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Soil quality — Determination of selected explosives and related compounds —

Part 2: Method using gas chromatography (GC) with electron capture detection (ECD) or mass spectrometric detection (MS)

Qualité du sol — Dosage d'une sélection d'explosifs et de composés apparentés —

Partie 2: Méthode utilisant la chromatographie en phase gazeuse (CG) avec détection à capture d'électrons (DCE) ou détection par spectrométrie de masse (SM)

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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.

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. www.iso.org/directives

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

ISO 11916 consists of the following parts, under the general title *Soil quality — Determination of selected explosives and related compounds*:

— *Part 1: Method using high-performance liquid chromatography (HPLC) with ultraviolet detection*

— *Part 2: Method using gas chromatography (GC) with electron capture detection (ECD) or mass spectrometric detection (MS)*

Soil quality — Determination of selected explosives and related compounds —

Part 2:
Method using gas chromatography (GC) with electron capture detection (ECD) or mass spectrometric detection (MS)

1 Scope

This part of ISO 11916 specifies the measurement of explosive and related compounds (nitroaromatics and nitroamines, as given in Table 1) in soils and soil materials. This part of ISO 11916 is intended for the trace analysis of explosives and related compounds by gas chromatography (GC) using electron capture detector(s) (ECD) or a mass spectrometer (MS) as detector.

This part of ISO 11916 can be used when reliable and specific identification of the compounds at low detection levels is required, e.g. for the evaluation of the toxic potential of soils contaminated with 2,6-DNT.

Under the conditions specified in this part of ISO 11916, concentrations as low as 0,05 mg/kg dry matter can be determined, depending on the substance. Similar compounds may be analysed using this method. This is, however, to be verified experimentally.

This method is not suitable for the analysis of hexogen (RDX), octogen (HMX), hexyl, tetryl and nitropenta (PETN).

Table 1 — Selected explosive and related compounds (nitroaromatics and nitroamines) for analysis

Compound	Abbreviation	CAS-RN[a]
Nitrobenzene	NB	98-95-3
1,3,5-Trinitrobenzene[b]	1,3,5-TNB	99-35-4
2-Nitrotoluene	2-NT	88-72-2
3-Nitrotoluene	3-NT	99-08-1
4-Nitrotoluene	4-NT	99-99-0
2,4-Dinitrotoluene	2,4-DNT	121-14-2
2,6-Dinitrotoluene	2,6-DNT	606-20-2
3,4-Dinitrotoluene	3,4-DNT	610-39-9
2,4,6-Trinitrotoluene	2,4,6-TNT	118-96-7
4-Amino-2,6-dinitrotoluene	4-A-2,6-DNT	1946-51-0
2-Amino-4,6-dinitrotoluene	2-A-4,6-DNT	35572-78-2

[a] CAS-RN: Chemical Abstract Service-Registry Number.

[b] 1,3,5-TNB gave poor interlaboratory trial results and its analysis could be problematic.

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 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*

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

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

3 Principle

Explosive materials in soils are extracted with methanol, using one of the following techniques:

— ultrasonic bath with ultrasonic waves as medium (USE);

— horizontal mechanical shaker at room temperature (MSE);

— Soxhlet apparatus that works isothermically at boiling temperature (SOX);

— pressurized liquid extraction (PLE).

By means of a liquid/liquid extraction, the analytes are re-solved from the methanolic extract into toluene. Traces of methanol in the organic phase are then washed out with water and discarded. The toluenic phase is dried, reconstituted, diluted (if necessary) and injected directly into a capillary gas chromatograph (GC). The analytes are detected by means of electron capture detection (ECD) or by mass spectrometry (MS).

Substances are verified either by running samples through two columns of different polarities with subsequent detection through ECD (simultaneous injection and operating with two ECD is recommended), or through MS detection utilizing known mass spectra and typical fragmentary ions.

WARNING — Take care when transporting, storing or treating explosive materials. High temperature, high pressure and static electricity shall be prevented when storing explosive materials. Small amounts of explosive materials should be kept moist in a cool, dark place. Soil samples containing explosives with a mass fraction of less than 1 % do not have a risk of explosion.

4 Interferences

Solvents, reagents, glassware, and other hardware used for sample processing may yield artefacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials shall therefore be demonstrated to be free of contaminants and interferences through the analysis of method blanks.

5 Reagents

5.1 General

All reagents shall be blank-free and of recognized analytical grade.

5.2 Chemicals

5.2.1 Water.

5.2.2 Acetone, C_3H_6O, for the cleaning of containers and devices.

5.2.3 Methanol, CH_3OH.

5.2.4 Toluene, $C_6H_5CH_3$.

5.2.5 Sodium chloride, NaCl, for phase separation.

5.2.6 Sodium sulfate, Na_2SO_4, anhydrous.

5.2.7 Diatomaceous earth or sea sand, pelletized and calcinated (for PLE).

5.3 Standard substances and solutions

5.3.1 Standard substances

5.3.1.1 Reference substances

Compounds listed in Table 1.

5.3.1.2 Method-checking standard

Suitable compound(s) not found in the sample, e.g. 2,5-DNT.

5.3.2 Standard solutions

5.3.2.1 General

All standard solutions used in this method shall be prepared as described below.

NOTE If commercially available certified standard stock solutions (Table 1) are used, calibration solutions are prepared in volumetric flasks by diluting the stock solutions with toluene (5.2.4) or methanol (5.2.3), for 5.3.1.2 respectively.

All dilution steps shall not exceed the factor 100.

5.3.2.2 Single-substance stock solutions

For the preparation, weigh 50 mg ± 0,1 mg of the reference substances into 50 ml measuring flasks (scale: mg/ml), fill up to the mark with toluene (5.2.4) and let them dissolve completely.

Transfer the stock solutions to amber-glass flasks and seal with PTFE-coated screw caps.

The stock solutions can be kept in the refrigerator at 2 °C to 6 °C in the dark for up to 1 year.

5.3.2.3 Multi-component stock solutions

Prepare multi-component stock solutions of different concentrations from the various single-substance stock solutions (5.3.2.2) by mixing and diluting with toluene (5.2.4).

At concentrations below 1 mg/ml, solutions should be checked after one week as reference substances may decompose.

For calibration standards, a minimum of 5 concentration levels is needed.

6 Apparatus

6.1 General

Usual laboratory apparatus and the following.

6.1.1 Amber glass containers with caps containing polytetrafluoroethene (PTFE) coated lining.

6.1.2 Amber glass vials with caps containing septa with polytetrafluorethene (PTFE) coated lining.

6.1.3 Amber glass conical bottles with ground-in stopper.

6.1.4 Perforated metal plate sieve, complying with ISO 565.

6.1.5 Analytical balance, with a precision of at least 0,1 mg.

6.1.6 Laboratory centrifuge, capable of producing an acceleration of at least 1 000*g*.

6.1.7 Filter and suitable filter discs, 0,45 µm pore size.

Any adsorption of the target analytes shall be avoided. No interfering material shall be eluated. PTFE or polyamide material is recommended.

6.2 Equipment for extraction

6.2.1 Temperature-controlled ultrasonic bath, 35 Hz, effective HF-power of at least 140 W.

Water bath capable of maintaining the temperature at (30 ± 5) °C or at (50 ± 5) °C during ultrasonic extraction.

6.2.2 Horizontal mechanical shaker

The shaker shall maintain a frequency of 100 cycles/min and offer a shaking width of about 10 cm.

6.2.3 Soxhlet apparatus

Extractor, whose extraction chamber and syphon are placed inside the steam chamber and suitably covered, or extractor with additionally heated extraction chamber, complete with boiling vessel, suitable heating mantle and reflux condenser, suitable for the extraction of a 50 g sample of soil with a hot solvent distillate through complete flooding of the extractive.

6.2.4 Pressurized liquid extractor (PLE)

Pressurized liquid extraction device, equipped with extraction cells made of stainless steel or other material capable of withstanding the pressure levels (890 hPa/2 000 psi) necessary for this procedure; vials for collection of extracts, 40 ml or 60 ml, pre-cleaned, open-top screw-cap with polytetrafluoroethylene (PTFE)-lined septum; filter disc, cellulose or glass fibre; cell cap sealing disc.

6.3 Equipment for re-solution (solvent exchange)

Microseparator, for the uptake of the toluenic extract.

6.4 Gas chromatographic system (GC) with ECD or MS

Gas chromatograph, equipped with a non-discriminating injection system, suitable capillary columns and electron-capture detector(s) (ECD) or mass selective detector (MS).

7 Procedure

7.1 Sample pretreatment, sample storage and determination of water content

While taking a field-moist sample, remove coarse impurities, e.g. plant residues and stones. Put the sample in an amber glass flask and store immediately in a cool, dark transport container.

Soil samples shall be analysed as soon as possible.

When sample treatment is proceeded within 1 week after sampling, store the sample in a dark place at (4 ± 2) °C. Samples that are stored for longer periods (i.e. > 1 week) prior to analysis, shall be stored at -20 °C.

Homogenize the sample by sieving through a sieve with an aperture of 2 mm (6.1.4).

For the determination of volatile nitroaromatics (2-NT, 3-NT, 4-NT, NB) a sample withdrawal is to be carried out, in order to minimize evaporative losses.

Samples that were primarily taken for the determination of volatile compounds may also be taken by filling them immediately (on-site) in an extraction vial containing methanol. Then, pretreat samples according to 7.2.2 or 7.2.3. These samples have to be considered and reported as non-homogenized unscreened random samples.

In order to calculate the dry matter based content of explosive compounds, determine the dry matter content of the field-moist soil in accordance with ISO 11465. Be aware of potential evaporation of volatile toxic contaminants.

7.2 Extraction

7.2.1 General

For extraction, the following four methods may be applied:

— extraction using ultrasonic waves (7.2.2);

— extraction using mechanical shaking (7.2.3);

— extraction using Soxhlet apparatus (7.2.4).

— pressurized liquid extraction (7.2.5).

The use of a method-checking standard is recommended. Method-checking standards have to be added prior to extraction. For the selection of suitable method-checking standards, refer to 5.3.1.2.

7.2.2 Extraction using ultrasonic waves

Take approximately 20 g of the field-moist and homogenized sample and weigh it into the extraction vial (6.1.1) with a precision of ± 0,1 g and add the method-checking standard (5.3.1.2), if used, with a concentration range of 1 mg/l to 10 mg/l in the final extract. Add 40 ml ± 0,1 ml of methanol (5.2.3) and seal with a cap containing a PTFE coated lining. Shake the vial briefly by hand, then apply ultrasonic extraction in the bath (6.2.1) for 16 h at (30 ± 5) °C or 4 h at (50 ± 5) °C.

During extraction, the water level in the bath should be at least 1 cm above the level of the solvent inside the extraction flasks.

After applying ultrasonic extraction, allow the soil particles to settle for 30 min. Do not open the vial before it has cooled down to room temperature. If necessary, filter an aliquot of the supernatant using a 0,45 µm PTFE or polyamide filter or centrifuge at 1 000*g* for 20 min.

It is recommended to lightly moisten the filter with solvent prior to filtration.

The total volume of the extract corresponds to the volume of solvent used for extraction plus the water content of the soil sample.

7.2.3 Extraction using mechanical shaking

Take approximately 20 g of the field-moist and homogenized sample and weigh it into the extraction vial (6.1.1) with a precision of ± 0,1 g and add the method-checking standard (5.3.1.2), if used, with a concentration range of 1 mg/l to 10 mg/l in the final extract. Add 40 ml ± 0,1 ml of methanol (5.2.3) and

seal with a cap containing a PTFE coated lining. Shake the vial briefly by hand, then place the extraction vial in a horizontal mechanical shaker (6.2.2) and shake for 16 h.

After shaking, allow the soil particles to settle for 30 min. If necessary, filter an aliquot of the supernatant using a 0,45 µm PTFE or polyamide filter, or centrifuge at 1 000*g* for 20 min.

It is recommended to lightly moisten the syringe filter with solvent prior to filtration.

The total volume of the extract corresponds to the volume of solvent used for extraction plus the water content of the soil sample.

7.2.4 Extraction using Soxhlet apparatus

The extraction is carried out isothermically (extraction sample in the thimble always at boiling temperature) in a Soxhlet apparatus (6.2.3). To ensure isothermic working conditions while using a classical Soxhlet, it shall be covered by the steam chamber of the solvent. When using an extractor such as Soxtec®[1)] or Büchi-extractors[2)], the solvent distillate in the thimble shall always be heated to its boiling point.

Take approximately 50 g of the field-moist and homogenized sample, weigh it into an extraction thimble with a precision of ± 0,1 g and add the method-checking standard (5.3.1.2), if used, with a concentration range of 1 mg/l to 10 mg/l in the final extract. Insert the thimble into the Soxhlet extractor, and add methanol (5.2.3) to the boiling vessel. The liquid level in the receiver (boiling vessel) should not drop below the upper rim of the heating mantle during extraction in order to prevent the formation of deposits on the inner wall of the vessel, because it may cause a loss of certain analytes.

Prior to analysis, check the absorption potential of extraction thimble material.

NOTE Experience has shown that the use of fibre-glass filters decreases the yield of TNB. Cellulose extraction thimbles seem to be most suitable.

The extraction is carried out for at least 4 h. When using a Soxhlet extractor, a cycle time of 6 min to 8 min should be reached. In every cycle the extractive shall be completely immersed in hot solvent distillate.

When the extraction is completed, let the extract cool down to room temperature before removing the reflux condenser.

The volume of the extract shall be determined or brought to a defined volume with methanol.

7.2.5 Pressurized liquid extraction (PLE)

Take approximately 20 g of the field-moist and homogenized sample, weigh it into a beaker with a precision of ± 0,1 g and add the method-checking standard (5.3.1.2), if used, with a concentration range of 1 mg/l to 10 mg/l in the final extract, and mix with a suitable amount of diatomaceous earth or sea sand. Transfer the whole content of the beaker into the extraction cell, refill the dead volume with diatomaceous earth or sea sand and close the cell.

Prepare the apparatus according to the manufacturer's instructions.

Fill the solvent container of the device with methanol and place the prepared cell(s) and the vial(s) collecting the extract inside the apparatus. Select the appropriate adjustment of parameters (see Table 2).

When the extraction is completed, the extract is held at a temperature of 20 °C. Since the extraction cells contain frits, filtration of the extracts is not necessary.

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1) Soxtec® is the trade name of a product supplied by Foss. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

2) Büchi-extractor is the trade name of a product supplied by BÜCHI Labortechnik AG. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

The volume of the extract shall be determined or brought to a defined volume with methanol.

Table 2 — Example of parameters and requirements for the PLE apparatus

Parameter	Requirement
Solvent	100 % methanol
Dimension of the cell, in ml	33
Preheat, in min	0
Heat, in min	5
Static, in min	15
Flush, in % of cell volume	60
Purge, in s	200
Cycles	1
Pressure, in hPa (psi)	890 (2 000)
Temperature, in °C	100

7.2.6 Re-solution (solvent exchange)

Pipette 10 ml of toluene (5.2.4) into a reagent bottle and add a defined aliquot of the methanolic extract. Add water to the above mixture with a volume ratio of at least 7:1 (water:methanolic extract), seal, shake vigorously and wait for separation of the phases, which may take several hours.

If difficulties arise during the phase separation of toluene and the methanolic water phase, the flask volume shall be further filled up with an aqueous saturated sodium chloride solution (5.2.5). The phases will then separate within several hours.

NOTE The effect of the salting-out on the distribution equilibrium of the analytes in the phases has been tested and can be neglected.

The phase separation may also be achieved through centrifugation, if necessary. During centrifugation, tubes shall be sealed to prevent the loss of volatile analytes and solvent.

For the separation of the toluene phase a microseparator is recommended.

Transfer the toluene phase into a small glass flask, containing anhydrous sodium sulfate (5.2.6). The dried toluenic extract is subsequently analysed.

7.3 Storage of extract

If the toluenic extract cannot be analysed immediately, it shall be stored in a refrigerator at (4 ± 2) °C in the dark. In case of precipitation, ensure that the precipitate is re-dissolved before analysis, e.g. through ultrasonication.

8 Gas chromatographic analysis

8.1 General

The analytes are separated by means of a capillary-column gas chromatograph with suitable columns and detected using electron-capture detection (ECD) or mass spectrometry (MS).

A defined volume of the extract, prepared according to Clause 7, shall be injected into the gas chromatographic system. The injected volume shall be the same for the extract and the standards.