INTERNATIONAL STANDARD

ISO 8165-1

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Water quality — Determination of selected monovalent phenols —

Part 1:
Gas-chromatographic method after enrichment by extraction

Qualité de l'eau — Dosage des phénols monovalents sélectionnés —
Partie 1: Méthode par chromatographie en phase gazeuse après enrichissement par extraction

Reference number
ISO 8165-1:1992(E)

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.

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.

International Standard ISO 8165-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Sub-Committee SC 2, *Physical, chemical, biochemical methods*.

ISO 8165 consists of the following parts, under the general title *Water quality — Determination of selected monovalent phenols*:

— *Part 1: Gas chromatographic method after enrichment by extraction*

— *Part 2: Method after derivatization with pentafluoro-benzoyl bromide*

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Introduction

In the determination of phenols by gas chromatography, several pretreatment methods may be applied depending on the problem to be solved. Basically, the extraction procedure described in this International Standard may be applied to all kinds of water. Compared with derivatization procedures, the limits of determination achievable with this procedure are not quite as low. On the other hand, the derivatization procedures are more likely to be interfered with by compounds such as amines and sometimes alcohols, therefore these procedures cannot be applied to all kinds of waste water.

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Water quality — Determination of selected monovalent phenols —

Part 1:
Gas-chromatographic method after enrichment by extraction

1 Scope

This part of ISO 8165 specifies a method for the determination of the phenols presented in table 1 in a concentration range from 0,1 µg/l to 1 mg/l. The concentration range depends on the nature of the phenols to be determined and on the gas chromatographic method used.

Other monovalent phenols may also be analyzed according to this procedure, the applicability, however, should be investigated for each particular case.

Table 1 — Phenols determinable using this method

Phenol
2-Methylphenol
3-Methylphenol
4-Methylphenol
2,4-Dimethylphenol
4-Ethylphenol
2,6-Di-*tert*-butyl-4-methylphenol
2-Phenylphenol
2-Benzylphenol
2-Benzyl-4-methylphenol
2-Chlorophenol
3-Chlorophenol
4-Chlorophenol
4-Chloro-2-methylphenol
4-Chloro-3-methylphenol
2,4-Dichloro-3,5-dimethylphenol
2-Cyclopentyl-4-chlorophenol
6-Chlorothymol
2,3-Dichlorophenol
2,4-Dichlorophenol
2,5-Dichlorophenol
2,6-Dichlorophenol
2,4,6-Trichlorophenol
2,3,5-Trichlorophenol
2,4,5-Trichlorophenol
2,3,6-Trichlorophenol
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol
2,3,5,6-Tetrachlorophenol
Pentachlorophenol
1-Naphthol
2-Naphthol
6-Chloro-3-methylphenol
2-Chloro-4-*tert*-butylphenol
4-Chloro-2-benzylphenol

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 8165. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 8165 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3:1985, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

3 Principle

Extraction of the unfiltered sample with diethylether and enrichment of the phenolic compounds in the extract under defined conditions. Gas chromatographic evaluation, using two capillary columns of different polarity (simultaneous splitting) and detection with a flame ionization detector (FID) or an electron capture detector (ECD) in the case of polychlorinated phenols.

4 Interferences

Surfactants, emulsifiers or high concentrations of polar solvents, such as acetone, methanol etc. will affect the extraction. Suspended particles in the water sample may also interfere with the extraction. A second liquid phase in the water sample (e.g. mineral oil compounds, highly volatile chlorinated hydrocarbons, emulsified fats and wax) hamper the pretreatment and the extraction. In this case, only the aqueous phase shall be investigated and the volume of the non-aqueous phase shall be reported with the results.

Interferences of the gas chromatographic system may have various reasons and shall be investigated by the applier with the aid of the operating manual.

5 Reagents

The content of monophenols in water and in the reagents used should be negligibly low. The blank of the water should be determined according to 8.3. If necessary, the water should be purified by distillation of water alkalized with sodium hydroxide (NaOH).

5.1 Sulfuric acid, $\rho = 1{,}84$ g/ml, diluted 1 + 3.

5.2 Sodium hydroxyde solution I, $c = 2$ mol/l.

5.3 Sodium hydroxide solution II, $c = 0{,}2$ mol/l.

5.4 Sodium sulfite (Na_2SO_3).

5.5 Methanol (CH_3OH).

5.6 Dioxane ($C_4H_8O_2$), freshly distilled if necessary.

5.7 Diethylether ($C_4H_{10}O$).

Normally diethylether is stabilized with 2,6-di-tert-butyl-phenol or 2,6-di-tert-butyl-4-methyl-phenol and has to be cleaned prior to use as follows.

Add 10 ml of sodium hydroxide solution I (5.3) to 500 ml of diethylether and distill over a 50 cm long Vigreux column. Discard a residue of 50 ml. The residue may contain peroxides and shall therefore be treated appropiately.

5.8 Silica gel, particle size 0,063 mm × 0,200 mm (equivalent to 70 × 230 mesh).

5.9 Diethylamine ($C_4H_{11}N$), freshly distilled if necessary.

WARNING — Diethylamine is toxic.

5.10 Sodium sulfate (Na_2SO_4), anhydrous.

5.11 Internal standard stock solution.

Dissolve, for example, 1 g of 2,4-dibromophenol or 2,5-dibromophenol in 1 litre of acetone.

1 ml of this solution contains 1 mg of phenol.

5.12 Internal standard solution.

Dilute, for example, 1 ml of internal standard stock solution (5.11) with acetone to 100 ml.

1 ml of this solution contains 10 µg of phenol.

5.13 Phenol stock solution.

Dissolve, for example, 10,0 mg of the respective phenol in methanol in a 100 ml measuring flask and dilute to volume with methanol. The solution contains 0,1 mg/ml of the respective phenol.

Instead of methanol, acetone may also be used.

For the simultaneous determination, several phenols may be dissolved in the respective volume of methanol.

Store the stock solutions in brown glass bottles, tightly stoppered, in a refrigerator.

5.14 Phenol standard solutions.

Pipette 10 ml of the stock solution (5.13) into a 100 ml measuring flask, and dilute to volume with methanol.

The solution contains 0,01 mg/ml of the respective phenol. Prepare the solutions freshly before use.

6 Apparatus

6.1 Storage bottles, brown glass, of capacity 250 ml and 1 000 ml.

6.2 Water bath.

6.3 Distillation apparatus for the distillation of solvents, e.g. a round-bottomed flask, of capacity 1 000 ml, distillation head, condenser, adapter, distillation receiver, e.g. a round-bottomed flask, of capacity 1 000 ml.

6.4 Distillation apparatus for concentration of the extract, consisting of a round-bottomed flask, of capacity 250 ml, with tapered tip, gas inlet tube, distillation head, thermometer, condenser, adapter, and distillation receiver, e.g. a round-bottomed flask, of capacity 50 ml. (See figure 1.)

6.5 Glass column, of length 20 cm and inner diameter 12 mm, tapered at the bottom, which is filled with 5 cm of silica gel (5.8), pre-cleaned with diethylether (see 5.7).

6.6 Shaking apparatus, linear shaker.

6.7 Separating funnels, with polytetrafluoroethylene (PTFE) cocks, of capacity 100 ml, 250 ml and 1 000 ml.

6.8 Measuring flasks, of capacity 5 ml, 10 ml and 1 000 ml.

6.9 Beakers, of capacity 100 ml, 250 ml and 1 000 ml.

6.10 Vigreux column, of length 50 cm.

6.11 Tapered round-bottomed calibrated flask, of capacity 10 ml.

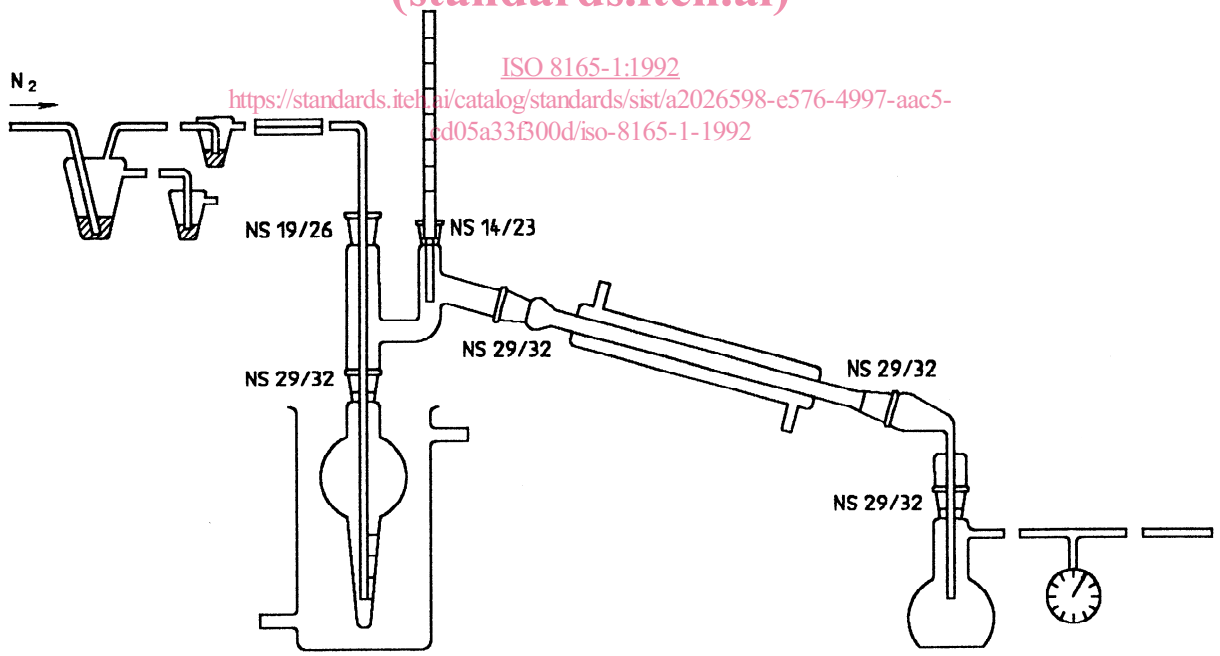

Figure 1 — Apparatus for the concentration of phenols from ether extracts under conditions of isothermic distillation

6.12 Sample bottles with PTFE-coated septum, of capacity 2 ml and 5 ml, or another device for storage of the extract.

6.13 Measuring cylinder, of capacity 250 ml.

6.14 Evaporator, e.g. Kuderna Danish evaporator.

6.15 Gas chromatograph, all-glass, with flame ionic detector or electron capture detector (for polychlorinated phenols) and gas supply according to the manufacturer's instructions.

6.16 Injection syringes, of capacity 1 µl, 5 µl, 10 µl, 50 µl and 100 µl.

6.17 Capillary columns for gas chromatography, (see table 2).

7 Sampling and sample preparation

Collect the samples in brown glass bottles with conical shoulder, of capacity 100 ml to 1 000 ml, to which 2 ml of sulfuric acid (5.1) per 1 000 ml of water sample has previously been added. Fill the bottles completely with the water sample.

Store the bottles at about 4 °C until they are to be analyzed. The pH should be less than 2, if not add more acid.

If the presence of oxidizing agents is suspected, especially in the presence of free chlorine, add approximately 0,1 g of sodium sulfite (5.4) to 1 litre of sample.

Carry out the enrichment within 48 h if possible.

Table 2 — Examples for possible separation conditions

Pair of capillary columns	Designation of capillary columns[1)]	Size of capillary columns		Carrier gas	Flow rate	Temperature programme
		Length m	Inner diameter mm		ml/min	
1	a	30 to 60	0,25 to 0,32	H_2 or He	< 5	General: 1 min at 60 °C 15 °C/min to 150 °C 5 °C/min to 240 °C[2)]
	b	30 to 60	0,25 to 0,32	H_2 or He	< 5	
2	c	30 to 60	0,25 to 0,32	H_2 or He	< 5	
	d	30 to 60	0,25 to 0,32	H_2 or He	< 5	
3	e	30 to 60	0,25 to 0,32	H_2 or He	< 5	
	f	30 to 60	0,25 to 0,32	H_2 or He	< 5	

1) See table 3 for trade names for the columns.

2) The temperature programme shall be adjusted to the respective separation programme.

Table 3 — Denotation of the columns given in table 2

Letter according to table 2	Trade name[1)]	Stationary phase
a, c, e	DB 5	95 % -Dimethyl/5 % diphenylpolysiloxane
b	DB 1701	86 % -Dimethyl/14 % -cyanopropylphenyl-polysiloxane
d	DB 225	50 % -Cyanopropylmethyl/50 % methylphenyl-polysiloxane
f	FFAP	"Free fatty acid phase" dinitroterephthalic acid

1) This information is given for the convenience of users of this part of ISO 8165 and does not constitute an endorsement by ISO of the products named. Equivalent products may be used if they can be shown to lead to the same results.

8 Procedure

8.1 Enrichment

8.1.1 General procedure

Place 800 ml of the acidified water sample in a separating funnel.

Add 1 ml of internal solution (5.12) and homogenize by mixing for 1 h.

Add 180 ml of diethylether (5.7).

After mixing and pressure compensation, mechanically shake for 5 min to extract the water sample. (The shaking frequency should be approximately 100 min^{-1}.)

Allow 30 min for phase separation, then discard the aqueous phase.

Transfer the ether phase to a separating funnel, of capacity 250 ml. (If necessary, filter the ether phase through a wad of silica glass wool, previously washed with diethylether.)

Shake the extract twice with 35 ml of sodium hydroxide solution II (5.3).

Allow 30 min for phase separation and transfer the alkaline aqueous phase to the separating funnel of capacity 100 ml (6.7).

Add 2 ml of sulfuric acid (5.1) and cool the funnel with water to ambient temperature. Shake the solution with 15 ml of diethylether (5.7) for 5 min, then wait 15 min.

Collect the ether phase in a stoppered flask, discard the aqueous phase.

8.1.2 Extraction of contaminated water

To purify, run the ether phase through a silica gel packed column (6.5), at a flow rate of approximately 2 ml/min.

Collect the ether phase in the concentrating flask of the distillation apparatus (6.4).

Rinse the vessels and the glass column with 10 ml of diethylether (5.7). Combine the washing with the extracts.

8.1.3 Concentration

Add 100 µl of diethylamine (5.9) and concentrate the ether solutions (see 8.1.1 and 8.1.2) by isothermal distillation carried out at ambient temperature (water bath, 20 °C to 22 °C) at 0,4 bar.

Pass nitrogen through the solution. This will help to prevent a delay in boiling and to preserve the phenolic compounds.

Adjust the nitrogen flow by means of a tubing clip, so that the individual bubbles may just be recognized.

Concentrate the extract to a residual volume of 100 µl to 200 µl.

Compensate the pressure. Rinse the gas distribution tube with 100 µl to 200 µl of dioxane (5.6), simultaneously rinsing the walls of the enrichment vessel by carefully rotating it.

Close the flask until the concentrate has gathered (this will take approximately 20 min).

Collect the residual solution with a syringe, determine its volume and transfer it to a small sampling bottle.

Carry out the gas chromatographic analysis as soon as possible, otherwise freeze the extract at − 20 °C. The maximum allowable storage time is one week.

NOTES

1 A water jet vacuum pump may be used to establish the vacuum pressure.

2 Other types of distillation apparatus are also suitable (e.g. Kuderna Danish).

3 Starting with a sample volume of 800 ml and a residual volume of 200 µl, the enrichment factor is 4 000. It may be increased to approximately 10^4 by altering the volumes, or reduced in the case of high concentrations by dilution with dioxane (5.6).

8.2 Gas chromatography

Check the suitability of the separating columns (see manufacturer's handbook).

Capillary columns, showing no or hardly any tailing and which give a separation onto the basis line, are suitable.

Due to the amount of possible interference, the substances are identified using two columns of different polarity.

In general, a flame ionization detector may be used as detector. This provides a linear relation between the concentration of the determinand and the detector signal. For polychlorinated phenols, an electron capture detector may be more suitable because of its higher sensitivity. The linear working range of this detector is limited; the specific response factor shall be determined for each substance.

In order to allow a reliable identification, the application of a mass selective detector may be applied.