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**Water quality — Determination of selected  
nitrophenols — Method by solid-phase  
extraction and gas chromatography with  
mass spectrometric detection**

*Qualité de l'eau — Dosage des nitrophénols sélectionnés — Méthode par  
extraction en phase solide avec détection par chromatographie en phase  
gazeuse et spectrométrie de masse*

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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.ch](mailto:copyright@iso.ch)  
Web [www.iso.ch](http://www.iso.ch)

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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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 17495 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Annexes A to D of this International Standard are for information only.

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## Introduction

Several methods may be applied to determine nitrophenols in water. This International Standard describes a gas chromatographic/mass spectrometric determination after solid-phase extraction and derivatization with diazomethane. It should be investigated whether and to what extent particular problems will require the specification of additional marginal conditions.

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# Water quality — Determination of selected nitrophenols — Method by solid-phase extraction and gas chromatography with mass spectrometric detection

**WARNING** — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate health and safety practices and to ensure compliance with any national regulatory conditions.

## 1 Scope

This International Standard specifies a method for the determination of selected nitrophenols (see Table 1) in drinking, ground and surface water in mass concentrations  $> 0,5 \mu\text{g/l}^{(1)}$ .

Table 1 — Nitrophenols to which this method is applicable

	CAS No.		CAS No.
2-Nitrophenol	88-75-5	2,4-Dinitrophenol	51-28-5
3-Nitrophenol	554-84-7	2,5-Dinitrophenol	329-71-5
4-Nitrophenol	100-02-7	2,6-Dinitrophenol	573-56-8
4-Methyl-2-nitrophenol	119-33-5	2,4-Dinitro-6-methylphenol	534-52-1
3-Methyl-4-nitrophenol	2581-34-2	2,6-Dimethyl-4-nitrophenol	2423-71-4
5-Methyl-2-nitrophenol	700-38-9	2,4-Dichloro-6-nitrophenol	609-89-2
3-Methyl-2-nitrophenol	4920-77-8	2,6-Dichloro-4-nitrophenol	618-80-4

CAS = Chemical Abstracts Service.

## 2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*.

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

1) See the results from the interlaboratory trial given in annex C.

ISO 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

ISO 8466-1:1990, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function.*

### **3 Principle**

Solid-phase extraction of the nitrophenols is carried out from the acidified sample, followed by solvent elution, derivatization with diazomethane and determination by gas chromatography and mass spectrometry.

It is absolutely essential that the tests described in this International Standard be carried out by suitably qualified staff.

### **4 Interferences**

#### **4.1 Interferences during enrichment**

In order to avoid losses, analyse the sample as soon as possible after sampling. If storage is unavoidable, store at 4 °C until sample pretreatment.

The commercially available adsorbance materials are often of varying quality. Considerable batch-to-batch variations in quality and selectivity of this material are possible.

The recovery may vary with the concentration, and shall therefore regularly be checked at different concentrations. Calibration and analysis shall be performed with material from one and the same batch only.

Suspended matter in the water sample (such as iron hydroxide, calcium carbonate) occurring on sampling, storage and sample preparation, as well as increased concentrations of microorganisms, may clog the packing. In this case the water sample may be filtered through a glass-fibre filter prior to the enrichment. A filtration step shall be mentioned in the test report.

Possible losses due to heating and volume reduction of the eluate may be reduced by the addition of a keeper (for example iso-octane)

#### **4.2 Interferences in the gas chromatograph**

The operating conditions shall be set in accordance with the manufacturer's instructions. These settings shall be checked at regular intervals.

General interferences, caused by the injection system or insufficient separation, can be eliminated with the help of special laboratory experience and the instrument manuals.

Excess diazomethane may cause instrument failure or damage, due to its high reactivity. Therefore care should be taken to remove excess diazomethane as far as possible by reducing the volume of the solution.

The use of alcohol as solvent should be avoided because any alcohol may destroy the deactivation layer (poly-siloxane) of the glass liner, leading to column load and an overload of the detector. In this case, the quantification of the analyte and the reproducibility of the result are no longer possible.

The stability of the analyte system should be checked (for example by application of a measuring standard).



## 5 Reagents

Reagents "for residual analysis" shall be used. Impurities of the reagents and of the water contributing to the blank shall be negligibly low. The blank shall be checked before use, especially prior to the use of a new batch.

**5.1 Water**, double-distilled or of comparable purity.

**5.2 Operating gases for the gas chromatograph/mass spectrometer**, in accordance with the manufacturer's instructions.

The operating gases shall be of high purity.

**5.3 Nitrogen**, high purity, minimum 99,996 % (volume fraction), for drying and eventually for concentration by evaporation.

**5.4 Hydrochloric acid**,  $c(\text{HCl}) = 2 \text{ mol/l}$ .

**5.5 Diethyl ether**,  $\text{C}_4\text{H}_{10}\text{O}$ , stabilized only with ethanol.

**5.6 Potassium hydroxide**, KOH, aqueous solution,  $\rho = 0,6$ .

**5.7 Ethanol**,  $\text{C}_2\text{H}_5\text{OH}$ .

**5.8 N-methyl-N-nitroso-4-toluenesulfonamide**, (Diazald)  $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_3\text{S}$ .

**5.9 Acetic acid**,  $\text{CH}_3\text{COOH}$ , aqueous solution, 10 % volume fraction (used to destroy diazomethane).

**5.10 Solvents**

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**5.10.1 Acetone**,  $\text{C}_3\text{H}_6\text{O}$ . <https://standards.iteh.ai/catalog/standards/sist/a51862a8-fab1-47c1-9b47-dfed9397c626/iso-17495-2001>

**5.10.2 Methanol**,  $\text{CH}_3\text{OH}$ .

**5.10.3 Ethyl acetate**,  $\text{C}_4\text{H}_8\text{O}_2$ .

**5.11 Methylated phenols**

Reference substances as methylated substances according to Table 1, with defined concentrations for the preparation of calibration solutions for gas chromatography (8.3)

**5.11.1 Standard stock solution** of methylated single substances

Weigh 50 mg of each of the reference substances into a 100-ml measuring flask, dissolve in ethyl acetate (5.10.3) or acetone (5.10.1) and bring to volume with ethyl acetate or acetone.

Store the solution in a refrigerator (about 4 °C). The shelf-life is limited (about 3 months) and the concentration shall be checked before use.

**5.11.2 Intermediate standard solution** of methylated single substances

Pipette into 100-ml measuring flasks 1 ml of the solution of the single substance (5.11.1), and bring to volume with ethyl acetate or acetone.

Store the solution in a refrigerator (about 4 °C). The shelf-life is limited (about 3 months) and the concentration shall be checked before use.

**5.11.3 Calibration solutions** for multipoint calibration (methylated phenols).

Prepare the calibration solutions by adequate dilution of the stock solutions (5.11.2) with ethyl acetate (5.10.3).

Store the solution in a refrigerator (about 4 °C). Their shelf-life is limited (about 3 months) and their concentration shall be checked regularly.

**5.12 Reference substances**

Reference substances (see Table 1) with defined concentrations for preparation of calibration solutions, for determination of the recovery (9.5) and for calibration over the overall procedure (9.3).

**5.12.1 Standard stock solutions** of non-methylated phenols

Weigh 50 mg of each of the reference substances in a 100-ml measuring flask, dissolve with acetone (5.10.1) or ethyl acetate (5.10.3) and bring to volume with ethyl acetate (5.10.3).

Store the solutions in a refrigerator (about 4 °C). Their shelf-life is limited (about 3 months) and their concentration shall be checked before use.

**5.12.2 Intermediate standard solutions** of non-methylated phenols

Pipette into 100-ml measuring flasks 1 ml of the solution of the single substances (5.12.1), and bring to volume with ethyl acetate (5.10.3)

Store the solutions in a refrigerator. Their shelf-life is limited (about 3 months) and their concentration shall be checked before use.

**5.12.3 Calibration solutions** for multipoint calibration (non-methylated phenols)

Prepare the calibration solutions by adequate dilution of the intermediate standard solutions (5.12.2) with solvent.

Store the solutions in a refrigerator. Their shelf-life is limited (about 3 months) and their concentration shall be checked regularly.

**5.13 Diazomethane solution**

**WARNING — Diazomethane is explosive, extremely toxic and severely irritating, causing pulmonary oedema when inhaled in high concentrations. Long-term, low-level exposure may lead to sensitization, resulting in asthma-like symptoms. Diazald and diazomethane should be regarded as toxic, carcinogenic and mutagenic. Handle with care.**

Diazomethane may be prepared in a distillation apparatus or in a commercially available equipment, preferably in a fume cupboard. An example of a preparation method is as follows.

In a 250 ml reaction flask, add 8 ml of the KOH solution (5.6) and 10 ml of ethanol (5.7).

Dissolve 5,0 g of Diazald (5.8) in 45 ml of diethyl ether (5.5) in a filter funnel.

Cautiously warm the reaction flask to about 60 °C (water bath) and, within 20 min, dropwise add the solution from the filter funnel.

Collect the diazomethane being formed during this process and the diethyl ether in the cooled trap (cooling with ice/NaCl).

After this reaction, add a further 10 ml of diethyl ether through the filter funnel and distil the remaining diazomethane.

Stopper the trap and store at about – 18 °C for not longer than 1 month.

Glassware used in the preparation of diazomethane or which has come into contact with Diazald should be cleaned with a 10 % aqueous solution of acetic acid (5.9). It is advisable to clean the apparatus after rinsing the filter funnel and the reaction flask by distillation of about 50 ml of ethanol (5.7).

#### 5.14 Internal standards

As internal standards, use two of the following phenols:

2,4-Dibromophenol,  $C_6H_4OBr_2$ , CAS No. 615-58-7

2,6-Dibromophenol,  $C_6H_4OBr_2$ , CAS No. 608-33-3

2,3,6-Trichlorophenol,  $C_6H_3OCl_3$ , CAS No. 933-75-5

2,4,6-Tribromophenol,  $C_6H_3OBr_3$ , CAS No. 118-79-6

Deuterated or  $^{13}C$ -labelled substances are suitable as well.

NOTE The internal standards are used for the control of the analytical procedure. The choice of the substances depends on the expected phenols to be determined.

Prepare a mixed standard solution of the two components in a concentration which gives peak heights in the upper part of the linear range.

Usually, a concentration of 10  $\mu g/ml$  is suitable; check the concentration prior to use.

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## 6 Apparatus

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Equipment or parts of it which may come into contact with the water sample or its extract should be free from residues causing significant blanks. It is recommended to use vessels made of glass or stainless steel.

**6.1 Flat-bottomed flasks**, preferably brown glass, 1 000 ml and 2 000 ml, with glass stoppers.

**6.2 Cartridges**, made of polypropene or glass, filled with solid-phase material, e.g. styrene/divinylbenzene polymer (see annex B).

**6.3 Vacuum or pressure assembly** for the enrichment step.

**6.4 Measuring flasks**, or graduated flasks with inert stopper, for the eluates.

In the case of autosampling, vials shall be made from glass and the septum covered with polytetrafluoroethene (PTFE).

**6.5 Apparatus** for preparing diazomethane, comprising:

- double-necked round-bottomed flask, 250 ml;
- filter funnel, 100 ml;
- distillation column, e.g. Vigreux column;
- distillation head;
- condenser, e.g. Liebig condenser;
- flask for absorption of diazomethane;