
**Soil quality — Determination of
total cyanide and easily liberatable
cyanide — Continuous-flow analysis
method**

*Qualité du sol — Détermination des cyanures totaux et des cyanures
aisément libérables — Méthode d'analyse en flux continu*

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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 17380 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

This second edition cancels and replaces the first edition (ISO 17380:2004), which has been technically revised.

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Introduction

Cyanides may be present in soil as cyanide ions and as complex cyanides. They can be determined as easily-liberatable cyanide or as total cyanide. Complex cyanide can be calculated by subtracting the easily-liberatable cyanide result from the total cyanide result. This International Standard specifies the determination of easily-liberatable cyanide, complex cyanides and total cyanide.

Methods using flow analysis automate wet chemical procedures and are particularly suitable for the processing of many analytes in water or soil extracts in large sample series at a high analysis frequency. The continuous flow analysis (CFA) method uses an automated dosage of the sample into a flow system (manifold) where the analytes in the sample react with the reagent solution on their way through the manifold. The sample preparation may be integrated in the manifold. The reaction product is measured in a photometric detector (e.g. flow cell photometer).^{[1],[2]}

In ISO 11262 a manual method for the photometric and volumetric determination of total cyanide in soil samples is described. It should be noted that the total cyanide results in soil samples as described in ISO 11262 may show slight differences from this International Standard. These differences are not considered to be very significant for this analysis. The easily-liberatable cyanide test has been removed from ISO 11262 because the validation data for this method were very poor.

For the analysis of cyanide in water ISO 14403-1^[6] and ISO 14403-2^[7] can be applied. The analytical procedure described in ISO 14403-2^[7] is identical to the one specified in this International Standard.

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Soil quality — Determination of total cyanide and easily liberatable cyanide — Continuous-flow analysis method

WARNING — Cyanide solutions are highly toxic. Appropriate measures shall be taken to avoid ingestion. Care should be taken in the disposal of these solutions.

1 Scope

This International Standard specifies a method for the photometric determination of the total cyanide and easily-liberatable cyanide content in soil using automated distillation/continuous-flow analysis.

The International Standard applies to all types of soil with cyanide contents above 1 mg/kg on the basis of dry matter, expressed as cyanide ion.

NOTE Sulfide concentrations in the sample higher than 40 mg/kg dry matter cause interference. This effect can be recognized by the split peaks and as a slow decrease of the detector signal and can only be prevented by diluting the sample extract.

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.

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

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

ISO 11262, *Soil quality — Determination of total cyanide*

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

total cyanide content

content of inorganic cyanide compounds consisting of the sum of the contents of easily-liberatable cyanide species and cyanide bound to metal cyanides, with the exception of thiocyanate ions and only partial breakdown of the cyanide bound in cobalt, gold, palladium and platinum cyanide complexes

3.2

easily-liberatable cyanide

content of inorganic cyanide compounds consisting of the sum of the contents of the easily-liberatable cyanide ions and the cyanide bound in simple metal cyanides (all expressed as CN) which are determined under the conditions of the method described in this International Standard

Note 1 to entry: The weakly complexed cyanide contained in tetracyanonickelate(II) and dicyanomercurate(II) is determined with the method for easily-liberatable cyanide. Up to 5 % of the strongly complexed cyanide in iron(III) hexacyanoferrate(II), hexacyanoferrate(III) and hexacyanoferrate(II) is determined with the method for easily-liberatable cyanide. Organic cyanide compounds (such as acetonitrile) are not determined.

Note 2 to entry: In connection with waste from the production of gold, “easily liberatable cyanide” is named “weak acid dissociable cyanide” [8].

3.3 complex cyanide content

total cyanide content less than the easily-liberatable cyanide content

4 Principle

4.1 Pretreatment of soil samples

The soil sample is extracted with 2,5 mol/l sodium hydroxide solution for 16 h. The extract is diluted 100 times, after which analysis of total and/or easily-liberatable cyanide is performed.

4.2 Determination of total cyanide content

Complex bound cyanide, present in the diluted extract (0,025 mol/l NaOH), is decomposed in a continuously flowing stream after addition of a buffer solution, with an initial pH of 3,8, by the effect of UV light. An UV-B lamp and decomposition coil of borosilicate glass are used. UV light with a wavelength of less than 290 nm is absorbed by the glass, preventing the photolytic conversion of thiocyanate into cyanide. The hydrogen cyanide present at these conditions is separated by in-line distillation at a heating bath temperature of $125\text{ °C} \pm 2\text{ °C}$ and then determined photometrically. The photometric determination is based on the reaction of cyanide with chloramine-T resulting in the formation of cyanogen chloride. This reacts with pyridine-4-carboxylic acid and 1,3-dimethylbarbituric acid to give a purple colour. The absorbance at 606 nm is then measured to determine the cyanide content. When an interference filter is used, a peak wavelength of $600\text{ nm} \pm 10\text{ nm}$ can be used.

NOTE Addition of the buffer solution, with an initial pH of 3,8 (5.2.1), to the sample flow containing 0,025 mol/l NaOH (ratio 1,0 sample : 0,42 buffer) leads to a final pH of 4,0. Varying the pH of the distillation between 3,8 and 5,7 leads to very small fluctuations in the recovery of hydrogen cyanide (only a few percent).

4.3 Determination of easily-liberatable cyanide content

Before distillation, and without UV decomposition, a zinc sulfate solution is added to the sample flow, such that any complex iron cyanide(s) present are precipitated as zinc-cyanoferrate complexes. The hydrogen cyanide present during these conditions is separated by distillation at a temperature of 125 °C and photometrically determined as described under 4.2.

NOTE The added zinc sulfate replaces a water reagent (see Table 1) used in the determination of total cyanide content.

5 Reagents

Only use reagents of recognized analytical grade and demineralized water or distilled water according to ISO 3696, Grade 1 or 2.

5.1 General reagents

5.1.1 Hydrochloric acid $w(\text{HCl}) = 37\%$.

5.1.2 Hydrochloric acid $c(\text{HCl}) = 1\text{ mol/l}$.

Dilute 83 ml of hydrochloric acid (5.1.1) with water to 1 000 ml.

5.1.3 Hydrochloric acid $c(\text{HCl}) = 0,1\text{ mol/l}$.

Dilute 100 ml of 1 mol/l hydrochloric acid (5.1.2) with water to 1 000 ml.

5.1.4 Sodium hydroxide solution $c(\text{NaOH}) = 2,5 \text{ mol/l}$.

Dissolve 100 g of NaOH in water and dilute with water to 1 000 ml. Store in a polyethylene bottle.

5.1.5 Sodium hydroxide solution $c(\text{NaOH}) = 1 \text{ mol/l}$.

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

5.1.6 Sodium hydroxide solution $c(\text{NaOH}) = 0,025 \text{ mol/l}$.

Dilute 25 ml of 1 mol/l sodium hydroxide (5.1.5) with water to 1 000 ml.

5.1.7 Detergent solution, polyoxyethylenelaurylether $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, $n \approx 23$.

Dissolve 30 g of polyoxyethylenelaurylether by adding small quantities to 100 ml water and mix thoroughly.

NOTE This solution is commercially available as Brij-35. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product. To dissolve the Brij-35, the temperature can be raised to 40 °C.

5.1.8 Indicator solution

Dissolve 0,02 g of p-dimethylaminobenzylindenerhodanine in 100 ml acetone. This solution can be stored for at least one week if kept in the dark and refrigerated (5 ± 3) °C.

5.1.9 Silver nitrate solution, $c(\text{AgNO}_3) = 0,01 \text{ mol/l}$

Dissolve 1,689 7 g of silver nitrate in approximately 400 ml water and dilute to 1 litre 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 in a brown glass bottle. Prepare a fresh solution monthly.

5.1.10 Silver nitrate solution, $c(\text{AgNO}_3) = 0,001 \text{ mol/l}$

Prepare daily from 0,01 mol/l silver nitrate (5.1.9). Add 25,00 ml of 0,01 mol/l silver nitrate to a 250 ml volumetric flask and dilute to 250 ml with water. Store this solution in the dark in a brown glass bottle.

5.1.11 20 % V/V Denatured ethanol

Mix 100 ml denatured ethanol with 400 ml water. This solution is stable for at least one year.

5.2 Reagents for determination of cyanide**5.2.1 Distillation buffer** (pH = 3,8)

Dissolve 50 g of citric acid, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ in 200 ml water. Add 120 ml sodium hydroxide solution 1 mol/l (5.1.5) and if necessary adjust the pH to 3,8 with sodium hydroxide solution 1 mol/l (5.1.5), and dilute to 500 ml with water. This solution is stable for three months if it is kept in the dark and refrigerated (5 ± 3) °C.

NOTE See Annex C for details of an alternative modified buffer to overcome flow stability problems observed with some continuous flow systems caused by the high concentration of citric acid in this reagent.

5.2.2 Zinc sulfate solution

Dissolve 10 g of zinc sulfate heptahydrate, $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$, in 750 ml water, mix and dilute to 1 000 ml with water. This solution is stable at least 1 year.

5.2.3 Buffer solution for photometric determination (pH = 5,2)

Dissolve 2,3 g of sodium hydroxide in 500 ml water. Add 20,5 g of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) and dilute to 975 ml with water. Adjust the pH of the solution to 5,2 with hydrochloric acid 1 mol/l (5.1.2) or sodium hydroxide solution 1 mol/l (5.1.5), add 1 ml detergent solution (5.1.7) and dilute to 1 000 ml with water. This solution is stable for three months if it is kept in the dark and refrigerated (5 ± 3) °C.

5.2.4 Chloramine-T solution

Dissolve 2,0 g of chloramine-T, $\text{C}_7\text{H}_7\text{ClNNaO}_2\text{S} \cdot 3 \text{H}_2\text{O}$ in 1 000 ml water. This solution is stable for one month if it is kept in the dark and refrigerated (5 ± 3) °C.

5.2.5 Colour reagent (pH = 5,2)

Dissolve 7,0 g of solid sodium hydroxide NaOH in 500 ml water. Add 16,8 g of 1,3-dimethylbarbituric acid, $\text{C}_6\text{H}_8\text{N}_2\text{O}_3$, and 13,6 g of pyridine-4-carboxylic acid, $\text{C}_6\text{H}_5\text{NO}_2$, and dilute to 975 ml with water. If necessary, adjust the pH of the solution to 5,2 with hydrochloric acid 1 mol/l (5.1.2) or sodium hydroxide solution 1 mol/l (5.1.5) and then dilute to 1 000 ml with water.

Stir vigorously for 1 h at 30 °C and then filter over a pleated filter. This solution is stable for three months provided it is stored in the dark and refrigerated (5 ± 3) °C, and filtered over a pleated filter before use.

5.2.6 Rinse solution for the sampler (0,025 mol/l sodium hydroxide)

Add 25 ml sodium hydroxide solution 1 mol/l (5.1.5) and dilute to 1 000 ml with water. This solution is stable for three months.

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5.3 Standard solutions for cyanide determination

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5.3.1 Stability

The concentrated standard solutions (5.3.2.1, 5.3.3.1 and 5.3.3.3) are stable for at least three months and the diluted standard solutions for at least one week provided they are stored in the dark and refrigerated (5 ± 3) °C.

5.3.2 Potassium cyanide standard solutions

5.3.2.1 Cyanide standard solution corresponding to 100 mg/l of cyanide ion

Dissolve 0,250 g of potassium cyanide KCN in sodium hydroxide solution 0,025 mol/l (5.1.6) and in a volumetric flask of 1 000 ml make up with sodium hydroxide solution 0,025 mol/l (5.1.6).

Transfer, by means of a pipette, into a beaker, 10 ml high standard cyanide solution with a content of 100 mg/l CN (5.3.2.1). Add 0,25 ml indicator solution (5.1.8). Perform a titration with the silver nitrate solution (5.1.10) until the colour changes from yellow to yellow-red (titration volume V_1).

Calculate the cyanide content in the standard cyanide solution with Formula (1):

$$\rho_{\text{CN}} = V_1 \cdot c_{(\text{AgNO}_3)} \cdot M_{(2\text{CN})} / V \quad (1)$$

where

ρ_{CN} is the cyanide content in the standard cyanide solution in milligrams per litre;

V_1 is the quantity of silver nitrate solution (5.1.9) used in millilitres;

$c_{(\text{AgNO}_3)}$ is the concentration of silver nitrate in millimoles per litre;

$M_{(2\text{CN})}$ is the molar mass of 2 CN (= 52 g/mol);

V is the volume of the standard cyanide solution in millilitres (in this case = 10 ml).

NOTE Commercially available standard solutions may also be used (e.g. potassium tetracyanozincate, $\text{K}_2\text{Zn}(\text{CN})_4$, $c(\text{CN} = 1\,000 \pm 2 \text{ mg/l})$).

5.3.2.2 Cyanide standard solution corresponding to 1 mg/l of cyanide ion

Transfer, by means of a pipette, 2,5 ml of the 100 mg/l cyanide solution (5.3.2.1) in a volumetric flask of 250 ml and fill to the mark with sodium hydroxide solution 0,025 mol/l (5.1.6).

5.3.3 Control solutions

5.3.3.1 Potassium thiocyanate solution corresponding to 100 mg/l of cyanide ion

Dissolve 0,373 g of potassium thiocyanate, KSCN (dried at 105 °C, stored in a desiccator), in sodium hydroxide solution 0,025 mol/l (5.1.6) and in a 1000 ml volumetric flask make up with sodium hydroxide solution 0,025 mol/l (5.1.6).

5.3.3.2 Potassium thiocyanate solution corresponding to 1 mg/l of cyanide ion

Transfer, by means of a pipette, 2,5 ml of the 100 mg/l standard thiocyanate solution (5.3.3.1) (equivalent to 100 mg/l CN^-) into a 250 ml volumetric flask and fill to the mark with sodium hydroxide solution 0,025 mol/l (5.1.6).

5.3.3.3 Potassium hexacyanoferrate solution corresponding to 100 mg/l of cyanide ion

Dissolve 0,211 g of potassium hexacyanoferrate, $\text{K}_3[\text{Fe}(\text{III})(\text{CN})_6]$ (dried at 105 °C, stored in a desiccator), in sodium hydroxide solution 0,025 mol/l (5.1.6) and in a volumetric flask of 1 000 ml make up with sodium hydroxide solution 0,025 mol/l (5.1.6).

5.3.3.4 Potassium hexacyanoferrate solution corresponding to 1 mg/l of cyanide ion

Transfer, by means of a pipette, 2,5 ml potassium hexacyanoferrate solution (5.3.3.3) (equivalent to 100 mg/l CN^-) into a 250 ml volumetric flask and fill to the mark with sodium hydroxide solution 0,025 mol/l (5.1.6).

5.3.3.5 Potassium hexacyanoferrate solution corresponding to 0,1 mg/l of cyanide ion

Transfer, by means of a pipette, 10 ml of 1 mg/l potassium hexacyanoferrate[III] solution (5.3.3.4) into a 100 ml volumetric flask and make up to the mark with sodium hydroxide solution 0,025 mol/l (5.1.6).

NOTE Solutions 5.3.3.2 and 5.3.3.5 are used to check the correct operation of the total cyanide method (see 9.2.4 and 9.2.5). Solutions 5.3.3.2 and 5.3.3.4 are used to check the correct operation of the easily-liberatable cyanide method (see 9.2.6 to 9.2.7).