

BS EN 16357:2013



BSI Standards Publication

**Carbonate liming materials —
Determination of reactivity —
Automatic titration method
with citric acid**

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National foreword

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

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Carbonate liming materials - Determination of reactivity - Automatic titration method with citric acid

Amendements minéraux basiques carbonatés -
Détermination de la réactivité - Méthode par titration
automatique à l'acide citrique

Carbonatische Kalke - Bestimmung der Reaktivität -
Automatisches Titrationsverfahren mit Citronensäure

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Foreword

This document (EN 16357:2013) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2014, and conflicting national standards shall be withdrawn at the latest by February 2014.

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Introduction

This method has been prepared to improve existing agricultural reactivity methods (see [1], [2], [3], [4] and [5]) for carbonate liming materials: duration, accuracy, representativeness, closer from soil conditions, automation.

Attention is drawn to the following critical steps:

- identification of the liming material type (influence on precision data);
- size distribution (influence on test portion preparation and amount);
- calibration of pH electrode (influence on titrator's pH adjustments);
- pH stat programme setting (influence on accuracy of added amounts of citric acid solution);
- suitability of PCC used to check calibration;
- stirring device (provides homogeneousness without grinding);
- additional uncertainty with neutralising value and MgO content determination.

1 Scope

This European Standard specifies a method for the determination of the reactivity of calcium carbonate and calcium magnesium carbonate liming materials. It assesses the speed and effectiveness of their neutralising potential by automatic titration with citric acid.

This method is applicable only to liming materials with a maximum particle size of 6,3 mm determined according to EN 12948.

NOTE For marble dolomite (BET procedure according to ISO 9277 below 500 m²/kg), see EN 14984.

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 1482-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

EN 12048, *Solid fertilizers and liming materials — Determination of moisture content — Gravimetric method by drying at (105 +/- 2) °C (ISO 8190, modified)*

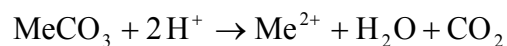
EN 12945, *Liming materials — Determination of neutralizing value — Titrimetric methods*

EN 12948, *Liming materials — Determination of size distribution by dry and wet sieving*

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

3 Principle

Limited decomposition of carbonates in a given time with acid according to the following reaction:



Titration under stable pH conditions (pH 4,5) with an automatic titration apparatus. The citric acid consumption during a given time (15 min) is a direct measure for the reaction of the liming materials being tested.

4 Apparatus

Usual laboratory apparatus and, in particular, the following:

4.1 pH meter with electrode.

This instrument is generally included in the automatic motor driven burette device.

4.2 Automatic motor driven burette, capacity 20 ml.

This kind of burette is generally equipped with all necessary accessories such as pH regulation programme (pH stat), automatic refilling device, pH electrode, continuous pH measurement and propeller stirring device.

Though a propeller stirring device is preferred, a magnetic stirring device (4.7) may be used, provided the central ring of the stirrer rod is thick enough and does not lead to grind the tested material. Make sure the rotation speed of the stirrer rod is fast enough to make homogeneous dispersion in the beaker. If not, increase the speed up to the necessary value.

The burette shall be able to deliver at least 0,05 ml of citric acid solution (5.3) per second. This is to ensure the first part of the reaction (pH dropping from initial pH value to target pH value (4,5) will not be a limiting factor for liming material dissolution speed). This figure is higher than the flow rate obtained with the fastest reaction observed in preliminary tests.

The burette shall be able to deliver its whole content in at least 4 000 steps to ensure accuracy for low amount of citric acid solution (5.3).

NOTE This condition is always fulfilled with modern titrators. All contemporary (less than 10 years old) titrators allow such accuracy: i.e. minimum step amount: 0,002 5 ml for a 10 ml burette, or 0,012 5 ml for a 50 ml burette. This is sufficient, even for low amounts. However, this accuracy is obtained only if correct (minimal) step volume in titrator setup is specified. If not, the precision of the method will be altered.

Use the burette only for the citric acid solution (5.3).

For liming materials coarser than 1 mm, use a 50 ml burette.

For most of products, a 10 ml burette is sufficient. However, a 20 ml burette is necessary for highly reactive chinks and precipitated calcium carbonate. Because refilling takes a significant time, this can bias the results. If volumes higher than 10 ml are expected, do not use the automatic refilling possibility and use a 20 ml or a 50 ml burette.

4.3 Glass beaker, capacity 100 ml.

For liming materials coarser than 1 mm, use a 200 ml beaker.

Minimum diameter in case of magnetic stirring device (4.7): 50 mm.

4.4 Stop-watch.

4.5 Balance, capable of weighing 10 g to the nearest 0,01 g.

4.6 Sample changer, optional.

If occurring, a beaker of water (5.1) shall be inserted between two samples.

4.7 Magnetic stirring device, optional, see 4.2.

Capable of minimum 500 min⁻¹ speed rotation.

Stirrer rod minimum length: 40 mm.

5 Reagents

All reagents shall be of recognised analytical grade.

5.1 Water, according to EN ISO 3696, grade 2.

5.2 Mono hydrated citric acid, C₆H₈O₇ · H₂O, crystallised or powder, molar mass: 210,14 g.

Do not use anhydrous citric acid having a different molar mass, which can partially hydrate when storing.

5.3 Citric acid solution, $\rho = 457,17$ g/l.

Preferably, use a fresh home-made solution as described below. Under these conditions, the solution concentration is conventionally supposed to be equal to the necessary one, $\rho_{ca} = 457,17$ g pure citric acid per litre.

The solution may be used for up to, at most, one month stored in a closed, dark glass vessel. If the solution has been stored more than one week, check its concentration by any means, for example by titration with a strong base (NaOH) solution of known concentration and report the result in the formula given in Clause 8.

Weigh 500 g of mono hydrated citric acid (5.2) to the nearest 0,1 g. Pour it quantitatively into a 1 l measuring vessel. Rinse the weighing material and pour the rinsing water into the vessel in a way that it takes any acid stuck on the edge or on the bottom. Add about 500 ml of water (5.1) to the measuring vessel. Heat the vessel until full dissolution (temperature about 80 °C). Let the vessel cool to ambient temperature. Make up to the volume with water to 1 l. Stir to get a homogeneous solution.

The pure citric acid content, ρ_{ca} , ($C_6H_8O_7$), in grams per litre of this solution is calculated according to Formula (1) as follows.

$$\rho_{ca} = \frac{500 \times 192,14}{210,14} = 457,17 \quad (1)$$

where

500 is the added mass of mono hydrated citric acid (5.2), in grams;

192,14 is the molar mass of anhydrous citric acid, in grams;

210,14 is the molar mass of mono hydrated citric acid, in grams.

5.4 Calcium carbonate, precipitated (or PCC), mass fraction, $w(CaCO_3)$ at least 99 %.

Commercial PCC for analysis is granted for its chemical characteristics. However, physical characteristics are not granted. As reactivity depends on fineness, even for PCC, it is essential to take as a reference a highly reactive PCC, such as commercial PCC from VWR / Prolabo / BDH, reference GPR, Rectapur, Ref 22296.294, Molar mass 100,09¹⁾, which will consume 15 ml after 15 min. This PCC was used in the ring test before launching measurements. By experience, some PCC do not meet this requirement. See also the note in 7.2.6.

5.5 Silicone defoamer.

5.6 Standard buffer solution, pH 4 (commercial solution, pH 4,01).

NOTE This solution has a limited lifetime.

5.7 Standard buffer solution, pH 7 (commercial solution, pH 6,98).

NOTE This solution has a limited lifetime.

6 Sampling and sample preparation

6.1 General

Sampling is not part of the methods specified in this document. A recommended sampling method is given in EN 1482-1.

Sample preparation shall be carried out in accordance with EN 1482-2.

1) This substance is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

This document specifies that samples are tested "as received" in order to allow immediate starting of all the necessary measurements (NV, MgO). No preliminary determination is required to calculate tested sample mass. However, make sure that sample moisture is the same in the reactivity test portion as in the neutralising value measurement.

Correcting factors are to be applied later on in the expression of results: actual citric acid concentration, exact mass of sample, as received neutralising value, MgO content. Such a procedure shortens the total necessary time for analysis because required measurements are made simultaneously, instead of successively. However, additional uncertainty introduced by the correction factors is not described in this document. Precision data mentioned in Clause 9 do not take into account this additional uncertainty. All implemented correction factors should be evaluated to quantify the additional uncertainty they introduce to expression of the reactivity.

NOTE This procedure is also better than drying the sample first and then titrate, because drying can perhaps modify fineness or physical presentation and consequently reactivity of some products.

6.2 Preparation of the test sample

Measure the moisture content of the tested material in accordance with EN 12048 and record the result for information.

Make sure there is no oxide or hydroxide in the material to be tested (pH with 1/10 dilution shall be below pH 10). An oxide or hydroxide fraction in the product will bias the result. Oxide or hydroxide chemical forms are not included in the scope of this method.

Use the test sample without any further preparation, e.g. grinding or drying.

NOTE The procedure (7.3.2) includes a standardized time of preliminary stirring.

6.3 Preparation of the test portion

Weigh 5,0 g of the test sample as received to the nearest 0,01 g, between 4,8 g and 5,2 g and record it.

For liming materials coarser than 1 mm, or presenting a presumable heterogeneousness, the test portion shall be prepared fraction wise in accordance with Annex A, and a test portion of 10 g shall be taken instead of 5 g. This can happen even if material particle size is finer than 1 mm. Keep in mind that representativeness of the product as delivered in the 5 g or 10 g test portion is the most important point.

Note that fraction wise sampling gives additional uncertainty. Consequently, this procedure (fraction wise sampling) should be used only if really necessary, otherwise, just increase the test portion up to 10 g.

7 Procedure

7.1 General

The determination shall be made under usual laboratory conditions, e.g. ambient temperature of (20 ± 2) °C.

Reagents shall be at the same room temperature.

As this method does not use a total but a partial reaction in a limited time, accuracy of results will strongly depend on trained and skilled staff. Do not proceed to measurements until it gets familiar with the method.

7.2 Calibrations

7.2.1 Calibrate the pH meter (4.1 or 4.2) with two buffer solutions, pH 4 (5.6) and pH 7 (5.7) to exactly the indicated values before each series of measurement. The pH electrode shall react quickly. Check that it can change from pH 4 to pH 7 within 5 s.

Check the sluggishness of the electrode and if necessary, clean it carefully with citric acid solution (5.3) and re-calibrate with the standard buffer solutions.

If the pH regulation system only accepts mV instead of pH as target value, register mV values during calibration at pH 4 and pH 7 and calculate by interpolation the mV value corresponding to the pH target value as 4,5.

This mV value may vary in the time for the same pH electrode.

This value has to be calculated each time a new series is being processed, just after calibration.

Checking and cleaning is more frequently required for liming materials containing clay.

7.2.2 Select the pH regulation programme (generally called "pH stat") and run set up adjustments.

A titration includes two successive steps that both consume citric acid solution. First, the pH lowers from about pH 9 to the targeted pH 4,5. Then, the regulation allows small solution flushes to keep the targeted pH. Some titrators allow dividing the titration into these two steps. They are called 'pretitration' (to reach target pH) and 'titration' or 'pH stat' (to maintain target pH). In this method, the lowering pH phase is part of the reaction, and shall not be removed. Choose the 'no pretitration' option in order to get the total consumption of solution (phase 1 + phase 2).

Generally, during titration, the target pH is obtained within 30 s to 2 min, depending on tested materials.

Let the system make an addition of citric acid solution as soon as deviations are higher than 0,01 pH (or 0,01 mV if the system only accepts target values as mV).

The system shall be able to deliver at least an amount of 0,5 ml within 10 s. This is to ensure that even with most reactive products, the flow rate will not be a limiting factor for the reaction.

Adjust the titration control so that the stepwise run of the titration is 0,001 ml. Set pH 4,5 as target pH value. Set the stirring device speed control to between 500 min^{-1} and 600 min^{-1} .

With automatic sample changer (4.6), programme a 30 s stirring time before beginning titration.

Set the end of reaction to 15 min. Even when target pH is reached, the reaction can continue, so the measurement shall be taken after precisely 15 min.

With automatic change of sample, insert a blank water (5.1) sample between two measurements, and programme the device to allow the stirrer to run during 30 s to rinse the pH electrode and if necessary (dolomites), flush 1 ml or 2 ml of solution to clean the capillary pipe. In case of samples containing clay (chalks), make sure the electrode remains clean.

NOTE In case of very reactive products, small projections can happen and particles can stick on the electrode or on top part of the beaker. This can bias results.

7.2.3 Fill the burette (4.2) with citric acid solution (5.3).

7.2.4 If required (see 5.3), check the effective concentration of citric acid solution (5.3) and record it.

An old solution can be more concentrated and will modify results. Using a fresh solution is recommended.

7.2.5 Set up the electrode (4.1 or 4.2) and the capillary pipe in the glass beaker (4.3) according to Figure B.1. In the reaction beaker, the stirring device shall be located in the middle. The pH electrode shall be 3/4 round after acid introduction pipe (see Figure B.1). This is to make sure that the added citric acid solution (5.3) is mixed with the content of the glass beaker before reaching the electrode (4.1 or 4.2). Avoid contact with the edge of the glass beaker.

7.2.6 For the exact adjustment of the operating conditions, start the stirrer device (4.2) and add $(5,00 \pm 0,01)$ g of precipitated calcium carbonate (5.4) to the stirred water in the glass beaker (4.3). Start the stop-watch (4.6) and commence the titration, by automatic addition of the citric acid solution (5.3) aiming the pH target value (7.2.2).

Check that the citric acid solution consumption is $(15,0 \pm 0,5)$ ml of citric acid (5.3) after 15 min. If the consumption of citric acid solution is below 14 ml, it can mean either:

- a) the PCC (5.4) is not of the correct analytical grade for its physical characteristics. This can happen because only chemical values are granted. Consumption below 10 ml will always mean that the used PCC is not suitable; or
- b) the settings of operating conditions are not correct and give lower values than expected.

In cases a) or b), first make sure operating conditions are as described in this document. Then test a highly reactive fine soft chalk. Generally, it approximately consumes an amount of 10 ml citric acid and PCC is assumed to reach much higher values (about 15 ml).

If chalk gives higher results than PCC, the relative results are not as expected, and the reference PCC is to be changed for another origin with higher reactivity. Test several PCCs until 15 ml consumption is obtained.

If chalk gives lower results than PCC (good relative results), check again the operating conditions.

NOTE Checking citric acid consumption for PCC is only an additional checking. The volume consumed with PCC is only used to check calibration. It does not have any influence on results themselves. If operating conditions are properly set, the results can be trusted, whatever the PCC.

If the material being tested foams very strongly, one drop of silicon defoamer (5.5) should be added to the solution.

7.3 Measurement

7.3.1 Set up the apparatus as described in 7.2.1 to 7.2.6.

7.3.2 Pour the weighed test portion (see 6.3) into the glass beaker (4.3). Pour water (5.1) in the 100 ml beaker (4.3) and adjust the level to 80 ml. For liming materials coarser than 1 mm, use a 200 ml beaker and adjust to 160 ml. Let the stirrer device run for 30 s. Start the stop-watch (4.6) and the titration procedure. In case of samples containing clay (chalks), clean the pH electrode after each titration.

NOTE In case of very reactive products, small projections can happen and particles can stick on the electrode or on top edge of the beaker. This can bias results.

7.3.3 Stop the titration after 15 min and record the amount of citric acid solution consumed with three significant figures.

7.3.4 Rinse and clean the pH electrode with water (5.1). Do not use a former rinsing beaker. Cleaning the pH electrode can require stronger cleaning solutions than water, depending on tested products. It is recommended to clean the pH electrode with a specific cleaning solution once every day.

For low reactive materials, i.e. that require less than 2 ml solution, such as dolomites, it is necessary to flush 1 ml or 2 ml of citric acid solution (5.3) after rinsing and cleaning to avoid capillary pipe contamination by the former sample.

NOTE With an automatic sample changer, these different steps can be pre-set and are automatically processed once beakers with samples and water have been prepared. As carbonates are nearly insoluble in water, the preliminary duration of contact between carbonate and water will have no influence.

7.3.5 Carry out the titration three times for each product to be tested. Take the mean acid consumption of the three titrations and record this average amount of citric acid solution (5.3) used.

7.4 Determination of neutralising value

Determine the neutralising value of the test sample as received in accordance with EN 12945, and record the result to the nearest 0,1 unit.

7.5 Determination of MgO content

Determine the MgO content of the test sample as received in accordance with a suitable method such as EN 12946 or EN 12947, and record it.

8 Calculation and expression of the results

Calculate the citric acid reactivity, R_{CA} , expressed in percentages of the liming material being tested, using Formula (2).

$$R_{CA} = 100 \times \left[\frac{V_{CA}}{12} \right] \times \left[\frac{C_{CA}}{457,17} \right] \times \left[\frac{5}{m_t} \right] \times \left[\frac{56}{NV_{AR}} \right] \times \left[\frac{((4-1) \times \text{MgO})}{21} + 1 \right] \quad (2)$$

where

V_{CA} is the mean volume consumption (7.3.5) of citric acid solution (5.3), in millilitres;

12 is the conventional reference amount, in millilitres, which the mean consumption is compared to;

C_{CA} is the actual concentration, in grams per litre, of the citric acid solution (5.3 and 7.2.4);

457,17 is the nominal concentration, in grams per litre of the citric acid solution (5.3);

5,0 is the dried standardized amount to be tested, in grams;

m_t is the mass of the as received test portion (see 6.3) of liming material, in grams;

56 is the neutralising value of pure dry calcium carbonate;

NV_{AR} is the neutralising value of the test sample, expressed on an as received basis (see 7.4);

MgO is the MgO content expressed in percent of as received product (see 7.5).

NOTE 1 MgO content is used to define a multiplying coefficient linked to MgO content that is equal to 1 when the sample contains no dolomite (0 % MgO), and equal to 4 when sample contains only dolomite (21 % MgO). This is made to balance the low rate of dissolution of dolomite in this conventional test, where dolomite is known to be more efficient in field conditions, even if less than calcium carbonates.

NOTE 2 For materials coarser than 1 mm, as both V_{CA} and m_t are multiplied, Formula (2) remains valid.

NOTE 3 For precipitated calcium carbonate or for exceptionally reactive materials, R_{CA} can exceed 100 %. This is normal, due to the conventional consumption reference (12 ml, where PCC gives 15 ml).

NOTE 4 R_{CA} is not a percentage of total possible dissolution (31,48 ml) (see [6]). It is only a percentage of conventional consumption reference (12 ml) made to express results in a traditional range from 0 % to about 100 % for nearly all traditional liming materials.

NOTE 5 Keep in mind that the reaction is stopped early before total dissolution. It allows quick assessment of material reactivity. Waiting total dissolution would be senseless, because citric acid is added in unlimited amounts. In such conditions, all products would have the same reactivity.

NOTE 6 Reactivity percentage, wrongly considered as a dissolution rate, does not mean that undissolved part will never react in soil. Field conditions of dissolution can bring different dissolution rates. It only gives an idea of the reaction speed of the material.

NOTE 7 For wet products, which are tested as received, moisture is taken into account through the as received neutralising value correction factor used in Formula (2).

9 Precision

9.1 Inter-laboratory tests

The precision data were derived from an inter-laboratory test involving 16 participants carried out in the year 2010 and analysing a range of several liming materials including limestone, dolomitic limestone, magnesian limestone and chalk of varying fineness or presentation. As some deviations obviously resulted from a lack of experience or training, which is not expected in routine measurement, all data coming from laboratories giving a mean value out of the range 90 % to 110 % of the median value of the level were been eliminated before calculation.

Repeatability and reproducibility were calculated according to ISO 5725-1 and ISO 5725-2.

The values derived from this test might not be applicable to concentration ranges and matrices other than those given.

In order to assess the uncertainty of the method itself, and to avoid uncertainty of correction factors that is cumulative, the statistical treatment of the ring test was made on consumption of citric acid solution (V_{CA}). However, to get the final precision of results, expressed as reactivity (R_{CA}) instead of ml citric acid solution (V_{CA}), laboratories shall consider the precision data of all the used methods mentioned in Formula (2). Otherwise, values in Table 1 underestimate the true uncertainty of the method.

9.2 Repeatability

The absolute difference between two independent single test results, obtained using 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, shall in no more than 5 % of the cases be greater than the repeatability limit r given in Table 1.

9.3 Reproducibility

The absolute difference between two single test results, obtained using the same method on identical test material in different laboratories with different operators using different equipment, shall in no more than 5 % of the cases be greater than the reproducibility limit R given in Table 1.

The repeatability limits, r , and reproducibility limits, R , expressed as absolute and relative percent values, are given in Table 1.

Table 1 — Mean values, repeatability and reproducibility limits

Liming material tested	Fineness 80 % passing μm	Number of laboratories	\bar{x} citric acid consumption ml	Repeatability limit r (absolute)	Reproducibility limit R (absolute)	Repeatability limit r % (relative)	Reproducibility limit R % (relative)
Limestone fine	56	12	6,668	0,693	1,280	10,4	19,2
Limestone coarse	691	14	4,919	0,617	0,816	12,5	16,6
Limestone granulated	3 860	8	6,981	1,120	1,080	16,0	15,5
Dolomite + limestone granulated	5 030	16	2,524	0,212	0,365	8,4	14,5
Magnesian limestone fine	138	11	4,415	0,510	0,721	11,6	16,3
Magnesian limestone coarse	712	14	2,527	0,356	0,453	14,1	17,9
Dolomite fine	113	6	0,627	0,106	0,107	16,9	17,0
Dolomite coarse	340	5	0,299	0,074	0,071	24,7	23,9
Chalk fine	851	10	8,617	0,919	1,200	10,7	13,9
Soft chalk coarse	1 080	11	9,508	1,127	1,404	11,9	14,8

NOTE 1 The analytical data used to calculate r and R is the volume of citric acid solution, in millilitres, poured for exactly 5 g of dry material within 15 min.

NOTE 2 For dolomite, of which r and R were higher in the ring test, the method has been improved to get better repeatability and reproducibility.

10 Test report

The test report shall contain at least the following information:

- a) all details necessary for the identification of the sample;
- b) a reference to this European Standard (EN 16357);
- c) the results and units in which the results have been expressed;
- d) any particular points observed in the course of the test;
- e) all operating details not specified in this document, or regarded as optional, together with details of any incidents that occurred when performing the method and that might have influenced the test result(s).

Annex A (normative)

Preparation of the test portion of liming materials coarser than 1 mm

A.1 General

For liming materials coarser than 1 mm or presenting a presumable heterogeneousness, determine the size distribution by dry sieving according to EN 12948 and store the different fractions. Select a maximum of three test sieves with different principal sizes to cover the range of the particle size expected. Compose the test portion of 5,00 g from the individual sieving fractions according to their proportion of the total test sample.

A.2 Calculation of mass fractions retained on the test sieves

The individual mass fractions of the total test sample, w_n , ($n = 1$ to 3), expressed in percent, shall be calculated using Formula (A.1):

$$w_n = \frac{m_n \times 100}{\sum m_n} \quad (\text{A.1})$$

where

m_n is the mass of the sieving fraction n in grams.

A.3 Calculation of the test portion to be weighed

The test portion $\sum m_i$ ($i = 1$ to 3) composed from the individual sieving fractions shall be calculated using Formula (A.2):

$$\sum m_i = \frac{w_i \times m_t}{100} \quad (\text{A.2})$$

where

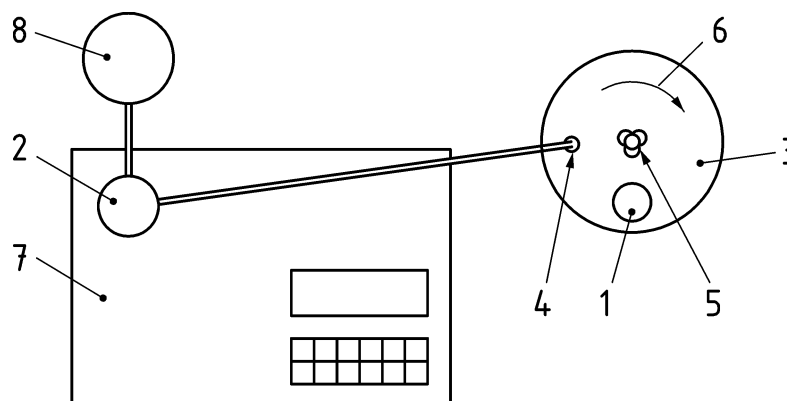
w_i is the mass fraction of individual fraction i of total test sample, in percent;

m_t is the mass of the test portion, in grams (= 5,00 g).

Annex B (normative)

Arrangement of the test apparatus

Arrange the elements of the test apparatus according to Figure B 1.



Key

- 1 pH electrode (4.1)
- 2 burette (4.2)
- 3 beaker (4.3)
- 4 citric acid solution introduction capillary pipe
- 5 stirrer device
- 6 direction of stir
- 7 titrator (4.2)
- 8 citric acid solution vessel (5.3)

Figure B.1 — Arrangement of the test apparatus — Plan view

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