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BSI Standards Publication

# Liming materials — Determination of the amount of residual finely ground carbonate in soils — Volumetric method

## National foreword

This Published Document is the UK implementation of CEN/TS 16375:2013.

The UK participation in its preparation was entrusted to Technical Committee CII/37, Fertilisers and related chemicals.

A list of organizations represented on this committee can be obtained on request to its secretary.

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**CEN/TS 16375**

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English Version

# Liming materials - Determination of the amount of residual finely ground carbonate in soils - Volumetric method

Amendements minéraux basiques - Détermination de la teneur en carbonate résiduel finement broyé dans les sols - Méthode volumétrique

Calcium-/Magnesium-Bodenverbesserungsmittel - Bestimmung der Menge feingemahlener Carbonatrückstände in Böden - Volumetrisches Verfahren

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# Contents

# Foreword

This document (CEN/TS 16375:2013) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

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# 1 Scope

This Technical Specification specifies a method for the determination of low contents (as < 5 g $CaCO_3$ per kilogram) of carbonate in soil samples. It applies to any type of carbonate liming material, such as limestone, chalk, and dolomite.

# 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

# 3 Principle

Hydrochloric acid is added to a soil sample to decompose any carbonates present. The reaction in simplified form reads as follows (Me means metal):

$$MeCO_3 + 2H^+ \rightarrow Me^{2+} + H_2CO_3$$

$$H_2CO_3 \rightarrow H_2O + CO_2 \text{ (gaseous)}$$

The volume of the carbon dioxide produced is measured with a measuring burette, and is compared with the volume of gas produced by increasing amounts of calcium carbonate added to test portions. To avoid making corrections for differences in temperature and pressure, all determinations are carried out under the same conditions, with a very strict control of ambient conditions and determination timing, e.g. air-conditioned room and water bath, short time during which the variation of atmospheric pressure is supposed to be constant.

# 4 Reagents

Use only reagents of recognized analytical grade.

**4.1 Water**, with a specific electrical conductivity not higher than 0,2 mS/m at 25 °C (conforming to grade 2 of EN ISO 3696).

**4.2 Hydrochloric acid**, $c$(HCl) = 4 mol/l.

Dilute 340 ml of 37 % hydrochloric acid in water (4.1) and then fill up to 1 000 ml with water (4.1).

**4.3 Sulfuric acid**, ($H_2SO_4$) solution 95 % to 97 %.

**4.4 Sodium sulfate**, ($Na_2SO_4$), powder, purity higher than 99 %.

**4.5 Internal liquid of the calcimeter**, 50 g/l of sodium sulfate (4.4) and 50 ml/l of sulfuric acid (4.3).

**4.6 Calcium carbonate**, ($CaCO_3$), powder, purity higher than 99 %.

# 5 Apparatus

**5.1 Apparatus for the volumetric measurement of produced gas**, inspired of Bernard calcimeter according to Figure 1.

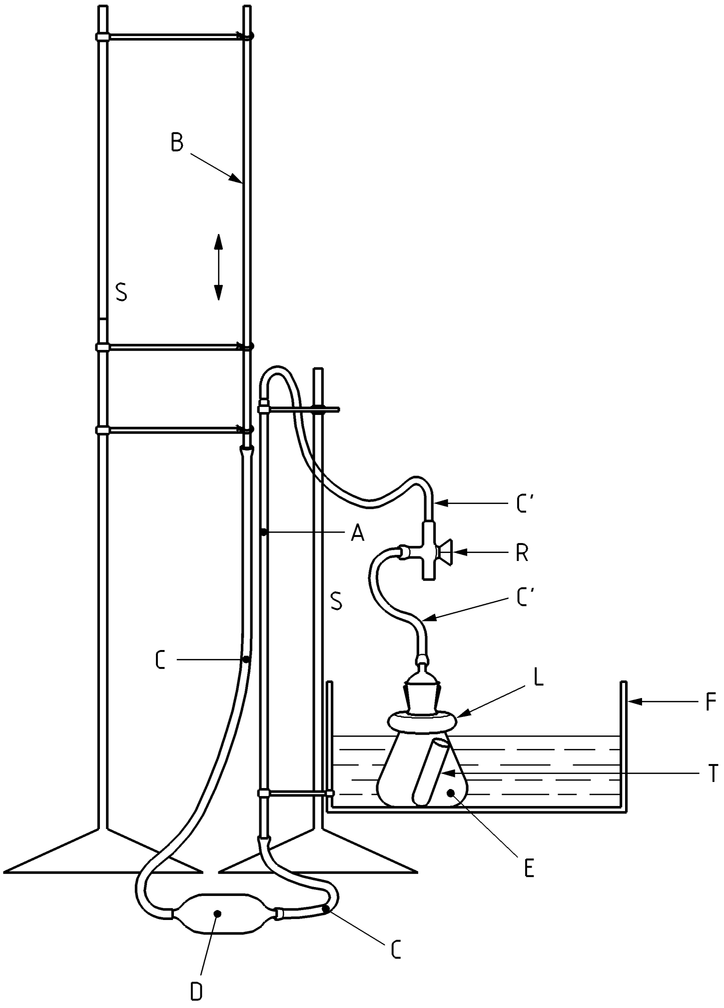
The apparatus is composed of a glass tube of 20 ml graduated every 0,02 ml. The total length shall not exceed 80 cm. Another non graduated glass tube with the same length and the same diameter is connected to the first glass tube with a transparent flexible pipe of about 1 m. A small volume of reserve of 50 ml can be inserted right at the inferior end of the graduated tube. The higher end of the graduated tube is connected by a standard flexible pipe to the Erlenmeyer flask (5.2) of attack.

The graduated tube is fixed vertically on a stand.

The non-graduated tube is held on a second stand, parallel to the first, but so that it is vertically mobile. Mark the tube to approximately 2 cm of its lower end.

The two tubes shall only be 1 mm or 2 mm away from each other.

The whole apparatus shall be dipped several hours in a surface-active cleaning liquid to eliminate any trace on the interior surface of the tubes which could hinder circulation and modify the levelling of the internal liquid. Rinse with demineralised water after treatment.



**Key**

| | |
|---|---|
| A | glass tube of 20 ml graduated every 0,02 ml |
| B | non-graduated tube |
| C | flexible pipe |
| C’ | standard flexible pipe |
| D | bulb of 50 ml |
| E | 200 ml Erlenmeyer flask with finely ground, gas tight glass stopper |
| F | water bath |
| L | metallic ring |
| R | 3 ways tap |
| S | stand |
| T | reaction tube (with hydrochloric acid) |

**Figure 1 — Calcimeter**

**5.2 200 ml Erlenmeyer flask**, with finely ground, gas tight glass stopper.

Erlenmeyer flasks of attack, with a capacity of 200 ml, are closed by a finely ground glass cup. The upper part of the cap is connected by 200 mm of standard flexible pipe to a 3 ways tap of polytetrafluoroethylene, PTFE), which is also connected to the flexible pipe coming from the graduated tube.

The waterproof of the glass cap is ensured by a thin silicone-grease layer.

**5.3 Water bath**, the volume of water shall be of at least 5 l and maintain at room temperature.

**5.4 Metallic ring**.

The Erlenmeyer flask of attack (5.2) is ballasted with a metallic ring and is kept in the water bath.

**5.5 Thermo stated room**.

The whole device is placed in a thermo stated room of a great thermal inertia or fit with a device of cold-hot regulation which ensures an uninterrupted constant temperature to ± 1 °C. Check the room temperature changes close to the device for 1 h.

The analysis may only start when the water bath temperature is equal to the room temperature.

Absence of important atmospheric pressure variation during the analysis shall be checked to the regional weather services.

**5.6 Glass tubes**, capacity of 20 ml.

Each tube shall have a length such to allow that:

- it can be vertically introduced into the Erlenmeyer flask using a finger,
- it can be maintained in sub-vertical position in the Erlenmeyer flask without its contents pours out,
- its contents can be completely emptied in the Erlenmeyer flask by inclining the Erlenmeyer flask at an angle lower than 90°.

**5.7 Thermometer**, with an accuracy of 0,2 °C.

**5.8 Analytical balance**, with an accuracy of 0,01 mg.

**5.9 Stop watch**.

# 6 Procedure

## 6.1 Preparation of the apparatus

**6.1.1** Fill the apparatus with the internal liquid (4.5). Use a small funnel connected by a flexible pipe at the higher end of the non-graduated tube. Eliminate air bubbles.

**6.1.2** Fill the tube until the liquid level match with the first higher graduation (position zero) of the graduated tube and the mark traced in the lower part of the non-graduated tube.

**6.1.3** Make sure that the two meniscuses' positions are on the same horizontal level (the apparatus is not connected to the Erlenmeyer flask at this point).

**6.1.4** Make the non-graduated tube slide downwards. The volume of liquid then goes down the graduated tube. Check, in several points of volume, the horizontal coincidence of the meniscuses.

**6.1.5** Reset the meniscuses to position zero.

**6.1.6** Lay the water bath close to the device.

**6.1.7** Let the whole device stabilize thermically for 0,5 h.

**6.1.8** Check that the water bath temperature is equal to the room temperature.

### 6.2 Sample preparation

NOTE Particular care is necessary to prepare the sample.

**6.2.1** The minimum amount of the sample for the laboratory shall be 500 g.

**6.2.2** Reduce all of the samples taken up to 2 mm, avoiding producing too many fine particles. A pestle and mortar should be used because they are undoubtedly the best system of crushing.

**6.2.3** Use a sieve with a pore size of 2 mm.

**6.2.4** Introduce the fine soil into a polyethylene flask. Leave an empty volume that shall be at least half of the flask. Stir upside down at 40 $\text{min}^{-1}$ for 2 h.

**6.2.5** Recover the whole sample or a part of the sample prepared in this way for the weighing of test portions.

### 6.3 Measurement procedure

**6.3.1** The reagents used (4.1 and 4.2) shall be at room temperature.

**6.3.2** Add to the Erlenmeyer flask (5.2) containing the test portion, 10 ml of water (4.1). Mix gently for 30 s.

**6.3.3** Pour carefully in a glass tube (5.6) 10 ml of hydrochloric acid (4.2). Avoid any contamination of the acid outside the tube.

**6.3.4** Introduce the tube vertically into the Erlenmeyer flask (5.2), by avoiding any discharge or splashes of acid outside the tube.

**6.3.5** Place the Erlenmeyer flask in the water bath by ballasting it with a metallic ring (5.4).

**6.3.6** Start the stopwatch (5.9), ($t$ = 0).

**6.3.7** Connect the Erlenmeyer flask (5.2) to the calcimeter with a finely ground, gas tight glass stopper slightly lubricated. Open and close the tap to connect the Erlenmeyer flask and the graduated tube.

**6.3.8** Check that the meniscus shows the position zero, if not open and close the tap.

**6.3.9** At time $t$ = 1 min, keep the Erlenmeyer flask at the top of the water bath and pour the acid contained in the tube as quickly as possible, by inclining the Erlenmeyer flask. Shake by hand, with a circular movement for 30 s.

**6.3.10** During this operation, the Erlenmeyer flask shall be handled by the neck not to transfer heat from the hands (use a fabric or a glove).

**6.3.11** Plunge the Erlenmeyer flask in the water bath again.

**6.3.12** Make the tube that is not graduated slide downwards to adjust the two meniscuses to the same level.

**6.3.13** At time $t$ = 3 min, shake the Erlenmeyer flask again as before for 30 s and plunge it again in the water bath.

**6.3.14** At time $t$ = 6 min, make coincide meniscuses on the same horizontal level and read the volume of released $CO_2$ to the nearest 0,02 ml.

**6.3.15** If combined magnesium and calcium is expected, read the volume at 20 min. Shake for 30 s every 5 min (for instance: at 8 min, 13 min, 18 min).

# 7 Method by controlled additions

## 7.1 General

This method is to be used when a sample of soil containing carbonate is not available.

## 7.2 Procedure

**7.2.1** Weigh 5 g, 10 g and 20 g of sample to the nearest 0,001 g in three different Erlenmeyer flasks. Let the Erlenmeyer flasks stabilize thermically close to the calcimeter.

**7.2.2** Begin measurement with the weakest test portion. Determine test portion, $m$, which corresponds to an awaited gas release from approximately 2 ml to 3 ml without going down lower than 2 g.

**7.2.3** Weigh in three different Erlenmeyer flasks the same test portion, $m$.

**7.2.4** In the second Erlenmeyer flask, add approximately 15 mg of powder $CaCO_3$ (4.6).

**7.2.5** In the third Erlenmeyer flask, add approximately 30 mg of powder $CaCO_3$ (4.6).

**7.2.6** Record the exact added weights to 0,01 mg.

**7.2.7** Mix $CaCO_3$ with the soil of the test portion and carry out measurements as indicated in 6.3.

## 7.3 Calculation and expression of the results

Determine by linear regression the relation of calibration between the degassed volume of $CO_2$ and the amount of $CaCO_3$.

Determine the measured volume of $CO_2$, $y_{(1)}$, in millilitre, by linear regression according to Formula (1).

$$y_{(1)} = ax + b \tag{1}$$

where

$x$ is the quantity of $CaCO_3$ added (0 mg; 15 mg; 30 mg);

$a$ is the slope of the linear regression straight line, in milligrams per millilitre;

$b$ is the ordinate value for $x$ = 0, in milligrams.

Calculate the slope, $a$, according to Formula (2) as follows:

$$a = \frac{n(\sum y_i x_i - \sum y_i \sum x_i)}{(n\sum x_i^2 - (\sum x_i^2)^2)} \tag{2}$$

Calculate the ordinate value, $b$, according to Formula (3) as follows:

$$b = \frac{(\sum y_i - a\sum x_i)}{n} \tag{3}$$

where

$x_i$ is the added level of $CaCO_3$: (0; 15; 30) milligrams;

$y_i$ is the measured volume in millilitres;

$n$ is the number of measurements, here $n$ = 3.

NOTE For the use of spread sheet software calculation facilities for the determination of $a$ and $b$ given in Formula (1) see the description in Annex A.

Express the quantity of $CaCO_3$ contained in the test portion by the ratio $\left| b/a \right|$.

Express the concentration in grams per kilograms by the ratio $\left| b/am \right|$ (where $m$ is expressed in grams).

# 8 Method by direct measurement

## 8.1 General

This method requires having a soil sample without any carbonate on which a preliminary calibration is made.

## 8.2 Choice of a pilot soil without carbonate

**8.2.1** Choose a non-hydromorphic soil with a well-balanced texture, with a relatively low content of organic matter, with a pH lower than 6, and containing no carbonate.

**8.2.2** Check with the calcimeter, that the gas volume produced at 6 min for a test portion of 20 g is equal to zero.

## 8.3 Calibration of the calcimeter

### 8.3.1 Procedure

**8.3.1.1** Weigh to the nearest 0,01 g, 20 g of soil without carbonate in a series of six Erlenmeyer flasks.

**8.3.1.2** Add in five Erlenmeyer flasks increasing amounts of powder $CaCO_3$ (4.6), between 5 mg and 40 mg to the nearest 0,01 mg.

**8.3.1.3** Mix carbonate with the soil sample.

**8.3.1.4** Carry out the measurements of these standards as indicated in 6.3.

### 8.3.2 Calculation and expression of the result

Determine by linear regression the relation of calibration between the amount of $CaCO_3$ added and the degassed volume.

Determine the added amount of $CaCO_3$, $y_{(4)}$, (0; 5 to 40), in milligrams, by linear regression according to Formula (4).

$$y_{(4)} = ax + b \tag{4}$$

where

$x$ is the measured volume, in millilitres;

$a$ is the slope of the linear regression straight line, in miligrams per millilitre;

$b$ is the ordinate value for $x$ = 0, in milligrams.

Calculate the slope, $a$, according to Formula (5) as follows:

$$a = \frac{n(\sum y_i x_i - \sum y_i \sum x_i)}{(n\sum x_i^2 - (\sum x_i^2)^2)} \qquad (5)$$

Calculate the ordinate value, $b$, according to Formula (6) as follows:

$$b = \frac{(\sum y_i - a\sum x_i)}{n} \qquad (6)$$

where

$y_i$ is the added level of $CaCO_3$: (0; 5 to 40) milligrams;

$x_i$ is the measured volume in millilitres;

$n$ is the number of measurements, here $n$ = 6.

NOTE For the use of spread sheet software calculation facilities for the determination of $a$ and $b$ given in Formula (4) see the description in Annex A.

## 8.4 Measurement of an unknown sample

### 8.4.1 Procedure

**8.4.1.1** Weigh 20 g ($m$) of sample to the nearest 0,01 g.

**8.4.1.2** If the amount of present carbonate involves a production of $CO_2$ exceeding the volume of the burette, the test portion may be reduced to 10 g.

**8.4.1.3** For a test portion lower than 10 g, calibrate the apparatus on a corresponding basis of pilot soil without carbonate.

**8.4.1.4** Immediately after the calibration of the apparatus, measure the unknown sample.

**8.4.1.5** Make a second measurement and calculate the average volume.

### 8.4.2 Calculation and expression of the results

Calculate the mass fraction, $w$, of $CaCO_3$ in grams per kilogram according to Formula (7).

$$w = (aV + b)/m \qquad (7)$$

where

$V$ is the average degassed volume, in millilitres;

$m$ is the mass of the test portion in grams.

Correct the content of $CaCO_3$ of the residual moisture of the prepared soil for the analysis to express the result on dry matter basis at 105 °C.

# 9 Precision

## 9.1 Inter-laboratory test

An inter-laboratory test has been carried out in 2010 with four participating laboratories and three different samples of limed soil. This test yielded the data given in Table 1. Repeatability and reproducibility were calculated according to ISO 5725-2. The values derived from this inter-laboratory test may not be applicable to concentration ranges and matrices other than those given in Table 1.

## 9.2 Repeatability

The absolute difference between two independent single test results, obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will in no more than 5 % of the cases exceed the values of *r* given in Table 1.

## 9.3 Reproducibility

The absolute difference between two single test results, obtained with the same method on identical test material in different laboratories by different operators using different equipment, will in no more than 5 % of the cases exceed the values of *R* given in Table 1.

**Table 1 — Mean values, repeatability and reproducibility limits**

| **Sample** Controlled amount $CaCO_3$ g/kg | **Number of labs** | **Mean value** g/kg | *r* | *R* | *r* % | *R* % |
|---|---|---|---|---|---|---|
| 0,0 | 2 | 0,056 | 0,054 | 0,055 | 96,33 | 98,10 |
| 0,4 | 4 | 0,399 | 0,089 | 0,166 | 22,34 | 41,69 |
| 0,9 | 4 | 0,865 | 0,109 | 0,154 | 12,62 | 17,86 |

## 10 Test report

The test report shall contain at least the following information:

a) all information necessary for the complete identification of the sample;

b) the test method used with reference to this document (CEN/TS 16375);

c) the test results obtained;

d) date of sampling and sampling procedure (if known);

e) date when the analysis was finished;

f) whether the requirement of the repeatability limit has been fulfilled;

g) all operating details not specified in this document, or regarded as optional, together with details of any incidents occurred when performing the method, which might have influenced the test result(s).

# Annex A
(informative)

## Using spread sheet software to calculate linear regression

For the use of spread sheet software calculation facilities for the determination of $a$ and $b$ given in Formula (1) and Formula (4) Table A.1 and the following description as an example is given.

**Table A.1 — Table of values**

| Cell reference | Column A | Column B |
|---|---|---|
| Line 1 | X | Y |
| Line 2 | 0 | 2 |
| Line 3 | 10 | 38 |
| Line 4 | 20 | 83 |
| Line 5 | 30 | 115 |

Explanation of the steps:

- Select the grey area.
- Click on the graphic assistant in the tool bar.
- Ask for a graphic representing data as a cloud of points on an X/Y scheme.
- You get a first graphic with your points.
- Then ask for the representation of a trend curve in the scrolling graphic possibilities.
- Choose the linear regression model and tick the regression formula display option.

You will then get on the same X/Y scheme:

- your $x\ y$ points,
- the linear trend straight line,
- the formula $y = ax + b$.

In the example: $y = 3{,}84x + 1{,}9$.

# Bibliography

[1] ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

[2] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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