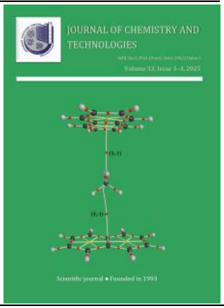
Journal of Chemistry and Technologies, 2025, *33*(4), 939-947

Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua
editorial e-mail: chem.dnu@gmail.com



UDC 502.521:623.454.24:623.454

DETERMINATION OF EXPLOSIVE COMPOUNDS IN SOIL BY HPLC-UV METHOD USING MODIFIED QUECHERS SAMPLE PREPARATION

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Received 6 August 2025; accepted 17 October 2025; available online 25 December 2025

Abstract

The method for analyzing explosives in soil was developed by HPLC-UV employing a modified QuEChERS sample preparation technique. The method of simultaneous determination of fourteen explosives in soil was validated according to the following criteria: specificity, linearity, limits of detection (LOD), limits of quantification (LOQ), accuracy, and precision. The chromatographic conditions for separation and determination of the explosives were optimized during the study. It was established that the most optimal mobile phase for the separation of fourteen explosives is water: formic acid in a ratio of 99.9 : 0.1 (by volume; eluent A) and methanol: formic acid in a ratio of 99.9 : 0,1 (by volume; eluent B). Chromatography was performed in isocratic mode (eluent A/B, 60/40). It was found that the correlation coefficients for fourteen explosives range from 0.998 to 0.999 ($R^2 > 0.995$). The limit of detection (LOD) and limit of quantification (LOQ) for explosives range from 0.012 to 0.081 mg/kg and 0.040 to 0.270 mg/kg, respectively. Percent recovery (R, %) in the range from 73.0 to 95.7 % indicates the acceptability of the explosives extraction procedure. The relative standard deviation (RSD, %) of the measurement results under conditions of repeatability ranged from 3.6 to 9.6 %. The obtained data suitability evaluation of method (validation) comply with the requirements of ISO 11916-1:2013 and method 8330A. The determined parameters of the proposed method also meet all the suitability assessment criteria and minimum permissible values according to Commission Decision 2002/657/EC. Therefore, the presented method is suitable for use in chemical analytical laboratories to determine the residual quantities of explosives in soils at the appropriate level.

Keywords: validation; explosives; soil; HPLC-UV; QuEChERS.

ВИЗНАЧЕННЯ ВИБУХОВИХ РЕЧОВИН У ГРУНТІ МЕТОДОМ HPLC-UV З ВИКОРИСТАННЯМ МОДИФІКОВАНОЇ ПРОБОПІДГОТОВКИ QUECHERS

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Анотація

Розроблена методика визначення вибухових речовин у грунті методом HPLC-UV з використанням модифікованої пробопідготовки QuEChERS. Оцінку придатності (валідацію) методики одночасного визначення чотирнадцяти вибухових речовин у пробах ґрунту методом HPLC-UV з використанням модифікованої пробопідготовки QuEChERS здійснювали за наступними критеріями: специфічність, лінійність, межа детектування (LOD), межа кількісного визначення (LOQ), правильність та прецизійність. У процесі дослідження були підібрані хроматографічні умови розділення та визначення вибухових речовин. Встановлено, що оптимальна рухома фаза для розділення на колонці чотирнадцяти вибухових речовин є вода : мурашина кислота в співвідношенні 99.9 : 0.1 (за об'ємом; елюент A) та метанол : мурашина кислота в співвідношенні 99.9 : 0.1 (за об'ємом; елюент B). Хроматографію проводили в ізократичному режимі (елюент A/B, 60/40). Встановлено, що коефіцієнти кореляції для чотирнадцяти вибухових речовин знаходяться в діапазоні від 0.998 до 0.999 (R2 > 0.995). Межа виявлення (LOD) та межа кількісного визначення (LOQ) для вибухових речовин складає від 0.012 до 0.081 мг/кг та від 0.040 до 0.270 мг/кг відповідно. Відсоток повернення (R, %) для проаналізованих концентрацій (0.2 мг/кг, 0.5 мг/кг та 1.0 мг/кг) був в межах від 73.0 до 95.7 %, що вказує на прийнятність процедури екстракції вибухових речовин з проб ґрунту. Відносне стандартне відхилення (RSD, %) результатів вимірювання в умовах збіжності склало від 3.6 до 9.6 %. Отримані дані оцінки придатності (валідації) методу відповідають вимогам, зазначеним в аналітичних методах ISO 11916-1:2013 та в методі 8330A. Визначені параметри запропонованої методики також відповідають усім критеріям оцінки придатності та мінімально допустимим значенням згідно з Commission Decision 2002/657/EC. Отже, представлена методика є придатною для застосовування в хіміко-аналітичних лабораторіях з метою визначення залишкових кількостей вибухових речовин у ґрунтах на належному рівні.

Ключові слова: валідація; вибухові речовини; грунт; HPLC-UV; QuEChERS.

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doi: 10.15421/jchemtech.v33i4.336927

Introduction

Military actions resulting from Russian aggression inflict substantial damage on Ukrainian society through fatalities, adverse impacts on human health, and the degradation of natural resources. Explosions, the destruction of oil depots, storage facilities for petroleum products, chemical substances, pesticides, mineral fertilizers, and other toxic compounds exert a detrimental influence on the ecological conditions of both individual settlements and entire regions of Ukraine. Among the most hazardous pollutants generated in territories exposed to shelling and affected by hostilities are explosive substances. Under current circumstances, there is a considerable risk of environmental contamination by explosives, and their concentrations in environmental objects must be appropriately monitored [2; 3].

An explosion is a process of extremely rapid transformation of an explosive substance into a large volume of highly compressed and heated gases, which, upon expansion, exert mechanical effects such as destruction, displacement, fragmentation, or ejection. According to the study by Breeze et al. [3], the investigation of explosive traces constitutes a critical component of forensic examination. It provides valuable information regarding the type of explosive material used, its qualitative and quantitative characteristics, the device parameters, as well as its structural features, including the main components and method of fabrication. Furthermore, Adegoke and Nic Daeid [1] demonstrated that one of the primary targets of forensic investigation is the residual amounts of explosive substances collected directly from the explosion site.

Explosives are chemical compounds or mixtures of compounds that, under certain external conditions, are capable of rapid chemical transformation accompanied by the release of energy and a large volume of gases.

Although a vast number of explosive substances are known today, only a few dozen are commonly used. According to Zapata and García-Ruiz [21], explosives are most frequently classified based on their intended application. This classification divides explosives into four main categories: high explosives (brisant), initiating explosives, propellants, and pyrotechnic compositions. Among these, initiating and high explosives are the most widely used.

It is also important to note that, from the standpoint of chemical analysis, high explosives attract the greatest attention, as they are most frequently encountered in forensic examinations. Common high explosives include 2,4-dinitrotoluene, 2,6-dinitrotoluene, 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene (TNT), RDX (hexogen), tetryl, and others.

In the context of criminal investigations involving the use of explosive devices, a pressing task is the identification of residual amounts of explosives—specifically nitroamines and nitroaromatic compounds—in soil samples collected from explosion sites using advanced chromatographic techniques. These methods include gas-liquid chromatography coupled with mass-selective and electron capture detectors, as well as high-performance liquid chromatography (HPLC) with ultraviolet (UV) and mass-selective detectors [9].

Each method presents its own advantages and limitations. For instance, according to ISO 11916-2:2013, gas-liquid chromatography is suitable only for the detection of nitroaromatic derivatives such as 2,6-dinitrotoluene and 2,4,6-trinitrotoluene (TNT), whereas compounds like RDX (hexogen), HMX (octogen), and tetryl cannot be identified using this method.

In recent years, increasing attention has been given to high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection, which enables selective and highly sensitive simultaneous determination of fourteen explosive compounds (including nitroamines and nitroaromatic compounds) within a single sample. Moreover, the study by Jeong et al. [8] highlights the application of the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) sample preparation technique, which allows for rapid and efficient extraction of residual target compounds and effective purification of the extract from matrix components.

Traditionally, the QuEChERS sample preparation technique has been employed for the determination of residual levels of pesticides from various chemical classes using gas or liquid chromatography coupled with mass spectrometry. However, recent studies indicate that QuEChERS, in its various modifications, can also be applied to the analysis of residual antibiotics [12], mycotoxins [17], and polychlorinated biphenyls [18].

Currently, the development of rapid and highly sensitive analytical methods for detecting explosive substances in soil and other matrices involves the use of advanced physicochemical and chromatographic techniques.

In the study conducted by Pan X. [13], the analysis of the explosive compound RDX (hexogen) and its metabolites in biological samples was performed using gas-liquid chromatography with an electron capture detector (GC-ECD). The authors report that RDX contaminates soil and water and is toxic to various organisms, including plants, animals, and microorganisms. Furthermore, RDX has been associated with genotoxic and neurotoxic effects, as well as an increased risk of carcinogenesis. RDX is also capable of biotransformation into N-nitroso derivatives (MNX, DNX, and TNX), which can accumulate both in the environment and in the tissues of living organisms.

Pawłowski et al. [14] demonstrated the successful application of the GC-ECD method for quality control during forensic investigations, specifically to assess the likelihood of contamination of explosive substances on the hands of investigators. The analytical procedure involved sample collection, extraction from a gauze swab, transfer of the extract, and instrumental analysis based on gas chromatography with electron capture detection (GC-ECD). The authors found that among the explosive substances, 2,4,6-trinitrotoluene (TNT) exhibited the highest level of contamination, followed to a lesser extent by RDX (hexogen).

Salem et al. [15] note that the most versatile method for determining residual amounts of explosives (nitro-substituted aromatic hydrocarbons) in various matrices, including soil, is gas-liquid chromatography coupled with mass spectrometric detection (GC-MS). This method enables highly sensitive and selective identification of thermally stable explosives using spectral mass databases.

In the study by Holmgren et al. [5], the development and validation of a novel and precise GC-MS method with chemical ionization for the determination of explosives in soil is presented. The authors propose using a solvent mixture of acetonitrile and dichloromethane in a 50:50 ratio at 30 °C for more efficient extraction of explosives from soil. This approach increased the recovery of more volatile products, improved accuracy, and significantly reduced analysis time compared to the conventional EPA 8330 method.

Despite the versatility of gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS), the analysis of explosives such as RDX (hexogen), HMX (octogen), tetryl, and pentaerythritol tetranitrate (PETN) presents certain challenges due to their thermal instability when using these methods. High-performance liquid chromatography with ultraviolet detection (HPLC-UV) overcomes the limitations of gas chromatography and enables the determination of all major explosive compounds and their metabolites, including RDX, HMX, nitroaromatic compounds, and nitroamines.

The study by Ünsal and Erkan [20] presents the development and validation of a method for the determination of explosives—including RDX (hexogen), HMX (octogen), 2,4,6-trinitrotoluene (2,4,6-TNT), tetryl, and others—using high-performance liquid chromatography with a diode array detector (HPLC-DAD). The optimal mobile phase for the column (XDB-C18, 5 µm, 4.6 × 150 mm) was a mixture of 22 % isopropanol (IPA) in water. The solvent used for both standard and test samples was a mixture of water and acetonitrile (60:40, v/v). The linear ranges for the analyzed explosives were 6.5–100 mg/L (R^2 = 0.998–0.999). Average recovery values ranged from 95.3 % to 103.3 %. The limits of detection (LOD) and quantification (LOQ) ranged from 0.09 mg/L to 1.32 mg/L and from 0.31 mg/L to 4.42 mg/L, respectively.

An increasing number of studies report the determination of explosive substances using high-performance liquid chromatography coupled with tandem mass spectrometric detection (LC-MS/MS). Şener et al. [16] developed a rapid LC-APCI-MS/MS screening and confirmation method for 18 residues of explosives and their metabolites in soil. The authors described a single-step extraction of explosives from the matrix (soil) using methanol. Additionally, the method was validated, yielding satisfactory metrological characteristics. Most recovery rates exceeded 80 %, while precision values were below 15 %. The limits of detection (LOD) and quantification (LOQ) ranged from 0.2 to 54.1 ng/g and from 0.3 to 190.0 ng/g, respectively.

Suppajariyawat and Gonzalez-Rodriguez (2021) conducted a study of organic explosives, including RDX (hexogen), 2,4,6-trinitrotoluene (TNT), tetryl, 1,3,5-trinitrobenzene (1,3,5-TNB), and pentaerythritol tetranitrate (PETN), using high-performance liquid chromatography coupled with high-resolution time-of-flight mass spectrometry (LC-QTOF/MS). Retention times, collision energies, precursor ions, and characteristic MS/MS spectra for each explosive compound were obtained via atmospheric pressure chemical ionization (APCI) in negative ion mode. The authors' results demonstrated that LC-QTOF/MS is a powerful method for the identification and confirmation of thermally labile organic explosives, in contrast to conventional GC-MS techniques.

The aim of the present study was to evaluate the suitability (validation) of a method for measuring the content of explosives (nitroamines and nitroaromatic compounds) in soils using HPLC-UV combined with a modified QuEChERS sample preparation technique.

Materials and methods

Laboratory investigations were conducted during 2024–2025 at a structural unit of the National University of Life and Environmental Sciences of Ukraine—the Ukrainian Laboratory of Quality and Safety of Agro-Industrial Products (accredited in accordance with the quality standard DSTU ISO/IEC 17025:2019 for the performance of analytical testing) [[6]].

Reagents. The study employed a mixture of analytical standards of nitroamines and nitroaromatic compounds (1000 µg/mL) produced by Restek. For QuEChERS sample preparation, anhydrous magnesium sulfate (Sigma-Aldrich, USA), sodium chloride (Merck, Germany), and HPLC-grade acetonitrile (Carlo Erba, France) were used. For preparation of the mobile phase in high-performance liquid chromatography, purified water obtained using a Millipore Direct-Q™ system, HPLC-grade methanol (Honeywell, USA), and formic acid (98.0–100 %, Sigma-Aldrich, USA) were utilized.

In this study, a certified reference material (CRM) of clean soil (Clean Sandy Loam) produced by Sigma-Aldrich was employed.

Preparation of calibration solutions. Calibration solutions were prepared by diluting the standard mixture of nitroamines and nitroaromatic compounds in a soil extract (blank samples) free of explosive residues (matrix-matched calibration). The concentrations of explosives in the calibration solutions were 2.0 µg/mL, 5.0 µg/mL, 10 µg/mL, 20 µg/mL, and 50 µg/mL.

Soil sample preparation using the modified QuEChERS method. The first stage of sample preparation was carried out in accordance with ISO 11916-1:2013 [6]. Ten grams of homogenized test soil sample were placed into a 50 mL centrifuge tube. Then, 10 mL of acetonitrile was added, and the mixture was vortexed for 1 minute followed by ultrasonic treatment in a water bath for 4 hours at 50 °C. After ultrasonic extraction, the sample was cooled to room temperature. The second stage of sample preparation was conducted following the modifications described in the literature by M. Mbisana et al. **Ошибка! Источник ссылки не найден.**. Subsequently, 5 mL of water was added and vortexed for 1 minute. Then, 4 g of anhydrous magnesium sulfate and 1 g of sodium chloride were added, and the mixture was vigorously shaken for 1 minute. The resulting mixture was centrifuged at 7000 rpm for 10 minutes. Using a pipette, 8 mL of the upper organic layer was transferred to a pear-shaped flask for evaporation. The extract was evaporated on a rotary evaporator at 40 °C. To the dry residue, 1 mL of methanol : water solution (50:50, v/v) was added and vortexed for 1 minute. The extract was then transferred to a 1.5 mL centrifuge tube and centrifuged at 15,000 rpm for 10 minutes. The obtained supernatant was filtered through a syringe filter with a pore size of 0.45 µm. The purified extract was subsequently transferred into vials and analyzed by HPLC-UV.

Chromatographic conditions. The determination of explosive substances (nitroamines and nitroaromatic compounds) in soil was performed using a Dionex Ultimate 3000 liquid chromatograph equipped with an ultraviolet (UV) detector (manufactured in the USA).

Separation of explosives was achieved on a C18 column (VDSpher 100 C18-M, 5 µm, 250×4.6 mm). Elution was carried out in isocratic mode using a mobile phase composed of eluents A and B in a 60 : 40 ratio. Mobile phase A consisted of water with 0.1 % formic acid, and mobile phase B was methanol with 0.1 % formic acid. The flow rate was set at 1.0 mL/min, with an injection volume of 10 µL. The UV detector wavelength was set at 315 nm.

The mass fraction of explosive compounds was calculated using the external standard method (absolute calibration) and expressed in mg/kg.

Method validation was performed in accordance with Commission Decision 2002/657/EC, which ensures compliance with EU Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results.

Results and discussion

Optimization of chromatographic conditions. Typically, methanol, acetonitrile, and water are used as mobile phases for the determination of explosives (nitroamines and nitroaromatic compounds).

In our study, two mobile phases were employed. During the initial optimization stage, methanol (eluent A) and water (eluent B) were used as the mobile phases. Chromatographic separation was performed under isocratic conditions with a 50 : 50 ratio of eluents A and B (According to the recommendations outlined in Method 8330A) [11]. The results demonstrated that this mobile phase composition did not achieve complete separation of explosive compounds such as 1,3-dinitrobenzene (1,3-DNB), tetryl, nitrobenzene (NB), and 2,4,6-trinitrotoluene (2,4,6-TNT). The incomplete chromatographic resolution of these components is likely due to their similar polar properties.

The chromatographic conditions related to the use of the second mobile phase were independently selected by the authors, taking into account the available C18 analytical column (VDSpher 100 C18-M, 5 µm, 250×4.6 mm).

The second mobile phase consisted of a mixture of water and formic acid in a ratio of 99.9 : 0.1 (v/v; eluent A) and a mixture of methanol and formic acid in a ratio of 99.9 : 0.1 (v/v; eluent B). Chromatographic separation was also performed in isocratic mode, but with a reduced volume fraction of the organic solvent–methanol–using a 60 : 40 ratio of eluents A to B. The use of this second mobile phase enabled complete separation of all explosive compounds (nitroamines and nitroaromatic compounds), allowing for their integration and quantitative analysis. Further reduction of the methanol volume fraction (eluents A/B, 70/30) resulted in decreased selectivity and prolonged chromatographic retention times.

Method validation. The validation of the method was carried out according to the criteria established by Commission Decision 2002/657/EC, including selectivity, linearity, limit of detection (LOD), limit of quantification (LOQ), accuracy (recovery), and precision.

Selectivity. To assess method selectivity, soil samples free of residual explosives (blank samples) and samples spiked with nitroaromatic compounds and nitroamines (explosives) at a concentration of 0.5 mg/kg were analyzed.

Comparison of chromatograms obtained from the blank soil samples and soil samples artificially enriched with explosive compounds demonstrated that the determination of explosive residues in soil was not affected by other sample components—matrix interferences (Figures 1 and 2).

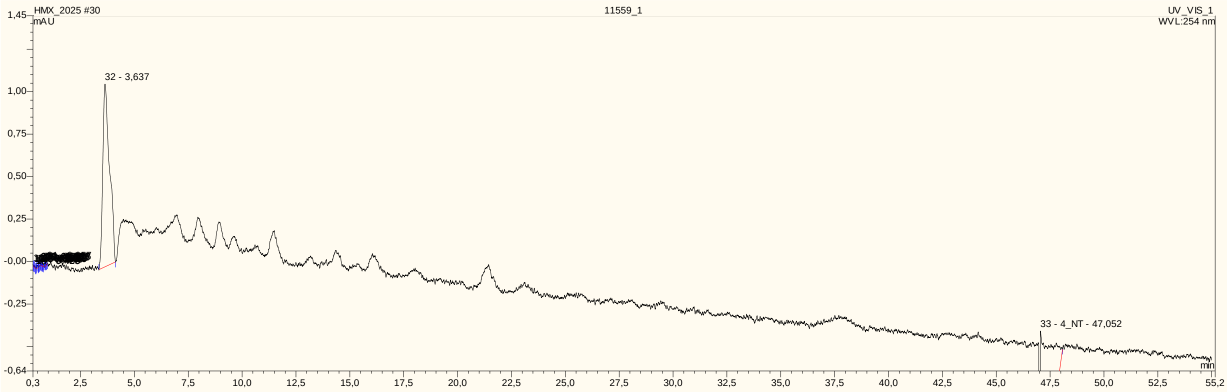

Fig. 1. Chromatogram of a blank soil sample

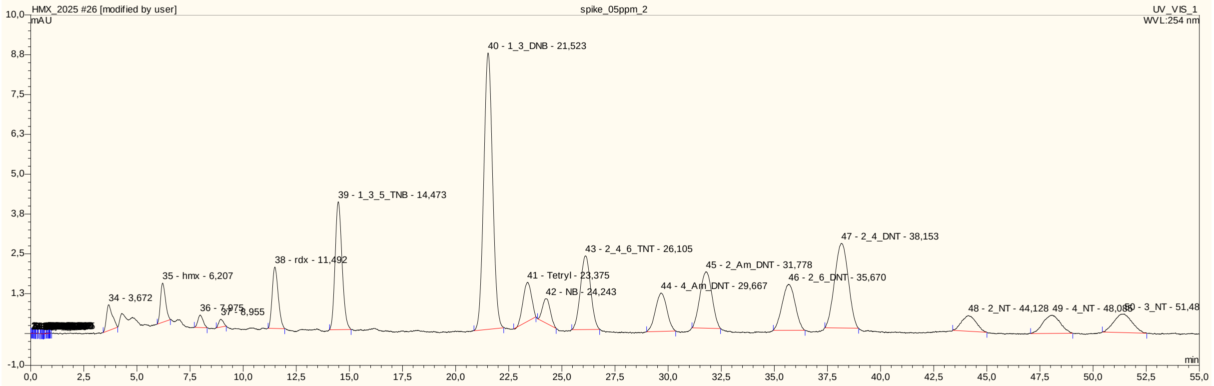

Fig. 2. Chromatogram of a soil sample containing explosive substances at a concentration of 0.5 mg/kg

Linearity. Five standard solutions with known concentrations of explosives (ranging from 2.0 to 50.0 µg/mL) were used to construct the calibration curve. For each standard solution, two analytical signal values (chromatographic peak areas) were obtained using the same batch of reagents and equipment. Regression analysis of the obtained data was performed using the least squares method with a linear model.

It was established that the calibration curves for all nitroaromatic compounds and nitroamines demonstrated R^2 values ranging from 0.998 to 0.999, which meet the required level of ≥ 0.995. Therefore, it can be concluded that the calibration curves for explosives are linear within the concentration range of 2.0 to 50.0 μg/mL.

Limit of detection (LOD) and limit of quantification (LOQ). The LOD and LOQ for each nitroaromatic compound and nitroamine were determined using artificially spiked soil samples with the standard mixture at the minimum concentration level of 0.2 mg/kg. LOD was defined based on a signal-to-noise ratio (S/N) of chromatographic peaks that is three times greater than the baseline noise (S/N = 3). LOQ was determined based on an S/N ratio ten times greater than the baseline noise (S/N = 10). The LOD and LOQ results for nitroaromatic compounds and nitroamines are presented in Table 1.

Table 1

LOD and LOQ results for nitroaromatic compounds and nitroamines in soil samples

Compound Name	LOQ (S/N = 10)	LOD (S/N = 3)
Octogen (HMX)	0.150	0.045
Hexogen (RDX)	0.150	0.045
1,3,5-Trinitrobenzene (1,3,5-TNB)	0.070	0.021
1,3-Dinitrobenzene (1,3-DNB)	0.040	0.012
Tetryl	0.170	0.051
Nitrobenzene (NB)	0.280	0.084
2,4,6-Trinitrotoluene (2,4,6-TNT)	0.100	0.030
4-Amino-2,6-dinitrotoluene (4-Am-DNT)	0.200	0.060
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	0.170	0.051
2,6-Dinitrotoluene (2,6-DN)	0.200	0.060
2,4-Dinitrotoluene (2,4-DNT)	0.100	0.030
2-Nitrotoluene (2-NT)	0.270	0.081
4-Nitrotoluene (4-NT)	0.270	0.081
3-Nitrotoluene (3-NT)	0.270	0.081

Source: Developed by the authors based on experimental data.

The limit of detection (LOD) and limit of quantification (LOQ) for explosives range from 0.012 to 0.081 mg/kg and from 0.040 to 0.270 mg/kg, respectively. The obtained LOD and LOQ values indicate that the determination of explosives in soil is feasible at their residual concentration levels.

Accuracy. The accuracy of explosives determination in soil was assessed using the "input-found" method. An analytical standard of the components under study (a standard mixture of nitroaromatic compounds and nitroamines) was added to soil samples (certified reference material (CRM) of a clean matrix) that did not contain residual amounts of explosives. After addition of the standard mixture, the concentrations of explosives in the soil were 0.2 mg/kg, 0.5 mg/kg, and 1.0 mg/kg. Following all stages of the modified QuEChERS sample preparation, the content of explosives was determined by HPLC-UV, and the recovery rate (R, %) was calculated for each model matrix (soil samples artificially spiked with explosives at levels of 0.2 mg/kg, 0.5 mg/kg, and 1.0 mg/kg).

The recovery coefficient (R, %) was calculated using formula (1).

$$R_i = \frac{C^{found} - C^0}{C^{added}} \times 100\ \% \qquad (1)$$

R_i is the recovery rate of the *i*-th component, %;
C^{found} is the concentration of the *i*-th component determined in the spiked sample, mg/kg;
C^{added} is the concentration of the *i*-th component added to the sample, mg/kg;
C^0 is the initial concentration of the *i*-th component in the sample, mg/kg.

It was found that the recovery rate (R, %) for nitroaromatic compounds and nitroamines at concentrations of 0.2 mg/kg, 0.5 mg/kg, and 1.0 mg/kg ranged from 73.0 % to 95.7 % (Table 2). Thus, the obtained recovery results for nitroaromatic compounds and nitroamines from soil samples (artificially spiked with explosives) using the modified QuEChERS sample preparation method fall within the acceptable range specified in ISO 11916-1:2013 and Method 8330A.

Table 2

Results of accuracy, precision, and uncertainty assessment for the determination of nitroaromatic compounds and nitroamines in soil (n = 5)

Compound Name	Spiked (mg/kg)	Found (mg/kg)	Recovery (R, %)	RSD (%)
Octogen (HMX)	0.2	0.179	89.5	6.32
	0.5	0.380	76.0	3.7
	1.0	0.91	91.0	4.7
Hexogen (RDX)	0.2	0.190	95.0	7.44
	0.5	0.41	83.0	5.1
	1.0	0.905	90.5	5.4
1,3,5-Trinitrobenzene (1,3,5-TNB)	0.2	0.191	95.7	6.27
	0.5	0.41	82.0	6.8
	1.0	0.965	96.5	6.5
1,3-Dinitrobenzene (1,3-DNB)	0.2	0.180	90.0	7.85
	0.5	0.42	85.0	8.3
	1.0	0.915	91.5	5.4
Tetryl	0.2	0.170	85.0	8.3
	0.5	0.370	74.0	7.6
	1.0	0.91	91.0	6.2
Nitrobenzene (NB)	0.2	0.175	87.5	4.0
	0.5	0.375	75.0	9.4
	1.0	0.925	92.5	3.8
2,4,6-Trinitrotoluene (2,4,6-TNT)	0.2	0.175	87.5	4.0
	0.5	0.39	78.0	3.6
	1.0	0.945	94.5	3.7
4-Amino-2,6-dinitrotoluene (4-Am-DNT)	0.2	0.173	86.5	4.1
	0.5	0.365	73.0	5.8
	1.0	0.885	88.5	5.5
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	0.2	0.171	85.5	4.1
	0.5	0.370	74.0	7.6
	1.0	0.935	93.5	5.3
2,6-Dinitrotoluene (2,6-DN)	0.2	0.155	77.5	4.5
	0.5	0.430	86.0	6.5
	1.0	0.94	94.0	6.0
2,4-Dinitrotoluene (2,4-DNT)	0.2	0.182	91.0	3.8
	0.5	0.425	85.0	4.9
	1.0	0.935	93.5	5.3
2-Nitrotoluene (2-NT)	0.2	0.179	89.5	3.95
	0.5	0.38	76.0	3.7
	1.0	0.925	92.5	3.8
4-Nitrotoluene (4-NT)	0.2	0.179	89.5	3.95
	0.5	0.42	84.0	6.7
	1.0	0.92	92.0	4.6
3-Nitrotoluene (3-NT)	0.2	0.182	91.2	4.26
	0.5	0.44	88.0	9.6
	1.0	0.92	92.0	4.6

Note: (1) R – Recovery rate; (2) RSD – Relative standard deviation

Source: Developed by the authors based on the conducted research

Precision. The precision of the HPLC-UV method for analyzing explosive substances in soil was assessed based on the repeatability of measurement results. The repeatability evaluation was conducted according to the following scheme:

- Model soil samples artificially spiked with explosive substances at concentrations of 0.2 mg/kg, 0.5 mg/kg, and 1.0 mg/kg were analyzed in five replicates;
- The experiment was performed under repeatability conditions (identical conditions using the same equipment, by the same analyst, within a short time interval);
- The relative standard deviation (RSD, %) of the obtained concentration values was calculated.

It was established that the relative standard deviation (RSD, %) of measurement results for the model soil samples under repeatability conditions for nitroaromatic compounds and nitroamines at concentrations of 0.2 mg/kg, 0.5 mg/kg, and 1.0 mg/kg ranged from 3.6 to 9.6 % (Table 2). Therefore, the RSD (%) values under repeatability conditions fall within the limits specified in ISO 11916-1:2013 and method 8330A [[6]]. The obtained repeatability assessment results indicate the absence of systematic errors in the developed methodology.

Analyzing recent scientific literature, we found no reports of the use of QuEChERS sample preparation or its modifications for the determination of nitroaromatic compounds and nitroamines (explosive substances) in soil. According to ISO 11916-1:2013[6], extraction of explosive substances is predominantly performed using acetonitrile with shaking (for 18 hours) or ultrasonic treatment (at 30 °C for 18 hours, or at 50 °C for 4 hours). Soxhlet extraction apparatus is also employed for extracting explosives, with methanol used as the solvent. According to method 8330A, residual explosive substances are extracted from soil using acetonitrile under ultrasonic conditions, followed by cleanup of the obtained extracts by liquid–liquid partitioning (aqueous calcium chloride solution–acetonitrile).

In our study, a modified QuEChERS sample preparation method was applied for the extraction of explosive substances. The modification consists of incorporating ultrasonic treatment of soil with acetonitrile at 50 °C for 4 hours during the initial extraction stage, followed by solvent concentration, and omitting the second stage of dispersive solid-phase extraction (dSPE) cleanup using a sorbent mixture (C18, PSA, and $MgSO_4$). This improvement in sample preparation conditions reduces the overall cost of the developed method by simplifying the sample preparation process and shortens the total analysis time. The introduction of a concentration step within the QuEChERS sample preparation modification enables the determination of explosive compounds in soil with enhanced method sensitivity (LOQ ranging from 0.040 to 0.270 mg/kg).

The results of the method validation for the determination of explosive substances in soil using HPLC-UV combined with a modified QuEChERS sample preparation demonstrated satisfactory metrological characteristics: $R^2 \geq 0.995$, LOD ranging from 0.012 to 0.081 mg/kg, LOQ ranging from 0.040 to 0.270 mg/kg, recovery (R) between 73.0% and 95.7 %, and relative standard deviation (RSD) between 3.6 % and 9.6%. Therefore, it can be concluded that the developed method complies with the requirements of ISO 11916-1:2013 and method 8330A, and is suitable for the determination of explosive substances at residual levels in soil.

Conclusions

The method for the determination of nitroaromatic compounds and nitroamines (explosive substances) in soil using HPLC-UV combined with a modified QuEChERS sample preparation procedure demonstrated satisfactory metrological parameters. The correlation coefficients (R^2) for the analyzed explosive compounds were ≥ 0.995. The limits of detection (LOD) and limits of quantification (LOQ) were sufficient for the identification and quantification of explosive residues in soil. The recovery rates ranged from 73.0 % to 95.7 %, indicating the acceptability of the proposed method based on the modified QuEChERS approach. The relative standard deviation (RSD) for repeatability was within the range of 3.6 % to 9.6 %. The results of the conducted study support the conclusion that the developed HPLC-UV method employing modified QuEChERS sample preparation complies with the requirements of ISO 11916-1:2013 and EPA Method 8330A, and can be applied in chemical-analytical and environmental laboratories.

References

[1] Adegoke, O., Nic Daeid, N. (2021). Colorimetric optical nanosensors for trace explosive detection using metal nanoparticles: advances, pitfalls, and future perspective. *Emerging Topics in Life Sciences. 5*(3), 367–379. https://doi.org/10.1042/ETLS20200281

[2] Aminzai, M. T., Yabalak, E., Kalderis, D., Gizir, A. M. (2024). Environmental remediation of emerging contaminants using subcritical water: A review. *Journal of Environmental Management*, *366*, 121800. doi: 10.1016/j.jenvman.2024.121800

[3] Breeze, J., Fryer, R. N., Nguyen, T. N., Ramasamy, A., Pope, D., Masouros, S.D. 2023. Injury modelling for strategic planning in protecting the national infrastructure from terrorist explosive events. *BMJ Mil Health, 169*(6), 565–569. https://doi.org/10.1136/bmjmilitary-2021-002052

[4] Council of the European Union. (1996). Council directive 96/23/EC of 29 April 1996 on measures to monitor certain substances and residues thereof in live animals and animal products and repealing Directives 85/358/EEC and 86/469/EEC and Decisions 89/187/EEC and 91/664/EEC. Official Journal of the European Communities.

[5] Holmgren, E., Ek, S., Colmsjö, A. (2012). Extraction of explosives from soil followed by gas chromatography–mass spectrometry analysis with negative chemical ionization. *Journal of Chromatography A, 1222*, 109–115. https://doi.org/10.1016/j.chroma.2011.12.014

[6] ISO 11916-1:2013. [Soil quality — Determination of selected explosives and related compounds. Part 1: Method using high-performance liquid chromatography (HPLC) with ultraviolet detection]. (In Ukrainian)

[7] ISO 11916-2:2013. [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)]. (In Ukrainian)

[8] Jeong, J., Koo, M., Lee, J.G. (2025). QuEChERS method development for the GC–MS analysis of polycyclic aromatic hydrocarbons in food. *Food Sci Biotechnol. 34*, 2749–2761. https://doi.org/10.1007/s10068-025-01910-2

[9] Mary Celin, S., Sharma, B., Bhanot, P., Kalsi, A., Sahai, S., Tanwar, R.K. (2023). Trends in environmental monitoring of high explosives present in soil/sediment/groundwater using LC-MS/MS. *Mass Spectrometry Reviews. 42*(5), 1727–1771. https://doi.org/10.1002/mas.21778

[10] Mbisana, M., Rebagamang, T., Mogopodi, D., & Chibua, I. (2023). Development and validation of a QuEChERS-LC-MS/MS method for determination of multiple mycotoxins in maize and sorghum from Botswana. Frontiers in fungal biology, 4, 1141427. https://doi.org/10.3389/ffunb.2023.1141427

[11] Method 8330A. [Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)]. (In Ukrainian)

[12] Negi, R., Kumar, A. Bhardwaj, P. (2025). Unveiling antibiotic residue contamination: assessing yak, dzomo, and hill cattle milk from himalayan region through QuEChERS-HPLC approach and health risk assessment. Food Sci Technol. 62, 635–643. https://doi.org/10.1007/s13197-024-06048-3

[13] Pan, X. (2021). Determination of the N-Nitroso Compounds in Mouse Following RDX Exposure. In: Pan, X., Zhang, B. (eds) *Environmental Toxicology and Toxicogenomics. Methods in Molecular Biology. 2326*, 315–325. https://doi.org/10.1007/978-1-0716-1514-0_23

[14] Pawłowski, W., Matyjasek, Ł., Cieślak, K., Karpińska, M. (2017). Contamination with explosives in analytical laboratory procedure. *Forensic Science International, 281*, 13–17. https://doi.org/10.1016/j.forsciint.2017.10.018

[15] Salem, A.M.B., Ismail, M., Oladipo, B. (2025). Systematic analysis of post-blast organic traces in soil, application of color tests, TLC, GC–MS, and ITMS. *Journal of Chromatography, A. 1746*, 465776. https://doi.org/10.1016/j.chroma.2025.465776

[16] Şener, H., Anilanmert, B., Mavis, M.E., Gursu, GG., Cengiz, S. (2022). LC-MS/MS monitoring for explosives residues and OGSR with diverse ionization temperatures in soil & hands: 30 minutes for extraction þ elution. *Acta Chromatographica. 34*(3), 304–314. https://doi.org/10.1556/1326.2021.00930

[17] Senin, S. A., Midyk, S. V., Korniyenko, V.I., Konovalova, O.Yu., Berezovskyi, O.V., Ladohubets, E.V., Harkusha, I.V. (2023). Determination of Mycotoxins in Wheat Grain by LC-MS/MS using Modified QuEChERS Sample Preparation. *Methods And Objects of Chemical Analysis. 18*(1), 22–28. https://doi.org/10.17721/moca.2023.22-28

[18] Senin, S.A., Midyk S.V., Korniyenko, V.I., Machuskyy, O.V., Baranov, Yu. S., Zemtsova, O.V. (2024). Determination of Polychlorinated Biphenyls in Sunflower Oil by GC-MS Using Modified QuEChERS Sample Preparation. *Methods And Objects of Chemical Analysis. 19*(4), 179–186. https://doi.org/10.17721/moca.2024.179-186

[19] Suppajariyawat, P., Gonzalez-Rodriguez, J. (2021). Application of LC– QTOF/MS for the validation and determination of organic explosive residues on Ionscan® swabs. *Science & Justice. 61*(6), 697–703. https://doi.org/10.1016/j.scijus.2021.09.001

[20] Ünsal, S.M., Erkan, E. (2022). Development and validation of a new RP-HPLC method for organic explosive compounds. *Turkish Journal of Chemistry. 46*(3). 923–928. https://doi.org/10.55730/1300-0527.3380

[21] Zapata, F., García-Ruiz, C. (2020). Chemical Classification of Explosives. *Critical Reviews in Analytical Chemistry. 51*(7), 656–673. https://doi.org/10.1080/10408347.2020.1760783

[22] Council of the European Union. (2022). Commission Decision of 14 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results (notified under document number C (2002) 3044), тext with EEA relevance 2002/657/ EC. Off. J. Eur. Union. 17.08.2002. L 221. 8–36.