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Soil quality — Determination of selected explosives and related compounds —

Part 3:
Method using liquid chromatography-tandem mass spectrometry (LC-MS/MS)

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

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Introduction

Currently two ISO standards exist for the analysis of explosives and related compounds in soil: ISO 11916-1(HPLC/UV method), ISO 11916-2(GC-ECD or MS). According to the results of inter-laboratory trial with ISO 11916-1, it showed some problematic aspects to analyze PETN, 1,3,5-TNB and tetryl. In case of ISO 11916-2, it also gave poor inter-laboratory trial results for 1,3,5-TNB. Therefore, it is necessary to develop new method effectively applicable to the determination of PETN, 1,3,5-TNB and tetryl. In addition to this, lower risk-based PRGs (Preliminary Remediation Goal), new regulatory concerns, and change of land use have created the atmosphere to apply more sensitive and selective instruments to determine explosive and related compounds. From the view of these aspects, liquid chromatography–tandem mass spectrometry (LC-MS/MS) is one of alternative methods for these purposes. LC-MS/MS method provides 10-20 times or more lower detection limit than that of HPLC/UV method. In this document, LC-MS/MS method is intended for the trace analysis of explosives and related compounds and applicable to 12 compounds (1,3-DNB, 1,3,5-TNB, 2,4-DNT, 2,6-DNT, 2,4,6-TNT, 4-A-2,6-DNT, 2-A-4,6-DNT, Tetryl, Hexyl, RDX, HMX, PETN) listed in ISO 11916-1(soil, HPLC/UV method) except for nitrobenzene, 2-nitrotoluene, 3-nitrotoluene and 4-nitrotoluene. In case of nitrobenzene and nitrotoluenes, they have the low sensitivity in LC-MS/MS measurement. In particular, this method is effective for the analysis of PETN, 1,3,5-TNB and tetryl when comparing with the method using HPLC. Also LC-MS/MS method is getting more familiar in ISO standard development (e.g. ISO/CD22104 Water quality--Microcystins, ISO/NP21677 Water quality--HBCD, ISO/CD21675 Water quality--PFAS).

Soil quality — Determination of selected explosives and related compounds — — Part 3: Method using liquid chromatography-tandem mass spectrometry (LC-MS/MS)

1 Scope

This part of ISO 11916 specifies the measurement of explosives and related nitrocompounds (as given in Table 1) in soil and soil materials. This document is intended for the trace analysis of explosives and related compounds by liquid chromatography–tandem mass spectrometry (LC-MS/MS). Generally, LC-MS/MS measurement shows the lower LOQ (limit of quantification) for each compound in Table 1 than that of high-performance liquid chromatography (HPLC) measurement.

Under the conditions specified in this document, concentrations as low as 0,005 mg/kg to 0,014 mg/kg-dry matter can be determined, depending on the substance. Similar compounds, in particular various nitroaromatics, by-products and degradation products of explosive compounds may be analyzed using this method. However, the applicability should be checked on a case-by-case basis.

Table 1 — Explosive and related nitrocompounds for analysis

Compound	Abbreviation	CAS-RN[a]
1,3-Dinitrobenzene	1,3-DNB	99-65-0
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4
2,4-Dinitrotoluene	2,4-DNT	121-14-2
2,6-Dinitrotoluene	2,6-DNT	606-20-2
2,4,6-Trinitrotoluene	2,4,6-TNT	118-96-7
4-Amino-2,6-dinitrotoluene	4-A-2,6-DNT	19406-51-6
2-Amino-4,6-dinitrotoluene	2-A-4,6-DNT	35572-78-2
N-Methyl-*N*-2,4,6-tetranitroaniline	Tetryl	479-45-8
2,4,6-Trinitro-*N*-(2,4,6-trinitrophenyl)aniline	Hexyl	131-73-7
1,3,5-Trinitrohexahydro-1,3,5-triazine	RDX	121-82-4
1,3,5,7-Tetranitroo ctahydro-1,3,5,7-tetrazocine	HMX	2691-41-0
Pentaerythrityltetranitrate	PETN	78-11-5

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 11465, Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method

3 Principle

Explosive materials in soils are extracted with acetonitrile by using one of the following techniques:

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

— horizontal mechanical shaker at room temperature (MSE);

There are two further extraction procedures such as pressurized liquid extraction (PLE) and soxhlet apparatus that works isothermically at boiling temperature (SOX). However, they might not be suitable for PETN, tetryl and 1,3,5-TNB.

The extract containing the analytes is either injected directly, or if necessary diluted prior to injection, into a reversed-phase high-performance liquid chromatograph–tandem mass spectrometer (LC-MS/MS).

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 artifacts 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.

Samples containing 2,4,6-trinitrobenzoic acid should not be extracted with acetonitrile as it may result in the overestimation of 1,3,5-TNB due to decarboxylation. To avoid this interference, methanol extraction can be an alternative method for 1,3,5-TNB.

5 Reagents

5.1 General

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

5.2 Chemicals

5.2.1 Water, with a electrical conductivity of ≥ 0.01 mS/m (25°C).

5.2.2 Acetonitrile, CH_3CN, HPLC grade or equivalent.

5.2.3 Methanol, CH_3OH, HPLCgrade or equivalent.

5.2.4 Ammonium acetate in water, 2,5 mmol/l.

For the preparation, weigh 96,3 mg of ammonium acetate($C_2H_7NO_2$) into 500 ml measuring flasks (scale: mg/ml), fill up to the mark with water (5.2.1). Prepare the reagent just before it is used. Before using as a mobile phase, filter the reagent using filter paper (6.1.7). After filtration, degas the filtrate using sonic bath or other methods.

5.2.5 Ammonium acetate in methanol, 2,5 mmol/l.

For the preparation, weigh 96,3 mg of ammonium acetate(C2H7NO2) into 500 ml measuring flasks (scale: mg/ml), fill up to the mark with methanol (5.2.3). Prepare the reagent just before it is used. Before using as a mobile phase, filter the reagent using filter paper (6.1.7). After filtration, degas the filtrate using sonic bath or other methods.

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 standards

Suitable compound(s) not found in the sample (i.e. 2,5-dinitrotoluene or 1,2-dinitrobenzene). It is recommended that the concentration of method-checking standards in the final extract is ranged from 0,04 mg/l to 0,1 mg/l. Before selecting the method-checking standards, confirm the applicability of those standards according to the analytical conditions of each laboratory.

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 are used, calibration solutions are prepared in volumetric flasks by diluting the stock solutions with acetonitrile (5.2.2).

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 acetonitrile (5.2.2) and let the reference substances dissolve completely.

Transfer the stock solutions to amber-glass flasks and seal with polytetrafluoroethylene (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 6 month.

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 acetonitrile (5.2.2).At concentrations below 1 mg/ml, solutions should be checked after one week as reference substances may decompose.

5.3.2.4 Calibration standard solutions

Calibration standard solutions are prepared by the dilution of multi-component stock solutions. The working range of 0,01 mg/l to 0,2 mg/l is recommendable. A minimum of 5 concentration levels is needed for the calibration.

6 Apparatus

6.1 General

Usual laboratory apparatus and the followings.

6.1.1 Amber glass containers with caps containing PTFE coated lining.

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

6.1.3 Amber glass conical bottles with ground-in stopper.

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

6.1.5 Laboratory centrifuge, capable of producing an acceleration of at least 1 000 G.

6.1.6 Membrane filter, 0,45 µm pore size.

Any adsorption of the target compounds shall be avoided. No interfering material shall be eluated. PTFE, polyamide or an equivalent 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.

6.3 Liquid chromatograph-tandem mass spectrometer (LC-MS/MS)

6.3.1 LC system, consisting of a pump that supports a pressure of at least 40 MPa (400 bar) and an injection system with an appropriate loop capacity depending on injection volume.

6.3.1.1 Stationary phase

Temperature-controlled columns packed with reversed phasematerial. The column should be selected from those made by filling 25 cm long stainless tubes with inner diameters within the range of 2,1mm to 4,6 mm with silica gel (particle diameter 5 µm) chemically bonded with octadecylsilyl (ODS) group or those with an equivalent separating ability. If the applicability is verified, other types of column can be used.

NOTE For verification purposes, where applicable, repeat the chromatographic separation using a column of different selectivity; CN reversed-phase column or phenyl-hexyl reversed-phase column are recommended.

6.3.1.2 Mobile phase

A solution made by mixing 2,5 mmol/l ammonium acetate in water (5.2.4) with 2,5 mmol/l ammonium acetate in methanol (5.2.5) can be used as a mobile phase.

6.3.2 Tandem mass spectrometer

The LC-MS/MS system should be capable of negative ion atmospheric pressure chemical Ionization (APCI). Use a triple quadrupole tandem mass analyzer (MS/MS) consisting of two successive quadrupole mass analyzer or a system with at least equivalent performance as a mass spectrometer. Also, multiple reaction monitoring (MRM) mode should be available for mass analysis.

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 analyzed as soon as possible. Before analyzing the sample, homogenize the sample through a sieve with an aperture of 2 mm.

Soil samples shall be stored in a dark place at (4 ± 2) °C. Samples thatare stored for longer periods (i.e. > than 1 week) prior to analysis, shall be stored at −20 °C.

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 two methods may be applied:

— extraction using ultrasonic waves;