INTERNATIONAL STANDARD

ISO 19747

First edition
2020-10

Fertilizers and soil conditioners — Determination of monosilicic acid concentrations in nonliquid fertilizer materials

Détermination des concentrations en silicium soluble dans les matières fertilisantes non liquides

Reference number
ISO 19747:2020(E)

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 134, *Fertilizers, soil conditioners and beneficial substances*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Although silicon is ubiquitous in nature, making up a quarter of the earth's crust[3], not all forms of silicon found in soils or fertilizer products are soluble and plant-available[4],[5]. The form of silicon in soils that is soluble and available for plant uptake is monosilicic acid. Worldwide, it has been estimated that annual removal of silicon from soils during crop production can amount to 239-255 mega tons annually, based on FAO 1998 global crop production estimates, and a conservative annual increase of 1 % through 2012. Although the first US patent on a solid Si fertilizer was issued in 1881[6], fertilizer manufacturers, governmental regulators and consumers had no means of evaluating nonliquid silicon fertilizer materials for their monosilicic acid supplying capacity to meet and replace plant uptake needs.

The first research into the use of silicon fertilizers was reported in 1840[7]. Additionally, increased plant silicon concentrations were first associated with reductions in rice (*Oryza sativa* L.) blast disease (*Magnaporthe grisea* M.E. Barr) over a century ago in Japan[8]. Since then, research has extended to other grasses and grains (e.g. barley (*Hordeum vulgare L.*)[9], corn (*Zea mays* L.)[10], oats (*Avena sativa* L.)[11], wheat (*Triticum aestivum* L.)[12], sugar cane (*Saccharum officinarum* L.)[13], pasture[14], turf grasses[15], and to dicotyledonous crops (e.g. cucumber (*Cucumis sativus* L.)[16], grapes (*Vitis vinifera* L.)[17], pepper (*Capsicum* L.)[18], pumpkin (*Curcubita pepo* L.)[19], soybean (*Glycine max* (L.) Merr.)[20], tomato (*Solanum lycopersicum* L.)[21]. Beneficial effects from silicon fertility have included increased stress tolerance (disease, insect, drought, salt, nutrient imbalance, UV-rays, low and high temperature) and yield increases with or without stress[4]. Other benefits from silicon supplements to soils have included CO_2 sequestration[22], reductions in metals toxicity[23], and reduced phosphorus run-off while increasing phosphorus use efficiency[24].

Considering the extensive research, a growing market, and the potential benefits from silicon fertility to global agriculture; it is important that a standard method exists to enable regulation of nonliquid silicon fertilizer materials based on their monosilicic acid supplying capacity. This is the first method developed which correlates well with plant silicon uptake while using commonly available laboratory equipment at a reasonable cost for the analysis. Reference the peer reviewed published version, single lab validated AOAC method[25].

Fertilizers and soil conditioners — Determination of monosilicic acid concentrations in nonliquid fertilizer materials

1 Scope

This document establishes a method for the determination of monosilicic acid concentrations in nonliquid fertilizer materials. Monosilicic acid is reported as silicon (Si).

This extraction method is applicable to the detection of monosilicic acid in nonliquid fertilizer products, blended products, and beneficial substances at silicon (Si) concentrations of 2 to 84 g/kg, with a limit of detection (LOD) of 0,6 g/kg Si, and a limit of quantification (LOQ) of 2 g/kg correlating well with plant uptake.

This method is not applicable to liquid silicon fertilizer sources due to an expected low bias of Si recovery and low correlation with plant uptake.

2 Normative References

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 8157, *Fertilizers and soil conditioners — Vocabulary*

3 Terms and Definitions

For the purposes of this document, the terms and definitions given in ISO 8157 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
monosilicic acid
inorganic molecule that is soluble in soil solution and is the form of silicon available for plant uptake

4 Principle

Monosilicic acid (reported as Si) from nonliquid Si fertilizer sources is extracted at ambient room temperature using a dilute Na_2CO_3-NH_4NO_3 extractant. The extractant solution is analysed by manual spectrophotometry at 660 nm using the heteropoly blue method[26].

5 Safety

General requirements: A minimum of standard laboratory personal protective equipment including safety glasses, gloves, and lab coats should be worn always. Consult individual SDS for chemicals listed and follow safety and handling conditions per individual SDS instructions.

6 Reagents

6.1 General requirements: Protect from sunlight. Store all reagents in a manner consistent with general laboratory practices. Store in temperatures between 20 and 24 °C unless otherwise noted.

6.2 Sodium carbonate solution, 0,094 M — fill a 19 l plastic dispensing bottle with 18 l water. Add 180 g anhydrous Na_2CO_3. Stir to dissolve.

6.3 Ammonium nitrate solution, 0,20 M — fill a 19 l plastic dispensing bottle with 18 l water. Add 288 g NH_4NO_3. Stir to dissolve.

Ammonium nitrate (NH_4NO_3): Is a strong oxidizing agent and should not be used near flames, heating or ignition sources, combustible materials, or reducing agents to avoid the potential for combustion or explosion hazards. NH_4NO_3 shall be separated from all organic materials present within the laboratory. Check with governmental agencies for any additional regulatory licensing requirements before obtaining or using NH_4NO_3.

6.4 Sodium carbonate-ammonium nitrate extractant solution, 9,4 pH — add 50 ml of each solution (6.2 and 6.3) to a plastic beaker, stir, and verify that the pH of the mixed solution is 9,4 using a pH meter.

Mixing of sodium carbonate and ammonium nitrate: Flexible vinyl gloves are to be worn when mixing Na_2CO_3 and NH_4NO_3, due to the caustic nature of this extractant. Care shall be taken to avoid eye or skin contact. If contact is made with eyes or skin, flush immediately with clean tap water and seek medical attention. Clean up any spills immediately.

6.5 Silicon 1000 mg/l stock solution, silicon standard — this solution, preferably 20 g/kg sodium hydroxide, is commercially available from numerous sources. Follow specific manufacturer's SDS for proper storage and shelf life.

6.6 Silicon spike solution, 500 mg/l — pipette 50 ml of a stock 1000 mg/l silicon standard into a 100 ml volumetric flask. Dilute to 100 ml with water.

6.7 Ammonium Molybdate solution, 0,42 M — add 75 g ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ to a 1 l beaker. Add 500 ml water. Dissolve. Slowly add 100 ml concentrated (18,4 M) sulfuric acid (H_2SO_4). Cool. Transfer to a 1 l volumetric flask. Dilute to 1 l with water.

WARNING — Handling of concentrated sulfuric acid: gloves, safety goggles, face shields, and lab coats should always be worn when handling concentrated sulfuric acid. Sulfuric acid is extremely corrosive and dehydrating, causing severe burns. Care shall be taken to avoid eye or skin contact. If contact is made with eyes or skin, flush immediately with clean tap water and seek immediate medical attention. To avoid the potential for fuming and spattering of concentrated sulfuric acid during dilution, always add sulfuric acid to water and do not add water to sulfuric acid.

6.8 Tartaric acid solution, 1,33 M — add 200 g tartaric acid ($C_4H_6O_6$)to a 1 l beaker. Add 700 ml water. Stir. Transfer to a 1 l volumetric flask. Dilute to 1 l with water.

6.9 Ascorbic acid solution, 0,017 M — add 3 g ascorbic acid ($C_6H_8O_6$)to 1 l volumetric flask. Dilute to 1 l with water. Stopper the flask and mix by inverting 10 times. Transfer to a plastic storage bottle. Cap tightly and refrigerate.

6.10 Intermediate silicon standard solution, 50 mg/l — dilute 5 ml of a stock 1000 mg/l silicon standard to 100 ml in a volumetric flask. Transfer immediately to a plastic storage bottle.

6.11 Cleaning solution for glassware, dilute 4 ml/l of Nitric Acid with de-ionized water (HNO_3).

6.12 Cleaning solution for flow cell, dilute 100 ml/l of HCl with de-ionized water.

7 Calibration standards

7.1 Blank: 0 mg/l Si — add 10 ml sodium carbonate–ammonium nitrate extractant solution (6.4) to a 1 l volumetric flask. Dilute to 1 l with water. Stopper the flask and mix by inverting 10 times.

7.2 Standard 1: 0,25 mg/l Si — add 10 ml sodium carbonate–ammonium nitrate extractant solution (6.4) to a 1 L volumetric flask. Add 5 ml intermediate silicon standard solution (6.10). Dilute to 1 l with water. Stopper the flask and mix by inverting 10 times.

7.3 Standard 2: 0,50 mg/l Si — add 10 ml sodium carbonate–ammonium nitrate extractant solution (6.4) to a 1 l volumetric flask. Add 10 ml intermediate silicon standard solution (6.10). Dilute to 1 l with water. Stopper the flask and mix well by inverting 10 times.

7.4 Standard 3: 1,0 mg/l Si — add 10 ml sodium carbonate–ammonium nitrate extractant solution (6.4) to a 1 l volumetric flask. Add 20 ml intermediate silicon standard solution (6.10). Dilute to 1 l with water. Stopper the flask and mix by inverting 10 times.

7.5 Standard 4: 2.0 mg/l Si — add 10 ml sodium carbonate–ammonium nitrate extractant solution (6.4) to a 1 l volumetric flask. Add 40 ml intermediate silicon standard solution (6.10). Dilute to 1 l with water. Stopper the flask and mix by inverting 10 times.

7.6 Spike sample: Prepare a spiked talc sample by drying (9.1.1) grinding (9.1.2) and weighing out (9.1.3) a 0,2 g talc [$Mg_3Si_4O_{10}(OH)_2$] test portion sample. Add 100 ml each of sodium carbonate (6.2) and ammonium nitrate (6.3) solutions using a plastic graduated cylinder. Before shaking (9.2) add 3 ml silicon spike solution (6.6) to the talc test sample. This talc-spiked test sample is processed and used for the matrix spike recovery test verifying that soluble (spike) rather than insoluble silicon (talc) is extracted and reported using this method.

8 Apparatus

As silica (SiO_2) is a constituent of commonly used laboratory glassware, and detection limits are at 0,6 g/kg Si, it is important to adhere to strict glassware cleaning instructions.

8.1 Glassware, to be thoroughly acid cleaned prior to use in reagent and calibration standard preparation by soaking in a 40ml/l HNO_3 solution (6.11) for 30 min and rinsing three times with deionized water. Allow glassware to air dry prior to use. Glassware items needed include 100 ml to 1 l volumetric flasks, 1 l beakers, and assorted 5 to 50 ml calibrated pipets. All glassware (including flasks and pipets) shall conform to Class A tolerances as recommended for routine laboratory applications.

8.2 Plastic ware, should be cleaned well with warm clean tap water, followed by triple rinsing with deionized water. Specific plastic ware items needed include: 50 to 1 l graduated cylinders, 200 ml nalgene volumetric flasks with screw closure; 250 ml nalgene erlenmeyer flasks with screw closure; 50 ml centrifuge or test tubes with screw closure; 250 ml to 1 l nalgene or fluorinated ethylene propylene (FEP) narrow-mouth storage bottles with screw closure; and 20 l wide-mouth dispensing bottles with screw closure (also nalgene or FEP).

8.3 pH meter, Accumet™[1)] AB15 Basic pH/mV benchtop meter or equivalent.

1) Accumet is the trademark of a product supplied by Fisher Scientific. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

8.4 Analytical balance, mettler AG200[2)], accuracy to 0,1 mg, or equivalent.

8.5 Shakers.

8.5.1 Touch agitator, thermolyne maxi mix II 12v vortex mixer, model M37615[3)] or equivalent.

8.5.2 Orbital platform shaker or wrist-action shaker.

8.5.2.1 Orbital platform shaker, labLine orbit[4)] shaker, model 3590 equipped with timer and adjustable rpm control, or equivalent.

8.5.2.2 Wrist-action shaker, burrell[5)] or equivalent.

8.6 Spectrophotometer and SpectraManager software package: jasco V-630[6)], equipped with a 10 mm flow cell, peristaltic sipper or equivalent and SpectraManager software package, or equivalent. Clean the flow cell at least 15 min before the start of test sample readings, and upon completion of readings by flushing the flow cell with a 100 ml/l (6.12) solution of HCl. Allow the acid solution to remain in the cell for a minimum of 5 min before dumping and disposing of the acid solution followed by passing water through the cell (about 100 ml). Read the absorbance (Á) value. If necessary, re-zero the instrument and continue flushing with water until the Á value is stable. For a manual cell, place the quartz cell in a dilute HCl solution (100 ml/l (6.12)) for a minimum of 5 min. Then rinse thoroughly with water three times. Blot dry with a soft tissue and visually examine for streaking or discoloration of the cell. Use a cotton-tipped swab to gently remove any stains, and then rinse the cell thoroughly with water three times. Repeat this process as needed. Check the Á of water to confirm a stable reading before test sample analysis.

8.7 Sample grinder, capable of grinding to a fineness passing a 300 µm sieve, micron bantam mill[7)] or equivalent.

8.8 Refrigeration unit: 0,31 m³ capacity, capable of maintaining a temperature of 4 °C (GE, Louisville, KY, example only, not a recommendation or similar brand).

8.9 Drying oven, convection oven capable of holding a constant temperature of 105 ± 2 °C (VWR). (Blue-M, Stabil-Therm, example only, not a recommendation or similar brand).

2) Mettler AG200 is the trademark of a product supplied by Mettler Toledo. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

3) thermolyne maxi mix II 12v vortex mixer, model M37615 is the trademark of a product supplied by Barnstead Thermolyne Corp., Dubuque, IA. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

4) labLine orbit is the trademark of a product supplied by Melrose Park. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5) This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

6) jasco V-630 is the trademark of a product supplied by Easton, MD. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

7) micron bantam mill is the trademark of a product supplied by Micron, Summit, NJ. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

9 Procedure

9.1 Sample preparation

9.1.1 Dry control test portions (e.g. Talc, Wollastonite) for 2 h at 105 ± 5 °C. All other fertilizer materials need not be dried and should be processed on an as-is moisture basis.

Test sample duplication — always make a duplicate of at least one of the unknown test samples.

9.1.2 Grind the test sample to pass a 300 µm sieve (USA standard No. 50).

9.1.3 Accurately weigh out a 0,2 g test portion and transfer to a 250 ml tared plastic flask, weigh again and record. This is the test portion weight.

9.2 Extraction

9.2.1 Add 100 ml each of the sodium carbonate (6.2) and ammonium nitrate (6.3) solutions to the test portion.

9.2.2 Cap flask tightly and shake solution at 140 rpm (table unit) or 60 rpm (wrist action shaker) at ambient temperature (25 °C) for 60 min. Before shaking add 3 ml of silicon spike solution (6.6) to the talc solution sample (7.6).

9.2.3 Remove from the shaker and let stand undisturbed for 5 days.

Begin a 5-day timer at the start of shaking (see 9.2.2).

9.3 Heteropoly blue analyses

9.3.1 At the end of 5 days, transfer via pipette, 2 ml (or 4 ml for materials expected to be 30 g/kg lower of Si) of resting extraction sample to a 200 ml polypropylene volumetric flask (do not move or agitate test solution prior to pipetting). Dilute to 200 ml with water. Stopper the flask and mix by inverting 10 times. Pipette 20 ml of diluted test solution into a plastic test tube[26].

9.3.2 Prepare silicon calibration standards; blank, and standards 1–4 (see 7.1-7.5), by pipetting 20 ml of each standard or blank solution into a plastic test tube.

9.3.3 Add 2 ml ammonium molybdate solution (6.7) to a test tube and mix well for 10 s using a touch agitator. Wait 10 min. Add 2 ml tartaric acid solution (6.8) to each tube. Stopper the test tube and mix well for 10 s using a touch agitator. Wait 5 min. Add 2 ml ascorbic acid solution (6.9). Stopper the test tube and mix well for 10 s using a touch agitator. Repeat for each test tube sample.

9.3.4 Allow test sample, blank, and standards to stand for 60 min for colour development. Colour gradation from blue to purple should be seen with increasing monosilicic acid concentration.

9.4 Manual spectrophotometer analyses

9.4.1 Set the spectrophotometer wavelength to 660 nm and mode to absorbance (A)[27].

9.4.2 Flush the flow cell or cuvette three times with water before initiating blank and standard sample readings. Flush again after reading standard 4, and after every three test samples.

9.4.3 Read and record A data for blank, standards, and test samples.

9.4.4 Determine the linear correlation equations using concentration versus A data by graphing or linear regression using computer software.

9.5 Calculations

9.5.1 Calculate the soluble (Si) in the fertilizer product test sample, using Formula (1).

$$\text{Si mg/kg} = [((\text{K} \times A) + \text{B}) \times V_i / W \times V_f / V_a] \quad (1)$$

where

K is the coefficient K1, or slope factor from standard curve;

A is the absorbance of test solution;

B is the intercept from the standard curve;

V_i is the initial volume in ml (200 ml for our test sample);

V_a is the test portion aliquot volume taken for dilution in ml, (2 or 4 ml);

V_f is the final volume in ml (200 ml for our sample);

W is the test portion weight in mg (200 mg for our sample).

9.5.2 Determine the Si spike recovery, using Formula (2).

$$S_r = (C_f - C_u) \times 100 / C_a \quad (2)$$

where

S_r is the Si spike recovery, in %;

C_f is the observed fortified test sample concentration, in mg/l;

C_u is the observed unfortified test sample concentration in mg/l;

C_a is the calculated concentration of spike using a test portion weight basis, rather than a solution basis (500 mg/l × 0,003 l/(0,2 g × 1000 mg/g) × 100 (mg/kg) for our test sample), in %.

9.6 Precision

To obtain precision, method repeatability standard deviation (SD) and repeatability RSD (observed) values were calculated for each test sample. Calculated values were compared to the PRSD (predicted) using the HorRat formula below.

$$P\ (\text{mg/kg}) = 2C^{-0,1505} \quad (3)$$

where

P is the precision method repeatability standard deviation, in mg/kg;

C is the sample concentration expressed as a mass fraction (or decimal part/hundred), in mg/kg.

9.7 Statistical analysis

A target range for HorRat values (RSDr/PRSD) was set at 0,3 to 1,3. Statistical analysis was performed using the statistical database in Microsoft Excel[30]. HorRat, References [28] and [29] are used to determine the precision (repeatability and reproducibility) of the analytical method.

9.8 Ring study

Results from the ring study of the method are summarized in Annex A.

Annex A
(Informative)

Report of the international laboratories ring study

A.1 Introduction

The international laboratories ring study of ISO 19747 has been conducted.

A.2 Precision

Statistical analysis of data from 6 laboratories on 8 test samples was performed using ISO 5725:1986, 22.2. HorRat values were determined using Formula (3) in 9.6.

A.3 Results

The results from the ring study are presented in Table A.1.

Table A.1 — Results from the ring study for ISO 19747

Product	Number of laboratories	Mean % Si	SD	SD%	*r*	*r*%	*R*	*R*%	HorRat *r*	HorRat *R*
Wollastonite	6	3,345	0,303 8	9,080 4	1,012	30,26	1,177	35,17	18,18	29,27
AgrowSil	6	1,294	0,139 3	10,768 7	0,478	36,93	0,951	73,47	19,24	70,52
AgrowSil dup	6	1,471	0,1646	11,191	0,548	37,3	0,811	55,14	19,81	51,92
Agrosilicio (Brazil)	6	3,471	0,8739	25,181 1	2,826	81,41	2,812	81,01	49,18	67,06
Mineral co-product (India)	6	3,955	0,261 3	6,606	0,882	22,31	0,864	21,84	13,74	17,73
SilStrong (China)	6	5,682	0,3496	6,1537	1,152	20,27	1,189	20,92	13,19	16,08
Magnesium silicate	6	0,052	0,063 2	121,591	0,211	405,22	0,204	393,29	130,34	611,37
AgrowSil (2017)	6	4,134	0,451 5	10,922 2	1,488	35,99	1,364	32,99	22,31	26,6

r: repeatability

R: reproducibility