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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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Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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.

When using an ECD, the two-column technique (two columns of different polarity) shall be applied. In this case, simultaneous injection is recommended (see NOTE). When using the specific MS, only a non-polar separation column is required.

NOTE When using ECD, simultaneous injection into a gas chromatograph equipped with two detectors is recommended because of significant time savings. However, the simultaneous injection technique does not allow optimization of the temperature program for each of the columns.

The device parameters are optimized and adjusted according to the manufacturer's instructions.

8.2 Gas chromatographic system

8.2.1 Gas chromatograph (GC)

Optimize the gas chromatograph (6.4) to achieve a separation of the analytes with a separation factor of at least 1,3 (see Annexes A and B).

The injection system shall ensure the injection of the analytes without discrimination.

8.2.2 Detector

8.2.2.1 Electron capture detector (ECD)

The ECD shall be operated under the premise that highest sensitivity is provided. Based on the default settings (set by the manufacturer), optimize the conditions for linearity of the detector response (see Annex A).

8.2.2.2 Mass spectrometric detector (MS)

A low-resolution mass spectrometer for electron impact ionization (EI) detection is used. The mass spectrometer is tuned in accordance with the manufacturer's instructions. Chromatograms are recorded in full scan or selected ion monitoring mode (SIM) (see Annex B). Examples for characteristic masses of the analytes are given in Table 3. To ensure a reliable analysis, it is recommended to use a suitable internal standard.

8.3 Calibration

The calibration is carried out by the external standard method.

The calibration solutions are prepared as described in 5.3.2. Take care to inject the same volume for calibration as for sample measurement.

The initial calibration serves to establish the linear working range of the calibration curve. This calibration is performed when the method is used for the first time and after maintenance and/or repair of the equipment.

The validity of the calibration shall be checked at the start and at the end of every sample series by a standard solution (5.3.2), consisting of compounds representing the retention range and substance polarities of all target analytes. The validity should additionally be proved after a maximum of 20 samples per series.

The recalibration has to cover the desired working range and is to be performed using a standard solution, whenever the validity checks show a deviation > 20 % from the expected concentration.

One feature of the resulting working range is the linear correlation between concentration and measured signal; this correlation shall be ensured for each analyte through at least five concentration levels. Working ranges exceeding the concentration decade are allowed as long as they are linear.

The pairs of varieties y_{ie} and c_{ie} obtained from the j calibrating solutions for the reference substances i are displayed graphically and visually tested for linear dependence. If this is fulfilled, the best-fit line is calculated through linear regression using Formula (1).

$$y_{ie} = a_i \times c_{ie} + b_i \quad (1)$$

where

y_{ie} is the measuring value (signal area or height, respectively) of the substance i depending on c_{ie} (unit depends on evaluation);

c_{ie} is the mass concentration of the substance i in toluenic solution (calibrating solution), in µg/ml;

a_i is the gradient of the reference line for substance i, in ml/µg;

b_i is the intercept on the ordinate of the reference line, same unit as measuring value; b_i can have positive and negative values.

Signals (peak area or peak height) are quantified by means of the calibrating function, see Formula (1).

8.4 Identification and quantification

8.4.1 General

The compounds are identified by comparison of the retention times of the respective measuring signals with current reference retention times. Deviations in retention times as large as 2 % or ± 0,03 min are acceptable.

8.4.2 Electron capture detection

With the two-column technique, an extract is examined chromatographically using two capillary columns of different polarity (see Annex A). Two individual results are obtained.

Tentative identification of an analyte occurs when a peak from a sample extract falls within the expected substance specific retention time (± 0,03 min or ± 0,2 %).

If the obtained signals (i.e. concentrations) fall within the expected repeatability standard deviation (< 10 %), then this is considered another proof of identity. Deviations larger than 10 % cannot be regarded as satisfactory and therefore do not represent secure results.

The smaller single result has to be reported.

If the concentrations determined by the respective columns differ by more than 50 % (based on the lower concentration), the result shall be marked as uncertain or be confirmed through another method, e.g. through method of standard addition or through MS detection. Another qualitative criterion may be a characteristic signal pattern typical for a certain area of examination.

8.4.3 Mass spectrometric detection

The mass spectrometric detection is carried out either in full scan mode (e.g. within the mass range of 50 amu to 300 amu) or in single ion monitoring (SIM) mode utilizing at least 3 characteristic fragments per analyte. Using SIM, the limit of quantification (LOQ) can be increased, accompanied by a loss of spectrometric information.

Besides the retention time, three additional identification points are necessary to provide proper identification. For GC/MS analysis, ISO 22892 describes the accurate procedure in detail.

The following ions are proposed in the SIM-mode (Table 3). It is also possible to use more than one ion for quantification. Ensure that the used ions are free of interferences caused by matrix components.

Table 3 — Characteristic fragments in the SIM mode (according to[3])

Compound	Diagnostic ion 1	Relative intensity	Diagnostic ion 2	Relative intensity	Diagnostic ion 3	Relative intensity
	amu	%	amu	%	amu	%
Nitrobenzene	77	100	123	52,6	51	43,1
1,3,5-Trinitrobenzene	75	100	213	82,1	63	29,1
2-Nitrotoluene	65	100	92	38,4	120	33,7
3-Nitrotoluene	91	100	137	73,6	65	55,7
4-Nitrotoluene	91	100	137	75,6	65	57,7
2,4-Dinitrotoluene	165	100	89	65,1	63	31,1
2,6-Dinitrotoluene	165	100	63	48,2	89	48,2
3,4-Dinitrotoluene	182	100	63	70,4	89	56,4
2,4,6-Trinitrotoluene	210	100	89	82,7	63	64,3
2-Amino-4,6-dinitrotoluene	78	100	180	71,0	197	53,4
4-Amino-2,6-dinitrotoluene	104	100	180	67,2	197	34,5

All mass fragments used for qualification and quantification in the SIM-mode have to be present and detected with a signal-to-noise ratio higher than 3 (s/n > 3). The fragment ratios shall be checked by using the recommendations of ISO 22892. In case of doubt, the identification should be double-checked by measurement in the full scan mode.

For detection in full scan mode, the identity has to be verified by comparison of the obtained spectra to the reference spectra taken under the same working conditions by each lab and GC-MS-system. The mass spectra of the sample should include all ions that have a relative intensity of more than 10 % in the reference spectra considering the fragmentation ratios using the specifications of the ISO 22892.

NOTE Besides the ionization in the above described electron impact ionization mode (EI), negative chemical ionization (NCI) mode is also a versatile tool for the detection of compounds mentioned in this method. The LOQ could be improved significantly by using NCI technology, but due to lower fragmentation, the spectrometric information is reduced. The higher specificity of NCI-detection to electron capturing compounds is able to reduce analytical noise caused by sample matrix effects. The use of mass spectrometry using NCI should be noted in the report. In case of doubt, the identification should be secured by measurement in the EI-mode.

9 Calculation of results

9.1 General

The mass concentration c_{ie} of an analyte in the toluenic extract is calculated after transposing Formula (1) to:

$$c_{ie} = \frac{y_{ie} - b_i}{a_i} \quad (2)$$

Only measuring signals within the calibration area may be quantified. If signals exceed the uppermost calibration mark, the respective extract is to be measured again after dilution of the sample. In this case, it is recommended not to exceed a higher dilution ratio than 1:100 per dilution step. Signals below the lowest calibration mark are considered not quantifiable.

In the case of MS detection, the most intense mass (base peak, main ion) or the sum of three characteristic masses (if present) serves as the measuring signal.

9.2 Calculation

The analyte concentration in the toluenic extract is primarily determined according to Formula (2). Taking the water content of the soil into consideration, this concentration in the extract is calculated according to Formula (3).

The mass concentration c_{is} of the analyte *i* in the solid sample is

$$c_{is} = c_i \times V_T \times \frac{100}{m_f \times w_{dm}} \times f_{dil} \quad (3)$$

where

c_{is} is the mass concentration of the substance *i* in the solid sample, in milligrams per kilogram of dry matter (mg/kg dm);

c_i is the mass concentration of the substance *i* in the toluenic extract, in micrograms per millilitre (µg/ml = mg/l), derived from Formula (2);

m_f is the mass of the soil used for extraction, in grams (g);

V_T is the volume of the toluene used for the re-solution, in millilitres (ml);

w_{dm} is the dry matter (dm) content of the soil sample, in percent of mass (%);

f_{dil} is the dilution factor of the toluenic extract.

If the original methanolic extract was divided into aliquots, apply Formula (4):

$$c_{is} = c_i \times \frac{V_T \times V_{Mtot}}{V_{Mali}} \times \frac{100}{m_f \times w_{dm}} \times f_{dil} \quad (4)$$

where

V_{Mtot} is the total volume of the methanolic extract based on the extraction method chosen (see 7.2.2, 7.2.3, 7.2.4, 7.2.5);

V_{Mali} is the volume of the methanolic extract (aliquot) that has been taken for the re-solution (solvent exchange) in toluene.

10 Quality assurance

To demonstrate the validity of the procedure, the use of a suitable method-checking standard (e.g. 2,5-DNT or other suitable compounds not found in the sample) is recommended. If it is not possible to choose a suitable standard, the efficiency of the extraction has to be checked frequently with the certified reference material.

The recovery rate of each single compound shall be determined, e.g. by spiking samples with other similar matrices parallel to the analysis of real samples or by performing the method of standard addition.

The determined extraction recoveries are not included in the calculation of the final result. Therefore, the constant control of the method recovery utilizing the entire analytical process, including all manual steps, has to be performed periodically. Reference materials are an adequate tool to carry out such experiments. The overall recovery rate shall be between 80 % and 110 % for each compound except 4-A-2,6-DNT and 2-A-4,6-DNT, which due to their lower solubility in toluene, provide lower recovery rates (approx. 40 % to 70 %).

A mathematical correction of the measured values of the samples in the case of lower recoveries is not permitted.

To prove the absence of contaminants during the procedure, include at least one blank analysis per series.

Monitor the accessibility of the lower limit of the working range by an adequate standard solution with every sample series. The signal-to-noise ratio of the resulting signals for each compound shall be ≥ 10, otherwise maintenance at the GC-system (e.g. shortening of the column or replacing the liner) should be performed.

The peak symmetry ($T = b/a$; measured at 10 % of peak height) should not exceed the value of 2 at any time for all analytes in order to allow proper integration and quantification.

For ECD a valuable tool to observe the proper chromatography is the peak area ratio of 4-A-2,6-DNT to TNT. This ratio should be 50 % to 150 % of the initial state (new liner, new column). This test should be carried out for any sample series.

11 Expression of results

Due to the measurement uncertainty, no more than two digits of the analytical result are significant. If, however, analytical results are included in further calculations, results are rounded to three digits (max). Contents < 1 mg/kg dry matter shall be indicated with a precision of 0,01 mg/kg dry matter.

12 Test report

This test report shall contain at least the following information:

a) the test method used, together with a reference to this part of ISO 11916 (ISO 11916-2);

b) all information necessary for complete identification of the sample;

c) the results of the determination according to Clause 11;

d) any details not specified in this part of ISO 11916 or that are optional, as well as any other factors that may have affected the result.

Annex A
(informative)

GC/ECD conditions

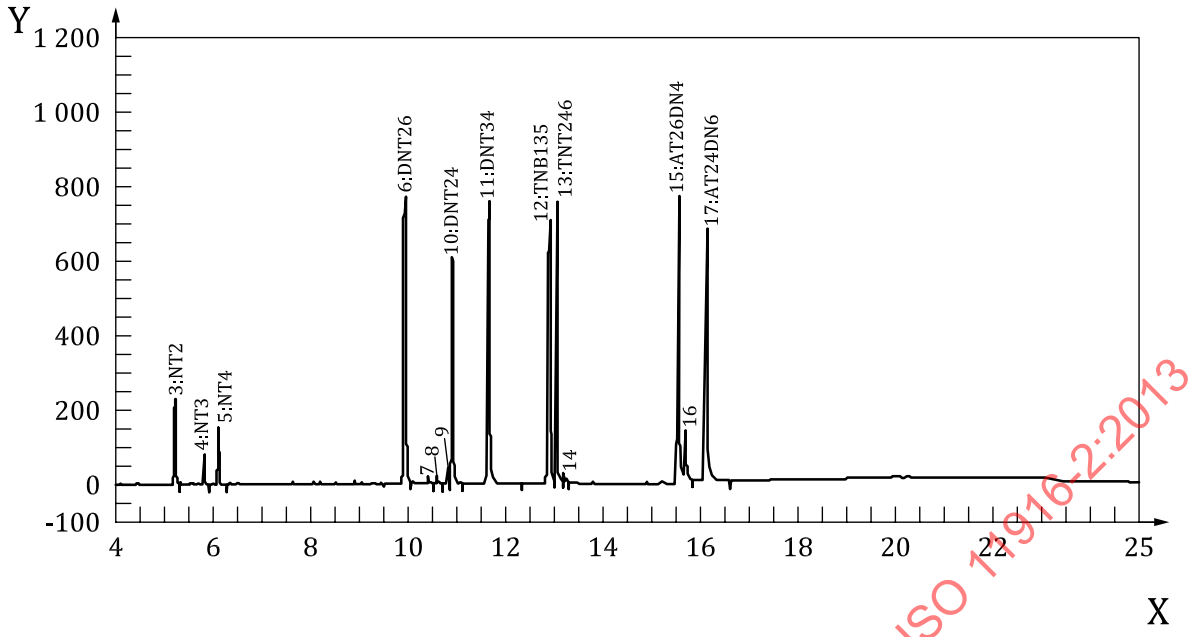
A.1 Example for GC/ECD conditions for the examination of 10 explosive compounds with two columns

Injection mode:	splitless (1 min)
Injection volume:	1 µl
Temperature of injector:	280 °C
Separating columns:	non-polar: J&W DB-5, 60 m × 0,32 mm internal diameter (ID), film thickness 0,25 µm; polar: J&W DB-17, 60 m × 0,32 mm ID, film thickness 0,25 µm; both columns connected to the injector
Carrier gas:	Hydrogen, 9 pressure, 3 ml/min
Temperature programme:	100 °C (4 min); 10 °C/min; 260 °C (4 min);
Detector:	ECD
Temperature of ECD:	370 °C

NOTE J&W DB-5 and DB-17 are the trade names of products supplied by Agilent. This information is given for the convenience of users of this document 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.

A.2 Examples of chromatograms for the effect of the 2 columns of different polarity with simultaneous injection

See Figures A.1 to A.4.

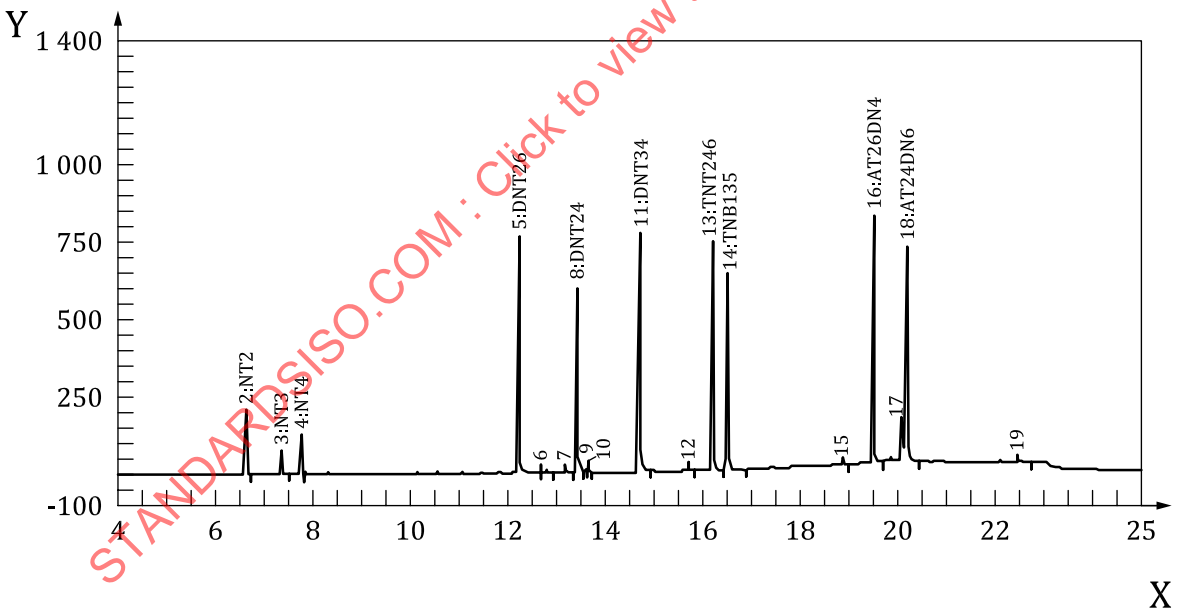


Key

X time, min

Y response, mV

Figure A.1 — Multi-component standard (Column DB-5 non-polar)

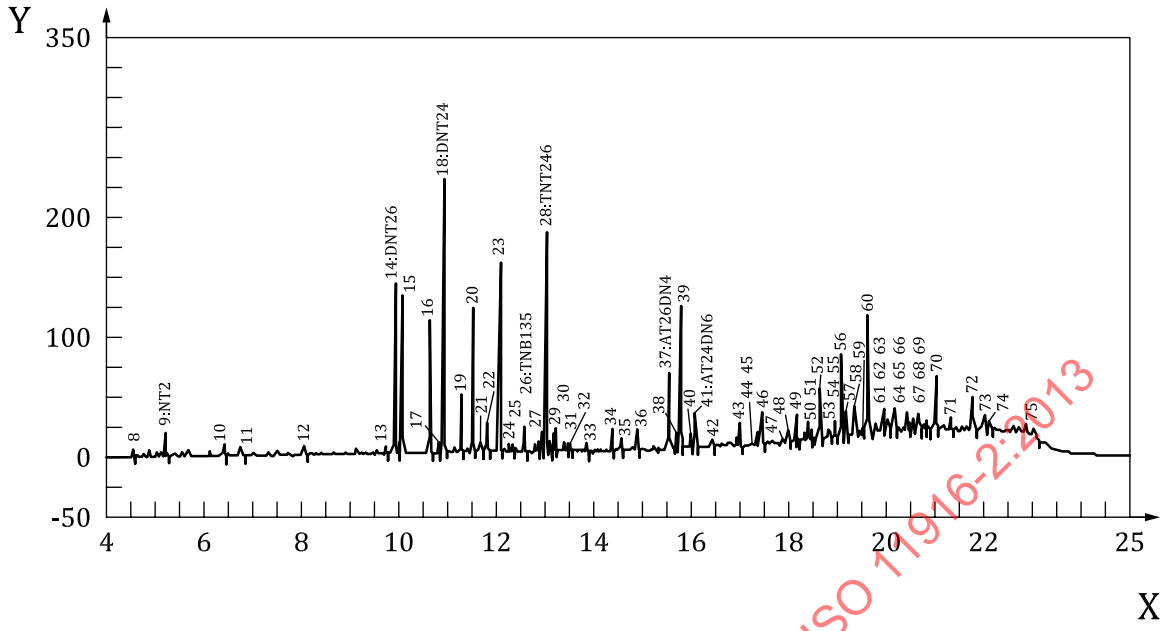


Key

X time, min

Y response, mV

Figure A.2 — Multi-component standard (Column DB-17 polar)

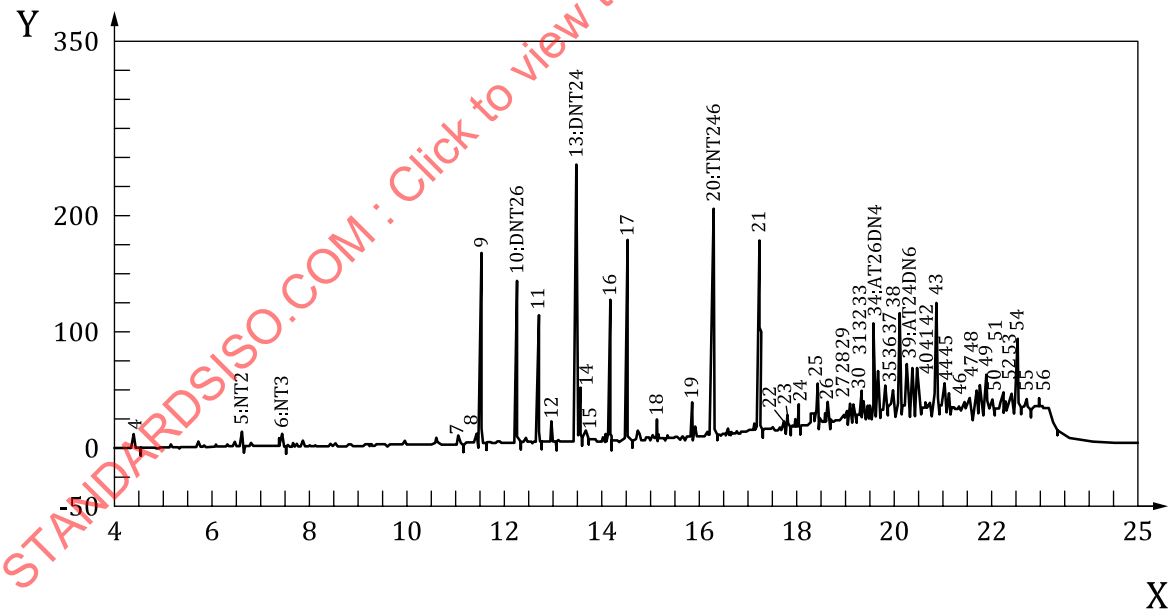


Key

X time, min

Y response, mV

Figure A.3 — Sample (Column DB-5 non-polar)



Key

X time, min

Y response, mV

Figure A.4 — Sample (Column DB-17 polar)

Annex B
(informative)

GC/MS conditions

B.1 Example for GC/MS conditions for the examination of 18 explosive compounds using SIM technique

Injection volume:	1 µl
Split mode:	Splitless, 1 min
Temperature of injector:	275 °C
Separating column:	DB-XLB 30 m × 0,25 mm ID, film thickness 0,25 µm
Pre-column:	Uncovered deactivated fused silica, ca. 2 m
Carrier gas:	Helium, 1 ml/min
Temperature programme:	70 °C (1 min); 20 °C/min; 300 °C (2 min)
Detector:	MSD
Transfer-line temperature:	320 °C
Modus:	SIM (Single Ion Monitoring)
Mass descriptor:	See Table B.1

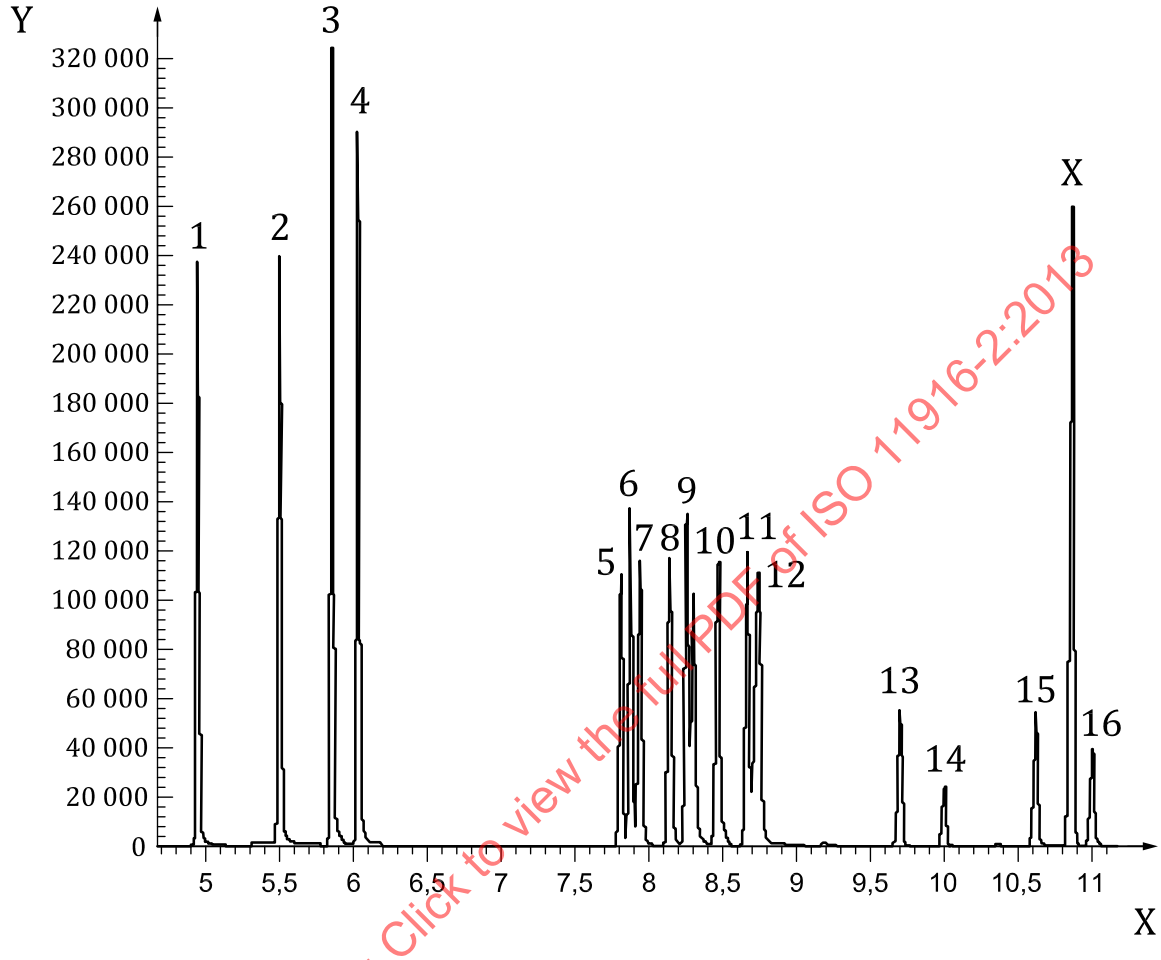
NOTE DB-XLB is the trade name of a product supplied by Agilent. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Table B.1 — Mass descriptors at about 3 cycles/second (quan. mass bold)

Compound group	Dwelling time	Mass window			
	ms	u (± 0,5 u)	u (± 0,5 u)	u (± 0,5 u)	u (± 0,5 u)
NB	70	51	77	**123**	
2-NT	70	65	92	**120**	
3-NT	70	65	91	107	**137**
4-NT	70	65	91	107	**137**
2,4-DNT	70	89	119	**165**	182
2,6-DNT	70	89	119	148	**165**
3,4-DNT	70	77	89	94	**182**
TNT	70	164	180	193	**210**
TNB	70	75	120	167	**213**
ADNT	70	104	**180**	197	

B.2 Example of chromatogram

See Figure B.1.



Key

X	time, min	Y	response, mV
1	Nitrobenzene	9	2,3-Dinitrotoluene
2	2-Nitrotoluene	10	2,4-Dinitrotoluene
3	3-Nitrotoluene	11	3,5-Dinitrotoluene
4	4-Nitrotoluene	12	3,4-Dinitrotoluene / 2-Amino-4-nitrotoluene
5	2,6-Dinitrotoluene	13	Trinitrotoluene
6	1,2-/1,4-Dinitrobenzene	14	Trinitrobenzene
7	1,3-Dinitrobenzene	15	4-Amino-2,6-Dinitrotoluene
8	2-Nitro-4-aminotoluene	16	2-Amino-4,6-Dinitrotoluene
		x	Method-checking standard

Figure B.1 — Multi-component standard

Annex C
(informative)

Precision data

C.1 Study concept and description of sample material

In 2011 the Fraunhofer Institute for Molecular Biology and Applied Ecology (IME) organized an interlaboratory validation study of a draft International Standard for the determination of selected explosives in soils on behalf of the German Environmental Agency (for details refer to UBA Final Report FKZ 3710 74 209).

Field samples of different sites contaminated by explosives were air-dried and sieved < 2 mm. Three individual mixtures were made from the sample materials in order to cover as many as possible of the explosive compounds listed in this part of ISO 11916. The mixtures were homogenized and subsamples were filled into brown glass bottles. The participants of the interlaboratory study received one sample (about 250 g dry weight) of each material. The draft version of this part of ISO 11916 served as a working instruction.

The test materials were prepared from sieved, but not ground, soil material originating from real contaminated sites. Due to well-known properties of soils contaminated with explosives, the homogeneity of the materials was partially not satisfactory. This was, in particular, true for the 2,4,6-trinitrotoluene (2,4,6-TNT) with variation coefficients (C_V) of up to 30 % in materials 1 and 3. Apart from that, variation coefficients were predominantly < 10 %. The homogeneity obtained in the test materials reflects the reality of samples originating from sites contaminated with explosives. Thus, the result of the interlaboratory study as presented below allows a realistic assessment of data determined according to this part of ISO 11916.

For quality assurance, a standard solution containing several explosives dissolved in toluene was sent to each participating laboratory. The concentration of each explosive substance in the standard solution was about 1,0 mg per litre which was communicated to the participants.

Tables C.1 to C.5 summarize the results of the interlaboratory study. Data evaluation was performed according to ISO 5725-2. Data listed are given as milligrams per kilogram of dry soil.

Table C.1 — GC-analysis data of extracts from mechanical shaking extraction (MSE)

Material 1	l	n	n_A	n_{AP} %	x	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
1,3,5-TNB	6	13	4	23,5	0,28	0,17	60,65	0,11	37,91
2,4-DNT	9	19		0,0	5,44	2,24	41,08	1,05	19,33
2,4,6-TNT	8	17	2	10,5	11,92	3,81	31,98	2,51	21,06
4-A-2,6-DNT	5	11	2	15,4	0,40	0,23	56,82	0,07	17,42
2-A-4,6-DNT	6	13		0,0	0,57	0,40	69,30	0,15	25,79
2,6-DNT	9	19		0,0	2,15	0,90	41,60	0,30	14,02
Material 2	l	n	n_A	n_{AP} %	x	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
1,3,5-TNB	7	15	2	11,8	3,98	5,16	129,45	0,51	12,70
2-NT	7	15		0,0	8,18	3,93	48,02	0,79	9,63
3-NT	8	17	2	10,5	1,29	1,04	81,01	0,12	9,18
4-NT	6	13	2	13,3	3,11	1,75	56,39	0,12	3,77
2,4-DNT	8	17	2	10,5	4,75	2,20	46,28	0,25	5,17
2,4,6-TNT	9	18		0,0	357,0	194,7	54,55	80,17	22,46
4-A-2,6-DNT	9	19		0,0	18,47	8,59	46,52	1,22	6,58
2-A-4,6-DNT	9	19		0,0	16,43	10,20	62,07	1,52	9,22
2,6-DNT	9	19		0,0	2,13	0,72	33,66	0,19	9,10
Material 3	l	n	n_A	n_{AP} %	x	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
1,3,5-TNB	7	15	2	11,8	1,57	1,62	103,25	0,13	7,97
2,4-DNT	7	15		0,0	0,42	0,17	40,10	0,06	14,80
2,4,6-TNT	9	18		0,0	122,7	54,63	44,53	31,29	25,51
4-A-2,6-DNT	9	19		0,0	7,75	2,51	32,41	1,22	15,68
2-A-4,6-DNT	9	19		0,0	6,17	2,90	46,98	1,29	20,93
2,6-DNT	4	9		0,0	0,12	0,03	22,31	0,03	22,31

Explanation of symbols

l	Number of laboratories after elimination of outliers
n	Number of single-analysis data without outliers
n_A	Number of outliers
n_{AP}	Number of outliers in %
x	Mean value in mg/kg dry matter
s_R	Standard deviation of reproducibility in mg/kg dry matter
$C_{V,R}$	Variation coefficient of reproducibility in %
s_r	Standard deviation of repeatability in mg/kg dry matter
$C_{V,r}$	Variation coefficient of repeatability in %

Table C.2 — GC-analysis data of extracts from ultrasonification (USE)

Material 1	l	n	n_A	n_{AP} %	x	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
1,3,5-TNB	6	13	4	23,5	0,25	0,15	60,40	0,04	16,00
2,4-DNT	9	19		0,0	5,77	2,44	42,25	1,66	28,73
2,4,6-TNT	9	19		0,0	11,44	3,41	29,80	1,83	16,04
4-A-2,6-DNT	6	13		0,0	0,33	0,11	33,43	0,08	23,80
2-A-4,6-DNT	6	13		0,0	0,45	0,26	58,54	0,11	24,39
2,6-DNT	9	19		0,0	2,55	0,61	23,89	0,20	7,83
Material 2	l	n	n_A	n_{AP} %	x	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
1,3,5-TNB	5	11	6	35,3	1,56	0,80	51,12	0,31	19,95
2-NT	9	19		0,0	8,38	4,21	50,24	0,78	9,35
3-NT	8	17	2	10,5	2,82	3,72	132,2	0,10	3,69
4-NT	9	19		0,0	3,92	1,39	35,48	0,38	9,77
2,4-DNT	8	16	3	15,8	4,55	2,21	48,65	0,20	4,42
2,4,6-TNT	8	15	3	16,7	263,9	105,2	39,84	12,15	4,60
4-A-2,6-DNT	8	16	3	15,8	19,11	7,78	40,69	0,69	3,61
2-A-4,6-DNT	9	19		0,0	19,21	12,61	65,67	2,01	10,45
2,6-DNT	9	19		0,0	2,42	0,87	35,94	0,27	11,08
Material 3	l	n	n_A	n_{AP} %	x	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
1,3,5-TNB	7	15	2	11,8	1,94	2,00	103,31	0,39	20,05
2,4-DNT	7	15		0,0	0,45	0,20	44,74	0,04	8,05
2,4,6-TNT	9	18		0,0	103,2	45,37	43,96	24,36	23,61
4-A-2,6-DNT	9	19		0,0	9,30	4,16	44,74	2,55	27,38
2-A-4,6-DNT	9	19		0,0	7,26	3,73	51,36	1,80	24,74
2,6-DNT	4	9		0,0	0,11	0,04	34,86	0,03	31,19
Explanation of symbols: See Table C.1.									