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

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

Reference number
ISO 17380:2004(E)

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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

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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.*

Introduction

Cyanides can be present in soil as cyanide ions and as complex cyanides. They can be determined as easily released cyanide or as total cyanide. Complex cyanide can be calculated by subtracting the easily liberated cyanide result from the total cyanide result. This International Standard specifies the determination of easily released 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 reacts 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).

A manual method for the photometric and volumetric determination of easily liberated cyanide, complex cyanide and total cyanide in soil samples is described in ISO 11262. It is important to note that the total cyanide results in soil samples as described in ISO 11262 can show slight differences from this International Standard. These differences are not considered to be very significant for this analysis. However, the easily released cyanide test is empirical and the result is defined by the method. The easily released cyanide test described in this International Standard (using an initial distillation pH of 3,8) varies from the easily released cyanide test in ISO 11262 (using a distillation pH of 4,0). Some difference in results can be expected between these two empirical methods (see 4.2).

Soil quality — Determination of total cyanide and easily released 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 the easily released cyanide mass fraction in soil using an automated-distillation continuous-flow analysis.

The International Standard applies to all types of soil with cyanide mass fractions above 1 mg/kg on the basis of dry matter, expressed on the basis of the 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 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 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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
total cyanide mass fraction
mass fraction of inorganic cyanide compounds consisting of the sum of the mass fractions of easily released cyanide species and that of cyanide bound in simple metal cyanides, with the exception of the cyanide bound in cobalt complexes and with thiocyanate ions

3.2
easily released cyanide mass fraction
mass fraction of inorganic cyanide compounds consisting of the sum of the mass fractions of the easily released cyanide ions and the cyanide bound in simple metal cyanides (all expressed as CN) that are determined under the conditions of the method described in this International Standard

NOTE The weakly complexed cyanide contained in tetracyanonickelate(II) and dicyanomercurate(II) is determined with the method for easily released cyanide. Up to 10 % of the strongly complexed cyanide in iron(III) hexacyanoferrate(II), hexacyanoferrate(III) and hexocyanoferrate(II) is determined with the method for easily released cyanide. Organic cyanide compounds (such as acetonitrile) are not determined.

3.3
complex cyanide mass fraction
total cyanide mass fraction less the easily released cyanide mass fraction

4 Principle

4.1 Pretreatment of soil samples

The soil sample is extracted with 2,5 mol/l sodium hydroxide solution. The extract is diluted 100 times, after which analysis of total and/or easily released 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. A 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 a buffer solution, with an initial pH of 3,8, to the sample flow of 0,025 mol/l NaOH (ratio 1,0:0,42) 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 released 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, $c(\mathrm{HCl}) = 1$ mol/l.

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

5.1.3 Hydrochloric acid, $c(\mathrm{HCl}) = 0{,}1$ 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, $c(\mathrm{NaOH}) = 2{,}5$ mol/l.

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

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

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

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

5.1.6 Sodium hydroxide solution, $c(\mathrm{NaOH}) = 0{,}025$ 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
$[(NaO_2C)CH(SO_3Na)CH_2CO]N(C_{12}H_{25})CH(CO_2Na)CH_2CO_2Na$

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

NOTE This solution is commercially available as Brij-35[1]. To dissolve the Brij-35, the temperature can be raised to 40 °C.

5.1.8 Indicator solution.

Dissolve 0,02 g 5-(*p*-dimethylaminobenzylindene)-rhodanine in 100 ml acetone. This solution can be stored for at least one week if kept in the dark and refrigerated (4 °C to 6 °C).

5.1.9 Silver nitrate solution, $c(\mathrm{AgNO_3}) = 0{,}01$ mol/l.

Dissolve 1,689 7 g of silver nitrate in approximately 400 ml water and dilute to 1 l 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 bi-weekly basis. Store this solution in the dark in a brown glass bottle. Prepare a fresh solution monthly.

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[1] Brij-35 is an example of a suitable product available commercially. This information is given for the convenience of users of ISO 17380 and does not constitute an endorsement by ISO of this product. Equivalent products may be used if they can be shown to lead to the same results.

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 Denatured ethanol, 20 % volume fraction.

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 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.

5.2.2 Zinc sulfate solution.

Dissolve 10 g zinc sulfate heptahydrate, $ZnSO_4{\cdot}7H_2O$, in 750 ml water, mix and dilute to 1 000 ml with water. This solution is stable for at least one year.

5.2.3 Buffer solution, for photometric determination, pH = 5,2.

Dissolve 2,3 g sodium hydroxide in 500 ml water. Add 20,5 g 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.

5.2.4 Chloramine-T solution.

Dissolve 2,0 g chloramine-T, $C_7H_7ClNNaO_2S{\cdot}3H_2O$, in 1 000 ml water. This solution is stable for three months if it is kept in the dark and refrigerated.

5.2.5 Colour reagent, pH = 5,2.

Dilute 7,0 g solid sodium hydroxide NaOH in 500 ml water. Add 16,8 g 1,3-dimethylbarbituric acid, $C_6H_8N_2O_3$, and 13,6 g 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, and filtered over a pleated filter before use.

5.3 Standard solutions for cyanide determination.

The concentrated standard solutions (5.3.1.1) 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 (less than 10 °C).

5.3.1 Potassium cyanide standard solutions.

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

Dissolve 0,250 g 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, the standard cyanide solution with a content of 100 mg/l CN (5.3.1.1). 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, designating the titration volume as V_1.

Calculate the cyanide concentration in the standard cyanide solution in accordance with Equation (1):

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

where

V_1 is the volume, in millilitres, of silver nitrate solution (5.1.9) used for the titration;

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

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

V is the volume, in millilitres (= 10), of the standard cyanide solution.

NOTE Commercially available standard solutions may also be used [e.g. potassium tetracyanozincate, $K_2Zn(CN)_4$, c(CN = 1 000 ± 2 mg/l)].

5.3.1.2 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 (5.3.1.1) into a volumetric flask of 250 ml and fill to the mark with sodium hydroxide solution 0,025 mol/l (5.1.6).

5.3.2 Control solutions.

5.3.2.1 Potassium thiocyanate solution, corresponding to 100 mg/l of cyanide ion.

Dissolve 0,373 g 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 1 000 ml volumetric flask make up with sodium hydroxide solution 0,025 mol/l (5.1.6).

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

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

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

Dissolve 0,211 g 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).

5.3.2.4 Potassium hexacyanoferrate solution, corresponding to 1 mg/l of cyanide ion.

Transfer, by means of a pipette, 2,5 ml of 100 mg/l potassium hexacyanoferrate solution (5.3.2.3) into a 250 ml volumetric flask and fill to the mark with sodium hydroxide solution 0,025 mol/l (5.1.6).

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

Transfer, by means of a pipette, 10 ml of 10 mg/l potassium hexacyanoferrate(III) solution (5.3.2.4) 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 5.3.2.2 and 5.3.2.5 are used to check the correct operation of the total cyanide method (see 9.2.4, 9.2.5 and 9.2.7). Solutions 5.3.2.2 and 5.3.2.4 are used to check the correct operation of the easily released cyanide method (see 9.2.4, 9.2.6 and 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, as 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 instrument as mentioned in ISO 14403 can be used.

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

A sample changer is used to set a sample time of 80 s and a rinsing time of 160 s.

For the UV decomposition (see Figure 1, item 3), 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 maximum wall thickness of 1 mm and an internal diameter of 2 mm. Borosilicate glass type DURAN 8330[2] 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 Figure 1, item 5) shall be placed vertically with at least 40 turns. 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, for a determination of total cyanide, the measurement of a thiocyanate solution with a concentration of 1 000 µg/l as CN gives a value of less than 10 µg/l CN. The coolers (see Figure 1, items 6 and 7 in) can be connected in line after the distillation equipment. The heating bath (see Figure 1, item 8) 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 Figure 1, item 9) shall be equipped with a continuous-flow cell with an optical path length of 50 mm and a filter of 600 nm ± 10 nm with a maximum bandwidth of 10 nm. The maximum absorption occurs at 606 nm and this wavelength should be used if a spectrometer is employed.

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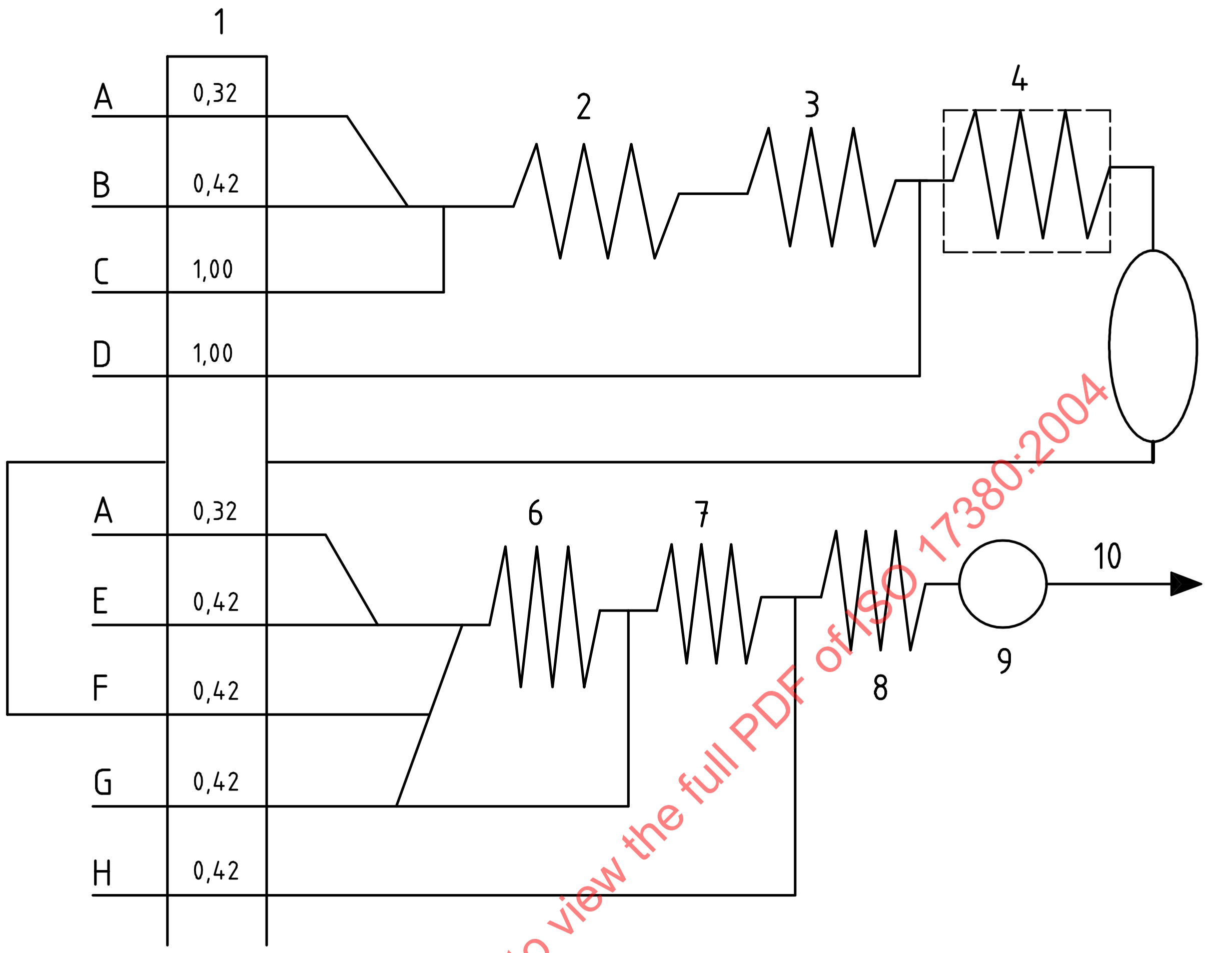
[2] DURAN 8330 is an example of a suitable product available commercially. This information is given for the convenience of users of ISO 17380 and does not constitute an endorsement by ISO of this product. Equivalent products may be used if they can be shown to lead to the same results.



Key

1 pumps (with flow rates, expressed in ml/min)
2 reaction coil (50 cm, ∅ int. 1 mm)
3 UV decomposition unit (312 nm)
4 heating bath (30 °C)
5 distillation unit (125 °C)
6 reaction coil (50 cm, ∅ int. 1 mm)
7 reaction coil (50 cm, ∅ int. 1 mm)
8 heating bath (37 °C, 100 cm, ∅ int. 1 mm)
9 detector (e.g. 1 cm optical path length), wavelength 590 nm to 610 nm
10 waste

A line for segmentation gas (air)
B line for buffer for distillation (5.2.1)
C line for sample
D line for $ZnSO_4$ solution (5.2.2) for easily released cyanide, or water for total cyanide (see Table 1)
E line for buffer solution for final photometric determination (5.2.3)
F line for resample
G line for chloramine-T trihydrate solution (5.2.4)
H line for colour reagent (5.2.5)

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

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

NOTE Good results are obtained with an apparatus generating 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 Extraction procedure

Take a field-moist soil sample, which can be stored for up to 4 days in a refrigerator at less than 10 °C (see note). Remove visible coarse constituents. As cyanide is labile, the test portion should be prepared in accordance with the procedure for volatile compounds, given in ISO 14507:2003, 8.2. Suspend a quantity of the sample equivalent to approximately 40 g 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 shaking machine 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) with water. Any other dilutions should be made with sodium hydroxide 0,025 mol/l solution (5.1.6). Analyse the diluted extract using the method for total and/or easily released cyanide as soon as possible but within 4 days. Care must be exercised when handling sodium hydroxide solutions (see warning 5.1.4).

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

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 analytical 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 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 in accordance with 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 released 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 Start operating the analysing system by first pumping water and then 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 Preliminary analysis checks should also be made to confirm that less than 10 % of the bound cyanide in hexacyanoferrate(III) is detected as easily released cyanide and that over 90 % 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, $R_{\mathrm{(CN)}}$, expressed in percent, in accordance with Equation (2):

$$R_{\mathrm{(CN)}} = X_{\mathrm{TS}} / X_{\mathrm{STD}} \times 100 \qquad (2)$$

where

X_{TS} is the measured value of the test solution;

X_{STD} is the measured value of the standard cyanide solution.

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) (5.3.2.3) 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 released cyanide, the system is suitable if the recovery of the 1 mg/l standard solution of hexacyanoferrate(III) (5.3.2.4) is less than 5 % [i.e. $R_{\mathrm{(CN)}}$ hexacyanoferrate < 5 %]. If levels of easily released cyanide higher than this are measured, significant breakdown of the hexacyanoferrate to cyanide has occurred. Prepare a fresh hexacyanoferrate solution and check that the lamp and the reaction coil material meet the specification (see 6.2).

9.2.7 Prior to analysis, checks should be made to confirm that the breakdown of thiocyanate occurring during the determination easily released and total cyanide is negligible. For total or easily released cyanide, no more than 10 µg/l or < 2 µg/l cyanide, respectively, shall be found on measurement of a thiocyanate solution of $c(\mathrm{CN}) = 1\,000$ µg/l (5.3.2.2); i.e. $R_{\mathrm{(CN)}}$ thiocyanate < 1 % or 0,2 %, respectively. If levels of easily released cyanide higher than this are measured, significant breakdown of the thiocyanate to cyanide has occurred. Prepare a fresh thiocyanate solution and check that 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, an aliquot amounting to 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 (5.3.1.2) into one of eight 100 ml volumetric flasks and making up to the mark with 0,025 mol/l sodium hydroxide solution (5.1.6). These eight 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 concentration, c_x, expressed in micrograms per litre. 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 tenth sample a control solution, e.g. a cyanide calibration solution containing 50 µg/l CN, in the sampler in order to correct for any deviation in the system.

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 into 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 salt, rinse with hydrochloric acid (5.1.2) for 30 min followed by a thorough rinsing with water. If the UV-decomposition spiral is contaminated with detergent, rinse for 15 min with 1 mol/l hydrochloric acid (5.1.2). Disconnect the coil and rinse with 20 % volume fraction denatured ethanol (5.1.11), followed by water.

10 Calculation of the cyanide mass fraction in the sample

Give the analysis result as the number of milligrams total and/or easily released cyanide per kilogram dry matter. Read for every peak the CN concentration from the calibration graph. Calculate the cyanide mass fraction, $W_{(\text{CN})}$ expressed in milligrams per kilogram, of the soil sample dried at 105 °C, in accordance with Equation (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_x is the cyanide concentration, expressed in micrograms per litre, of the diluted extract as determined from the calibration graph;

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 (9.4), and is equal to 1 if no further dilution is used;

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

W_{dm} is the dry matter mass fraction, expressed as a percentage in accordance with ISO 11465, of the soil;

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

Round the results in accordance with Table 2.

Table 2 — Rounding of analytical results for soil samples

Range of mass fraction values, $W_{(CN)}$, for cyanide mg/kg	**Rounded to nearest** mg/kg
$W_{(CN)} \leqslant 1$	< 1
$1 < W_{(CN)} \leqslant 10$	0,1
$10 < W_{(CN)} \leqslant 50$	1
$50 < W_{(CN)} \leqslant 100$	5
$100 < W_{(CN)} \leqslant 1\,000$	10
$1\,000 < W_{(CN)}$	50

11 Precision

An inter-laboratory trial was organized to test the procedures specified in this International Standard. In this trial, the amount of easily released 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 repeatability coefficient of variation, CV_r, and the reproducibility coefficient of variation, CV_R, of the results of these analyses are given in Annex A. The values have been calculated in accordance with ISO 5725-2:1994.

12 Test report

The test report shall contain the following information:

a) reference to this International Standard;

b) complete identification of the sample;

c) the results of the determinations, expressed in milligrams per kilogram on a dry-mass basis, rounded in accordance with Table 2;

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