

# Carbonate Analysis By Modified Pressure Calcimeter Method

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## **Problem:**

Soil organic carbon analyses using high temperature induction furnace combustion methods have become increasingly popular because of advances in instrumentation. Combustion methods, however, also include carbon from  $\text{CaCO}_3$  and  $\text{CaMg}(\text{CO}_3)_2$  found in calcareous soils. Separate analysis of the inorganic carbon must be done to correct soil carbon data from combustion methods.

Soil carbonate analysis methods typically utilize acid dissolution with the consumption of  $\text{H}^+$  or the determination of Ca and Mg, or  $\text{CO}_2$  production (Loeppert and Suarez, 1996). Quantitative determination of carbonates can be accomplished using the gravimetric method based on the reaction of HCl with soil carbonates and the gravimetric loss of  $\text{CO}_2$  as described by the U.S. Salinity Laboratory Staff (1954). This method however is not practical for large sample runs and is not suitable for low concentrations of carbonate. The direct measurement of  $\text{CO}_2$  is preferred due to its simplicity and because it is a direct measure of carbonate when precautions are used to eliminate organic matter oxidation which would give a positive interference. The analysis of  $\text{CO}_2$  by pressure calcimeter method described by Loeppert and Suarez (1996) is a direct, accurate and inexpensive method, but the complexity of the pressure calcimeter apparatus makes large sample runs impractical.

## **Objective:**

To develop a fast, efficient and precise inorganic carbon method by modification of the pressure calcimeter method that covers the complete analytical range.

## **Method Modification:**

We modified the pressure calcimeter by using Wheaton serum bottles (20 mL and 100 mL volumes) sealed with butyl rubber stoppers and aluminum tear-off seals as the reaction vessel and a pressure transducer monitored by a digital volt meter.



## MODIFIED PRESSURE CALCIMETER METHOD

### Apparatus Description

The modified calcimeter apparatus (Fig. 1) consists of a pressure transducer (Model 280E Serta, 0-105 kPa, output .03-5.03 VDC from Setra systems, Inc., Boxborough, MA)<sup>1</sup> connected to a power supply (24 volt DC) with 14 gauge wire, and a digital voltmeter wired in line to monitor output from the transducer. Attached to the base of the pressure transducer is 20 cm of clear laboratory Tygon R-3603 tubing (9.5 mm i.d.) connected to an 18 gauge Luer-loc hypodermic needle with a particle filter (0.6  $\mu$ m for removing particles from carrier gas, Leco # 768-980) spliced in the middle of the tubing to prevent any reflux from reaching the pressure transducer. A 20 mL Wheaton serum bottle serves as the reaction vessel for soils containing up to 15 %  $\text{CaCO}_3$  and a 100 mL bottle for soils above 15 %  $\text{CaCO}_3$ , in which a 2 mL (0.50 dram) auto-sampler vial is inserted containing the acid reagent of 6M HCl containing 3% by weight of  $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$  (Fig. 2). The  $\text{FeCl}_2$  is used to eliminate the release of  $\text{CO}_2$  from organic matter. The 2 mL of acid reagent is able to neutralize up to 60 %  $\text{CaCO}_3$ .

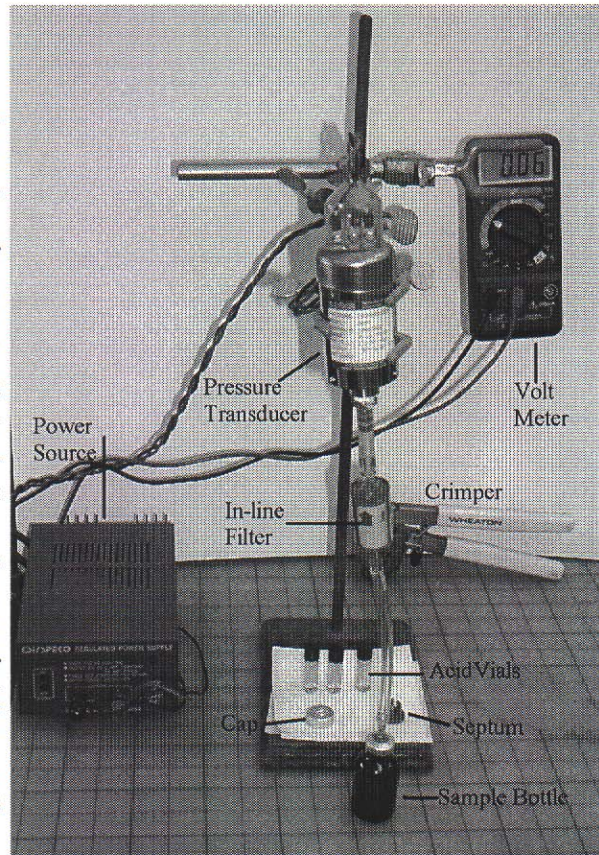


Figure 1.

### Analysis Procedure

A sample is weighted to 1.00 or 0.50 g and transferred to a Wheaton serum bottle. The vial containing 2 mL of 6M HCl is then slowly dropped into the serum bottle.

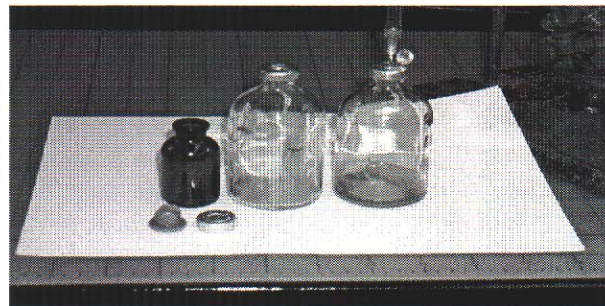


Figure 2.

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<sup>1</sup>Mention of a commercial product does not imply Colorado State University or USDA endorsement of that product over similar products.



The bottle is then sealed with a 2-prong gray butyl rubber stopper and crimped closed with a aluminum tear-off cap using a hand crimper.

Once the serum bottle with the sample and acid vial is sealed (reaction vessel), the reaction is started by vigorously shaking the 20 mL serum bottle or gently swirling the 100 mL serum bottle assembly, to spill the acid vial within the reaction vessel which allows acid to contact the soil. After a set reaction time, 2 to 6 hours for most soils, samples and standards are measured for CO<sub>2</sub> evolution by removing the aluminum tear-off seal cap, which exposes the butyl rubber stopper, and inserting the 18 gauge hypodermic needle that is attached to the pressure transducer and voltage meter. The voltage output is recorded to two decimal places after approximately 3 to 5 seconds.

A calibration curve is developed by mixing reagent grade CaCO<sub>3</sub> with oven-dried at laboratory sand which was powder ground to 80 mesh. Standards can be made based on a final weight of 20.0000 of sand and CaCO<sub>3</sub> to obtain IC concentrations of 0.20, 0.25, 0.50, 1.0, 2.0, 5.0, 10.0, and 15.0 %CaCO<sub>3</sub> for the 20 mL Wheaton serum bottles. The calibration curve for the 100 mL Wheaton serum bottle was obtained using IC concentrations of 0.50, 1.0, 5.0, 10.0, 20.0, 30.0, and 50.0 %CaCO<sub>3</sub>. A 1.00 g sample of each standard is transferred into the serum bottles. A calibration curve is analyzed during each run of samples along with 4 blanks, the mean of which is used as the zero concentration in the linear regression to account for changes in room temperature and pressure.

## Results and Conclusions

Gravimetric inorganic carbon determination of six soils, representing a wide range of soil carbonates from the North American Proficiency Testing program, showed a strong correlation when regressed against inorganic carbon from the modified pressure calcimeter method ( slope of 0.99,  $r^2 = 0.998$ ). The method detection limit (MDL) when using the 20 mL serum bottles as the reaction vessel was calculated to be 0.14 % CaCO<sub>3</sub>. In addition to MDL, a limit of quantitation (LOQ) was empirically derived from examining the inflection point in the curve of relative standard deviation (RSD), which is the standard deviation divided by the mean in percent vs. increasing analyte concentration. This is defined as the lowest level at which analytical measurement becomes meaningful. The limit of quantification, was 0.25 %CaCO<sub>3</sub> for the 20 mL reaction vessel. The 100 mL serum bottle used as the reaction vessel had a MDL of 0.35 % CaCO<sub>3</sub> with a LOQ of 2.0 CaCO<sub>3</sub>. When using a 100 mL Wheaton serum bottle as the reaction vessel with a 0.50 g sample size, soils containing up to 100 % CaCO<sub>3</sub> equivalent can be analyzed within the voltage output range of the pressure transducer.

The modification of the pressure calcimeter apparatus lends itself to the large sample output needed in commercial and research laboratories. It produces accurate and precise results using simplified techniques and minimal equipment investment. Batch runs of 120 samples per day are possible using a six hour reaction time and 3 to 5 second per sample time for reading output volts from the pressure transducer after puncturing the reaction vessel rubber stopper. Changes in laboratory temperature and pressure can affect the pressure change in the reaction vessel, and therefore a calibration curve is needed for each batch to correct for these changes. By changing the reaction vessel volume size and/or the sample size, the complete analytical range can be analyzed with high precision.