TECHNICAL SPECIFICATION

ISO/TS 17182

First edition
2014-12-15

Soil quality — Determination of some selected phenols and chlorophenols — Gas chromatographic method with mass spectrometric detection

Qualité du sol — Dosage de quelques phénols et chlorophénols sélectionnés — Méthode par chromatographie en phase gazeuse avec détection par spectrométrie de masse

Reference number
ISO/TS 17182:2014(E)

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Published in Switzerland

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Foreword

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

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Soil quality — Determination of some selected phenols and chlorophenols — Gas chromatographic method with mass spectrometric detection

WARNING — Phenols and chlorophenols are both toxic and corrosive and should be handled with care. Methanol and acetonitrile are toxic and acetic acid is corrosive. Latex or nitrile gloves and eye protection should be worn at all times. Spills should immediately be wiped up with adsorbent tissue and placed in sealed containers used for the disposal of toxic chemicals. Samples should be treated as toxic and harmful. Extreme care shall be taken through all steps of the extraction procedure, which shall be performed in a fume hood. All solvent wastes shall be collected and treated as hazardous waste. Thus, there is a contamination risk in the laboratory.

1 Scope

This International Standard describes the gas chromatographic determination of phenols, methyl phenols, di-methylphenols and tri-methylphenols (see Table 1) and selected chlorophenols (see Table 2) by using mass spectrometric detection in soil samples. This method can also be used for other solid samples, such as sediments and solid wastes. This International Standard describes an acidic liquid extraction of soil, followed by acetylation and then liquid/liquid extraction. Determination takes place by gas chromatography and mass spectrometric detection.

With this method, phenols and chlorophenols can be determined at the lowest of mass concentrations ranging from approximately 0,01 mg/kg to 0,1 mg/kg depending on the component sensitivity and the quantity of sample used. In some cases, complete separation of isomers cannot be achieved. Then the sum is reported.

NOTE With this method, other higher methylated phenols can also be analysed provided that the suitability and the validity of the method is proven.

Table 1 — Target phenolic compounds with relevant mass fractions of respective acetylated compounds for MS-detection

Compound	CAS-RN[a]	Chemical formula	Acetylated compounds Fragmentation[b]			
			1st mass	Relative intensity %	2nd mass	Relative intensity %
phenol	108-95-2	C_6H_6O	94	100	66	26
2-methylphenol (o-cresol)	95-48-7	C_7H_8O	108	100	107	68
3-methylphenol (m-cresol)	108-39-4	C_7H_8O	108	100	107	85
4-methylphenol (p-cresol)	106-44-5	C_7H_8O	108	100	107	92
2,3-dimethylphenol	596-75-0	$C_8H_{10}O$	122	90	107	100
2,4-dimethylphenol	105-67-9	$C_8H_{10}O$	122	100	107	85
2,5-dimethylphenol	95-87-4	$C_8H_{10}O$	122	100	107	90
2,6-dimethylphenol	576-261-1	$C_8H_{10}O$	122	100	107	92

[a] Chemical abstract service registry number.

[b] Spectral database for organic compounds (SDBS).

Table 1 *(continued)*

Compound	CAS-RN[a]	Chemical formula	Acetylated compounds Fragmentation[b]			
			1st mass	Relative intensity %	2nd mass	Relative intensity %
3,4-dimethylphenol	95-65-8	$C_8H_{10}O$	122	99	107	100
3,5-dimethylphenol	108-68-9	$C_8H_{10}O$	122	100	107	68
2,3,5-trimethylphenol	697-82-5	$C_9H_{12}O$	136	87	121	100
2,3,6-trimethylphenol	2416-94-6	$C_9H_{12}O$	136	90	121	100
2,4,6-trimethylphenol	527-60-6	$C_9H_{12}O$	136	10	121	85
3,4,5-trimethylphenol	527-54-8	$C_9H_{12}O$	136	70	121	100
2-ethylphenol	90-00-6	$C_8H_{10}O$	107	100	122	48
3-ethylphenol	620-17-7	$C_8H_{10}O$	122	48	107	100
4-ethylphenol	123-07-9	$C_8H_{10}O$	107	100	122	35
4-propylphenol	645-56-7	$C_9H_{12}O$	107	100	136	25
4-isopropylphenol	99-89-8	$C_9H_{12}O$	121	100	136	28
2-hydroxybiphenyl	90-43-7	$C_{12}H_{10}O$	170	100	141	23
Internal standards						
2-fluorophenol	367-12-4	C_6H_5FO	112	100	64	58
4-fluorophenol	371-41-5	C_6H_5FO	112	100	64	18
3-fluoro-2-methyl-phenol	452-72-2	C_7H_7FO	126	100	97	29
4-fluorocatechol	367-32-8	$C_6H_5FO_2$	128	100	75	28

[a] Chemical abstract service registry number.

[b] Spectral database for organic compounds (SDBS).

Table 2 — Target chlorophenolic compounds with relevant mass fractions of respective acetylated compounds for MS-detection

Compound	CAS-RN[a]	Chemical formula	Acetylated compounds Fragmentation			
			1st mass	Relative intensity %	2nd mass	Relative intensity %
2-chlorophenol	95-57-8	C_6H_5OCl	128	100	130	34
3-chlorophenol	108-43-0	C_6H_5OCl	128	100	130	29
4-chlorophenol	106-48-9	C_6H_5OCl	128	100	130	35
2,6-dichlorophenol	87-65-0	$C_6H_4OCl_2$	162	100	164	67
2,4-dichlorophenol	120-83-2	$C_6H_4OCl_2$	162	100	164	66
2,5-dichlorophenol	583-78-8	$C_6H_4OCl_2$	162		164	
3,5-dichlorophenol	591-35-5	$C_6H_4OCl_2$	162	100	164	66
2,3-dichlorophenol	576-24-9	$C_6H_4OCl_2$	162	100	164	66
3,4-dichlorophenol	95-77-2	$C_6H_4OCl_2$	162	100	164	66
2,4,6-trichlorophenol	88-06-2	$C_6H_3OCl_3$	196	100	198	98

[a] Chemical abstract service registry number.

Table 2 *(continued)*

Compound	CAS-RN[a]	Chemical formula	Acetylated compounds Fragmentation			
			1st mass	Relative intensity %	2nd mass	Relative intensity %
2,3,6-trichlorophenol	933-75-5	$C_6H_3OCl_3$	196	100	198	100
2,3,5-trichlorophenol	933-78-8	$C_6H_3OCl_3$	196	100	198	100
2,4,5-trichlorophenol	95-95-4	$C_6H_3OCl_3$	196	96,1	198	100
2,3,4-trichlorophenol	15950-66-0	$C_6H_3OCl_3$	196	100	198	98
3,4,5-trichlorophenol	609-19-8	$C_6H_3OCl_3$	196	100	198	100
2,3,4,5-tetrachlorophenol	4901-51-3	$C_6H_2OCl_4$	230	—	232	—
2,3,5,6-tetrachlorophenol	935-95-5	$C_6H_2OCl_4$	230	79	232	100
2,3,4,6-tetrachlorophenol	58-90-2	$C_6H_2OCl_4$	230	78	232	100
pentachlorophenol	87-86-5	C_6HOCl_5	264	66	266	100

[a] Chemical abstract service registry number.

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 10381-1, *Soil quality — Sampling — Part 1: Guidance on the design of sampling programmes*

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

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

ISO 18512, *Soil quality — Guidance on long and short term storage of soil samples*

ISO 22892, *Soil quality — Guidelines for the identification of target compounds by gas chromatography and mass spectrometry*

3 Principle

The method described here is based on two steps. The first step includes a solid/liquid extraction: the phenols are extracted from field moist soil with methanol at low pH. The second step is the derivatization of phenols obtained in an aliquot of methanol in aqueous carbonate solution with acetic anhydride; the derivatives formed are extracted from this sample with cyclohexane. The cyclohexane fraction is analyzed by gas chromatography with mass spectrometric detection.

4 Interferences

4.1 Interference with sampling and extraction

Standard laboratory glassware, appropriately cleaned and free of interfering compounds. Do not use any kind of plastic containers, since phenols can be adsorbed to these. Plastic materials can also contribute their impurities to the sample material. Surfactants, present in the sample, might disturb the proper extraction of phenols.

4.2 Interference with GC-MS determination

Substances which have the same or nearly the same retention time of the target analytes and which give the same mass fragments (i.e. isomeric phenols other than stated in the table) might interfere with the determination.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and water of at least grade 1 as defined in ISO 3696.

Only commercially available certified standards of high purity shall be used.

5.1 Products used in their commercially available form

5.1.1 Gas chromatography gases, of a purity as recommended by the gas chromatography manufacturer.

5.1.2 Methanol, CH_3OH, with a mass fraction of 99,5 %.

5.1.3 Cyclohexane, C_6H_{12} or other hydrocarbon solvent like heptane.

5.1.4 Hydrochloric acid, HCl, concentrated, with a mass fraction of 37 %.

5.1.5 Sodium hydroxide, NaOH.

5.1.6 Potassium carbonate, K_2CO_3.

5.1.7 Acetic anhydride, $(CH_3CO)_2O$, anhydrous.

5.1.8 Sodium sulfate, Na_2SO_4, anhydrous.

Weigh portions of 2 g of sodium sulfate into test tubes with polytetrafluoroethylene (PTFE) lined caps. Dry the test tubes at (550 ± 20) °C for 4 h ± 30 min without caps. Take them to a desiccator and let them cool. When cooled, put on the caps and store the tubes at room temperature. Sodium sulfate can also be dried in bigger portions and stored in a desiccator after cooling. Weigh portions of 2 g into tubes when needed.

5.1.9 Selected phenol and chlorophenol standards, listed in Table 1 and Table 2.

5.1.10 Selected fluorophenol standards, listed in Table 1 as internal standard.

NOTE Other compounds such as isotopic and deuterated phenols which might not interfere with the GC-MS measurement can also be used as internal standards.

5.2 Aqueous solutions

5.2.1 Sodium hydroxide solution, NaOH, c(NaOH) = 0,1 mol/l.

5.2.2 Sodium hydroxide solution, NaOH, c(NaOH) = 0,5 mol/l.

5.2.3 Potassium carbonate solution, K_2CO_3, $c(K_2CO_3)$ = 0,1 mol/l.

5.2.4 Potassium carbonate solution, K_2CO_3, $c(K_2CO_3)$ = 5,2 mol/l.

5.3 Standard solutions of phenols

5.3.1 Internal standard solution

5.3.1.1 General

Fluorophenols can be used as suitable internal standard.

5.3.1.2 Stock solution

Prepare the stock solution by weighing fluorophenols (5.1.10) and dissolving it in methanol (5.1.2). A suitable concentration is 1 mg/ml. Divide the stock solution into 5 ml bottles with tight caps, 1,5 ml to each, and store at –18 °C.

NOTE Stock solutions are stable for at least half a year when stored in the dark at 4 °C. They are stable at least one year at –18 °C.

5.3.1.3 Working solution

Prepare this working solution by diluting the stock solution (5.3.1.2) with distilled water. A suitable concentration is 100 µg/ml.

5.3.2 Individual standard phenol solutions

5.3.2.1 General

Typical concentrations of standard solutions are given in Annex A.

5.3.2.2 Stock solution

Weigh out each of the phenol standards (5.1.9) into the same or into separate measuring flasks and dissolve them in methanol (5.1.2). A suitable concentration is 0,5 mg/ml. Divide the stock solution(s) into 5 ml bottles with tight PTFE lined caps, 1,5 ml to each, and store at –18 °C.

NOTE Stock solutions are stable for at least half a year when stored in the dark at 4 °C. They are stable at least one year at –18 °C.

5.3.2.3 Working solution

Dilute stock solution(s) (5.3.2.2) with distilled water to one working solution. A suitable concentration is 50 µg/ml.

6 Apparatus and equipment

6.1 General requirements

Standard laboratory glassware appropriately cleaned and free of interfering compounds. Do not use any kind of plastic containers, since the phenols can adsorb to these or plastic materials can contribute their impurities to the sample material.

6.2 Gas chromatography system

6.2.1 Gas chromatograph, equipped with a non-discriminating injection system, capillary column, and a mass spectrometric detector (GC-MS).

6.2.2 Capillary columns, each comprising a 5 % phenyl-methyl silicone stationary phase coated onto fused silica capillary column or an equivalent chemically bonded phase column. Their dimensions should be sufficient to separate the critical pairs mentioned below. In general, column length should be at least 30 m. Internal diameter 0,25 mm and film thickness 0,2 µm.

Sufficient resolution (0,7) between the chromatographic peaks of critical pairs as m-cresol and p-cresol shall be set as quality criteria for the capillary column. Otherwise, the sum of both isomers is to be reported.

6.3 Ultrasonic bath

6.4 Shaking device, with horizontal movement (200 strokes per min to 300 strokes per min).

7 Sampling

Take samples according to ISO 10381-1 and pre-treat the samples according to ISO 14507.

Samples shall be taken in glass vessels with PTFE caps. It is recommended that the vessel be filled completely.

Store the samples in the dark in the laboratory according to ISO 18512. Phenols may be subject to microbial conversion under certain conditions. It is recommended that samples are frozen if they are stored for more than 2 days.

As phenols in soil are subject to biodegradation, some of the phenols are volatile; the sample containers should be filled on site with methanol to preserve the phenols. Bottles containing reagent should be pre-weighed in the laboratory before filled with sample material and re-weighed on receipt in the laboratory.

8 Procedure

8.1 Test portion

At least 10 g with an accuracy of 0,01 g of field moist soil is taken directly from the vessel. The sample is taken with a spoon or a spatula by mixing the soil as well as possible.

8.2 Dry matter content

The dry matter content of the soil shall be determined in a subsample of the same vessel according to ISO 11465.

8.3 Blank sample

Blank samples shall be treated exactly the same way as normal samples but the test portion (8.1) is replaced by 10 g of sample matrix known to be free of phenols.

8.4 Standard sample

Standard samples shall be treated exactly the same way as normal samples but the test portion (8.1) is replaced by 50 µl of standard working solution (5.3.2.3) and 10 g of sample matrix known to be free of phenols.

8.5 Extraction

Take a test portion of 10 g soil and place it in a conical flask. Add 50 µl of internal standard working solution (5.3.1.3), 75 ml of methanol (5.1.2), and 0,5 ml of hydrochloric acid (5.1.4).

In case of high concentrations, more of the internal standard should be added.

Sonicate the sample for 10 min and then shake for at least 30 min with 200 strokes per min to 300 strokes per min. Allow the sample to settle and transfer an aliquot of the methanol extract (e.g. 10 ml) to a separating funnel with 50 ml of potassium carbonate aqueous solution (5.2.3).

Some types of soil are acidic, contain carbonates, or have a high buffer capacity. In these cases, the amounts of acid and base added are not enough to reach sufficiently low pH. When phenols are to be analysed in these types of soil, check the pH-values to be pH < 3 in the extraction step.

8.6 Acetylation

8.6.1 Acetylation of extract

Acetylate the phenols and chlorophenols in 50 ml potassium carbonate solution (5.2.3) as follows: Add 2 ml of sodium hydroxide aqueous solution (5.2.2) and 1 ml of acetic anhydride (5.1.7) to the extract and shake the mixture vigorously for 2 min to release any carbon dioxide formed in the funnel. Let the mixture stand for 10 min while shaking occasionally, and then add 10 ml of cyclohexane (5.1.3). Shake the funnel and let the two phases separate. Transfer as large a portion as possible of the cyclohexane phase to a tube containing 2 g of Na_2SO_4 (5.1.8) for drying. After shaking, transfer the cyclohexane solution to another vial with Na_2SO_4 and store at 4 °C. Analysis of the acetylated phenols shall be done as soon as possible (within 48 h) since the acetates are rather labile towards hydrolysis.

8.6.2 Acetylation of control samples

Take 50 µl of standard working solution and add it to a separation funnel with 50 ml of potassium carbonate solution (5.2.3) and shake the funnel. Add 2 ml of sodium hydroxide aqueous solution (5.2.2) and 1 ml of acetic anhydride (5.1.7) to the separation funnel and shake the mixture vigorously for 2 min to release any carbon dioxide formed in the funnel. Let the mixture stand for 10 min while shaking occasionally, and then add 10 ml of cylohexane (5.1.3). Shake the funnel and let the two phases separate. Transfer as large a portion as possible of the cyclohexane phase to a tube containing 2 g of Na_2SO_4 (5.1.8) for drying. After shaking, transfer the cyclohexane solution to another vial with Na_2SO_4 and store at 4 °C. Analysis of control samples shall be done as soon as possible (within 48 h).

8.7 Gas chromatographic analysis

Set up the GC-MS system equipped with appropriate columns (6.2.2). Optimize the gas flows to obtain sufficient separation. Ensure a stable condition. An example of gas chromatographic conditions and temperature programme is given in Annex B. The mass spectrometer is tuned in accordance with the manufacturer's instructions. Chromatograms are recorded in full scan or selected ion mode (SIM). Examples for characteristic masses of analytes are given in Table 1 and Table 2.

Use ISO 22892 for identification of the analytes.

8.8 Calibration

Use extracted and acetylated standard samples (8.4) as calibration solutions. Calibration solutions should be prepared according to 8.4 by adding a constant definite volume of internal standard working solution (5.3.1.3) adding different volumes of working solution (5.3.2.3). For each compound, a separate calibration function shall be established, consisting of at least five measurement points. It is permissible to examine several compounds in one calibration.

The calibration function obtained for a particular compound is valid only for the established concentration range and the respective sample preparation used. It depends on the operational conditions of the entire analytical system.

Calibration shall be based on peak height or area and on the response of the internal standard.

