
**Water quality — Determination of certain
explosives and related compounds —
Method using high-performance liquid
chromatography (HPLC) with UV
detection**

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*Qualité de l'eau — Dosage de certains explosifs et de composés
apparentés — Méthode utilisant la chromatographie en phase liquide à
haute performance (CLHP) avec détection UV*

ISO 22478:2006

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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 22478 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

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Introduction

Explosives and related compounds are frequently encountered in groundwater areas near to soil sites contaminated by armaments waste and may also be found in drinking water taken from nearby catchment areas. The range of pollutants will depend on the waste concerned, but will not, as a rule, include all the compounds listed in Table 1. Instead, samples of groundwater containing such pollutants may contain numerous other substances, such as nitro- and dinitrobenzoic acid, nitrophenols and aromatic amines. The compounds listed in Table 1 are frequently used for exploratory examinations of armaments waste.

When using this International Standard, it may be necessary in some cases to determine whether and to what extent particular problems will require the specification of additional conditions.

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Water quality — Determination of certain explosives and related compounds — Method using high-performance liquid chromatography (HPLC) with UV detection

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

IMPORTANT — It is absolutely essential that tests conducted in accordance with this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies a method for determination of certain explosives, in particular nitrotoluenes, nitroamines and nitrate esters, and related compounds (by-products and degradation products), such as those listed in Table 1, in drinking water, groundwater and surface water.

Depending on the type of sample and the compound to be analysed, the lower limit of the working range for nitroaromatics and nitramines can be assumed to be between 0,1 µg/l and 0,5 µg/l (in some cases, the lower limit may be extended down to 0,05 µg/l). The lower limit of the working range for nitrate esters may be assumed to be higher (0,5 µg/l or more).

Similar compounds, in particular other nitroaromatics, may also be determined by this method, but its applicability will have to be checked in each individual case.

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, *Water for analytical laboratory use — Specification and test methods*

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

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

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

3 Principle

The substances in the water sample are concentrated by solid-phase extraction using a polystyrene/divinylbenzene-based adsorbent. After elution with a solvent mixture, the eluate is concentrated and the substances are separated by high-performance liquid chromatography (HPLC) and analysed using a UV photodiode array (UV-PDA) detector.

Table 1 — Explosives and related compounds determined by this method (the compounds listed here are particularly likely to be encountered in water samples containing armaments waste)

Name	Abbreviation ^a	Other name	CAS ^b No.	Molar mass g/mol	Reference No./ letter in example chromatograms in Clause			
					A.1	A.2	A.3	B.1
2,4,6-Trinitrophenol	PA	Picric acid	88-89-1	229,1	1	2	1	a
1,3,5,7-Tetranitro-octahydro-1,3,5,7-tetrazocine	HMX	Octogen	2691-41-0	296,2	2	1	2	b
1,3,5-Trinitro-hexahydro-1,3,5-triazine	RDX	Hexogen	121-82-4	222,1	3	3	4	d
2,2',4,4',6,6'-Hexanitrodiphenylamine	—	Hexyl	131-73-7	439,2	4	19	3	c
Ethylene glycol dinitrate	EGDN	—	628-96-6	152,1	5	4	5	e
Diethylene glycol dinitrate	DEGN	—	693-21-0	196,1	6	5	6	f
1,3,5-Trinitrobenzene	1,3,5-TNB	—	99-35-4	213,1	7	6	7	g
1,3-Dinitrobenzene	1,3-DNB	—	99-65-0	168,1	8	7	9	i
<i>N</i> -Methyl- <i>N</i> -2,4,6-tetranitroaniline	CE	Tetryl	479-45-8	287,2	9	8	8	h
Glycerol trinitrate	NG	Nitroglycerine	55-63-0	227,1	10	9	10	j
2,4,6-Trinitrotoluene	2,4,6-TNT	TNT	118-96-7	227,1	11	10	11	k
4-Amino-2,6-dinitrotoluene	4-A-2,6-DNT	—	19406-51-6	197,1	12	11	12	l
2-Amino-4,6-dinitrotoluene	2-A-4,6-DNT	—	35572-78-2	197,1	13	12	13	m
2,6-Dinitrotoluene	2,6-DNT	—	606-20-2	182,1	14	13	14	n
2,4-Dinitrotoluene	2,4-DNT	—	121-14-2	182,1	15	14	15	o
2-Nitrotoluene	2-NT	—	88-72-2	137,1	16	15	17	q
Pentaerythritol tetranitrate	PETN	Nitropenta	78-11-5	316,2	17	18	16	p
4-Nitrotoluene	4-NT	—	99-99-0	137,1	18	16	18	r
3-Nitrotoluene	3-NT	—	99-08-1	137,1	19	17	19	s
Diphenylamine	DPA	—	122-39-4	169,24	20	—	—	—

^a Standard abbreviations, some of Anglo-Saxon origin.
^b Chemical Abstracts Service.

The structural formulae of selected compounds are given in Figure 1.

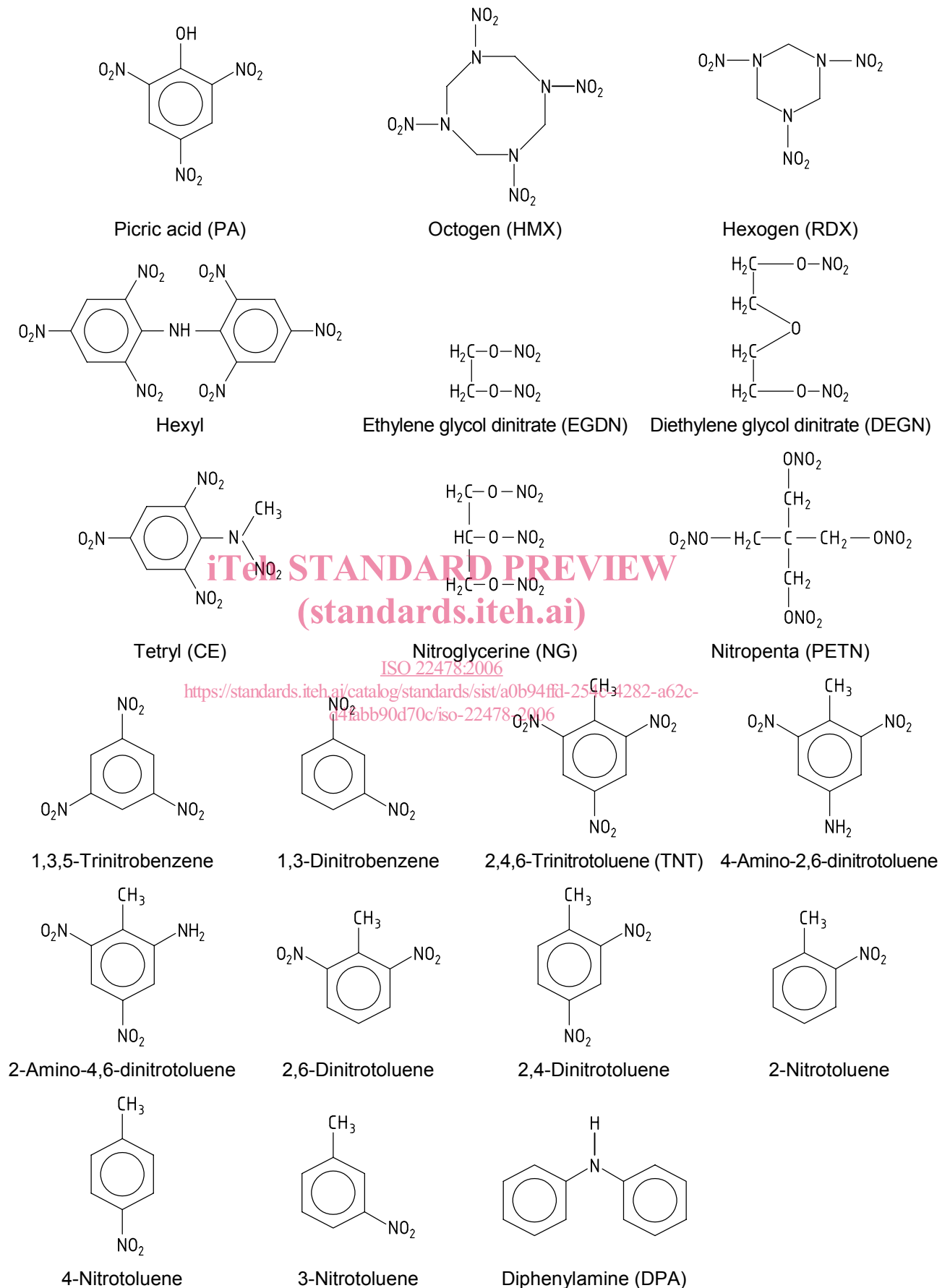


Figure 1 — Structural formulae of selected explosives

4 Interference

4.1 Sampling

To avoid interference, collect samples as specified in Clause 7, observing the instructions given in ISO 5667-1, ISO 5667-2 and ISO 5667-3.

4.2 Filtration

If the sample contains suspended matter, first filter it through a borosilicate glass fibre filter to prevent blockage of the solid phase concentrating cartridge and record this operation in the test report.

4.3 Concentration by evaporation

Mononitrotoluenes may be lost when the eluates are evaporated as specified in 8.2.

4.4 Chromatography

Asymmetrical peaks and peaks that are wider than normal may indicate incompletely resolved peaks or peak overlapping due to compounds with similar retention times and/or absorption at the same or at a similar wavelength to those of the compounds being determined. To detect peak overlaps, check the peak purity and compare the UV spectrum with that of a reference material.

Interference may also be caused by humic matter eluted in the same range as the analytes being determined.

4.5 Exposure to light

Reference solutions, samples and sample extracts may decompose on exposure to light. This is particularly important in the case of tetryl (see Annex C). Therefore a detailed investigation of the recovery of tetryl should be carried out.

4.6 Determination of hexogen

When determining small concentrations of hexogen, interference may be caused by high concentrations of nitroaromatics.

5 Reagents

The reagents shall not have blank values that would interfere with the HPLC analysis.

If available, use reagents of HPLC grade or residue grade. The solvents shall not contain any measurable UV-absorbing substances that interfere with the method.

5.1 Water, complying with grade 1 as defined in ISO 3696. The water shall not contain any measurable quantities of UV-absorbing substances that interfere with the determination.

5.2 Nitrogen, purity not less than 99,996 % by volume, for drying the adsorbent and, if necessary, for concentrating the eluates.

5.3 Helium, purity not less than 99,996 % by volume, for degassing the eluent if a vacuum degasser is not used.

5.4 Microporous polystyrene/divinylbenzene adsorbent, with a high specific surface area (e.g. greater than 900 m²/g). Other adsorbents may be used provided that the recovery rate is greater than 85 % for octogen (HMX) at a concentration of 1 µg/l in a 1 l sample.

5.5 Methanol, CH₃OH.

5.6 Acetonitrile, CH₃CN.

5.7 Sodium chloride, NaCl.

5.8 Potassium dihydrogen phosphate solution, $c(\text{KH}_2\text{PO}_4) = 0,025 \text{ mol/l}$ (3,40 g/l).

5.9 Orthophosphoric acid, $w(\text{H}_3\text{PO}_4) = 85 \%$.

5.10 Reference compounds, as listed in Table 1, some of which are obtainable only as commercial solutions with a specified mass concentration.

5.11 Solutions of reference compounds, prepared as follows:

Add methanol (5.5) to 100 mg of the reference compound in a 100 ml volumetric flask, dissolve the reference compound and make up to volume with methanol.

Prepare solutions of hexyl and octogen using acetonitrile (5.6) because of their poor solubility in methanol.

Store the solutions at a maximum of 6 °C, protected from light; their shelf-life is limited (six months at most).

5.12 Stock solutions, prepared as follows:

Transfer 1 ml of each of the solutions of reference compounds (5.11) to a separate 100 ml volumetric flask and make up to volume with methanol (5.5).

Store the solutions at a maximum of 6 °C, protected from light; the solutions are stable for up to six months.

5.13 Reference solutions for multipoint calibration, prepared as follows:

Prior to each calibration, prepare at least five dilutions of each of the stock solutions prepared in 5.12, preferably using a methanol/water mixture (50 + 50 parts by volume) as solvent.

Store the reference solutions at a maximum of 6 °C, protected from light; check their concentrations regularly as their stability is limited.

5.14 Buffer solution, to improve gradient elution of hexyl and picric acid, prepared by adjusting the pH of a 0,025 mol/l solution of potassium dihydrogen phosphate (5.8) to 3,2 using orthophosphoric acid (5.9).

6 Apparatus

Those parts of the apparatus that come into contact with the sample or the extract shall be free of compounds that may produce blank values. The apparatus shall be made of materials that do not adsorb the compounds under investigation and that provide protection from light, e.g. brown glass, stainless steel or perfluorinated plastics.

6.1 Brown-glass narrow-necked flat-bottomed flasks, 1 000 ml.

6.2 Vacuum or pressure equipment, for sample enrichment.

6.3 Glass fibre filter, diameter of fibres 0,75 µm to 1,5 µm, of borosilicate glass containing an inorganic binder.

6.4 Solvent-resistant micromembrane filter, e.g. polyamide or cellulose membrane, pore size of 0,2 µm to 0,45 µm, for filtration of HPLC extracts.

6.5 Glass or polypropene cartridges, packed with a polystyrene/divinylbenzene-based adsorbent (5.4).

6.6 Glass volumetric flasks, 1 ml, 10 ml and 100 ml.

6.7 Graduated cylinder, 100 ml.

6.8 pH-meter, with electrodes.

6.9 Equipment for concentrating the eluates by evaporation, e.g. a rotary evaporator, regulatable for constant vacuum and with a temperature-controlled water bath, or stripping equipment using nitrogen gas.

6.10 Glass vessels, for collecting and concentrating the eluates by evaporation (e.g. tapered flask with cylindrical graduated extension).

6.11 Glass sample bottles, with inert closure (e.g. PTFE-coated septum), for storing the extracts.

6.12 High-performance liquid chromatograph, consisting of:

- a) an analytical pump system for isocratic or gradient elution;
- b) a manual or automatic sample introduction device;
- c) a degassing device;
- d) a column thermostat;
- e) a photodiode array (PDA) detector with a wavelength range of e.g. 200 nm to 400 nm;
- f) a data evaluation system;
- g) an analytical column (examples of suitable column types are given in Annex A).

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7 Sampling

Fill carefully cleaned brown-glass flat-bottomed flasks with the water to be examined. Store the samples immediately after sampling and during transport at not more than 4 °C, protected from light (e.g. in a cool box). Extract the sample, if possible, within three days after collection since the concentration of explosives and related compounds is more stable in the organic eluates than in the samples. If storage cannot be avoided, keep the sample at about 4 °C in the dark.

Carry out the determination as soon as possible after extraction.

8 Procedure

8.1 Conditioning of adsorbent

Use not less than 0,2 g of polystyrene/divinylbenzene adsorbent (5.4) in a cartridge (6.5) for each 1 000 ml of sample. Add 3 ml of methanol (5.5) over a period of 5 min and wash with 3 ml of acetonitrile (5.6) and then with 10 ml of water. Ensure that the adsorbent does not run dry.

8.2 Concentration and elution

If necessary, filter the sample through a glass fibre filter (6.3) to remove suspended matter.

Take e.g. 1 000 ml of the sample to be examined and dissolve in it about 5 g of sodium chloride (5.7). Pass the sample through the adsorbent conditioned as in 8.1 at a flow rate of up to 1 000 ml/h and then flush with 1 ml of water (5.1). Dry the adsorbent in a stream of nitrogen (5.2) for not less than 10 min.