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Determination of explosives in environmental soil samples by gas chromatography ion trap mass spectrometry

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ABSTRACT

A rapid, accurate and reproducible method was developed for quantitative determination of thirteen explosive compounds in soil at trace levels (μg/kg) by gas chromatography-ion trap mass spectrometry. Explosives were extracted from soil by sonication with acetonitrile, followed by cleanup with silica cartridge and florisil. Two calibration curves were drawn and the correlation coefficients (r2) for each explosive were ranged from 0.995-0.999 and 0.984-1.000 for calibration curves 1 and 2, respectively. The method provided detection limits ranging from 0.98 μg/g for nitrobenzene (NB) to 0.01 μg/g for 3,5-DNA. The method was validated by different analysis. The method gave good recovery (60.49-97.65 %), good precision (0.99-25.38 %), excellent reproducibility, and proved to be suitable to real routine work sample analysis. The effectiveness of the method appeared by the analysis of soil samples in several soil samples from test fields in Kuwait.

KEYWORDS

Determination;
Explosives,
Soil sample;
GC-ITMS.

INTRODUCTION

Gas chromatography (GC) is a reasonable technique for the determination of explosives, having nitroaromatic groups, but not for those having nitrate esters or nitroamines, which mostly undergo thermal decomposition[1].

Some sources of explosives contaminant which may include testing, storage, production and disposal to the environment by defense practicing. Explosives are group of compounds, which are toxic, mutagenic and have a great potential to persist in the environment[2,3]. Contamination of soil and groundwater with the explosives occur due to manufacturing, storage and demilitarization of weapons[4]. Explosives in soil are harmful, as they are toxic in nature and may undergo photocatalytic degradation and biodegradation like reduction, oxidation, exchange reaction, and they may undergo metabolic transformation[5].

High performance liquid chromatography (HPLC) and GC are routinely practiced for the determination of explosives in a variety of sample matrices such as soil[6-9], drinking and groundwater[10,11]. Various methods have been reported for the detection of explosives such as, 4-amino-2,6-dinitrotoluene (2,6-DNT-4A), and 2-amine-4,6-dinitrotoluene (4,6-DNT-2A) are derivative compounds of TNT, which have immediate risks to human health, even at very low levels (ppb)[12,13]. Tetryl

TABLE 1 : GC-EI-SIS-MS (ion trap) operational conditions for the analytical method of explosives

Ion preparation parameters	
Mass isolation window	1.0
Isolation time	5 ms
Excitation time	5 ms
Ejection amplitude	20 V
Broadband amplitude	30 V
Modulation rate	30 µs/ step
Ionization parameters	
Ion trap temperature	220^0C
Transfer line temperature	310^0C
Manifold temperature	80 ^{0}C
Front line temperature	260^0C
Axial modulating voltage	4.0 V
Emission current	40 µA
Electron multiplier voltage	1550 V
Scan rate	0.45 s/scan
Pre-scan ionization time	1500 µs
Target TIC	40,000
Maximum ionization time	45,000
RF pump value	650 *m/z*
Background mass	45 *m/z*
Count threshold	1 counts
Isolation window	3.0 *m/z*

(2,4,6-N-tetranitro-N-methylaniline) is known to be mutagenic and causes dermatitis to humans[14].

HPLC was used widely for the determination of explosives. It is ideal for the analysis of analytes that are thermally labile and do not vaporize easily. However, HPLC technique suffers from poor resolution and low sensitivity[15]. The usefulness of GC/ mass spectrometry (MS) method lies in the sensitivity and the selectivity. GC has been recently introduced in the trace analysis of explosives. Explosives have been reported for the analysis of water samples[16,17].

The authors concern was to extend the effort to develop an analytical method with high sensitivity for soil samples using GC/MS, in order to detect explosives and to confirm the identity of the compounds response.

The United States EPA method 8330, using HPLC/ UV, applicable to soil and water samples, requires ultrasonic extraction for 18 h[7]. EPA method 8095 utilized GC/ electron capture detector (ECD) and method detection limits were improved when compared with method 8330[6].

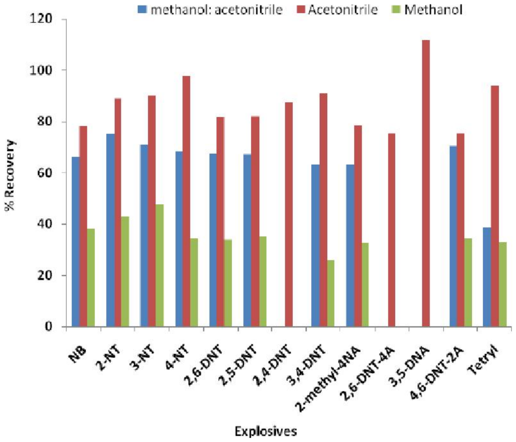

Figure 1 : Recoveries of the extracted spiked soil using different solvents

Several methods have been reported for the determination of explosives using solid phase microextraction followed by GC/MS in soils[18-20], water[21] and urine[22]. High performance liquid chromatography-mass spectrometry (HPLC-MS), using both atmospheric pressure chemical ionization and electrospray ionization mode were also cited in the literature for water samples[23], animal exposure[24], and in soil[25].

The site selected to collect the soil sample appeared to be a strong candidate for explosive soil contamination within the territory of Al-Mutla'a area. However, this area was extensively bombarded during the Iraqi invasion to Kuwait in 1990. Samples were collected carefully from the area in order to investigate the soil contaminant of explosive residues.

This paper deals with the steps as follows: sample collection, preservation and handling, extraction of the target analytes, separation of the selected analytes, and quantification. GC/MS was used for the separation and quantification steps because of its specificity.

The objective of this study was to develop a GC/ MS (ion trap) method for the analysis of explosive contamination in soil. Concentration of the explosives in soil may exceed acceptable levels. Thus, a study to determine the fate of such compounds in soil was needed. However, a fast and accurate extraction method was developed to quantify these compounds at µg/g levels in soil.

To the best of the authors knowledge, analyzing these compounds in soil samples in Kuwaiti environ-

TABLE 2 : Calibration data, concentration range, correlation coefficient, regression equation and method detection limit

No.	Explosives	Calib. range (1) (pg/µl)	Corr.Coeff (1) (r^2)	Regres. equa. (1)	Calib.range (2) (pg/µl)	Corr.Coeff (2) (r^2)	Regres. Equa (2)	LOD (µg/g)	LOQ (µg/g)	Ret.Time (R_t)	m/z
1	NB	619-9297	0.997	Y=0.1581x	6.198-30.99	0.992	Y=0.011x	0.98	9.84	3.64	120/122
2	2-NT	614.4-9216	0.999	Y=8.6095x	6.144-24.576	0.984	Y=0.627x	0.51	5.12	4.33	120/122
3	3-NT	569.4-8825	0.997	Y=0.0285x	5.694-28.47	0.969	Y=0.0158x	0.07	0.8	4.68	120/122
4	4-NT	615.1-9226.5	0.995	Y=0.1329x	6.151-30.755	0.993	Y=0.03x	0.19	1.89	4.89	120/122
5	2,6-DNT	118.5-1777.5	0.999	Y=6.5104x	1.185-5.925	0.989	Y=0.017x	0.11	1.11	6.98	164/166
6	2,5-DNT	117.9-1768.5	0.997	Y=3.9498x	1.185-5.925	0.996	Y=0.734x	0.13	1.30	7.33	164/166
7	2,4-DNT	118.5-1777.5	0.997	Y=6.1566x	1.185-5.925	0.999	Y=0.87x	0.03	0.25	7.57	164/166
8	3,4-DNT	139.5-2095.5	0.999	Y=0.0359x	1.395-6.975	0.995	Y=0.053x	0.14	1.38	7.99	180/182
9	2-methyl-4NA	117.2-1758	0.998	Y=3.7518x	1.395-6.975	0.996	Y=0.0581x	0.25	2.51	8.72	150/152
10	2,6-DNT-4A	118.5-1777.5	0.999	Y=2.8036x	1.172-5.86	0.998	Y=0.5157x	0.24	2.37	9.98	180/182
11	3,5-DNA	123.8-1857	0.999	Y=0.2791x	1.238-6.19	0.993	Y=0.3952x	0.01	0.14	10.09	180/182
12	4,6-DNT-2A	118.5-1777.5	0.997	Y=5.4040x	1.185-5.925	0.996	Y=0.503x	0.17	1.65	10.25	180/182
13	TETRYL	118.5-1777.5	0.996	Y=0.0298x	6.198-30.99	1.000	Y=0.029x	0.09	0.97	10.67	192/194

TABLE 3 : Intra-day and inter-day recovery, precision of the explosive in soil samples

No.	Explosives	Conc.spiked (pg/µl)	Intra-day precision		Inter-day precision		Conc.spiked (pg/µl)	Reproducibility	
			Rec.(%)	RSD(%)	Rec.(%)	RSD(%)		Rec.(%)	RSD(%)
1	NB	9297	68.98	11.43	68.91	20.79	6198	75.59	3.06
2	2-NT	9216	83.31	9.55	70.12	16.56	6144	72.27	14.89
3	3-NT	8825.7	81.27	0.99	78.88	14.39	5694	80.78	8.54
4	4-NT	9226.5	88.13	25.38	66.68	5.83	6151	85.45	3.03
5	2,6-DNT	1777.5	96.91	6.61	93.13	11.52	1185	99.20	9.76
6	2,5-DNT	1768.5	74.58	9.98	60.49	13.84	1179	67.39	10.56
7	2,4-DNT	1777.5	75.47	6.91	89.54	13.36	1185	98.99	7.39
8	3,4-DNT	2095.5	77.07	14.97	62.39	18.30	1395	84.87	14.86
9	2-methyl-4NA	1758	86.92	19.89	76.29	2.73	1172	99.99	13.21
10	2,6-DNT-4A	1777.5	74.10	11.94	96.57	13.35	1185	100.35	9.34
11	3,5-DNA	1857	80.24	9.02	64.87	20.54	1238	96.02	8.17
12	4,6-DNT-2A	1777.5	91.01	8.77	97.65	12.32	1185	96.17	1.30
13	TETRYL	1777.5	91.36	4.19	86.49	4.93	1185	81.86	7.05

ment has not been reported in the literature.

Additionally, this is the first report that investigated the determination of explosives in Kuwait soil. The optimized method was successfully applied to the soil extract samples from test fields in Al-Mutla'a,Kuwait area.

EXPERIMENTAL

Instruments

A Varian CP-3800 GC coupled with a Saturn 2200 ion-trap spectrometry (Varian, Walnut Crek, CA, USA) was used for the analysis. Samples were separated in a factor four ™ capillary column (VF-5ms; 15 m×0.25 mm×0.25 µm). Varian 8200 CX Autosampler was used for all sample injection. Helium was used as a carrier gas at 1 ml/ min constant flow rate. Oven temperature was controlled as follows: 60°C held for 1.0 min, increased at 15°C/min to 150°C and finally increased at a rate of 20°C/min to 250°C and held for 5 min.

The injection volume was 1 µl, and the injection was in a splitless mode. Operational ion-trap conditions are listed in TABLE 1. Automatic gain control (AGC) was utilized to optimize the sensitivity by filling the trap with the target ions. The values were optimized

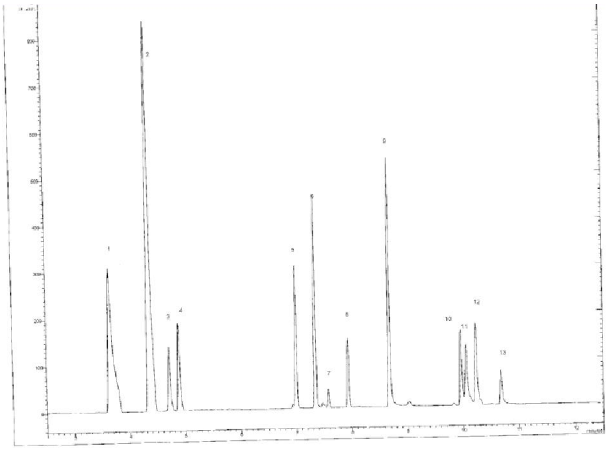

Figure 2 : Typical GC/MS (ion trap) chromatogram of a standard mixture of explosives using VF-5ms; 15 m; 0.25 mm; 0.25 µm column. Peak annotation was as in TABLE 2. Explosives concentration (pg/µl): (1) NB=9297; (2) 2-NT= 9216; (3) 3-NT= 8825.7; (4) 4-NT= 9226.5; (5) 2,6-DNT= 1777.5; (6) 2,5-DNT= 1768.5; (7) 2,4-DNT= 1777.5; (8) 3,4-DNT= 2095.5; (9) 2-methyl-4NA= 1758; (10) 2,6-DNT-4A= 1777.5; (11) 3,5-DNA= 1857; (12)4,6-DNT-2A= 1777.5 and (13) tetryl= 1777.5

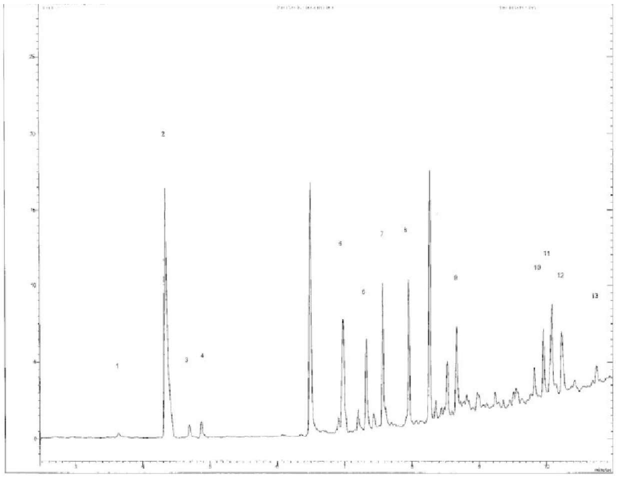

Figure 3 : Typical GC/MS (ion trap) chromatogram of explosives spiked to soil sample, using VF-5ms; 15 m; 0.25 mm; 0.25 µm column. Peak annotation was as in TABLE 2. Explosives concentration (µg/g): (1) NB=30.99; (2) 2-NT= 30.72; (3) 3-NT= 28.47; (4) 4-NT= 30.755; (5) 2,6-DNT= 5.925; (6) 2,5-DNT= 5.895; (7) 2,4-DNT= 5.925; (8) 3,4-DNT= 6.975; (9) 2-methyl-4NA= 5.86; (10) 2,6-DNT-4A= 5.925; (11) 3,5-DNA= 6.19; (12) 4,6-DNT-2A= 5.925 and (13) tetryl= 5.925

to 5000 for the electron impact ionization (EI) mode. The operational conditions for GC-EI-EI-SIS-MS are shown in TABLE 1. Perfluorotri-n-butylamine was used as a reference gas.

Chemicals and reagents

All the chemicals and reagents were used of HPLC-grade, acetonitrile, methanol and acetone supplied by Baker J.T. (Deventer, The Netherlands). Acc Standard (New Haven, USA) supplied the studied standards.

The groups of explosives selected for analysis were as follows: 2,5-dinitrotoluene (2,5-DNT)= 100 µg/ml in acetonitrile; 2-methyl-4 nitroaniline (2-methyl-4-NA)= 100 µg/ml in acetonitrile; 3,4-dinitrotoluene(3,4-DNT)= 100 µg/ml in acetonitrile; Explosive stock solution A= 100 µg/ml in acetonitrile: methanol, which contains 2 amino-4,6-DNT; 4-amino-2,6-DNT; tetryl (2,4,6-tetranitro-N-methylaniline) and 2,6-DNT; 2,4-DNT; and explosive stock solution B, which contains nitrobenzene (NB)= 500.2 µg/ml; 2-nitrotoluene (2-NT)= 495.5 µg/ml; 3-nitrotoluene (3-NT)= 495.8 µg/ml; 4-nitrotoluene (4-NT)= 495.8 µg/ml and 3,5-dinitroaniline (3,5-DNA)= 99.9 µg/ml. All standards were prepared by a serial dilution of the stock solution in acetonitrile (Fisher Scientific, Pittsburgh, PA, USA). Standards were prepared daily and stored in amber vials at 25°C in the dark. Calibration curves were conducted by plotting concentration of the analyte against peak area response.

Two calibration solutions were prepared. Calibration solution 1 was prepared by mixing explosives group 1 to group 5 and diluted to 10 ml with acetonitrile, different amounts were taken for each concentration levels such as 0.01 ml, 0.05 ml, 0.10 ml and 0.15 ml. However, calibration solution 2 was prepared by taking 0.10 ml from calibration solution 1 and diluted to 10 ml with acetonitrile and then taking 5 different amounts such as 0.01 ml, 0.02 ml, 0.03 ml, 0.04ml, 0.05 ml. Correlation coefficient, calibration range, regression equation, and method detection limits are presented in TABLE 2.

Soil sample extraction and cleanup

Samples were prepared by taking 5 g of soil, sonicated for 30 min with 25-ml acetonitrile solvent. The soil samples were spiked with known concentration of explosives. Different amounts of the stock solutions were utilized to obtain the required concentration in the spiked soil samples.

Silica SPE cartridge of 1000 mg, filled with 1-g florisil and sodium sulfate (EMD-Chemical- Darmstadt-Germany), was used to clean up the extracts.

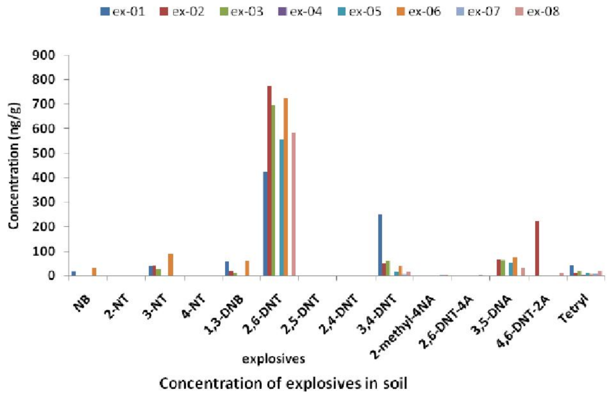

Figure 4 : Distribution of explosives level in Kuwait soil (Al-Mutla'a)

The cartridges were conditioned with acetonitrile (10 ml). Samples were then loaded, eluated (5 ml acetonitrile) and collected into 10-ml graduated tubes. The cleaned sample was concentrated to 1.0 ml under nitrogen gas, and ready for GC/MS analysis.

RESULTS AND DISCUSSION

Effect of different solvents in explosive recovery

Three different solvents were utilized to extract the explosives from soil samples. Acetonitrile was found to be a suitable solvent for the extraction. Its recovery varied from 75.21% to 116.20%. Other solvents provided poor recoveries. The extract chromatogram exhibited clean and sharp peaks. No interferences with other compounds were observed. The clean chromatogram indicated that the cleanup method was efficient. However, all explosives were completely separated, and the response of GC/MS was satisfactory for each explosives compounds. Figure 1 shows the recoveries of the extracted spiked soil using different solvents.

Linearity of the calibration solutions

Under the chromatographic conditions described, GC/MS showed a linear response for each analyte. At higher concentration in which calibration 1 was conducted, the response was linear with excellent correlation coefficient (r^2= 0.995-0.999) for each analyte (TABLE 2). For a lower concentration range, a good fit was obtained for the concentration versus the GC/MS response, with a good correlation coefficient (r^2= 0.969-1.000) (TABLE 2).

Reproducibility of the calibration data and stability of the retention time

Different standard solutions for the calibration curve were analyzed daily, in order to check the sensitivity of the peak response related to each explosive. The obtained data of the standard (4 points; n= 6) showed that the recoveries and the relative standard deviation were varied between 70.92 and 110.81% ± 1.62 and 15.52%, respectively. The standard deviation rates of the retention times were found to range from 0.09 to 1.45% for the tested explosives. The obtained results indicated that the reproducibility of the standard and the retention times were stable. No large differences in retention times were observed after injecting large amount of real soil samples.

Sonication extraction time

The sonication extraction time for all explosives in acetonitrile was investigated at different time intervals (min) as follows: 15, 30, 45, 60, 1 h:30 min and 2 h. The results indicated that 30 min of sonication was satisfactory to the extraction, and a good recovery was obtained for each explosive.

Chromatogram of the explosives

A total ion chromatogram from GC/MS (ion trap) standard mixture of explosives is shown in figure 2. A very good response was obtained for all the explosives tested. However, the chromatogram of the analysis of soil sample from Al-Mutla'a and few peaks corresponding mainly to 2,6-DNT, 3,4-DNT, 3,5-DNA, 4,6-DNT-2A and tetryl were found. A typical chromatogram from a spiked soil sample is shown in figure 3.

Limit of detection (LOD) and limit of quantification (LOQ)

The LOD for each explosives was calculated based on S/N= 3 and the LOQ based on S/N= 10. All LODs were less than 1 μg, ranging from 0.98 μg/g for NB and 0.01 μg/g for 3,5-DNA (TABLE 2).

Precision and accuracy of the GC/MS method

Three replicates of different concentrations of the standard solution were spiked to soil samples in order to determine the precision and recovery of the developed method. Recovery was determined by comparing the obtained concentration to the spiked concen-

TABLE 4 : Levels of explosives in different kind of soils collected from Al-Mutla'a

No.	Explosives	Conc.(μg/g) Ex-01	Conc.(μg/g) Ex-02	Conc.(μg/g) Ex-03	Conc.(μg/g) Ex-04	Conc.(μg/g) Ex-05	Conc.(μg/g) Ex-06	Conc.(μg/g) Ex-07	Conc.(μg/g) Ex-08
1	NB	18.0	ND	ND	ND	ND	ND	ND	ND
2	2-NT	ND	ND	ND	ND	ND	ND	ND	ND
3	3-NT	37.6	40.8	25.0	ND	ND	ND	ND	ND
4	4-NT	ND	ND	ND	ND	ND	ND	ND	ND
5	2,6-DNT	425	775.2	695.4	ND	555.8	727.6	ND	586.6
6	2,5-DNT	ND	ND	ND	2.0	ND	ND	ND	ND
7	2,4-DNT	ND	ND	ND	1.98	ND	ND	ND	ND
8	3,4-DNT	250.0	49.2	61.0	ND	15.4	37.6	8.57	15.8
9	2-methyl-4NA	ND	ND	ND	ND	ND	ND	4.0	4.0
10	2,6-DNT-4A	ND	ND	ND	ND	ND	ND	3.89	ND
11	3,5-DNA	ND	67.6	63	0.83	54.4	74.8	ND	32.4
12	4,6-DNT-2A	ND	223.2	ND	ND	ND	ND	ND	12.8
13	TETRYL	44.4	10.2	19	4.85	12.6	6.2	11.49	20.8

tration. Precision was reported as relative standard deviation (RSD). The intra-day precision was evaluated by repeated injections (n= 3) of the same soil samples on one day. The inter-day precision was calculated by repeated injections of the same soil samples on six different days. The obtained values were quantified using the calibration curves established.

The precision observed, as (RSD), ranged from 0.99-25.38 %, and 2.73-20.79% for intra-day and inter-day analysis, respectively.

Recoveries were obtained ranging from 68.98-96.91% and 60.49-97.65% for intra-day and inter-day analysis, respectively. The results for precision and accuracy are given in TABLE 3.

Reproducibility of the method was assessed; standard concentrations corresponding to each analytes used in the calibration were spiked to soil samples. Each solution was determined in duplicate on three consecutive days and the RSD at each concentration for each analyte was calculated. The results are illustrated in TABLE 3.

Soil samples

Contaminated soil samples with explosives were collected from ten different locations based on the extensive use for ammunitions. The locations were selected, based on extensive practice bombarding during the Gulf War. These locations were suspected of being contaminated with various explosives.

The collected soil samples were dried at room temperature (20-25°C). Five grams of each sample was weighed, and 25 ml of acetonitrile was added, and placed in ultrasonic bath for 30 min. The sediment in the extracts was allowed to settle out of suspension. The extract was treated according to the cleanup procedure, described previously.

Figure 4 shows the distribution behavior of the extract of explosive-contaminated soils obtained from the locations. The soil contaminants and their concentrations were found to vary from the samples to other. Highest concentrations of 2,6-DNT, 3,4-DNT, 3,5-DNA and tetryl were found in the contaminated soils. However, 2-NT and 4-NT could not be detected in all samples. In addition, 2,5-DNT and 2,6-DNT were only detected in one sample. TABLE 4 presents the levels of explosives in different kinds of soil samples.

CONCLUSIONS

A method for determining a mixture of explosives in soil was demonstrated with good separation and identification by GC/MS (ion trap). Several parameters were checked and optimized to obtain quantitative results. Detection limits for GC/MS (ion trap) were found to be in the μg/g range for the explosives used in this method.

The developed method is sufficiently accurate, sensitive and precise and it was successfully applied to assay of the explosives. The method can be recommended to be used for routine analysis of explosives contaminant in soil samples in the laboratory.

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