubation studies, the amount of time allowed for the reactions to occur can have an effect on the resulting pH measurements. This is particularly important when using a weak base, which takes time to dissociate completely. It is possible that the time required for a complete reaction is long enough to allow secondary, biological reactions, such as decomposition to begin, causing variation in results. Sometimes, an amendment such as CaSO_4 is combined with the substrate. This addition can stabilize the acid–base reactions over time (W.R. Argo, Blackmore Co., Inc. Belleville, Mich., personal communication). The Ca^{2+} background in this amendment provides can enhance the dissociation of H^+ from exchange sites in organic materials. CaSO_4 is also incorporated occasionally into greenhouse substrates as a fertilizer.

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Table 1. Effects of the amount of water added to substrate and incubation duration on resulting pH measurements.

Incubation time	Water added (% CC)	Avg pH	SD
5 h	95	6.23 b	0.0991
	100	6.22 b	0.0673
	120	6.10 a	0.0612
	150	6.03 a	0.0695
14 d	95	6.29 b	0.0489
	100	6.42 c	0.0313
	120	6.44 c	0.0665
	150	6.55 d	0.0353
Tukey's HSD _{0.05}		0.09	

The first objective of this study was to evaluate the effects of water amount (W), solution procurement method (SP), type of base (B), time allowed (T) and the addition of CaSO_4 to develop a protocol for titrating soilless substrates. The second objective was to develop a titration curve for sphagnum peatmoss that could be used to determine the neutralization requirement for any specified pH level.

Materials and Methods

For all experiments, the substrate consisted of sphagnum peatmoss and perlite (Sun Gro Horticulture, Bellevue, Wash.) in a volume ratio of 3:1 and amended with the proprietary wetting agent used by Sun Gro in their commercial soilless substrates. All experiments were a complete random design (CRD) with 10 replications. The experimental unit for each study consisted of 50 g of substrate (fresh weight) placed in a lidded, plastic seed germination dish ($10.2 \times 10.2 \times 2.6$ cm). Substrate was amended with specified amounts of deionized water and bases and the dishes were incubated at 20 °C for specified amounts of time.

Moisture content (MC) is the amount of water contained in fresh substrate. MC was determined on a weight basis by filling three 500-mL beakers with substrate. The filled beakers were weighed to obtain a fresh weight (FW), placed in a laminar flow oven at 105 °C for 48 h and then weighed a final time to obtain the oven-dry weight (ODW). MC was calculated by subtracting ODW from FW.

Container capacity (CC) is the amount of water that can be held by the substrate against gravitational forces. CC was also determined on a weight basis by filling ten, weighed incubation dishes with 50 g (FW) substrate, each. Water was added until it was just glistening on the substrate surface. The dishes were allowed to stand for 1 h, to ensure that all the substrate pore spaces had become water-filled. During this time, additional water was added, as needed, to maintain its level at the substrate surface. After 1 h, the dishes were covered with lids in which nine, evenly spaced holes (0.48-cm-diameter) had been drilled. Dishes were inverted, top down, on racks, and were allowed to drain thoroughly (thirty minutes). After draining, the lids were removed and the dishes and contents were weighed to obtain the drained weight (DW). Water weight was calculated by subtracting the dish weight-plus-substrate FW from DW. MC was added

to water weight to obtain CC of oven-dry substrate by weight.

Solution pH for all studies was measured using an ion sensitive electrode and pH meter (Extech Instruments, Waltham, Mass.). The meter was calibrated with a pH 7.0 and 4.0 standard before the first measurement and after every 10 subsequent measurements.

Data for the W, SP, B, and T± CaSO_4 experiments were analyzed using analysis of variance and means were separated by Tukey's HSD (PROC GLM, SAS Institute, Cary, N.C.). The titration curve was generated with and without CaSO_4 by regressing pH against milliequivalents of base (Microsoft Excel, Microsoft Corp.).

Water amount. For W, dolomitic limestone was added to the substrate at a rate of 6 g·L⁻¹. Dishes were filled with 50 g substrate (FW) and water was added to achieve either 95%, 100%, 120%, or 150% CC, by weight. Dishes were incubated for either 5 h or 14 d. Funnels were lined with a double layer of cheesecloth and were then placed in beakers. After incubation, the entire contents of each dish were scraped into the cheesecloth-lined funnels and the solution was squeezed through the cheesecloth and pH was measured.

Solution procurement method. The effects of three substrate solution procurement methods on solution pH were evaluated: SQ, PT, and SME. For all three, dolomitic limestone was added to the substrate at a rate of 6 g·L⁻¹. Substrate (50 g, FW) was added to each incubation dish and water was pipetted in to obtain 95% CC. The dishes were incubated for either 5 h or 14 d.

For SQ, solution was extracted through cheesecloth-lined funnels as described for W (above) and solution pH was measured. For PT, the contents of each dish were scraped into cheesecloth-lined funnels. Then, an amount of deionized water equal to 95% CC, by weight, was poured over the surface to displace the substrate solution. The leachate was collected and pH determined. For SME, after incubation, water was added until the contents were just glistening. The dishes were allowed to stand for 30 min so equilibrium could be attained between substrate and solution. Then, solution was procured as for SQ and pH was measured.

Type of base. The effects of sodium hydroxide (NaOH) and calcium hydroxide [$\text{Ca}(\text{OH})_2$] on solution pH were studied in B. Since NaOH is highly soluble, it was added to deionized water to make a basic solution that provided 2 meq alkalinity. $\text{Ca}(\text{OH})_2$, being less soluble, was incorporated as a solid into the substrate, also to provide 2 meq alkalinity, as each dish was filled. The basic solution or deionized water [for the $\text{Ca}(\text{OH})_2$ treatments] was added to achieve 95% CC. Substrate solution pH was procured using SQ and solution pH measured after 0, 2, 4, 8, 24, 48, and 96 h incubation.

Incubation time with and without CaSO_4 . CaSO_4 is frequently used by growers as a sulfur (S) fertilizer, since S deficiency is known to occur in some areas of the country. CaSO_4 is also thought to help stabilize the acid-base reactions between peatmoss substrates and liming materials (W.R. Argo, personal communication). In T, $\text{Ca}(\text{OH})_2$ was incorporated with substrate in each dish to provide 6 meq alkalinity and was

Table 2. Effects of solution procurement methods and incubation duration on solution pH.

Incubation time	Solution procurement method	Avg pH	SD
5 h	Squeeze	6.27 a	0.1724
	Saturated media extraction	6.52 cd	0.0360
	Pour-through	6.61 d	0.0367
14 d	Squeeze	6.25 a	0.1226
	Saturated media extraction	6.34 ab	0.0352
	Pour-through	6.44 bc	0.0298
Tukey's HSD _{0.05}		0.11

Fig. 1. The effects of 2 meq NaOH or $\text{Ca}(\text{OH})_2$ in 50 g substrate on substrate solution pH over time. Each symbol is based on 10 observations and vertical bars represent ± standard error.

Fig. 2. The effects of 6 meq $\text{Ca}(\text{OH})_2$ with and without CaSO_4 on substrate solution pH over time. Each symbol is based on 10 observations and vertical bars represent $\pm$ standard error.

Fig. 3. Titration of 3 peatmoss : 1 perlite (by volume) substrate with $\text{Ca}(\text{OH})_2$, with and without CaSO_4 . Each symbol is based on 10 observations and vertical bars represent $\pm$ standard error. Regression equation for + CaSO_4 : $y = -0.0002x^3 + 0.003x^2 + 0.2223x + 3.8295$; $r^2 = 0.9962$. Regression equation for - CaSO_4 : $y = -0.0002x^3 + 0.005x^2 + 0.189x + 4.0962$; $r^2 = 0.9983$.

tested with and without CaSO_4 added at a rate of $1 \text{ g} \cdot \text{L}^{-1}$ (253 mg/dish). Deionized water was pipetted into the dishes to achieve 95% CC. Substrate solution pH was procured using SQ and solution pH was measured after 0, 1, 2, 4, 24, 48, and 96 h incubation.

Titration curve. The substrate was titrated with and without CaSO_4 at the same rate as in T. The titrating base used was $\text{Ca}(\text{OH})_2$, which was incorporated with the substrate to provide 0 to 24 meq alkalinity in 1 meq increments. Water was added to achieve 95% CC. The dishes were incubated for 24 h. Solution was procured via SQ and its pH was measured. There were seven replications.

Results and Discussion

Water amount. A stable and equal pH reading was seen in the 95% CC and 100% CC water treatments at 5 h ($P = 0.3725$) and 95% CC at 14 d ($P = 0.0404$), as shown in Table 1. After 5 h of incubation, solution pH decreased as water amount increased. Conversely, after incubation for 14 d, solution pH increased with increasing water. The former phenomenon may be explained by the previously mentioned theory of Davis (1943), in which the greater amounts of water enhanced the dissociation of H^+ from the substrate exchange sites. At 5 h, the short period of time was possibly not long enough for the carbonate from the dolomitic limestone to dissociate sufficiently to neutralize the additional H^+ released. However, after 14 d, the limestone may have been dissociated completely and the H^+ concentrations had reached equilibrium between the substrate and the solution, thus producing the well-documented dilution effect. Our goal was to supply enough water to ensure complete contact of bases with substrate while avoiding the dissociation or dilution of H^+ in the measuring solution. Consequently, the best overall level of water addition for the purposes of this study was 95% of CC.

Solution procurement method. Only the SQ method provided consistent results at both 5 h and 14 d (Table 2). This is fortuitous because SQ yields unaltered substrate solution, hence the actual pH condition, in the substrate. The SME and PT methods resulted in higher pH levels at 5 h, and PT did so at 14 d indicative of water dilution. This was anticipated in the SME procedure as explained earlier, but not in PT. In the laboratory, the transfer of substrate from germination dishes to funnels in the PT method created macropore channels. These channels allowed the added deionized water to pour freely through the substrate instead of displacing the substrate solution.

Type of base. NaOH produced higher pH values at all times ($P < 0.0001$) than $\text{Ca}(\text{OH})_2$ as shown in Fig. 1. This result was expected due to the higher affinity of the divalent cation Ca^{2+} for substrate exchange sites than the monovalent Na^+ . This greater affinity allowed Ca^{2+} to displace more H^+ than Na^+ , creating a more acidic solution. These data were collected in a system where only 2 meq base were applied to 50 g peatmoss resulting in pH levels mostly between 4.5 and 5.0.

Incubation time with and without CaSO₄.

The addition of CaSO₄ resulted in significantly lower pH values at all times (0, 24, and 48 h, $P = 0.0028$; 1, 2, and 96 h, $P < 0.0001$; 4 h, $P = 0.0030$; Fig. 2). At this low level of alkalinity, it is possible that the additional Ca²⁺ displaced H⁺ on the substrate exchange sites in excess of the amount of base available to neutralize them. CaSO₄ did not consistently reduce the variability of the pH measurements, but did hasten the acid–base reaction to completion. Regardless of the presence or absence of CaSO₄, the acid had been completely neutralized when the dishes were incubated for 24 h.

Titration curve. When alkalinity is provided to result in solution pH measurements ranging from ≈ 4.0 to 8.0, it is clear that the addition of CaSO₄ exerts the greatest influence in the low pH range (Fig. 3). Significant differences occurred between the two curves at and below pH 5.0. In the pH range in which plants are grown, there was no effect of CaSO₄. Since there are many experimental factors that can significantly influence pH measurements, care must be taken when developing a titration

curve relating solution pH to milliequivalents of base. If the information provided from such a titration curve is to be used as a means of comparison, it is necessary to match the experimental methods used for creating the curve to the systems to which the resulting information will be applied.

Conclusions

The titration curve developed here will subsequently be used to compare the neutralization requirements of various sphagnum peatmoss samples, and also to determine and compare the neutralization capacities of various limestones. From the results of these studies, incorporating Ca(OH)₂ into the substrate, adding water to achieve 95% CC, incubating for 24 h at 20 °C, and procuring solution for pH measurement using SQ comprise the most appropriate protocol for developing a titration curve for the intended purpose. In addition, it is not necessary to incorporate CaSO₄ into the procedure unless one is considering a crop grown at pH 5.0 or lower and preplant Ca in addition to that supplied by limestone is used.

Literature Cited

- Davis, L.E. 1943. Measurement of pH with the glass electrode as affected by soil moisture. *Soil Sci.* 56:405–422.
- Faber, W.R. and P.V. Nelson. 1984. Evaluation of methods for bulk solution collection from container root media. *Commun. Soil Sci. Plant Anal.* 15:1029–1040.
- Reddy, S.S. 2001. Putting pH to the test... But which one? *GrowerTalks* 65(3):108–112.
- Scoggins, H.L., D.A. Bailey, and P.V. Nelson. 2001. Development of the press extraction method for plug substrate analysis: Quantitative relationships between solution extraction techniques. *HortScience* 36(5):918–921.
- Sparks, D.L. *Environmental Soil Chemistry*. Academic Press, San Diego. 1995.
- Thomas, G.W. 1996. Soil pH and acidity. In: *Methods of soil analysis. Part 3. Chemical methods*. Soil Sci. Soc. Amer.–Amer. Soc. Agron., Madison, Wis.
- Warncke, D.D. and D.M. Krauskopf. 1983. Greenhouse growth media: testing and nutrition guidelines. *Mich. State Univ. Coop. Ext. Ser. Bul.* E-1736.
- Wright, R.D. 1986. The pour-through nutrient extraction method procedure. *HortScience* 21:227–229.