INTERNATIONAL STANDARD

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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

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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.

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.

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 hexocyanoferrate(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 °C ± 2 °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 nm ± 10 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 $w(\mathrm{HCl}) = 37\ \%$.

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

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

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

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

5.1.4 Sodium hydroxide solution $c(NaOH) = 2{,}5$ 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 $c(NaOH) = 1$ 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 $c(NaOH) = 0{,}025$ 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 $C_{12}H_{25}(OCH_2CH_2)_nOH$, $n \approx 23$.

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, $c(AgNO_3) = 0{,}01$ 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, $c(AgNO_3) = 0{,}001$ 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, $C_6H_8O_7 \cdot H_2O$ 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, $ZnSO_4 \cdot 7\ H_2O$, 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 ($KHC_8H_4O_4$) 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, $C_7H_7ClNNaO_2S \cdot 3\ H_2O$ 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, $C_6H_8N_2O_3$, and 13,6 g of pyridine-4-carboxylic acid, $C_6H_5NO_2$, 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.

5.3 Standard solutions for cyanide determination

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):

$$\rho_{\mathrm{CN}} = V_1 \cdot c_{(\mathrm{AgNO_3})} \cdot M_{(\mathrm{2CN})} / V \qquad (1)$$

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;

$c_{(\mathrm{AgNO_3})}$ is the concentration of silver nitrate in millimoles per litre;

$M_{(\mathrm{2CN})}$ 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, $K_2Zn(CN)_4$, c(CN = 1 000 ± 2 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 of 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, $K_3[Fe[III](CN)_6]$ (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).

6 Apparatus

6.1 Standard laboratory glassware and laboratory equipment

Use brown or green coloured laboratory glassware to prevent the breakdown of complex cyanides or thiocyanate by daylight.

6.2 Continuous flow analysis system

A typical continuous flow analysis system is shown in Figure 1. This type of continuous flow automatic distillation apparatus is available commercially from a number of manufacturers (see Annex B).

NOTE The same system as mentioned in ISO 14403-2 can be used. Continuous flow system cyanide manifold design varies slightly from manufacturer to manufacturer. The key issue is ensuring suitable validation data are obtained by the user before employing the method for routine analysis.

The specification given below is an example of a “fit for purpose system”. For every individual apparatus optimal conditions have to be established and validated.

A sample changer is used to set appropriate sample and rinsing times (for example 80 and 160 s resp.).

For the UV decomposition (see 3 in Figure 1), a UV-B lamp with an emission maximum of (312 ± 5) nm of at least 8 W power shall be used. The decomposition coil shall be made from borosilicate glass with a capacity of approximately 13 ml and approximately 45 turns with a coil diameter of 30 mm; the tube shall have a wall thickness of max. 1 mm and an internal diameter of max. 2 mm. Borosilicate glass type DURAN 8330[1)] is recommended. The equipment shall be designed such that no UV light with a wavelength of less than 290 nm can reach the flow of fluid.

The distillation coil (see 5 in Figure 1) with at least 40 turns shall be placed vertically. The distillation heater temperature shall be adjusted to 125 °C with an accuracy of 1 °C. The distillation equipment shall be designed in such way that, on determination of total cyanide, less than 10 µg/l CN is found while measuring a thiocyanate solution with a concentration of 1 000 µg/l as CN. The reaction coils (coolers) (see 6 and 7 in Figure 1) after the distillation equipment can be connected in line. The heating bath (see 8 in Figure 1) shall be set to 37 °C ± 2 °C and the reaction coil shall be designed such that a retention period of approximately 4 min is achieved.

The photometer (see 9 in Figure 1) shall be equipped with a continuous flow cell with optical path length of 50 mm and a filter of 600 nm ± 10 nm with a band width of max. 10 nm. The maximum absorption occurs at 606 nm and this wavelength should be used if a spectrometer is employed.

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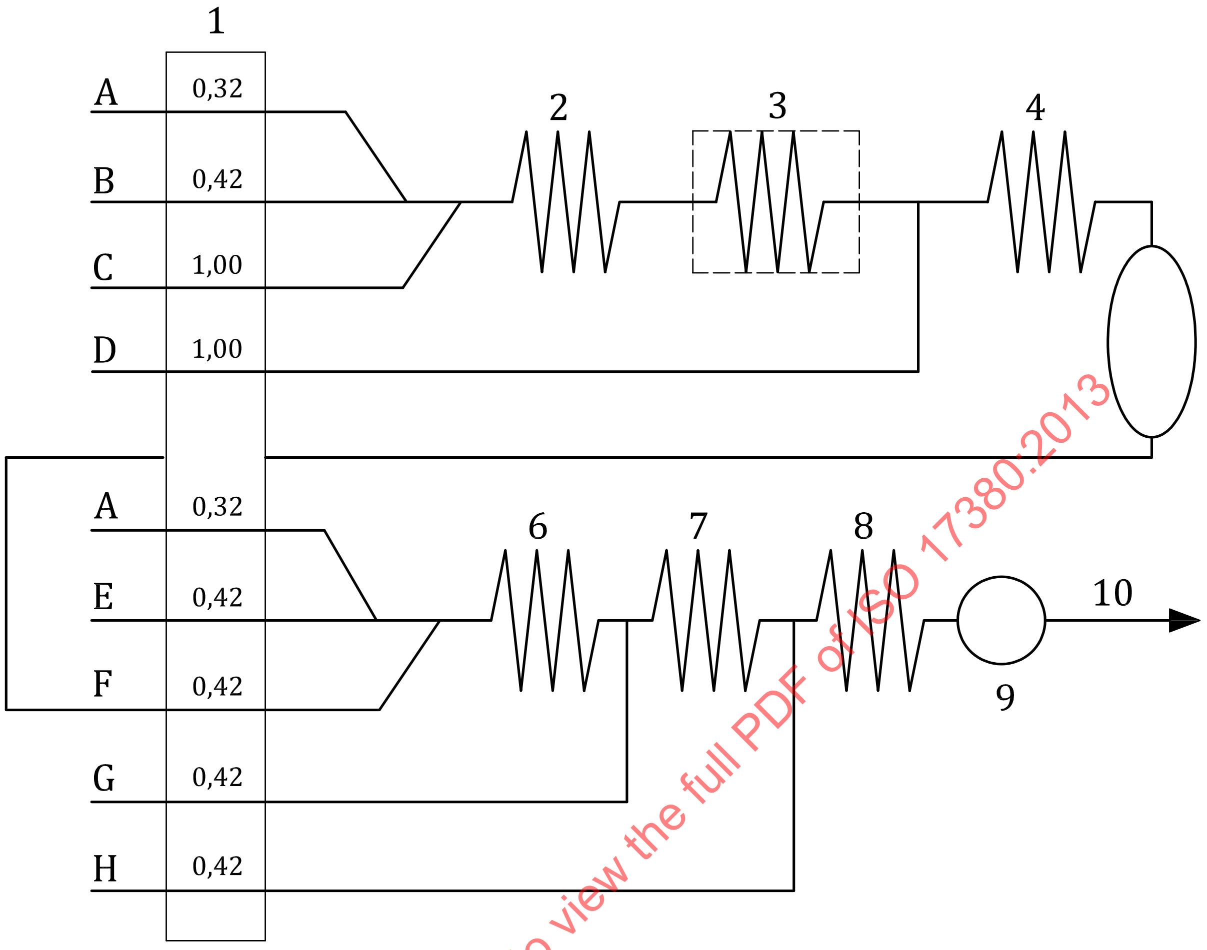
1) DURAN 8330 is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.



Key

A	Segmentation gas (air)
B	Buffer for distillation (5.2.1)
C	Sample
D	$ZnSO_4$ solution (5.2.2) for easily-liberatable cyanide, or water for total cyanide (see Table 1)
E	Buffer solution for final photometric determination (5.2.3)
F	Resample
G	Chloramine-T trihydrate solution (5.2.4)
H	Colour reagent (5.2.5)

1	Pump (flow rates in ml/min)
2	Reaction coil (50 cm, Ø int. 1,5 mm)
3	UV-B lamp (decomposition coil) (312 nm ± 5 nm)
4	Reaction coil (50 cm, Ø int. 1,5 mm)
5	Distillation coil (125 °C ± 1 °C)
6	Reaction coil (50 cm, Ø int. 1,5 mm)
7	Reaction coil (50 cm, Ø int. 1,5 mm)
8	Heating bath (37 °C ± 2 °C, 100 cm, Ø int. 2 mm)
9	Photometer (e.g. 50 mm optical path length), wavelength 590 nm to 610 nm
10	Waste

Figure 1 — Typical continuous flow system for the photometric determination of easily-liberatable and total cyanide (10 µg/l to 100 µg/l) with a distillation procedure

6.3 Shaking machine

Shaking machine with a shaking motion which allows an optimal contact between the sample and the extraction liquid.

NOTE Good results are obtained with an apparatus with a horizontal movement (motion) of 180 strokes per minute and a stroke length of 5 cm with the 500 ml polyethylene extraction vessels in horizontal position.

7 Sampling, sample preparation and extraction

Take a field moist representative soil sample, stored for up to four days in a refrigerator at (5 ± 3) °C; (see NOTE 1). Remove visible coarse constituents, as cyanide is labile the test portion should be prepared according to ISO 14507. Follow the procedure for volatile compounds, given in 8.2 of ISO 14507:2003. Suspend a quantity of the sample equivalent to approximately 40 g of dry matter, accurate to 0,1 g in 200 ml sodium hydroxide solution 2,5 mol/l (5.1.4) in a 500 ml polyethylene bottle. Shake for 16 h using the apparatus specified in 6.3. During this period, prevent irradiation by light, to minimize the decomposition of complex cyanides. Afterwards filter the suspension using a fit to purpose analytical filter paper. Dilute the extract by a factor of 100 (f_1) water. Any other dilutions should be made with 0,025 mol/l sodium hydroxide solution (5.1.6). Analyse the diluted extract using the method for total and/or easily-liberatable cyanide as soon as possible but within 4 days. Care must be exercised when handling sodium hydroxide solutions (see NOTE 2).

NOTE 1 A stability study has demonstrated that refrigerated soil samples are stable for at least four days.[4]

NOTE 2 2,5 mol/l sodium hydroxide is extremely corrosive to human tissue. It is essential that adequate eye protection is worn when handling sodium hydroxide solutions.

NOTE 3 Extraction by shaking for 1 h with 1 mol/l sodium hydroxide solution has been found to be adequate for many samples. Before using this modification, the user should validate this extraction with a wide range of typical samples.

8 Working range

The continuous flow analysis system shown in Figure 1 has a working range from 2 μg/l to 100 μg/l cyanide (expressed as CN). For a sample aliquot equivalent to 40 g of dry matter, this corresponds to 1 mg/kg to 50 mg/kg cyanide after the 100 fold dilution of the sodium hydroxide extract.

9 Procedure

9.1 General

Before performing the continuous flow analysis, consult the equipment operating instructions.

9.2 Checking analysis system for correct function

9.2.1 Adjust the continuous flow analysis system according to Table 1 depending on the determination to be performed.

Table 1 — Adjustment of continuous flow analysing system

Continuous flow analysis part/ medium	Part/parameter to be used	Setting for determination of	
		Total cyanide	Easily-liberatable cyanide
UV decomposition	Borosilicate glass coil UV-B lamp	On	Off
Solution	After UV lamp	Water	Zinc sulfate solution (5.2.2)
Distillation	Temperature	125 °C	125 °C
	Distillation buffer pH (5.2.1)	3,8	3,8
Photometric final determination	Colour reagent pH (5.2.5)	5,2	5,2
	Wavelength	600 nm ± 10 nm	600 nm ± 10 nm

9.2.2 Set the analysing system into operation at first by pumping water and afterwards the reagents (5.2) into the system. Set the baseline of the automatic recorder, after it has stabilized, to 10 scale divisions. Measure in succession two standard cyanide solutions with a concentration of 100 µg/l (see 9.3) in order to set the full-scale deflection to 90 scale divisions, followed by two blanks to monitor the baseline.

9.2.3 Check that the system is working correctly before proceeding according to the instructions of the manufacturer.

9.2.4 Prior analysis checks should also be made to confirm that less than 5 % of the bound cyanide in hexacyanoferrate[III] is detected as easily-liberatable cyanide and that over 95 % of the bound cyanide in hexacyanoferrate[III] is detected as total cyanide. Also there should be negligible breakdown of thiocyanate ion to cyanide (see 9.2.5, 9.2.6 and 9.2.7). Calculate the recovery using Formula (2):

$$R_{(\mathrm{CN})} \text{ test solution} = (\text{measured value test solution/measured value 100 µg/l cyanide solution}) \times 100 \tag{2}$$

9.2.5 The system is suitable for the measurement of total cyanide if the recovery of the 100 µg/l standard solution of hexacyanoferrate[III] (5.3.3.5) expressed as cyanide is at least 90 %. A recovery of hexacyanoferrate[III] less than 90 % indicates inadequate effectiveness of the UV decomposition (i.e. $R_{(\mathrm{CN})}$ hexacyanoferrate < 90 %). In this case clean the system (9.5) and, if necessary, replace the lamp.

9.2.6 For the determination of easily-liberatable cyanide, the system is suitable if the recovery of the 1 mg/l standard solution of hexacyanoferrate[III] (5.3.3.4) is less than 5 % (i.e. $R_{(\mathrm{CN})}$ hexcyanoferrate < 5 %). If higher levels of easily-liberatable cyanide than this are measured, significant breakdown of the hexacyanoferrate to cyanide has occurred. Prepare a fresh hexacyanoferrate solution, check the lamp and the reaction coil material meet the specification (see 6.2).

9.2.7 Prior to analysis checks should be made confirm negligible breakdown of thiocyanate occurs when determining easily-liberatable and total cyanide. For total or easily-liberatable cyanide no more than 10 µg/l cyanide of either species shall be found on measurement of a thiocyanate solution of c(as CN) = 1 000 µg/l (5.3.3.2) (i.e. $R_{(\mathrm{CN})}$ thiocyanate < 1 %). If higher levels of easily-liberatable cyanide than this are measured, significant breakdown of the thiocyanate to cyanide has occurred. Prepare a fresh thiocyanate solution, check the lamp and the reaction coil material meet the specification (see 6.2).

9.3 Calibration graph

Prepare a series of calibration standards by transferring by means of a pipette 0,5 ml; 1 ml; 2 ml; 4 ml; 5 ml; 6 ml; 8 ml and 10 ml of the 1 mg/l standard cyanide solution (5.3.2.2) respectively in a 100 ml volumetric flask and making up to the mark with 0,025 mol/l sodium hydroxide solution (5.1.6). These solutions contain 5 µg/l, 10 µg/l, 20 µg/l, 40 µg/l, 50 µg/l, 60 µg/l, 80 µg/l and 100 µg/l CN respectively (before the corrections for the concentration found on titration of the standard solution, see Clause 10). They should be prepared daily. Measure the entire calibration series. Plot a graph of the peak heights h_x of the calibration standards against the cyanide content c_x in µg/l. The calibration graph should be linear under these conditions.

NOTE The response of the system to sodium hydroxide concentration is effectively constant over the range 0,010 mol/l to 0,25 mol/l NaOH.

9.4 Measurement of samples

Dilute the diluted sample extract f_2 with 0,025 mol/l sodium hydroxide solution (5.1.6) until the cyanide concentration lies within the measurement range, but preferably no lower than 10 % of the highest concentration of the working range.

Place after every 20th sample a control solution, e.g. a cyanide calibration solution containing 50 µg CN per litre and then a blank solution in the sampler in order to correct for any change in sensitivity or baseline drift.

9.5 Cleaning of the analysis system

After the distillation bath has been shut down and cooled below 100 °C, the manifold is first rinsed by pumping water through the system. At suitable intervals, or at least every two months rinse the system with sodium hydroxide solution $c(\text{NaOH}) = 0{,}1$ mol/l for 30 min to remove any dirt.

If the system is contaminated with a residue of salts, rinse with hydrochloric acid (5.1.2) for 30 min followed by thoroughly rinsing with water. If the UV-decomposition spiral is contaminated (e.g. with detergent), rinse for 15 min with 1 mol/l hydrochloric acid (5.1.2). Disconnect the coil and rinse with 20 % v/v denatured ethanol (5.1.11), followed by water.

10 Calculation of the cyanide content in the sample

Give the analysis result as the number of mg total and/or easily-liberatable cyanide per kilogramme dry matter. Read for every peak the CN concentration from the calibration graph. Calculate the cyanide content in the soil sample expressed in milligrams per kg using Formula (3):

$$W_{(\text{CN})} = W_x \times f_1 \times f_2 \times \frac{V + \left(\frac{100 - W_{\text{dm}}}{100} \times m\right)}{1000 \times m} \times \frac{100}{W_{\text{dm}}} \qquad (3)$$

where

$W_{(\text{CN})}$ is the cyanide content of the sample dried (105 °C), in milligrams per kilogram;

W_x is the cyanide content in the diluted extract determined from the calibration graph in micrograms per litre;

f_1 is the initial dilution factor (= 100) of the sample extract to the diluted extract (Clause 7);

f_2 is any further dilution factor of the diluted sample extract in order to get the cyanide concentration of the diluted extract within the measurement range (9.3); If no further dilution is used then $f_2 = 1$.

V is the volume of sodium hydroxide solution used for the extraction in millilitres (= 200 ml);

W_{dm} is the dry matter content of the soil expressed as a percentage (according to ISO 11465);

m is the original mass of the sample aliquot taken, in grams.

Report the results to two significant figures at most.

11 Precision

An inter-laboratory trial was organized to test the procedures specified in this International Standard. In this trial, the amount of easily-liberatable and total cyanides was determined by a number of laboratories on three soils.

The repeatability standard deviation (S_r), the reproducibility standard deviation (S_R), the relative repeatability standard deviation ($C_{V,r}$) and the relative reproducibility standard deviation ($C_{V,R}$) of the results of these analyses are given in Annex A.

12 Test report

The test report shall contain the following information:

a) a reference to this International Standard;

b) complete identification of the sample;

c) the results of the determination in mg/kg on a dry matter basis;

d) any details not specified in this International Standard or which are optional, as well as any factor which may have affected the results.

Annex A

(informative)

Recovery and repeatability

In an intralaboratory trial the recovery and repeatability for standard solutions of the methods described in this International Standard, the following results were obtained.[3]

See Tables A.1, A.2 and A.3.

Table A.1 — Results achieved for standard solutions

Standard solution	**N** **Measurements**	**Cyanide content** µg/l	**Total cyanide content**		**Easily-liberatable cyanide content**	
			Mean recovery %	Relative standard deviation	Mean recovery %	Relative standard deviation
KCN	40	50	98,8	1,9	98,9	1,9
$Fe_4[Fe(CN)_6]_3$	10	65,4	87,3	2,9	4,2	0,8
$K_3Fe[III]\ (CN)_6$	25	50	98,3	0,9	4,6	0,6
$K_4Fe[II]\ (CN)_6$	25	50	99,5	2,2	4,5	0,6
$Ni[II]\ (CN)_4$	25	50	99,0	2,2	99,3	1,9

In an interlaboratory trial the following validation data were obtained using the method described in this International Standard. Data are calculated according to ISO 5725-2.[5]

Table A.2 — Results achieved for determination of easily-liberatable cyanide in soil samples

	Easily-liberatable cyanide								
Sample	***N***	**N Measurements**	$\overline{X}$ mg/kg	S_r mg/kg	S_R mg/kg	$C_{V,r}$ %	$C_{V,R}$ %	***r*** mg/kg	***R*** mg/kg
Soil I	12 (0)	24	1,70	0,150	0,609	8,8	35,8	0,42	1,65
Soil II	12 (0)	24	5,18	0,409	1,40	7,9	27,1	1,15	3,93
Soil III	12 (0)	24	16,3	1,19	3,91	7,3	24,0	3,36	11,0
Standard	11 (1)	22	24,1	0,530	1,13	2,2	4,7	1,45	3,18

N is the number of laboratories left over after rejection of statistical outliers according to ISO 5725-2;
() is the number of rejected results;
$\overline{X}$ is the mean value, in milligrams per kilogram (mg/kg);
S_r is the repeatability standard deviation, in milligrams per kilogram (mg/kg);
$C_{V,r}$ is the relative repeatability standard deviation, in per cent (%);
S_R is the reproducibility standard deviation, in milligrams per kilogram (mg/kg);
$C_{V,R}$ is the relative reproducibility standard deviation, in per cent (%);
r is the repeatability, in milligrams per kilogram (mg/kg);
R is the reproducibility, in milligrams per kilogram (mg/kg).

Table A.3 — Results achieved for determination of total cyanide in soil samples

	Total cyanide								
Sample	***N***	**N° Measurements**	$\overline{X}$ mg/kg	S_r mg/kg	S_R mg/kg	$C_{V,r}$ %	$C_{V,R}$ %	***r*** mg/kg	***R*** mg/kg
Soil I	14 (0)	28	7,73	0,356	1,03	4,6	13,3	0,99	2,89
Soil II	14 (0)	28	31,8	0,795	3,34	2,5	10,5	2,21	9,35
Soil III	13 (1)	26	193	5,98	20,8	3,1	10,8	16,8	58,2
Standard	12 (2)	24	63,8	1,21	6,12	1,9	9,6	3,18	1,72

N is the number of laboratories left over after rejection of statistical outliers according to ISO 5725-2;
() is the number of rejected results;
$\overline{X}$ is the mean value, in milligrams per kilogram (mg/kg);
S_r is the repeatability standard deviation, in milligrams per kilogram (mg/kg);
$C_{V,r}$ is the relative repeatability standard deviation, in per cent (%);
S_R is the reproducibility standard deviation, in milligrams per kilogram (mg/kg);
$C_{V,R}$ is the relative reproducibility standard deviation, in per cent (%);
r is the repeatability, in milligrams per kilogram (mg/kg);
R is the reproducibility, in milligrams per kilogram (mg/kg).