A Gasometric Procedure to Measure Residual Lime in Container Substrates

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Abstract. Unreacted residual limestone in the container substrate is key in buffering pH change over time. Our goal was to develop a substrate test protocol to measure residual lime [in units of CaCO3 equivalent (CCE)] by applying a strong mineral acid (HCl) to a substrate sample and measuring the evolved CO2 gas with a gasometric method based on a Chittick apparatus. In one experiment, CaCO3 was added to a substrate that had previously been neutralized to pH 7.35 with Ca(OH)2 so that there would be minimal CaCO3 reaction with the substrate at this high pH. The gasometric method was then used to estimate residual CCE. Measured CCE and applied CaCO3 were similar, indicating reliable CCE estimation. In a second experiment, a pH titration method was used to quantify the relationship between substrate-pH and milliequivalents of reacted base and providing an additional validation of the estimated reacted and residual CCE. The gasometric method demonstrated declining residual CCE over time as a dolomitic limestone reacted to raise substrate-pH and increasing residual CCE as applied CaCO3 concentration increased. Residual CCE in a substrate is an important property that should be considered for pH control and management in greenhouse crop production. Our results indicate that the gasometric system may be useful for optimizing lime application rate, lime source, or management of residual CCE during crop production.

Liming materials are incorporated into container substrates to neutralize acidity and to provide calcium (Ca) and magnesium (Mg). Liming materials differ in their reactivity rate, which in turn determines the proportion of base that remains as unreacted “residual” limestone in the substrate. Research has shown that most pH buffering in container substrates comes from residual lime (Argo and Biernbaum, 1996). However, a test method is currently lacking to quantify the concentration of residual lime [in units of calcium carbonate (CaCO3) equivalents (CCE)] in container substrates.

The most common liming materials used in greenhouse substrates are carbonate-based limestones: calcite (CaCO3 with 40% Ca), calcitic [CaMg(CO3)2], with greater than 30% Ca and less than 5% Mg, dolomitic [CaMg(CO3)2] with less than 30% Ca and greater than 5% Mg, and доломит [CaMg(CO3)2] with 22% Ca and 13% Mg. When carbonate-based limestones react with acid from proton sources such as acidic peat, then calcium (Ca2+) or magnesium (Mg2+), water (H2O), and carbon dioxide (CO2) gas result:

\[
\text{CaCO}_3 (\text{calcite}) + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \text{(gas)} \quad [1]
\]

\[
\text{CaMg(CO}_3\text{)}_2 (\text{dolomite}) + 4\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{H}_2\text{O} + 2\text{CO}_2 \text{(gas)} \quad [2]
\]

Our hypothesis, based on research measuring CCE in agronomic soils (Dreimanis, 1962; Hülsemann, 1966), was that the unreacted lime concentration (on the left side of Eqs. 1 and 2) could be determined in a soilless substrate by addition of a strong acid and subsequent measurement of released CO2 gas through volume displacement. The volume of CO2 gas evolved by the chemical reaction can be determined with a Chittick apparatus (or variants thereof), which is easily constructed from basic laboratory glassware and tubing (Fig. 1; Dreimanis, 1962). Once the device is calibrated by use of prepared CaCO3 standards, 1) media samples are introduced and reacted with HCl, 2) the volume of CO2 released is measured, and 3) the amount of residual lime is calculated with either a CO2-CaCO3 standard curve or the Ideal Gas Law with a known air temperature and air pressure.

Soil CCE content can be determined by either measuring the CO2 evolved when treated with acid or the use of empirical standard curves relating pH to known carbonate content. The first method includes several procedures differing in how evolved CO2 is quantified. The liquid displacement (i.e., Chittick) method on which our technique is based has been widely used (Dreimanis, 1962; Hülsemann, 1966) to measure the volume of CO2 evolved on application of strong acid. The gravimetric method for measuring CaCO3 (Allison and Moodie, 1965) is another well-known procedure and appears in other soil analysis manuals (Goh et al., 1993). In the gravimetric procedure for measuring CaCO3, a soil sample is combined with excess 4 M HCl and the loss in weight incited by CO2 evolution is converted to CCE using an equation based on formula weights. The gravimetric method uses an Erlenmeyer flask as the reaction vessel and involves periodically removing and replacing a rubber stopper while the flask is swirled to promote CO2 evolution. Loss of H2O vapor along with CO2 contributes to the loss in weight each time the stopper is removed and thus increases the calculated CCE content. A resolution problem can also occur because the flask and stopper together weigh well over 100 g along with a soil sample of 1 to 10 g, whereas the loss in weight for a typical soil is only tenths of a gram.

The second method involves the reaction of the soil carbonates with 0.4 M acetic acid and then measuring pH after allowing the acid-soil solution time to reach equilibrium. The pH value is converted to an equivalent CaCO3 content by means of an algorithm obtained in separate calibration runs with pure CaCO3 (Moore et al., 1987). The problem mentioned by Moore et al. (1987) is that appreciable CaCO3 content can be estimated even for acidic soils, apparently as a result of neutralization of dilute acetic acid by clay and organic matter.

Our goal was to develop and test a gasometric method for quantifying residual lime in a container substrate and describe a recommended protocol. To improve confidence that the gasometric method was a valid approach, specific objectives were to compare estimated CCE against 1) applied CaCO3 under high pH conditions, and 2) a pH titration method to relate substrate-pH with milliequivalents of reacted CaCO3. The method was then used to quantify the effect of 3) dolomitic limestone on residual CCE and substrate-pH over time, and 4) increasing applied CaCO3 on residual CCE and substrate-pH. Additional experiments were run to identify potential sources of measurement...
error. The conclusion of this article describes a recommended protocol.

**Materials and Methods**

The gasometric system. A gasometric system adapted from a Chittick device (Dreimanis, 1962) was described by Huang et al. (2007) for measuring the reaction rate of different carbonate limestone sources and particle size fractions (Fig. 1). The gasometric system consisted of a gas-measuring burette, acid-dispensing burette, level burette, 1-L decomposition flask, and a magnetic stirrer. CaCO₃ equivalent was calculated based on volumetric measurement of CO₂ through displacement of a solution in the measuring burette.

The CO₂ volume could be related to moles of CaCO₃ using the Ideal Gas Law:

\[ N_{\text{CO}_2} = \frac{P_{\text{CO}_2}V_{\text{CO}_2}}{RT} \]  

where \( N_{\text{CO}_2} \) represents the moles of CO₂ liberated (\( N_{\text{CO}_2} \) also equals the moles of carbonate material decomposed according to the stoichiometry of Eqs. [1] and [2]), \( P_{\text{CO}_2} \) represents CO₂ partial pressure (Pa), \( V_{\text{CO}_2} \) represents the volume of CO₂ (L) liberated after subtracting the volume of HCl from the displaced gas volume, \( R \) is the universal gas constant (0.008314 L Pa K⁻¹mol⁻¹), and \( T \) is temperature (K) (°C + 273.2).

**Initial calibration of the system.** The precision and accuracy of estimated CaCO₃ was tested by comparing estimated CaCO₃ against a weighed amount of CaCO₃ (Fig. 2) ranging from 0.01 to 8.0 mmol (0.001–0.8 g). For each measurement, 0.005 L of 6 M HCl was added to the decomposition flask to react with the standard CaCO₃. The volume of CO₂ was recorded after complete CaCO₃ reaction, with a 5-min reaction time, subtracting the volume of the HCl from the displaced gas volume.

Overall, the system accurately and precisely measured CaCO₃ (Fig. 2A–B) when the sample was CaCO₃ (without substrate). The device successfully determined CaCO₃ content as low as 0.01 (0.001 g) up to 8.0 (0.8 g) mmol, although errors occurred when standard CaCO₃ was less than 0.5 mmol (0.05 g) in the sample (Fig. 2A). If the system was used to measure lime incorporated into a substrate, 0.01 to 8.0 mmol would be equivalent to CCE at 0.02 to 16 g CCE (0.02–16 kg m⁻²) of substrate for a sample volume of 0.050 L of substrate.

To measure residual lime incorporated into a peat-based substrate, the gasometric system needed to be further calibrated. To do this, subsamples of an experimental substrate composed of 70% peat + 30% perlite by volume were measured in 0.05- or 0.1-L sample volumes in a beaker with the substrate packed to similar bulk density as would occur in an irrigated and drained container. The peat source used in all experiments was Canadian Sphagnum peat (Sun Gro Horticulture, Vancouver, Canada) with long fibers and little dust (Von Post scale 1–2; Puustjarvi and Robertson, 1975). These subsamples were placed into 1-L decomposition flasks. The dry bulk density for peat and 70% peat + 30% perlite was 128 and 147 g L⁻¹, respectively. The medium contained 150 mL water per liter before analysis. Deionized water was added to the substrate at 1.5 times the sample volume (i.e., 0.075 or 0.15 L for the substrate sample of 0.05 or 0.1 L, respectively). The flask was then attached to the gasometric system. The system was closed and 6 M HCl was introduced into the decomposition flask at half the sample volume (0.025- or 0.05-L aliquot of 6 M HCl for 0.05- or 0.1-L substrate samples, respectively). The sample in the flask was constantly stirred using a magnetic stirrer, and a heat isolation pad was placed between the top surface of the stirrer and the bottom of the decomposition flask. The reaction time was 10 min for reagent CaCO₃ and 30 min (Dreimanis, 1962) for horticultural limestone. After reaction, the apparatus was left to stand for 2 min for temperature and pressure within the apparatus to reach room conditions. The temperature and barometric pressure of air surrounding the apparatus was then measured.

The amount of residual lime can be calculated using either the Ideal Gas Law with a known air temperature and air pressure or with a CO₂–CaCO₃ standard curve. The standard curve appropriate to residual CCE measurement was generated by adding a range in weights of CaCO₃ to the decomposition flask along with a fixed volume of deionized water rather than with a fixed volume of container substrate. Standard weights of CaCO₃ of 0, 0.02, 0.05, 0.10, 0.20, and 0.30 g were added to the decomposition flasks followed by a given volume of deionized water (0.075 or 0.15 L for a corresponding substrate sample size of 0.05 or 0.1 L, respectively) in a factorial manner.

![Fig. 1. A gasometric system for CO₂ measurement adapted from Chittick apparatus [AOAC Official Method 923.02; diagram from Huang et al. (2007)]. The decomposition flask (A) was connected through the side hose connection by rubber tube (B) provided with a stopcock (C) to a graduated gas-measuring burette (D), which was connected in turn with a level burette (E) using a rubber tube. To measure residual carbonate lime in the substrate, a 1-L wide-mouth filter flask (A) was fitted with a one-hole rubber stopper with an extended tip of a 10-mL acid-dispensing burette (F) passed through the hole. A magnetic stirrer (not shown here) was also introduced into the gasometric system for residual lime measurement. A heat isolation pad should be placed between the top surface of the stirrer and the bottom of the decomposition flask to isolate possible heat from the magnetic stirrer motor.](Image 113x155)

![Fig. 2. Calibration of the gasometric system using reagent CaCO₃. Reagent CaCO₃ was weighed to the nearest 0.1 mg, ranging from 0.0 to 8.0 mmol (0.8 g), and was introduced into the decomposition flask without peat substrate. For each measurement, 0.005 L of 6 M HCl was added to the decomposition flask to react with the standard, and the volume of CO₂ was recorded until complete reaction. (A) Detailed view for standard CaCO₃ at low weights below 1.0 mmol. (B) The relationship between the estimated and weighed CaCO₃ for the complete range in sample weights (0–8.0 mmol). Symbols represent individual measurements.](Image 215x336)
The flask was then attached to the gasometric system and an aliquot of 6 M HCl (i.e., 0.025 or 0.05 L of 6 M HCl for corresponding substrate sample size of 0.05 or 0.1 L, respectively) was added for complete CaCO₃ reaction. After 10 min of reaction time, the volume of released CO₂ was recorded and was plotted as a function of corresponding standard CaCO₃ weight. During the course of residual CCE measurement, the room air temperature was kept stable, and the air pressure was assumed constant. For each experiment and substrate sample size, a different set of standard curves were developed, which were used in the analysis described in the figures. However, the calculated CCE using a standard curve (CCE₃) and the calculated CCE using the Ideal Gas Law (CCE₁) were very similar. Over all the experiments, the r² equaled 0.999 for the relationship CCE₃ = (1.032 ± 0.015)CCE₁ – (0.109 ± 0.031).

After initial calibration of the system, we validated results using the following two methods.

A. Validation by incorporating reagent-grade CaCO₃ into a preneutralized substrate. By adding CaCO₃ to a substrate that was already at a high pH, we expected minimal lime reaction. Therefore, the applied CaCO₃ should be similar to the measured CCE, and this would provide a validation of CCE measurements. CaCO₃ was incorporated at three concentrations (0.5, 1.0, or 2.0 g per liter of substrate) into a 70% peat + 30% perlite (including 95% confidence intervals) for the 0.05- and 0.1-L substrate sample volumes are plotted over time.

Effect of CaCO₃ incorporation rate on substrate-pH and residual CaCO₃ equivalent. As additional CaCO₃ is added to a peat substrate, a plateau in the concentration of reacted lime is expected above pH 7.0 because of reduced solubility of CaCO₃ at high pH. Application of additional lime beyond that plateau in pH level is expected to result in an increasing proportion of unreacted lime, which should be measurable as residual CCE. To evaluate whether the gasometric system could quantify these trends, reagent CaCO₃ was incorporated into a peat substrate at a rate of 3, 6, 9, or 12 g CaCO₃-L⁻¹ of substrate, and pH and residual CCE were measured 14 d later with three replicates per lime rate. Reacted lime was calculated by subtracting applied CCE minus the residual CCE (g CCE-L⁻¹ of substrate).

Results and Discussion

Validation by incorporating CaCO₃ into a preneutralized substrate. Increasing the amount of reagent CaCO₃ incorporated into a previously neutralized 70% peat + 30% perlite mix resulted in an increased residual CCE (Fig. 3). The ideal recovery rate (calculated as the measured residual CCE/incorporated CaCO₃) for this procedure would equal 100%. With a 0.05-L sample, the recovery rate ranged from 89% to 102% depending on the incorporated CaCO₃ concentration compared with 86% to 95% for the 0.1-L sample.

This validation experiment assumed that none of the applied CaCO₃ reacted with the substrate because the substrate-pH was raised to pH 7.35 with Ca(OH)₂ before the CaCO₃...
was applied. However, if a portion of the applied CaCO₃ did indeed react, that would reduce the recovery rate. We measured the substrate-pH within 6 h after CaCO₃ incorporation, and the substrate-pH increased 0.13 and 0.24 pH units for CaCO₃ rates of 0.5 and 1.0 g L⁻¹, respectively. This indicated that there was partial lime reaction in the preneutralized substrate, which would contribute to some of the error in CaCO₃ recovery from Figure 3.

Validation against a pH titration procedure. The titration of 70% peat + 30% perlite with reagent CaCO₃ showed an approximately linear pH response with increasing CaCO₃ application rate up to a pH near 7.0 (Fig. 4), which was consistent with the trend observed by Rippy and Nelson (2005). The residual CCE estimated by the pH titration method was compared with the residual CCE from the gasometric method in Figure 5, and the CCE estimated with both methods had a relationship nearly 1:1 with r² = 0.997.

Effect of dolomitic limestone on residual CaCO₃ equivalent and substrate-pH over time. Figure 6 illustrates how reaction over time of a dolomitic limestone-incorporated rate in CCE at 1.42 g L⁻¹ resulted in an increase in substrate-pH and a corresponding decrease in the remaining residual lime. By day 27, substrate-pH had reached pH 4.9, and the lime had reacted completely as indicated by zero detectable residual CCE. Given the demonstrated ability to track change in residual CCE over time, the method could be used during crop production to identify change in the buffering capacity of a substrate (and therefore the potential for rapid and undesirable pH change).

Effect of applied CaCO₃ on substrate-pH and residual CaCO₃ equivalent. The gasometric method quantified the expected trend in residual CCE with increasing applied CaCO₃ concentration. Substrate-pH increased 3.4 with no applied CaCO₃ to pH 7.2 after application of CaCO₃ at 6 g L⁻¹ (Fig. 7A). There was only a slight increase in pH (from pH 7.2 to 7.5) as applied CaCO₃ increased from 6 to 12 g L⁻¹ of substrate. The measured residual CCE was zero for CaCO₃ rate at 3 g L⁻¹, and the residual CCE increased from 0.32 g L⁻¹ up to 6.08 g L⁻¹ after application of CaCO₃ from 6 to 12 g L⁻¹ (Fig. 7B). Correlated with pH, the calculated amount of reacted lime increased as increasing CaCO₃ application rate from 3 to 6 g L⁻¹, but increased only slightly for CaCO₃ rate between 6 and 12 g L⁻¹ (i.e., the amount of reacted lime in CCE was 5.68, 5.77, and 5.92 g L⁻¹ for applied CaCO₃ at 6, 9, and 12 g L⁻¹, respectively). For a given substrate and limestone source combination, the gasometric method could be used to identify residual CCE at different lime incorporation rates, which would be a useful tool for developing substrates that have high buffering capacity.

Potential sources of error. Generally, the gasometric system could accurately and consistently measure residual lime in CCE from 0.02 up to 16 g L⁻¹ of substrate. We found inadequate precision for samples with low alkalinity content (CCE less than 0.05 g L⁻¹). Temperature and air pressure should be kept stable during experimental runs, ideally under the same conditions as occurred during development of the standard curve. Dry peat-based samples were found to release non-CO₂ gas to the system that caused erroneously high CO₂ readings (data not shown), which can be easily corrected by moistening a dry substrate sample with deionized water (1 part water:1 part dry substrate) and left overnight before it is attached to the gasometric system. Because lime and media components are added to container substrates on a volume basis, rather than by substrate weight, we chose to measure CCE on a per liter basis. For applicable results, it is therefore important that the bulk density of the gasometric sample be prepared at a similar level to the substrate bulk density in a container.

Application of noncarbonate lime materials such as hydrated lime [Ca(OH)₂] and CaO could also contribute to CO₂ readings when the corresponding substrate-pH is greater than 7.0 because of potential absorption of CO₂ from the air. It is important to note, however, that pH 7.0 is above the normal pH range for greenhouse crops. We tested the amount of CO₂ released using the gasometric method when reagent Ca(OH)₂ was applied at different rates in a 70% peat + 30% perlite substrate (with corresponding substrate-pH from 3.9 to 8.1). There were no CO₂ readings observed unless substrate-pH was greater than 7.0 (unpublished data). Carbonate content (as a contaminant) in Ca(OH)₂ and bicarbonate arising from CO₂ adsorption in the air at high pH may have contributed to the CO₂ readings. Highly soluble carbonate or bicarbonate has a very rapid reaction rate (less than 1 min) in the gasometric system based on our observations of nearly instant CO₂ gas release when reagent-grade CaCO₃ or bicarbonate fertilizer salts were tested.

![Fig. 4. Titration of 70% peat + 30% perlite with reagent CaCO₃ showed an approximately linear pH response with increasing application rate of base up to a pH near 7.0. Symbol represented the means ± se with n = 3.](image)

![Fig. 5. The relationship between estimated CaCO₃ equivalent (CCE) using a gasometric system and the estimated CCE using a pH titration curve. Dolomitic limestone was incorporated into the substrate in CCE at 1.42, 2.86, and 5.71 g L⁻¹. Symbols represent individual measurements. Data are included from days 0, 1, 2, 8, and 27.](image)

![Fig. 6. Changes in residual CaCO₃ equivalent (CCE) and corresponding substrate-pH over time after incorporation of a dolomitic limestone (passed through a 100 mesh but retained on a 200 mesh; 75–150 μm) into a 70% peat + 30% perlite substrate in CCE at 1.42 g per liter of substrate. Substrate moisture was maintained at 20% container capacity at room temperature (22 °C). Symbols represent means of three measurements ± sd.](image)

![Fig. 7. Substrate-pH response (A) and residual CaCO₃ equivalent (CCE) using the gasometric system in a peat substrate and the corresponding reacted CCE (B) 14 d after CaCO₃ was incorporated into a peat substrate at a rate of 3, 6, 9, and 12 g L⁻¹ of substrate. Each sample represents the average of three replicates, and error bars represent 95% confidence intervals. Reacted lime was calculated by subtraction of the applied CCE minus the estimated residual CCE (g L⁻¹ of substrate).](image)
Lime reaction time in HCl solution is influenced by lime type (calcitic and dolomitic), lime particle size distribution, and chemical purity. We evaluated the reaction rate of 25 commercial horticultural lime stones in the gasometric system and found that duration required for 90% recovery with a 0.2 g lime sample varied from an average 1.8 min for calcitic limestone to an average 18 min for dolomitic limestone. There was considerable variability in reaction time between individual limestone samples with 90% reaction occurring anywhere from 1 to 50 min because of factors such as limestone particle size (data not shown).

Substrate components can potentially contribute carbonate, particularly vermiculite. We measured the CCE of five horticultural sources of vermiculite, one source of coir, and five sources of perlite. Measured CCE averaged (mean ± std) 2.04 ± 1.76, 0.13 ± 0.08, and 0.20 ± 0.18 g L⁻¹ for vermiculite, coir, and perlite, respectively. The measured CCE in coir and perlite was very low and would probably be neutralized when these materials are mixed with acidic peat. In contrast, the measured CCE in vermiculite had similar neutralizing characteristics as carbonate limestones and was not completely neutralized when blended with peat. The CCE measured in vermiculite required 20 to 30 min to reach a complete reaction in the system. The two U.S.-mined vermiculite samples had lower CCE (0.31 and 0.38 g L⁻¹) compared with the South African vermiculite sources (1.48, 2.37, and 2.76 g L⁻¹). When a fine-grade South African horticultural vermiculite sample was mixed with the peat at different ratios (0%, 25%, 50%, 75%, and 100% by volume) at high moisture (95% container capacity), substrate-pH at day 7 increased from 3.26 for 100% peat up to 8.47 for 100% vermiculite, and measured CCE increased from 0 to 4.95 g L⁻¹. Because different sources of vermiculite varied widely in neutralizing power, further research is needed to compare effects of vermiculite source, particle size, and application rate on residual CCE.

Other potential sources of carbonate alkalinity that could affect gasometric measurements in substrates include irrigation water and bicarbonate fertilizers. Both carbonate and bicarbonate will produce one mole of CO₂ per mole, although one mole of carbonate has twice the base strength as bicarbonate. The gasometric system is unable to distinguish between bicarbonate and carbonate, except indirectly by reaction time. We have analyzed potassium bicarbonate in the gasometric system (published data) and found that this form of alkalinity reacts completely within a few seconds. In addition, soluble bicarbonate in irrigation water is neutralized rapidly (outside of the gasometric system) when applied to a substrate with pH below 7. Argo et al. (1996) found that high alkalinity (CaCO₃ at 320 mg L⁻¹) water applied to a peat medium at substrate-pH 5.9 to 6.3 caused a spike in CO₂ within 10 min because of reaction with peat acidity, and the bicarbonate was mostly neutralized within 180 min after the irrigation event.

Substrate pH buffering can be contributed by noncarbonate sources that would not be measured with the gasometric method, for example, phosphates or substrate cation exchange capacity. However, Argo and Biernbaum (1996) found that the low bulk density of components typically used in container substrates means that residual lime had a greater effect than cation exchange capacity on pH buffering.

**Conclusions and Suggested Protocol**

Residual CCE in a substrate is an important property that should be considered for pH control and management in greenhouse crop production. The results shown in Figures 6 and 7 indicate that the gasometric system is a useful tool for optimizing lime application rate and management of residual CCE during crop production. For different lime sources, it would be possible to quantify the reacted and residual CCE at a given lime incorporation rate to a particular substrate. It may be possible to identify a desirable minimum residual CCE for adequate pH buffering to avoid a rapid pH drop during production. If residual CCE was found to be close to zero, corrective actions such as a basic drench may be useful for crops sensitive to iron/manganese toxicity at low pH.

Results from the gasometric method were closely matched with those estimated by the validation experiments using preneutralized media or pH titration. These results suggested the following procedure for CCE determination in a container substrate using the gasometric system:

**1. System calibration and standard curve development:** The system should be calibrated as shown in Figure 2. A standard CO₂ (mL)–CaCO₃ (g) curve is recommended for CCE determination if the air temperature and air pressure are stable or, alternatively, the Ideal Gas Law should be used for each experimental run after measurement of the air temperature, air pressure, and volume of evolved CO₂ in the gas-measuring burette. To prepare a standard CO₂ (mL)–CaCO₃ (g) curve, weigh reagent-grade CaCO₃ samples to the nearest 0.1 mg and place in 1-L decomposition flasks. Sample weights of 0.05, 0.10, 0.20, 0.30, and 0.40 g are suggested if the total solution is 0.1 L of deionized water. Using the same procedure for measuring the volume of CO₂ released in the substrate samples, the suggested reaction time is 10 min.

**2. Substrate sample size:** Measure 0.050 or 0.1 L to the nearest 1-mL substrate samples and transfer into 1-L decomposition flasks. The recommended substrate sample is 0.1 L if the expected residual CCE is less than 0.5 g L⁻¹ and 0.05 L if CCE is larger than 0.5 g L⁻¹. The substrate sample should contain CCE at least 0.05 g for accuracy.

**3. Volume of deionized water and volume of 6 M HCl:** Add 0.075 L of deionized water into the 1-L decomposition flask that contains the 0.05-L substrate sample, place a magnetic stir bar in the flask, then attach the flask to the gasometric system. After the system is closed, add 0.025 L of 6 M HCl into the decomposition flask through the acid-dispensing burette. For a 0.1-L substrate sample, the volumes of deionized water and 6 M HCl are 0.15 and 0.05 L, respectively.

**4. Reaction time:** The recommended average time for general grade dolomite and calcite is 30 min. As a general guideline, the experimental run is finished when the CO₂ volume reading is stable for at least 5 min.

**5. Procedure:** In addition to the detailed procedure described in the article by Huang et al. (2007), a magnetic stirrer is introduced into the gasometric system. The sample should be constantly stirred during the lime dissolution period. A heat isolation pad should be placed between the top surface of the stirrer and the bottom of decomposition flask to isolate possible heat from the magnetic stirrer motor.

**Literature Cited**


