INTERNATIONAL STANDARD

ISO 11262

First edition
2003-09-15

Soil quality — Determination of cyanide

Qualité du sol — Dosage des cyanures

Reference number
ISO 11262:2003(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

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.

ISO 11262 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Introduction

Cyanides may be present in soil as cyanide ions and as complex cyanides. They can be determined as easily released cyanide, as complex cyanide or as total cyanide. This International Standard specifies the determination of easily released cyanides, complex cyanides and total cyanide.

This International Standard addresses, in particular, the following two subjects:

a) liberation and absorption of hydrogen cyanide;

b) determination of cyanide ions:

   1) photometric method;

   2) titrimetric method using an indicator.

Soil quality — Determination of cyanide

WARNING — Hydrogen cyanide and its salts are toxic, thus care shall be exercised in the manipulation of cyanide-contaminated samples. Volatile hydrogen cyanide (with a smell of bitter almonds) is released from acidified solutions containing cyanide salts. Since hydrogen cyanide gas is highly toxic, do not acidify samples except in accordance with the defined procedures in Clause 7. Carry out all work in a fume hood and wear suitable plastic gloves when handling contaminated samples.

Place analytical wastes containing cyanides in a special lidded container in the laboratory for temporary storage. Clearly mark this container with labels such as "Toxic waste" or "Cyanides". Periodically empty the container and dispose of the wastes containing cyanides as "special waste" via an appropriate waste management contractor.

1 Scope

This International Standard is applicable to as-received soil samples, and specifies two quantification methods for the determination of easily released and complex cyanides. It is not always necessary to determine easily released cyanide prior to the measurement of complex cyanide. In this instance, the first part of the distillation process is omitted so that only the total cyanide is determined. The methods are applicable to soil containing between 0,5 mg/kg and 10 000 mg/kg of total cyanide. The methods and corresponding ranges of cyanide in the aliquot taken from the relevant absorption solution are as follows:

a) photometric method:

   This method is applicable for cyanide contents of 0,5 mg/kg to 50 mg/kg in the original field-moist sample.

b) titrimetric method using an indicator:

   This method is applicable for cyanide contents of above 50 mg/kg in the original field-moist sample.

2 Normative references

The following referenced documents are indispensable for the application 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 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

ISO 9297, *Water quality — Determination of chloride — Silver nitrate titration with chromate indicator (Mohr's method)*

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

ISO 14507:2003, *Soil quality — Pretreatment of samples for determination of organic contaminants*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
easily released cyanide
compounds containing cyanide groups which can form hydrogen cyanide at pH 4 under reflux conditions

NOTE The extraction method given in 7.4.2 for easily released cyanide provides significantly higher results than free cyanide methods using acidification at room temperature. These other methods determine only the hydrated cyanide ion, whereas the method of 7.4.3 determines the hydrated cyanide ion together with some complex cyanides.

Consequently the result for complex cyanides using these other methods differs from that using the present method. Easily released cyanide will determine the hydrated cyanide ion and some complex cyanides.

3.2
complex cyanide
cyanide liberated (as HCN) under the conditions specified in 7.4.3 after the distillation of easily released cyanides

3.3
total cyanide
sum of easily released and complex cyanides, i.e. all compounds which form hydrogen cyanide under the conditions of this method

4 Principle

Easily released cyanide is extracted from the soil sample by treatment at pH 4 under reflux. This liberates the cyanide as hydrogen cyanide, which is absorbed by an aqueous solution of sodium hydroxide. Zinc sulfate is used to suppress the release of cyanide ion from complex cyanides. Complex cyanides have greater stability and so are extracted using orthophosphoric acid under reflux conditions. Tin(II) and copper(II) salts are added to suppress the interference from sulfur compounds and catalyse the decomposition of complex cyanides.

Cyanide ion in the sodium hydroxide absorber solutions is determined

— either photometrically (see Clause 8) by a procedure based on the reaction of cyanide with chloramine-T with the formation of cyanogen chloride. This reacts with pyridine-4-carboxylic acid and 1,3-dimethylbarbituric acid to form a coloured complex, the absorbance of which is measured at 600 nm,

— or titrimetrically (see Clause 9) by a titrimetric procedure involving titration with silver nitrate. When in excess relative to the $Ag(CN)_2^-$ ion, silver ions form a red-coloured complex with the end-point indicator, 5-(dimethylaminobenzylidene) rhodanine:

$$Ag^+ + CN^- \rightarrow AgCN$$

$$AgCN + CN^- \rightarrow Ag(CN)_2^-$$

$$Ag^+ + Ag(CN)_2^- \rightarrow Ag[Ag(CN)_2]$$

Trace of $Ag[Ag(CN)_2]$ + rhodanine indicator → red colour.

5 Reagents

All reagents shall be of recognized analytical grade and the water used shall conform to grade 2 of ISO 3696. All reagents are stable for at least three months unless stated otherwise.

5.1 Reagents for liberation and absorption of cyanide.

5.1.1 Orthophosphoric acid, β-(H_3PO_4) w = 85 % (mass fraction), ρ = 1,69 g/ml.

5.1.2 Sodium hydroxide solution, c(NaOH) = 1 mol/l.

Dissolve 40 g NaOH in water and dilute with water to 1 000 ml. Store in a polyethylene bottle.

5.1.3 Hydrochloric acid solution, c(HCl) = 1 mol/l.

Dilute 83 ml of concentrated hydrochloric acid w = 37 % (mass fraction), ρ = 1,18 g/ml with water to 1 000 ml.

5.1.4 Zinc(II) sulfate solution.

Dissolve 100 g of zinc(II) sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) in water and dilute with water to 1000 ml.

5.1.5 Buffer solution, pH 4,0 ± 0,2.

Dissolve 10,2 g of potassium hydrogen phthalate ($C_8H_5KO_4$) in warm water and make up to 1 000 ml. Store at a temperature below 10 °C.

5.1.6 Phenolphthalein solution.

Dissolve 0,03 g of phenolphthalein in 100 ml ethanol.

5.1.7 Tin(II) chloride solution.

Dissolve 5 g of tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) in 40 ml of the hydrochloric acid solution (5.1.3) and dilute with water to 100 ml. Prepare a fresh solution daily.

5.1.8 Copper(II) sulfate solution.

Dissolve 200 g of copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) in water and dilute with water to 1 000 ml.

5.2 Reagents for the photometric determination of cyanide ions.

5.2.1 Sodium hydroxide solution, c(NaOH) = 0,8 mol/l.

Dissolve 32 g NaOH in water and dilute with water to 1 000 ml. Store in a polyethylene bottle.

5.2.2 Glacial acetic acid, φ = 20 % (vol. fraction)

Dilute 100 ml of glacial acetic acid (ρ = 1,049 g/ml) to 500 ml in a graduated cylinder with water.

NOTE 100 % glacial acetic acid (ρ = 1,049), 96 % glacial acetic (ρ = 1,06 g/ml) are commonly available.

5.2.3 *N*-Chloro-4-methylbenzenesulfonamide sodium salt solution (Chloramine-T).

Dissolve 0,5 g of chloramine-T trihydrate ($C_7H_7ClNNaO_2S \cdot 3H_2O$) in water in a 50 ml volumetric flask and dilute to the mark. Prepare a fresh solution daily.

5.2.4 Colour reagent

Dilute 7,0 g of sodium hydroxide NaOH in 500 ml of water. Add 16,8 g of 1,3-dimethylbarbituric acid, $C_6H_8O_3N_2$, and 13,6 g of 4-pyridine carboxylic acid, (isonicotinic acid) $C_6H_5NO_2$, and dilute to 1 000 ml with water. Mix well for 1 h at 30 °C and then filter (pore size 8 µm) through a pleated filter.

This solution can be kept for at least one week provided it is stored below 10 °C in the dark, and filtered through another pleated filter (pore size 8 µm) before use.

5.2.5 Potassium cyanide standard solution corresponding to 100 mg/l of cyanide ion.

Dissolve 250 mg of potassium cyanide (KCN) in the 0,8 mol/l sodium hydroxide solution (5.2.1) and dilute with the same sodium hydroxide solution to 1 000 ml in a volumetric flask. Standardize this solution by titration with the 0,01 mol/l silver nitrate solution (5.3.1), once each day if numerous determinations are carried out (see Clause 9). Store at a temperature below 10 °C.

5.2.6 Potassium cyanide standard solution corresponding to 10 mg/l of cyanide ion.

Dilute 10,00 ml of solution (5.2.5) to 100 ml in a volumetric flask using 0,8 mol/l sodium hydroxide solution (5.2.1). Prepare daily.

5.2.7 *p*-Nitrophenol, ρ = 0,1 % in ethanol.

Dissolve 0,1 g *p*-nitrophenol in 100 ml of ethanol.

5.3 Reagents for the titrimetric determination of cyanide ions.

5.3.1 Silver nitrate solution, $c(AgNO_3)$ = 0,01 mol/l.

Dissolve 1,689 7 g of silver nitrate in approximately 400 ml water and dilute to 1 000 ml in a volumetric flask with water.

Check the actual concentration of the 0,01 mol/l silver nitrate by titration with sodium chloride according to ISO 9297 on a two-weekly basis. Store this solution in the dark.

5.3.2 Silver nitrate solution, $c(AgNO_3)$ = 0,001 mol/l.

Prepare daily from 0,01 mol/l silver nitrate (5.3.1). Add 25,00 ml of 0,01 mol/l silver nitrate to a 250 ml volumetric flask and dilute to 250 ml with water. Cover flask in aluminium foil to exclude light.

5.3.3 Indicator solution

Dissolve 0,02 g of 5-(4-dimethylaminobenzylidene) rhodanine in acetone and dilute with acetone to 100 ml. This solution is stable for up to one week if kept in the dark at ambient temperature.

6 Apparatus

Usual laboratory equipment and, in particular, the following.

6.1 Apparatus for the liberation and absorption of hydrogen cyanide

Use the apparatus shown in Figure 1. The round-bottomed flask (9) shall be triple-necked, have a capacity of at least 500 ml and have standard conical joints (for example 29/32 central neck, 19/24 side necks). A water-cooled Liebig condenser (3) (for example 16 cm long and 30 mm outer diameter), a 50 ml dropping funnel (5) and air inlet tube (7), shall be fitted. Connection to the absorption vessel (2) (for example 20 cm long and 2,5 cm inner diameter) is via a distillation tube (1). Standard joints are fitted to this tube to enable connection to the Liebig condenser and the absorption vessel (2). A glass tube (for example, 15 cm long by 1,3 cm outer diameter) extends into the absorption vessel and this is fitted with a No. 2 glass frit sinter (4) of porosity class P 160 in accordance with ISO 4793 to ensure efficient bubbling of the liberated HCN through the absorption fluid.

The recovery factor (f_r) of the distillation apparatus should be determined using a potassium cyanide standard for easily released cyanide and potassium ferricyanide for total cyanide. A mid-range calibration standard should be used (see 8.4 and 9.3).

6.2 Suction device

A pump capable of sucking up to 30 l/h air through the apparatus in Figure 1 is required. A low-power piston pump is recommended. This shall be fitted with a fine control valve [see (13), Figure 1] between the pump and the Drechsel bottle [see (6), Figure 1]. The Drechsel bottle is used to ensure that if a sample contained a very high level of cyanide, no HCN would be liberated to atmosphere.

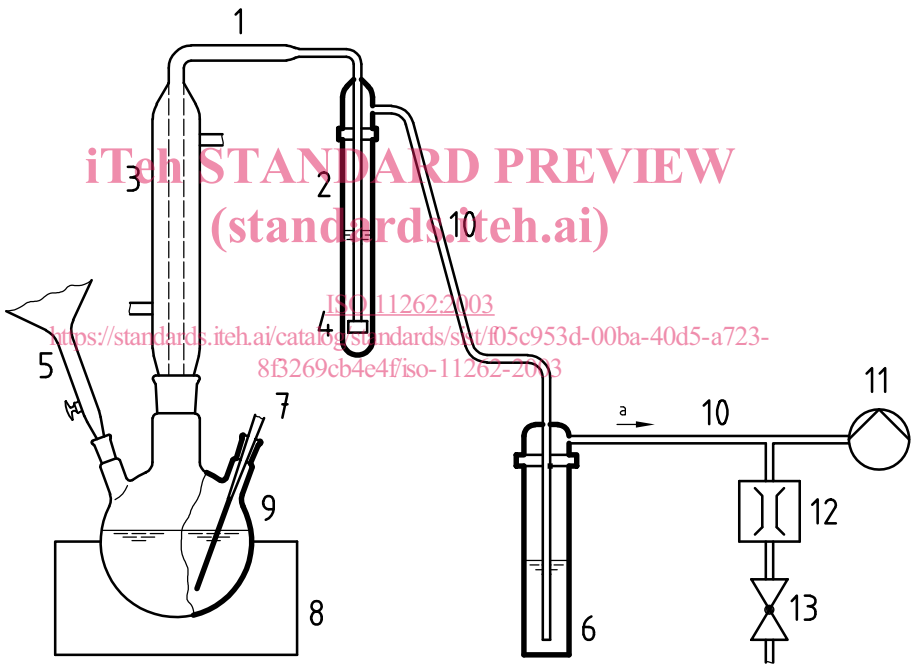
NOTE A single flowmeter [see (12), Figure 1] can be used to give a visual estimation of a flow rate of 10 l/h to 20 l/h. All other Drechsel bottle flows can then be set visually without using flowmeters. If such a flowmeter is used, the flowrate needs to be defined as a function of the volume of the apparatus, and should be checked by the determination of recovery rates.

6.3 Photometer, set to a wavelength of 600 nm, with cells of optical path length 10 mm.

6.4 Magnetic stirrer.

6.5 Burette, of capacity 10 ml.

6.6 Mechanical shaker.



Key

1 distillation tube
2 absorption vessel
3 Liebig condenser
4 glass frit sinter
5 dropping funnel
6 Drechsel bottle
7 air inlet tube
8 heating device
9 500 ml 3-necked round-bottomed flask
10 plastic tubing
11 pump
12 flowmeter
13 fine control valve
a Direction of flow.

Figure 1 — Apparatus for distillation of cyanide in soils