INTERNATIONAL
STANDARD

ISO
11048

First edition
1995-05-01

Soil quality — Determination of water-soluble and acid-soluble sulfate

Qualité du sol — Dosage du sulfate soluble dans l'eau et dans l'acide

Reference number
ISO 11048:1995(E)

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11048 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Annex A of this International Standard is for information only.

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Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

Soil quality — Determination of water-soluble and acid-soluble sulfate

Section 1: General

1.1 Scope

This International Standard specifies procedures for the preparation of water and acid extracts of air-dried soils and soil-like materials. The sulfate content of these extracts is determined by a gravimetric method in which barium chloride is added to the water or acid extract and the precipitate of barium sulfate is dried and weighed. The sulfate content is then calculated from the mass of the material used in the analysis and the mass of barium sulfate precipitated.

This International Standard is applicable to all types of air-dried soils, for example pretreated according to ISO 11464.

This International Standard consists of seven sections:

Section 1: General

Section 2: Pretreatment of samples and determination of dry matter contents

Section 3: Extraction of soil with water at a mass:volume ratio of 1 soil:5 water

Section 4: Extraction of soil with water at a mass:volume ratio of 1 soil:2 water

Section 5: Extraction of soil with dilute hydrochloric acid

Section 6: Determination of sulfate in solution by a gravimetric method using barium chloride

Section 7: Precision of method and test report

1.2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 9280:1990, *Water quality — Determination of sulfate — Gravimetric method using barium chloride.*

ISO 11464:1994, *Soil quality — Pretreatment of samples for physico-chemical analyses.*

ISO 11465:1993, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method.*

1.3 Principle

Samples of air-dried soil are extracted with:

— dilute hydrochloric acid; or

— water in a mass:volume ratio of soil:water of 1:2 or 1:5.

The sulfate content of these extracts is determined by a gravimetric method in which barium chloride is added to the water or acid extract and the precipitate of barium sulfate is dried and weighed. The sulfate content is then calculated from the mass of soil used in the analysis and the mass of barium sulfate precipitated.

Section 6 is similar to ISO 9280.

It is recognized that other acceptable methods for the determination of sulfate are available but these are not covered by this International Standard. Suitable methods may include: direct barium titrimetry, inductively coupled plasma emission spectrometry, flow injection analysis using a turbidimetric method, continuous flow indirect spectrophotometry using 2-aminoperimidine, air-segmented continuous flow colorimetry using methylthymol blue, and ion chromatography. Reference should be made to the appropriate international and national standards for information regarding the applicability and limitations of such methods.

1.4 Applicability and limitations

The procedures in sections 3 and 4 are considered to be relevant to the extraction of sulfate from soils and may be relevant to the assessment of the "availability" of sulfate to plants (a variety of extractants have been used for this purpose and none were shown to be generally applicable to all soil types and climates). It should be noted that there is no verified relation between water-extractable sulfate and the need for sulfur fertilization. The procedure in section 4 is also relevant to the potential for the attack of sulfates on building materials, especially concrete.

The use of the procedures described in sections 4, 5 and 6 should enable a distinction to be made between the presence of sulfates that are highly soluble in water and those of limited solubility such as gypsum ($CaSO_4 \cdot 2H_2O$).

Section 6 is applicable to concentrations of sulfate ion (SO_4^{2-}) in solution of 10 mg/l and above, i.e. in relation to the methods in sections 3 and 4 to minimum water-soluble concentrations in air-dried soil of about 50 mg/kg and 20 mg/kg [0,005 % (*m/m*) and 0,002 % (*m/m*)] respectively and, in relation to the method in section 5, to a minimum acid-soluble concentration in air-dried soil of about 500 mg/kg [0,05 % (*m/m*)].

If concentrations in solution are lower than this, a concentration step will be required, or a more sensitive analytical procedure than that described in section 6 should be used [e.g. ion chromatography, inductively coupled plasma (ICP) spectrometry or atomic emission spectrometry (AES)].

In most instances, complete characterization of a soil, in terms of the concentrations and nature of sulfates present, will require that determinations are made following the procedure in section 5 and in either section 3 or section 4 or both, whichever is the more appropriate for the purpose of investigation of the soil.

The methods described should be suitable for a range of "soils" including agricultural soils and materials from polluted sites. However, no method can be expected to be universally applicable, and users must recognize this fact and be prepared to deal with the analytical difficulties that may sometimes be encountered. Soils containing sulfides may require special attention (see note 7 to 5.1).

"Soils" from some polluted sites, for example former gasworks sites and colliery spoil tips, may contain a variety of sulfur species (e.g. elemental sulfur, sulfate, sulfite, thiosulfate, thiocyanate) that may be transformed from one to another under changing chemical conditions and/or microbial action. The presence of other ions may affect solubilities. Thus, in these circumstances, particular care may be required in sample handling and preparation, and in the interpretation of the results.

The limitations of the method in section 6, in terms of acceptable concentrations of other ions, are defined.

The tests described are strictly empirical and thus cannot be considered to measure the true sulfate content in soil, although reproducibility should be good.

Because of the limited solubility of some sulfates (e.g. calcium sulfate) and possible interferences from other ions, a single extraction following the procedure described in section 3 may not give a true measure of the "total water extractable" sulfate. This potential problem can be tackled either by repeating the extraction one or more times on the same sample, or by substantially increasing the water:soil ratio. Another option is to use a "buffered" extraction solution which will enhance the solubility of the sulfates present, but such procedures are beyond the scope of this International Standard.

If calcium is the only cation present, sulfate ion in solution will not exceed 1 441 mg SO_4^{2-}/l at 20 °C. This means that the maximum amount of sulfate that can be extracted from such a soil by the procedure in section 3 is about 7 205 mg SO_4^{2-}/kg (10 g soil:50 ml water) and by the procedure in section 4 is about 2 882 mg SO_4^{2-}/kg (50 g soil:100 ml water).

Section 2: Pretreatment of samples and determination of dry matter contents

2.1 Scope

In this section, procedures are described for the preparation of air-dried test samples for use in the extraction procedures described in sections 3 to 5 of this International Standard.

2.2 Determination of dry matter content

Determine the dry matter content of the field-moist and air-dried materials in accordance with ISO 11465, but at a temperature not exceeding 75 °C to 80 °C (there is a danger if gypsum is present that water of crystallization will be lost at higher temperatures).

2.3 Preparation of soil samples for extraction with water in the mass:volume ratio 1 soil:5 water, or for extraction with dilute acid

2.3.1 Apparatus

The following items of apparatus, additional to those specified in ISO 11465, allow the preparation of a single test sample.

2.3.1.1 Desiccator, containing anhydrous silica gel.

2.3.1.2 Glass container, capable of holding approximately 10 g of soil and fitted with a ground glass stopper.

2.3.2 Preparation of test sample

Prepare each test sample for analysis from the laboratory sample as follows.

> Dry and prepare a laboratory sample passing a 2 mm sieve of sufficient size, for all the tests to be performed following the procedures described in ISO 11464.
>
> Divide the material passing the 2 mm sieve by successive riffling or another approved means (see ISO 11464) to produce a sample weighing approximately 100 g.
>
> Mill this fraction to pass a 250 µm sieve.
>
> Subdivide the sample by successive riffling to obtain a test sample weighing approximately 10 g (additional test samples can be taken at this stage if required).
>
> Place the test sample in a suitable glass container (2.3.1.2) and dry at a temperature of not more than 40 °C. The test sample shall be deemed to be dry when the differences in successive weighings at intervals of 4 h do not exceed 0,1 % (*m/m*) of the test sample.
>
> Allow the test sample(s) to cool in a desiccator (2.3.1.1).

NOTES

1 It is assumed that any material retained on the 2 mm test sieve will not contain sulfates. This is generally true, but certain soils may contain lumps of gypsum larger than 2 mm in diameter and in such cases the gypsum should be removed by hand, crushed to pass a 2 mm test sieve and incorporated into the fraction passing the sieve.

2 Other suitable mechanical sample dividers may be used instead of the riffle boxes, provided that their size is suitable for the sizes and gradings of the samples to be obtained, or, alternatively, manual coning and quartering may be used.

2.4 Preparation of soil samples for extraction with water in the mass:volume ratio of 1 soil:2 water

2.4.1 Apparatus

The following items of apparatus, additional to those specified in ISO 11465, allow the preparation of a single test sample:

2.4.1.1 Desiccator, containing anhydrous silica gel.

2.4.1.2 Glass container, capable of holding approximately 125 g of soil and fitted with a ground glass stopper.

2.4.1.3 Glass container, capable of holding approximately 50 g of soil and fitted with a ground glass stopper.

2.4.2 Preparation of air-dried soil test sample

Prepare each test sample for analysis from the laboratory sample as follows.

Dry and prepare a laboratory sample passing a 2 mm sieve of sufficient size, for all the tests to be performed following the procedures described in ISO 11464.

Divide the material passing the 2 mm sieve by successive riffling to produce a sample weighing approximately 125 g.

Mill this fraction to pass a 250 µm sieve.

Subdivide the sample by successive riffling to obtain a test sample weighing approximately 50 g (additional test samples can be taken at this stage if required).

Place the test sample in a suitable glass container (2.4.1.3) and dry at a temperature of not more than 40 °C. The test sample shall be deemed to be dry when the differences in successive weighings at intervals of 4 h do not exceed 0,1 % (*m/m*) of the test sample.

Allow the test sample(s) to cool in a desiccator (2.4.1.1).

NOTES

3 It is assumed that any material retained on the 2 mm test sieve will not contain sulfates. This is generally true, but certain soils may contain lumps of gypsum larger than 2 mm in diameter and in such cases the gypsum should be removed by hand, crushed to pass a 2 mm test sieve and incorporated into the fraction passing the sieve.

4 Other suitable mechanical sample dividers may be used instead of the riffle boxes, provided that their size is suitable for the sizes and gradings of the samples to be obtained, or, alternatively, manual coning and quartering may be used.

Section 3: Extraction of soil with water at a mass:volume ratio of 1 soil:5 water

3.1 Principle

A procedure is described for the determination of the water-soluble sulfate content of soil, for which a 1 part by mass soil:5 parts by volume water extract is first prepared.

Determination of sulfate ions in solution is subsequently made using the gravimetric method described in section 6 of this International Standard.

NOTE 5 If calcium is the only cation present, the sulfate content of the aqueous extract will not exceed 1 441 mg SO_4^{2-}/l at 20 °C. Sulfate contents in excess of this figure in the soil-water extract, or in the groundwater, as determined in this test, therefore indicate the presence of other more soluble sulfate salts.

3.2 Preparation of 1:5 water extract

3.2.1 Reagent

The following reagent is required for preparing the water extract.

3.2.1.1 Distilled water or water of equivalent purity, in accordance with grade 3 of ISO 3696.

3.2.2 Apparatus

The following items of apparatus are required for preparing the water-soluble sulfate extract from a single test sample.

3.2.2.1 Extraction bottle, of capacity approximately 100 ml.

3.2.2.2 Buchner funnel, of diameter about 100 mm.

3.2.2.3 Vacuum filtration flask, of capacity approximately 500 ml, to take the funnel.

3.2.2.4 Filter papers, of medium grade, porosity = 8 µm.

3.2.2.5 Source of vacuum, for example a filter pump.

3.2.2.6 Length of rubber tubing, to fit the vacuum pump and filter flask.

3.2.2.7 Mechanical shaker or stirrer, capable of keeping 10 g of soil in continuous suspension in 50 ml of water.

3.2.2.8 Balance, capable of weighing to an accuracy of 0,001 g.

3.2.3 Preparation of air-dried soil test sample

Prepare an air-dried test sample following the procedure described in 2.3 of this International Standard.

3.2.4 Preparation of extract

Carry out the extraction at a temperature in the range 20 °C to 25 °C.

The 1 soil:5 water extract for the determination of the water-soluble sulfate content is obtained from a single air-dried test sample as follows.

Transfer a test portion of mass 10 g ± 0,1 g to the extraction bottle (3.2.2.1).

Add 50 ml ± 0,5 ml of distilled water (3.2.1.1) to the extraction bottle which shall then be stoppered tightly, placed in the shaker (3.2.2.7) and agitated for 16 h.

Filter the soil suspension into a clean and dry flask (3.2.2.3) through a suitable filter paper (3.2.2.4) placed in the Buchner funnel (3.2.2.2).

Retain the filtrate for measurement of the sulfate content.

Record the volume of the filtrate (V_E).

3.3 Determination of dry matter content

Determine the dry matter content of the air-dried material following the procedure described in 2.2 of this International Standard.

Section 4: Extraction of soil with water at a mass:volume ratio of 1 soil:2 water

4.1 Principle

A procedure is described for the determination of the water-soluble sulfate content of soil, for which a 1 soil:2 water extract is first prepared (see note 5 to 3.1).

Determination of sulfate ions in solution is made using the gravimetric method described in section 6 of this International Standard.

4.2 Preparation of 1:2 water extract

4.2.1 Reagent

The following reagent is required for preparing the water extract.

4.2.1.1 Distilled water or water of equivalent purity, in accordance with grade 3 of ISO 3696.

4.2.2 Apparatus

The following items of apparatus are required for preparing the water-soluble sulfate extract from a single test sample.

4.2.2.1 Beaker, of capacity 500 ml, preferably conical, with glass rods and cover glasses.

4.2.2.2 Buchner funnel, of diameter about 100 mm.

4.2.2.3 Vacuum filtration flask, of capacity approximately 500 ml to take the funnel.

4.2.2.4 Filter papers, of medium grade, porosity = 8 µm.

4.2.2.5 Source of vacuum, for example a filter pump.

4.2.2.6 Length of rubber tubing, to fit the vacuum pump and filter flask.

4.2.2.7 Mechanical shaker or stirrer, capable of keeping 50 g of soil in continuous suspension in 100 ml of water.

4.2.2.8 Extraction bottle, of capacity approximately 250 ml.

4.2.2.9 Pipette, of capacity 100 ml.

4.2.2.10 Balance, capable of weighing to an accuracy of 0,001 g.

4.2.2.11 Watch glass, capable of holding 50 g of soil.

4.2.3 Preparation of air-dried soil test sample

Prepare an air-dried test sample weighing approximately 50 g following the procedure described in 2.4 of this International Standard.

4.2.4 Preparation of extract

Carry out the extraction at a temperature of 20 °C to 25 °C.

The 1 soil:2 water extract for the determination of the water-soluble sulfate content is obtained from each of the prepared test samples as follows.

> Weigh an air-dried test sample of 50 g ± 0,5 g onto a watch glass (4.2.2.11) and transfer it to a clean and dry extraction bottle (4.2.2.8).
>
> Add 100 ml ± 1 ml of distilled water (4.2.1.1) to the extraction bottle (see note 6), which shall then be stoppered tightly, placed in the shaker (4.2.2.7) and agitated for 16 h.
>
> Filter the soil suspension into a clean and dry beaker (4.2.2.1) through a suitable filter paper (4.2.2.4) placed in the Buchner funnel (4.2.2.2).
>
> Retain the filtrate for measurement of the sulfate content.
>
> Measure the volume of the filtrate (V_E).

NOTE 6 If a centrifuge is available, it will probably prove more convenient to use a centrifuging tube for the extraction. The suspension can then be centrifuged instead of filtered and 25 ml of the clear supernatant liquid can be used for analysis after appropriate dilution, if required.

4.3 Determination of dry matter content

Determine the dry matter content of the air-dried material following the procedure described in 2.2 of this International Standard.

Section 5: Extraction of soil with dilute hydrochloric acid

5.1 Principle

A procedure is described for the determination of the acid-soluble sulfate content of soil for which an acid extract is first prepared.

Acid-soluble sulfates, which include virtually all naturally occurring sulfates, are extracted from a soil sample with dilute hydrochloric acid.

Determination of sulfate ions in solution is made using the gravimetric method described in section 6 of this International Standard.

Soils containing sulfides may require special attention (see note 7).

NOTE 7 The acid extraction method determines the total sulfate content of the soil at the time of testing and any sulfides which may be present are destroyed during the extraction process (see note 10). If sulfides are present, it is possible that these may oxidize in the long term to produce additional sulfates. If the presence of sulfides is suspected and the possible oxidation of these in the future is a cause of concern, the total sulfur content should be measured. The difference in the total sulfur content and the acid-soluble sulfate content, both expressed in terms of percentage SO_4, gives a measure of the amount of sulfide present. Sulfides may be present in shales and mudstones and they are frequently found in waste materials and by-products such as minestone (colliery spoil) and slags.

5.2 Preparation of acid extract

5.2.1 Reagents

The following reagents are required for preparing the acid extract. They shall be of recognized analytical grade.

5.2.1.1 Distilled water or water of equivalent purity, in accordance with grade 3 of ISO 3696.

5.2.1.2 Dilute hydrochloric acid.

Carefully mix 500 ml ± 10 ml of concentrated hydrochloric acid (relative density 1,18) with water and dilute to 1 litre in a measuring cylinder.

Store in a glass or polyethylene bottle. The solution is stable indefinitely.

5.2.1.3 Dilute ammonia solution.

Dilute 500 ml of ammonia (relative density 0,880) to 1 litre with water.

5.2.1.4 Silver nitrate solution, $c(\mathrm{AgNO_3}) \approx 0{,}1$ mol/l.

Dissolve 17 g ± 1 g of silver nitrate in about 800 ml of water and dilute to 1 litre in a measuring cylinder. Store the solution in an amber-glass container.

5.2.1.5 Concentrated nitric acid, relative density 1,42.

5.2.1.6 Red litmus paper.

5.2.2 Apparatus

The following items of apparatus are required for preparing the acid-soluble sulfate extract from a single test sample.

5.2.2.1 Two beakers, of capacity 500 ml, preferably conical, with glass rods and cover glasses.

5.2.2.2 Electric hotplate, capable of being controlled to boil the contents of the beaker without causing undue overheating.

5.2.2.3 Filter papers, of medium grade (porosity = 8 µm), hardened medium grade (porosity = 8 µm) and fine grade (porosity = 2,5 µm) to fit the funnel.

5.2.2.4 Glass rod, about 150 mm to 200 mm long and 3 mm to 5 mm in diameter.

5.2.2.5 Wash bottle, preferably made of plastics, containing distilled water or water of equivalent purity.

5.2.2.6 Glass filter funnel, of diameter about 100 mm.

5.2.2.7 Dropping pipette, of capacity 10 ml.

5.2.2.8 Fume cupboard.

5.2.2.9 Measuring cylinder, of capacity 100 ml.

5.2.2.10 Balance, capable of weighing to an accuracy of 0,001 g.

5.2.3 Preparation of air-dried soil test sample

Prepare an air-dried test sample following the procedure described in 2.3 of this International Standard.

5.2.4 Preparation of extract

The acid extract for the determination of the acid-soluble sulfate content is obtained from the air-dried test sample as follows.

a) Transfer about 2 g of the analytical sample (see note 9) to a 500 ml beaker (5.2.2.1), reweigh the beaker and calculate the mass (m_S) of the analytical sample by difference.

b) Add 100 ml ± 1 ml of dilute hydrochloric acid (5.2.1.2) to the test portion; if frothing occurs, care should be taken to ensure that no material is lost (see note 10).

c) Cover the beaker with a cover glass, heat the contents to boiling and simmer gently for 15 min in a fume cupboard (5.2.2.8).

d) Rinse the underside of the cover glass back into the beaker with distilled water (5.2.1.1) and add a few drops of concentrated nitric acid whilst the suspension continues to boil.

e) Add dilute ammonia solution (5.2.1.3) slowly, preferably from a dropping pipette (5.2.2.7), with constant stirring, to the boiling suspension until the sesquioxides are precipitated and red litmus paper (5.2.1.6) is turned to blue by the liquid (see note 11).

f) Filter the suspension through a hardened filter paper (5.2.2.3) into a 500 ml conical beaker (5.2.2.1). Wash the filter paper with distilled water until the washings are free from chloride, as indicated by an absence of turbidity when a drop is added to a small volume of silver nitrate solution. Record the total volume (V_E) of the extract (the final volume of the filtrate should preferably not exceed 200 ml).

NOTES

8 Samples from contaminated sites (e.g. former gasworks) may be contaminated with cyanides. There is therefore a possibility of the release of hydrogen cyanide (HCN) on addition of acid. Samples should either be screened for cyanides first or all acid additions should be made in an efficient fume cupboard.

9 The mass of sample to be used depends on the amount of sulfate present. Ideally a mass should be chosen that will produce a precipitate of barium sulfate weighing approximately 0,2 g.

10 Materials containing sulfides will release hydrogen sulfide (H_2S) on acidification and this can be detected by its smell. In these cases, there is a danger that this procedure will cause overestimation of the sulfate content because of sulfide oxidation. If the material contains sulfides, place 10 times the mass of the acid sample in a 500 ml beaker and heat to boiling. Remove from the heat source and, whilst stirring the acid solution, sprinkle the weighed analytical sample onto the acid.

11 If a heavy voluminous precipitate of sesquioxides forms when ammonia is added to neutralize the acid [step e)], some sulfate may be entrapped which will not be removed by washing and could lead to low results. In this case, a second precipitation is recommended. This is done by carefully removing the filter paper with the precipitate and replacing it in the original beaker. Dilute hydrochloric acid is added and the contents stirred until the sesquioxides have dissolved (20 ml of dilute hydrochloric acid should be sufficient). Bring the contents to the boil and repeat the process from step e).

5.3 Determination of dry matter content

Determine the dry matter content of the air-dried material following the procedure described in 2.2 of this International Standard.

Section 6: Determination of sulfate in solution by a gravimetric method using barium chloride

6.1 Scope

A gravimetric method is specified for the determination of sulfate in water extracts and dilute acid extracts of soils obtained using the procedures described in sections 3 to 5 of this International Standard. It closely follows the method described in ISO 9280. For information on potentially interfering substances, see 6.8.

A sulfate concentration (expressed as SO_4^{2-}) in the range of 25 mg/l to 5 000 mg/l can be determined, using the specified test portion (6.6.1). It is possible to determine higher concentrations by taking a smaller test portion from the laboratory sample (i.e. the acid or water extract).

The lower limit of detection (with nine degrees of freedom) of the method described in ISO 9280 is $SO_4^{2-} = 10$ mg/l.

6.2 Principle

Acidification of the laboratory sample with hydrochloric acid, followed by boiling with barium chloride solution for at least 20 min to promote coagulation of the precipitate of barium sulfate. Filtration through a tared sintered-glass crucible, washing the precipitate free from chloride, drying at 105 °C and reweighing when cool. The increase in mass of the crucible is due to the barium sulfate precipitate formed by the reaction of barium with sulfate ions in the sample.

6.3 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity, in accordance with grade 3 of ISO 3696.

6.3.1 **Dilute hydrochloric acid**, $c(\text{HCl}) = 6$ mol/l.

Carefully mix 500 ml ± 10 ml of concentrated hydrochloric acid (relative density 1,18) with water and dilute to 1 litre in a measuring cylinder.

Store in a glass or polyethylene bottle. The solution is stable indefinitely.

6.3.2 **Barium chloride dihydrate**, 100 g/l solution.

WARNING — Barium chloride is poisonous and harmful if swallowed.

Dissolve 100 g ± 1 g of barium chloride dihydrate ($BaCl_2{\cdot}2H_2O$) in about 800 ml of water, warming the mixture to aid dissolution. Cool the solution and dilute to 1 litre in a measuring cylinder.

Store in a glass or polyethylene bottle. The solution is stable indefinitely.

6.3.3 **Sodium hydroxide solution**, $c(\text{NaOH}) = 5$ mol/l.

WARNING — Sodium hydroxide solution is hazardous on contact with skin and eyes.

Dissolve 20 g of sodium hydroxide in 100 ml of water whilst stirring.

Store the solution in a polyethylene bottle.

6.3.4 **Methyl orange indicator**, about 1 g/l solution.

Dissolve 100 mg of methyl orange in about 50 ml of water, warming the mixture to aid dissolution. Cool the solution and dilute to 100 ml in a measuring cylinder.

Store in a glass or polyethylene bottle. The solution is stable indefinitely.

6.3.5 **Silver nitrate solution**, $c(\text{AgNO}_3) \approx 0{,}1$ mol/l.

Dissolve 17 g ± 1 g of silver nitrate ($AgNO_3$) in about 800 ml of water and dilute to 1 litre in a measuring cylinder.

Store in an amber-glass bottle. The solution is stable indefinitely if protected from light.

6.3.6 **Ethanol** (C_2H_5OH) or **rectified spirit** (95 % ethanol, 5 % water).

6.3.7 **Sodium chloride**, 100 g/l solution.

Dissolve 10 g ± 0,1 g of sodium chloride (NaCl) in about 100 ml of water.

Store the solution in a glass or polyethylene bottle.

6.3.8 Sodium carbonate (Na_2CO_3), anhydrous.

NOTE 12 When accurately standardized solutions are required, it may be more convenient to obtain them already standardized in concentrated form and to dilute them in accordance with the manufacturer's instructions.

6.4 Apparatus

Usual laboratory equipment and

6.4.1 Sintered-glass crucibles, of capacity about 30 ml and porosity value of 4.

6.4.2 Buchner flask, equipped with a safety guard for vacuum filtration.

6.4.3 Analytical balance, capable of weighing to an accuracy of 0,000 2 g.

6.4.4 Platinum evaporating basin, of capacity 250 ml.

6.5 Sampling and sample preparation

6.5.1 Sample handling

Collect laboratory extracts in glass or polyethylene bottles and analyse shortly after filtration or store at 2 °C to 5 °C for not more than one week.

Fill the sample bottles completely to exclude air and thus eliminate the risk of oxidation of samples containing sulfide or sulfite.

NOTE 13 Samples low in organic matter may be kept for longer periods, but tests should be carried out to ensure that the samples are sufficiently stable.

6.6 Procedure

6.6.1 Test portion

The volume of the test portion shall be between 10 ml and 200 ml and shall contain not more than 50 mg of sulfate ions. Withdraw the test portion from the laboratory sample (the water or acid extract) using a pipette. Record accurately the volume (V_A) of the test portion.

NOTE 14 The volume (V_E) of the water or acid extract (the laboratory sample) will be required for calculation of the result in terms of the concentration of sulfate ions, in milligrams per kilogram of air-dried soil, and should have been recorded as part of the procedures described in sections 3 to 5.

6.6.2 Pretreatment

Measure the test portion (6.6.1) into a 500 ml beaker and add 2 drops of methyl orange indicator (6.3.4). Neutralize the test portion with dilute hydrochloric acid (6.3.1) or sodium hydroxide solution (6.3.3) according to the initial pH. Add 2 ml ± 0,2 ml of dilute hydrochloric acid and then, if necessary, add water to bring the total volume in the beaker to 200 ml ± 20 ml. Boil the contents of the beaker for at least 5 min.

If the solution is clear after boiling, proceed to 6.6.3. If insoluble material is present, filter the hot mixture through a fine-porosity ashless filter paper and wash it with a small amount of hot water, combining the washings with the filtrate. Transfer the solution quantitatively to a 500 ml beaker and proceed to 6.6.3.

NOTES

15 If it is suspected that the insoluble material retained by the filter paper contains insoluble sulfate and it is desired to include this in the final result, retain the filter paper and carry out the procedure given in 6.9.2.

16 If silica is present in the test portion at concentrations likely to interfere (see 6.8), follow the pretreatment method given in 6.9.1.

17 If organic substances are present in the test portion at concentrations considered likely to interfere (see 6.8), follow the pretreatment method given in 6.9.1.

6.6.3 Precipitation

Boil the solution produced at the end of the pretreatment (6.6.2) and slowly add, using a pipette, 10 ml ± 5 ml of hot (about 80 °C) barium chloride solution (6.3.2). Heat the solution for at least 1 h, then allow to cool and stand overnight at 50 °C ± 10 °C.

NOTE 18 Slow addition of the hot barium chloride reduces the possibility of coprecipitation. Subsequent heating aids coagulation of the precipitate and renders it more crystalline, reducing coprecipitation even further.

6.6.4 Filtration

6.6.4.1 Procedure

Dry a sintered-glass crucible (6.4.1) by heating it to 105 °C for 1 h and let it cool in a desiccator.

Accurately weigh the crucible, to the nearest 0,000 2 g. Record the mass of the crucible (m_1) and then fit it onto the Buchner flask (6.4.2). Filter the precipitate using gentle suction. Use a rubber-tipped glass rod to dislodge any precipitate remaining in the beaker and rinse out with cold water into the crucible. Wash the precipitate in the crucible with chloride-free cold water.

6.6.4.2 Test for chloride in the washings

Collect about 5 ml of the filtrate from 6.6.4.1 in a small beaker containing about 5 ml of silver nitrate solution (6.3.5). To ascertain whether the washings and hence the barium sulfate precipitate are free from chloride, observe the mixture and check that no turbidity is formed. Otherwise continue washing.

It is also important to check that no chloride remains on the underside of the rim of the crucible.

6.6.5 Drying and weighing

Remove the crucible and dry it at 105 °C ± 2 °C for about 1 h. Transfer the crucible to a desiccator and weigh it accurately when it has cooled to room temperature. Return the crucible to the drying oven for a further 10 min and repeat the cooling and weighing. Provided that the second mass differs by not more than 0,000 2 g from the first, record the second mass (m_2). Otherwise repeat the drying, cooling and weighing until two successive masses do not differ by more than 0,000 2 g.

NOTE 19 Shorter drying periods may be obtained if the precipitate is washed with three 5 ml portions of ethanol (6.3.6).

6.6.6 Blank test

Follow a procedure identical to that described in 6.6.3 to 6.6.5, but using 200 ml ± 20 ml of water.

Subtract the crucible mass recorded before filtration in 6.6.4 from that recorded after filtration in 6.6.5, to give the mass m_0, in grams, of the blank.

6.7 Expression of results

6.7.1 Calculation of concentrations in test portions

Calculate the mass m, in grams, of barium sulfate in the test portion, using the following equation:

$$m = m_2 - m_1 - m_0$$

where

m_0 is the mass, in grams, of the blank calculated in 6.6.6;

m_1 is the mass, in grams, of the crucible recorded in 6.6.4;

m_2 is the mass, in grams, of the crucible recorded in 6.6.5.

Calculate the sulfate concentration $\rho_1\left(\mathrm{SO}_4^{2-}\right)$ in the solution, in milligrams per litre, using the following equation:

$$\rho_1\left(\mathrm{SO}_4^{2-}\right) = \frac{m \times 0{,}411\,6}{V_\mathrm{A}} \times 10^6$$

where

m is the mass, in grams, of barium sulfate precipitate;

V_A is the volume, in millilitres, of the test portion (see 6.6.1);

0,411 6 is the gravimetric factor (sulfate/barium sulfate).

Conversion factors for other units of concentration are given in table 1.

Table 1 — Conversion factors

	$\rho(\mathrm{SO}_4^{2-})$ mg/l	$c(\mathrm{SO}_4^{2-})$ mmol/l	$\rho(\mathrm{S})$ mg/l
$\rho\left(\mathrm{SO}_4^{2-}\right) = 1$ mg/l	1	0,010 41	0,333 8
$c\left(\mathrm{SO}_4^{2-}\right) = 1$ mmol/l	96,06	1	32,06

6.7.2 Calculation of sulfate concentration in soil

Calculate the sulfate concentration $\rho_2\left(\mathrm{SO}_4^{2-}\right)$ of the soil, in milligrams per kilogram of air-dried soil, from the following equation:

$$\rho_2\left(\mathrm{SO}_4^{2-}\right) = \frac{\rho_1\left(\mathrm{SO}_4^{2-}\right) \times V_\mathrm{E}}{m_\mathrm{S}} = \frac{m \times 0{,}411\,6 \times 10^6 \times V_\mathrm{E}}{m_\mathrm{S} \times V_\mathrm{A}}$$

where

$\rho_1\left(\mathrm{SO}_4^{2-}\right)$ is the measured sulfate concentration in the extract, in milligrams per litre (calculated in 6.7.1);

V_E is the total volume, in millilitres, of the extract;

m_S is the mass, in grams, of sample taken.

Table 2 — Repeatability and reproducibility standard deviations

Sample	Test portion volume ml	Mass concentration of sulfate mg/l	s_r mg/l	VC_r %	s_R mg/l	VC_R %
1	200	50	3,3	—	—	—
2	20	210	3,3	1,6	6,9	3,3
3	20	583	8,4	1,4	12,4	3,3
4	20	1 160	9,3	0,8	11,6	1,0
5	20	1 500	21,3	—	—	—
6	20	5 000	29,4	—	—	—

s_r	is the repeatability standard deviation
VC_r	is the repeatability variation coefficient
s_R	is the reproducibility standard deviation
VC_R	is the reproducibility variation coefficient

Details of samples

1,5,6: Standard solutions, data from the United Kingdom, one laboratory, 9 degrees of freedom.

2: Data from Germany, 10 laboratories, 37 degrees of freedom.

3: Data from Germany, 10 laboratories, 35 degrees of freedom.

4: Data from Germany, 9 laboratories, 32 degrees of freedom.

6.7.3 Repeatability and reproducibility of sulfate determination in test solution

Repeatability and reproducibility standard deviations determined for the method described in ISO 9280 are given in table 2. Those obtained during an interlaboratory trial of the procedures described in this International Standard are given in annex A.

6.8 Interferences

Sulfide and sulfite interfere if the samples are unduly exposed to air causing oxidation to sulfate before analysis. Otherwise, any sulfide and sulfites present at the beginning of the analysis are removed as hydrogen sulfide and sulfur dioxide gases respectively by boiling during pretreatment (6.6.2).

Organic compounds present in substantial amounts (for example a sample with a permanganate index > 30 mg O_2/l) may interfere by absorption or coprecipitation. The procedure described in 6.9.1 may be used to overcome this difficulty.

Amounts of other inorganic ions in the test portion (6.6.1) below which no interference is likely are given in table 3.

Table 3 — Tolerances to other ions

Ion	Expressed as	Maximum mass concentration mg/l
Chromate	CrO_4^{2-}	10
Phosphate	PO_4^{3-}	10
Nitrate	NO_3^-	100
Silicate	SiO_2	2,5
Calcium	Ca^{2+}	100
Iron(III)	Fe^{3+}	50

6.9 Special cases

6.9.1 Removal of organic compounds

Measure the test portion (6.6.1) into a platinum evaporating basin and add 2 drops of methyl orange indicator (6.3.4).

Neutralize the test portion with dilute hydrochloric acid (6.3.1) or sodium hydroxide solution (6.3.3) according to the initial pH and then add 2,0 ml of dilute hydrochloric acid. Evaporate almost to dryness on a water bath and then add 5 drops of sodium chloride solution (6.3.7) to the remaining liquid. Evaporate to complete dryness and then heat the basin to a dull red heat (about 700 °C) over a bunsen flame or in a muffle furnace to form an ash.

Allow to cool and then moisten the ash with about 10 ml of water. Add 5 drops of dilute hydrochloric acid (6.3.1) and evaporate to dryness on a water bath. Then allow to cool slightly, add 10 ml ± 1 ml of water and transfer quantitatively to a 500 ml beaker. Proceed as described in 6.6.2, beginning with "add 2 drops of methyl orange indicator...".

6.9.2 Determination of sulfate in insoluble material

Place the filter paper from 6.6.2 in a platinum evaporating basin (6.4.4) covered with a lid and either heat over a low bunsen flame or place in a muffle furnace at room temperature and bring the muffle furnace up to a temperature of 500 °C to burn off the paper. Mix the ignited residue with 4 g ± 0,1 g of anhydrous sodium carbonate (6.3.8) and heat strongly to fuse the mixture, maintaining it in a melted state for 15 min. Allow to cool.

Add 50 ml of water to the platinum dish, warm to dissolve the fused mixture and then filter the solution through a coarse filter paper. Wash the filter paper with 20 ml of water. With the combined filtrate and washings, proceed as described in 6.6.2 to 6.6.6 beginning with "add 2 drops of methyl orange indicator...".

Note that there is a strong evolution of carbon dioxide when the acid is added.

Calculate the additional sulfate concentration $\rho_3\left(\mathrm{SO}_4^{2-}\right)$, in milligrams per litre, as described in 6.7 and add it to the soluble sulfate concentration determined on the filtrate produced during pretreatment (6.6.2) to arrive at the total sulfate concentration.

6.10 Notes on procedure

6.10.1 Cleaning the used sintered-glass crucibles

Barium sulfate can be removed from the crucibles after the analysis by soaking them overnight in a solution containing about 5 g of disodium ethylenediaminetetraacetate (EDTA, disodium salt) and about 25 ml of ethanolamine ($NH_2CH_2CH_2OH$) per litre of water. After soaking, wash the crucibles by drawing water through under suction before drying and re-use in subsequent analyses.

Section 7: Precision of method and test report

7.1 Repeatability and reproducibility

The results of an interlaboratory trial of the three extraction methods and of the sulfate determination are presented in annex A.

7.2 Test report

The test report shall include the following information:

a) a reference to this International Standard;

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

c) details of the preparation of the test sample;

d) whether any of the special case procedures were used;

e) a statement of repeatability achieved;

f) the results, expressed to an appropriate number of significant figures, and the method of expression used;

g) details of any operation not specified in this International Standard, or regarded as optional, as well as any factor which may have affected the results.

Annex A
(informative)

Results of an interlaboratory trial

An interlaboratory trial was organized to test the procedures specified in this International Standard. In this trial, the concentration of acid-soluble and water-soluble sulfate in four soils, and the sulfate content of one solution, were determined by 11 laboratories.

The characteristics of the soils analysed are given in table A.1.

The repeatability (*r*) and reproducibility (*R*) of the results of the analyses of the solution obtained by the laboratories are given in table A.2.

The repeatability (*r*) and reproducibility (*R*) of the results of the analyses of the soils are given in tables A.3 to A.5.

The values have been calculated according to ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

Table A.1 — Characteristics of the soils used for the interlaboratory trial for the determination of sulfate

Soil	Description
A	Natural soil (C) with added gypsum — water-soluble sulfate governed by limited solubility of gypsum
B	Natural soil (C) with added sodium sulfate — highly water-soluble sulfate
C	Natural soil
D	Soil/fill from industrially polluted site

Table A.2 — Results of the interlaboratory trial for the determination of sulfate in the test solution

Number of laboratories retained after eliminating outliers	10
Number of outliers (laboratories)	1
Number of accepted results	20
Mean value, mg/l	5 247
Repeatability standard deviation (s_r), mg/l	58
Repeatability relative standard deviation, %	1,11
Repeatability limit ($r = 2,8 \times s_r$), mg/l	164
Reproducibility standard deviation (s_R), mg/l	273
Reproducibility relative standard deviation, %	5,20
Reproducibility limit ($R = 2,8 \times s_R$), mg/l	764

Table A.3 — Results of the interlaboratory trial for the determination of acid-soluble sulfate in test soils

Soil	A	B	C	D
Number of laboratories retained after eliminating outliers	7	8	10	7
Number of outliers (laboratories)	0	0	0	0
Number of accepted results	14	16	20	14
Mean value, % of air-dried soil	1,397	2,836	0,175	1,048
Repeatability standard deviation (s_{r}), % of air-dried soil	0,099	0,265	0,019	0,080
Repeatability relative standard deviation, %	7,07	9,35	10,93	7,65
Repeatability limit ($r = 2{,}8 \times s_{\mathrm{r}}$), % of air-dried soil	0,276	0,742	0,054	0,225
Reproducibility standard deviation (s_{R}), % of air-dried soil	0,099	0,339	0,092	0,168
Reproducibility relative standard deviation, %	7,10	11,97	52,51	16,06
Reproducibility limit ($R = 2{,}8 \times s_{\mathrm{R}}$), % of air-dried soil	0,278	0,950	0,258	0,472

Table A.4 — Results of the interlaboratory trial for the determination of sulfate soluble in a 1 soil:5 water extract

Soil	A	B	C	D
Number of laboratories retained after eliminating outliers	11	10	11	10
Number of outliers (laboratories)	0	0	0	0
Number of accepted results	22	20	22	20
Mean value, % of air-dried soil	0,738	2,785	0,095	0,636
Repeatability standard deviation (s_{r}), % of air-dried soil	0,032	0,083	0,007	0,016
Repeatability relative standard deviation, %	4,28	2,98	7,33	2,59
Repeatability limit ($r = 2{,}8 \times s_{\mathrm{r}}$), % of air-dried soil	0,088	0,233	0,020	0,046
Reproducibility standard deviation (s_{R}), % of air-dried soil	0,068	0,234	0,094	0,096
Reproducibility relative standard deviation, %	9,29	8,40	35,37	15,14
Reproducibility limit ($R = 2{,}8 \times s_{\mathrm{R}}$), % of air-dried soil	0,192	0,655	0,263	0,270