08.53 CALCIMETER

OPERATING INSTRUCTIONS

Contents

On these operating instructions

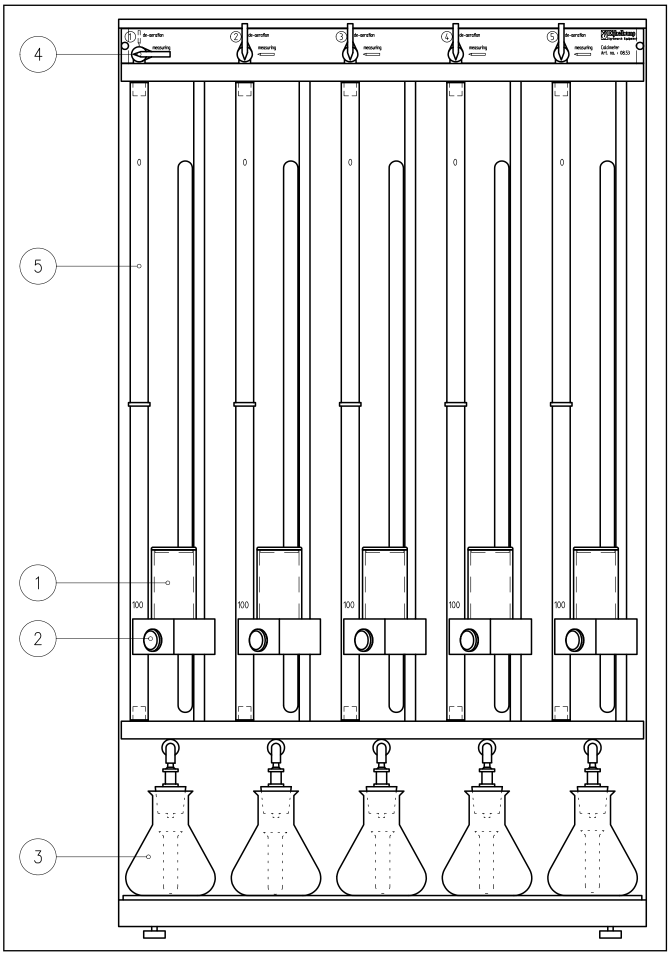
☞ **If the text follows a mark (as shown on the left), this means that an important instruction follows.**

⚠ **If the text follows a mark (as shown on the left), this means that an important warning follows relating to danger to the user or damage to the apparatus.The user is always responsible for its own personal protection.**

Text **Italic indicated text indicates that the text concerned appears in writing on the display(or must be typed).**

1. Introduction

The carbonate content of the soil is a sure indication of the fertility of the soil. To be able to determine the carbonate content of the soil Eijkelkamp (together with Dutch research institutes) developed a calcimeter that meets the standard NEN-ISO 10693.
The calcimeter by Eijkelkamp is suitable for the simultaneous determination of the carbonate content in 5 samples. The calcimeter works in accordance with the method of Scheibler. The method Scheibler involves a determination of the carbonate content in the soil based on a volumetric method. The carbonates present in the sample are converted into CO_2 by adding hydrochloric acid to the sample. As a result of the pressure of the CO_2 released, the water in a burette (graduation in ml) that is de-aerated, rises. The difference in level measured is an indication for the released quantity of CO_2, from which the carbonate content can be calculated. The carbonate content is expressed as an equivalent calcium carbonate content.



Advantages by comparison to other methods (for instance the Wesemael- and Anderson methods) are:

- ☐ No oven required to dry the silica gel.
- ☐ No other chemicals needed.
- ☐ No long waiting periods.
- ☐ No very accurate weighing equipment needed.
- ☐ Less vulnerable glass parts.
- ☐ It is easier to determine the content using the volumetric method then by weighing the gas.

2. Information

The device (see drawing)

- ☐ On top of the device twoway cocks (4) have been mounted. These work as follows:
  - By turning the handle in an upward position the reaction vessel (3) as well as the burette (5) are de-aerated; this is the de-aeration position.
  - By placing the handle in a horizontal position the de-aeration is closed and the reaction vessel is connected with the burette; this is the measuring position as well as the testing position.

- ☐ The buffer vessels (1) can be moved up- and downward by holding the buffer holder and pressing the black button (2) with the thumb. The blocking of the buffer vessel is now relieved and the vessel can be shifted.

- For measurement the burettes should be filled with water. For this purpose the buffer vessels need to be shifted to the highest position (cock in de-aeration position). Now water can be poured into the vessels. This will then flow into the burettes.
  Remove trapped air bubbles by moving the buffer up and down a few times.

With the buffer vessel in the highest position water should be added until the level in the burette has risen to 0 ml.

☞ **Remove excess water from the vessel as it would cause problems.**

3. Testing for leakage

Close the burette by turning the cock to the test position, with the buffer vessel is in its top position. Push the silicone stopper in the empty Erlenmeyer flask (reaction vessel) and bring the buffer vessel all the way down. There will be underpressure in the burette. After 60 minutes setting time the water level should be stable.

4. Required substances

- Prepared sampling material according to ISO 11464, air dried, assuming that the fraction of the particles is smaller then, or equal to 2 mm, sieved and divided into laboratory samples.
  In a sub sample the moisture content is determined according to NEN-ISO 11465.
- Calcium carbonate ($CaCO_3$) powder.
- Hydrochloric acid c(HCl) = 4 mol/l.
  Dilute 340 ml concentrated HCl (p = 1.19 g/ml) with water to 1000 ml.
- Water with a quality suitable for analysis; with a specific conductivity of no more than 0.2 mS/m at 25°C (according to quality degree 2 as mentioned in ISO 3696).

5. Preparation

Part of the laboratory sample (appr. 2.5 g) is treated on a watch glass with approx. 1 ml hydrochloric acid. The carbonate content is estimated based on the time the bubbling lasts. Based on these estimates the quantity of the sample for the analysis is determined. See NEN-ISO 10693 page 4, paragraph 7.1.

Intensity of effervescence	**Carbonate content g/kg**	**Mass of test portion g**
None or only limited	<20	10
Clear, but for a short time	20 till 80	5
Strong, for a long time	80 till 160	2,5
Very strong, for a long time	>160	≤ 1

6. The measurement

Fill a reaction vessel with a little calcium carbonate ($CaCO_3$). Place the test tube with hydrochloric acid in the reaction vessel using a pair of tweezers (prepare a reaction vessel for each burette). Close the reaction vessel using the stopper. Place the cock in the measuring position and by tilting the reaction vessel, enable the hydrochloric acid to flow out of the test tube and over the calcium carbonate ($CaCO_3$), initiating the reaction.
Allow this to stand for a day so that the water in the burette becomes saturated with CO_2 so that during the actual measurement no CO_2 is lost. This makes the measuring result substantially more accurate.

For every series of measurements you should execute two blank determinations (to obtain a zero/reference value) and two determinations of 0.2 en 0.4 g $CaCO_3$ for calibration.
The measurements should preferably be executed in a temperature controlled room (temperature difference will influence the measurements significantly).

6.1 Blank determinations

Fill 2 reaction vessels with 20 ml of water each for the blank determinations. The determinations of the samples and the standards commence with a starting level of 3 ml; this is set using the buffer vessels. The starting level of 3 ml is required to allow rising of the water level in the burette. This may sometimes occur in practice when almost no CO_2 evolves, but a small quantity is absorbed.

The determination of the blanks commences with starting values of 20 and 80 ml. The main reason for this is that differences in the measured values at the lower or at the top end of the burette may be caused due to diffusion or a difference in pressure. Applying both levels may yield an acceptable average. Place the reaction vessels on the calcimeter so that there is no further need to move them.
Now fill a small test tube with 7 ml hydrochloric acid and place it in a reaction vessel using a pair of tweezers.

☞ **No acid should be spilled on the material to be analysed before the stopper has been placed on the reaction vessel and the cock has been placed in the measuring position. Dampen the stopper before placing it on the reaction vessel. Subsequently turn the cock down to the measuring position. Repeat this with every reaction vessel.**

By tilting the reaction vessel, the hydrochloric acid flows from the test tube over the material to be analysed and the reaction is initiated. The gas produced will lower the level of the fluid in the burette and raise the level in the buffer vessel. Do not allow this difference in level to exceed 3 ml. If the difference were to exceed 3 ml, the CO_2 would come under pressure, which would increase its solubility in water. This will yield a less accurate result. Shake the reaction vessel every now and again to allow the reaction to proceed to as near completion as possible.
Shake for 5 minutes. When the volume no longer varies, note this volume. If the volume continues to increase, shake until the volume becomes stable (do not shake for longer than 1 hour).

6.2 Calibration

Before calibration weigh 0.2 and 0.4 g (dried) $CaCO_3$ to an accuracy of 1 mg and transfer these quantities to 2 reaction vessels and add 20 ml of water to each of these.
The determinations of the samples and the standards commence with a starting level of 3 ml; this is set using the buffer vessels.
The starting level of 3 ml is required to allow the water level in the burette to rise. This may sometimes occur in practice when almost no CO_2 evolves, but a small quantity is absorbed.
Place the reaction vessels on the calcimeter so that there is no further need to move them.
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Shake for 5 minutes. When the volume no longer varies, note this volume. If the volume continues to increase, shake until the volume becomes stable (do not shake for longer than 1 hour). (The measured values lie round 40 and 80 ml CO_2).

6.3 Soil sample (analysis sample)

For the preliminary determination, weigh the correct quantity of prepared samples to an accuracy of 1 mg. Transfer this quantity to a reaction vessel and add 20 ml of water.
Place the reaction vessels on the calcimeter so that there is no further need to move them.
Now fill a small test tube with 7 ml hydrochloric acid and place it in a reaction vessel using a pair of tweezers.

☞ **No acid should be spilled on the material to be analysed before the stopper has been placed on the reaction vessel and the cock has been placed in the measuring position. Dampen the stopper before placing it on the reaction vessel. Subsequently turn the cock down to the measuring position. Repeat this with every reaction vessel.**

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Shake for 5 minutes. When the volume no longer varies, note this volume. If the volume continues to increase, shake until the volume becomes stable (do not shake for longer than 1 hour).

For soil containing carbonates that are harder to dissolve, such as shells, this may take somewhat longer. It is generally accepted that the reaction is complete when no further bubbling can be observed. Bring the burette and the buffer vessel to the same level and read the volume. If this has been done for all five reaction vessels, the measurement is complete.

7. Notes

- The change in volume during the determination of the blanks should not exceed 1.0 ml.
- More water should be added to soil with a high content of organic material.
- Other gasses produced (e.g. hydrogen sulfide in anaerobic sulfide containing soil) leads to an overestimation of the carbonate content. In these cases the produced gas should be purified after which the produced CO_2 can be quantified in an other way.

☞ **Do not use solvents and cleaning agents when cleaning the device (especially the synthetic parts).**

8. Calculation

Calculate the changes in volume of the gas produced by the sample (V_1), the calcium carbonate standards (V_2) and the blanks (V_3) by subtracting the initial value in the calibrated tube from the final value. The carbonate content is calculated with the formula:

$$w\,(CaCo_3) = 1000 \times \frac{m_2\,(V_1 - V_3)}{m_1\,(V_2 - V_3)} \times \frac{100 + w(H_2O)}{100}$$

Where:

$w\,(CaCo_3)$ = the carbonate content =, in grams per kilogram, of the oven-dried soil
m_1 = the mass, in grams, of the test portion
m_2 = the mean mass, in grams, of the calcium carbonate standards
V_1 = the volume, in millilitres, of carbon dioxide produced by reaction of the test portion
V_2 = the mean volume, in millilitres, of carbon dioxide produced by the calcium carbonate standards
V_3 = the volume change, in millilitres, in the blank determinations (this value can be negative)
$w(H_2O)$ = the water content, expressed as a percentage by mass, of the dried sample, determined according to ISO 11465

The result is rounded to a whole number.

9. Repeatability

The difference between two singular measuring results, obtained under repeatable circumstances should not exceed the values indicated in table 2 of NEN-ISO 10693, page 5, paragraph 9.

Carbonate content g/kg	**Acceptable differences**
0 till 50	3 g/kg
> 50 till 150	6% of the value
> 150 till 180	9 g/kg
> 180	5% of the value

10. Standards

More information on sample preparation, calculations and repeatability can be found in the standard ISO 10693.