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Extraction of explosives from soil followed by gas chromatography–mass spectrometry analysis with negative chemical ionization

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ABSTRACT

A new, simple and accurate method for extraction of explosives from soil was developed and validated. The method includes one hour gentle extraction of compounds from soil in acetonitrile:dichloromethane 50:50 at 30 °C. Further analysis was made with GC–MS using cool on-column injection and negative chemical ionization. The method increased the recovery of the more volatile products, generated higher accuracy and was extensively time-saving compared to the conventional EPA (US Environmental Protection Agency) 8330 method. Applications are demonstrated on commercial reference materials.

1. Introduction

Analysis of explosives in soil matrices is used as one of the tools for characterization of hazardous sites, forensic investigations, acts of terrorism and the detection of landmines and unexploded ordnance. Soil matrices are complex materials and can be grouped into several types such as magnetite/dolomite, till (glacially deposited material), laterite and sand. A large part of these soils is composed of non-volatile or semi-volatile substances, largely of inorganic origin [1]. Though, up to 20% (w/w) of the soil can consist of a very large number of organic compounds formed in natural degradation processes [2]. Bioremediation has been applied in order to reduce explosives either on-site or in large slurry reactors [3], but widely differing results of degradation were achieved [4]. The concentrations of explosives in soil from contaminated areas can vary considerably and be as high as up to water saturation levels [5] or as low as in the sub ng/g level [6], inferring that moderate to very sensitive techniques of analysis are required for identification and quantification of these compounds.

The traditional sample work-up procedure often employed in this field is the EPA method 8330 [7,8], which is based on ultrasonic assisted extraction with acetonitrile as solvent. The drawbacks of the method are that it is time-consuming and that many steps in the extraction method, such as drying, homogenization, desorption, filtration etc., may cause both losses of compounds intended for analysis and contamination of the final sample. As an alternative extraction method, solid phase micro extraction (SPME) has been applied, which requires an additional step to convert the samples into aqueous solutions [6]. Supercritical fluid extraction (SFE) has also been applied [9,10] as well as the more recently explored technique of pressurized liquid extraction (PLE) [11,12]. Microwave assisted extraction (MAS) is another possibility to extract energetic materials without decomposition [13]. In spite of its almost one century of usage, Soxhlet extraction is still effective and can be applied to explosives in soil samples [14], even though it is regarded as time- and solvent consuming. Due to extended times of analysis for traditional methods, a 20 min on-site extraction with acetone followed by a bio-sensor response technique has been developed, yielding a limit of detection (LOD) of 0.5 μg/g soil [15]. This should be compared to the 0.001 mg/kg LOD achieved by ordinary laboratory techniques, *vide supra*. As an intermediate to these techniques Hewitt et al. [16] used a portable gas chromatograph with a thermionic ionization detector and an on on-site acetone extraction technique of soil.

The heterogeneity and the quality of the soil influence the requirements on the sample preparation method [17], since the final sample extract must contain a matrix that will not contaminate or deteriorate the chromatographic system. For example, a fresh or partly decomposed plant material, which often is encountered in soil samples, contains a number of compounds that may

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disturb the final chromatographic analysis, if no adequate sample work-up procedure has been used. Waxes, chlorophyll and other compounds can contaminate the chromatographic system, giving complex chromatograms, or even ruin the stationary phase of the column.

The nitro-groups present in an explosive molecule, either in conjugated or non-conjugated systems, make the polarity of explosives vary considerably. This infers that a clean and robust GC-system is required for the use of cool on-column injections, in order to avoid excessive adsorption phenomena in the GC, which leads to poor peak shapes.

If all types of organic explosives are to be determined in the same extraction and separation step, the requirements on the methods are extraordinary, since the analytes represents the full range of polar properties. Recently, a complete separation of all these compounds was performed by the aid of a porous graphic carbon (PGC) column [18]. This was later confirmed by Tachon et al., who used a slightly modified mobile phase system [19].

In the present study, a new time-saving, simple and efficient extraction method based on the liquid extraction of soil matrices using a combination of dichloromethane and acetonitrile as solvent have been evaluated. In spite of its negative environmental properties, a small volume (5 ml) of dichloromethane was included in the extraction procedure in order to enhance the extraction efficiency and reduce the time of extraction. Furthermore, a mass spectrometer (MS) operating in negative chemical ionization (NCI) mode has been employed to give a selective, sensitive and versatile detection. Zitrin and Yinon were the pioneers of the analysis of explosives with GC and MS in the NCI mode [20]. They described the ionization of nitroaromatic compounds with chemical ionization, though they used the positive mode (PCI). Sigman et al. published the LODs of numerous explosives in 2001 [21]. His group used both NCI and PCI in their work. Further work in this area at Thermo Fischer was only published as application notes and not in a peer-reviewed journal [22,23]. Our method is similar to the one more recently published by Collin et al. [24], but our method can be used for more explosives and has lower LODs. Our observations on the choice of ionization gas are in accord with those of Lee et al. [25].

2. Materials and methods

2.1. Chemicals

Three groups of explosives were studied. These are listed as nitroaromatics in Table 1, cyclic nitramines in Table 2 and nitrate esters in Table 3. All tables are found in the Supplementary material. All compounds were supplied by Analytical Standards, Sweden, except for the perdeuterated internal standard perdeutero-2,4-dinitrotoluene (2,4-DNT-d_6), which was synthesized in our laboratory.

Solvents used for extraction were acetonitrile (HPLC Isocratic grade, J.T. Baker) and dichloromethane (LiChrosolv, Merck, Sweden). *iso*-Butane (AGA, Sweden) was used as reaction gas for the chemical ionization and Helium (AGA, Sweden) was used as carrier gas as GC mobile phase.

2.2. Soils

Three commercially available reference soils with origin in the USA were purchased for the evaluation of the method of analysis presented in this work, see Table 4 (Supplementary material). The concentrations of explosives in each soil were given both as certified values and as values from by EPA SW846 (3rd edition) extraction and analysis by EPA method 8330 [4]. This includes extraction using acetonitrile in an ultrasonic bath followed by HPLC analysis. All soil samples were purchased via LGC Promochem, Sweden and contained specified amounts of explosive residues. Data of the soil samples can be found in Tables 5–7 (Supplementary material).

2.3. Extraction procedure

All certified soils with specified levels of a multitude of explosives were extracted. They contained nitroaromatics, nitramines and nitrate esters that represent almost all military and some civilian explosives in current use.

Soil (0.25–0.6 g) was weighed into silanized, ambered glass vials. DNT-d_6 (247.50 ng in acetonitrile) was added as internal standard to all vials. A magnetic stirring bar and acetonitrile (5 ml) were added to each vial. The vials were then sealed and stirred at 30 °C for 30 min. Dichloromethane (5 ml) was added and the stirring continued for another 30 min. The suspension was then filtered through micro filters (Acrodisc, AP-4559T from Pall Life Sciences, provided by VWR International AB, Sweden) into the same type of vials. The extracts were either analyzed directly or stored at −25 °C prior to analysis.

2.4. Analysis

All analyses were carried out on an Agilent 6890N GC coupled to a stand-alone capillary GC detector (Agilent mass spectrometer 5975 MSD XL inert MSD). The column used was a HP-5MSI (5% phenylmethylsiloxane), 6 or 30 m × 0.25 mm, FT 0.25 μm. Cool on-column injections were performed. The injector was programmed to follow the oven program temperature. The 5975 MSD was operated in SIM (Selected Ion Monitoring) mode with negative chemical ionization. The ionization gas was *iso*-butane. The MS interface temperature was held at 250 °C, the MS source temperature was set to 180 °C and the MS quadrupole temperature was operated at 180 °C.

In order to quantify all of the compounds accurately, two GC–MS methods were used. For nitramines (including tetryl) and nitrate esters, method 1 was used. For nitroaromatics, method 2 was used. The following GC temperature programs were used: method 1, which is quicker, can be used for all compounds, if complete separation of all isomers is not required. This method can be used for screening to detect the presence or absence of almost all analytes. If detailed analysis of the different isomers of dinitrotoluenes, trinitrotoluenes, aminodinitrotoluenes and diaminonitrotoluenes is required, the longer method 2 must be used.

Method 1: Initial temperature 80 °C for 0.5 min followed by a temperature ramp at 20 °C/min to 160 °C immediately followed by another temperature ramp at 60 °C/min to 320 °C. This was kept for 2 min. Helium was used as carrier gas and operated in constant flow mode. The inlet pressure was set to 14.8 psi corresponding to a flow rate of 1.5 ml/min (45 cm/s). The column length was 6 m. The temperature of the ion source and the quadrupole was 180 °C.

The nitramines and nitrate esters analyzed with this method are listed in Tables 2 and 3. Identification of each compound was made by the use of retention times and the specific mass fragments, also given in Tables 2 and 3 (Supplementary material).

The internal standard 2,4-DNT-d_6 was recorded on ions m/z = 188, 172, and 158. The first ion was used for quantification.

Method 2: The following method was applied for nitroaromatics: the oven was programmed to an initial temperature of 80 °C for 3 min followed by a temperature ramp of 5 °C/min to 125 °C and held for 8 min, followed by a temperature ramp of 5 °C/min to 210 °C, directly followed by another temperature ramp of 60 °C/min to 320 °C which was held 4 min. Helium was used as carrier gas and the GC operated in constant flow mode. The inlet pressure was set to 12.8 psi, which corresponds to a flow rate of 1.3 ml/min (42 cm/s).

The column length was 30 m. The temperature of the ion source and the quadrupole was 180 °C.

The nitroaromatics analyzed with this method are listed in Table 1 (Supplementary material). Identification of each compound was made by the use of retention times and the specific mass fragments, also given in Table 1.

The internal standard 2,4-DNT-d_6 was recorded on fragments m/z = 188, 172 and 158. The first ion was used for quantification.

3. Results and discussion

In Tables 1–3 (Supplementary material), basic data for all the 30 compounds studied are given. These are energetic materials that can be expected to be found at military training ranges, impact areas, hazardous waste areas and mine fields.

3.1. Chemical properties

The explosives in this study display a great range of properties. The most important factor in the extraction is the solubility of the different compounds in the solvent mixture. Nitroaromatics and nitrates esters are highly soluble in organic solvents, whereas the cyclic nitramines (*i.e.* RDX and HMX) are less soluble. Another factor that influences the extraction is the acid–base properties of the analytes. For instance, picric acid will be a salt in all soil matrices. This compound was not present in the certified soils and the yield could thus not be evaluated. The same is true for the diaminonitrotoluenes, which depending on the pH of the soil either will be in their neutral state or protonated as salts. All other compounds, *i.e.* all analytes in the certified soils, are in their neutral state in all normal soils.

3.2. Thermal stability

The thermal stability is important for any explosive to be put into charges. Thermal stability in this sense means that the compound must be stable to all conditions encountered in normal service and for storage. The most thermally unstable compounds in this study are the nitrate esters NG and PETN. These compounds require stabilizers not to decompose and cause accidents. One way to evaluate the thermal stability is accelerated ageing in heat flow calorimeters [23]. However, the requirements on thermal stability are different in a GC column. The choice of analysis method is governed by the thermal stability of the analytes on the column in combination with their boiling points and the analysis time.

To prevent any thermal decomposition of the analytes, split-splitless techniques were avoided and on-column injection was used. The thermal stability of PETN is insufficient to allow the use of the longer method 2, whereas the use of the shorter method 1, *vide supra*, could successfully be applied. The same is true for HMX, which requires no stabilizers for storage. Consequently the two aforementioned compounds could be analyzed with method 1 due to sufficient stability.

3.3. Ionization and fragmentation

The ionization pattern of the analytes was completely different between the different groups of the analytes. The nitrate esters (NG and PETN) only displayed the NO_3^- ion, even though there are some fragments with low relative intensity, and no molecular ion peaks. Neither of the non-aromatic nitramines (RDX and HMX) had any molecular ion peak. They had the same fragments, but with different relative intensities. Due to the large difference in retention time, both compounds could be quantified. The aromatic nitramine tetryl showed an ionization pattern, which pertained neither to the aliphatic nitramine nor to the nitroaromatic family. It shared some traits from both groups. It had no molecular peak and lost only exocyclic fragments. The nitroaromatics, on the other hand, ionized as their radical anions. This is possible due to the delocalization over the aromatic ring. The fragments are listed in Tables 1–3 (Supplementary material).

3.4. Limit of detection

Limits of detection (LOD) are presented for the GC–MS method for all compounds investigated. These values are calculated from the standard deviation, s, of the lowest concentration of the calibration graph, giving LOD = 3 s/a_1 where a_1 is the local slope of the calibration line. The LOD values are based on GC–MS runs of the standards compounds in Tables 1–3 dissolved in acetonitrile and diluted in steps of ten giving five levels of concentration. Mostly the LOD is well below 1 pg giving a sample LOD below the 4 ng/kg level when applied to samples in the lower gram interval. The calibration line is truly heteroscedastic, giving a standard deviation that decreases with decreasing amount of compound registered by the mass spectrometer. A slight non-linearity of the calibration line can be observed for most of the compounds when a squared term is included in the data fitting. Though, the curvature is so weak that a fitting to a linear calibration line never gives any experimental data points outside of the 95% confidence limits of expected data distribution of neither the linear nor the log–log plot.

3.5. Extraction and GC–MS

The extraction method applied in this work is based on desorption of target compounds by the use of high solvent strength at slightly elevated temperatures (30 °C) for a short time (60 min) with the aim of getting a fast and non destructive dissolution of target compounds without the addition of salt. The acetonitrile is added first, since this will dissolve all water in the soil. This leads to a very fine dispersion of the soils sample, and thus to a very good contact between all particles and the solvent. The addition of dichloromethane will make the extract immiscible with water. The particles will still have a good contact with the solvent mixture, thanks to the stirring. As the organic phase is immiscible with water, there are little or no salts and other highly hydrophilic compounds in the obtained extracts. Compared to EPA 8330, this procedure simplifies the extraction considerably.

The extraction and GC–MS method were applied to three different types of soil. Certified values of explosives and results achieved by the present method are presented in Tables 5–7 (Supplementary material). The certified values are obtained by the use of the EPA 8330 method. This yielded some striking differences to our results. In general, the concentrations given by our methods are well above the certified values of the commercial soils for volatile compounds. These results have been repeated by us in ten independent experiments and are well beyond all insignificances. The results indicate that our method is both less destructive to the analytes and more efficient with respect to desorption than the methods used for achieving the certified values. The drying and grinding included in the EPA 8330 method could possibly lead to losses of target compounds. In an experiment at our laboratory, a reference soil was placed in a closed vessel followed by the evacuation of air through a C18 cartridge. Analysis of this cartridge yielded easily detectable amounts of the more volatile analytes (*e.g.* nitro- and dinitrotoluenes and benzenes). This experiment indicated that the drying process of EPA 8330 produces loss of target compounds.

EPA 8095 describes the analysis of explosives by GC–MS after extraction as outlined in EPA 8330. EPA 8095 uses split-splitless injection. According to our experience, this injection method can lead to decomposition of the analytes in this study. Another drawback is the changes of the liner in the split-splitless system, which

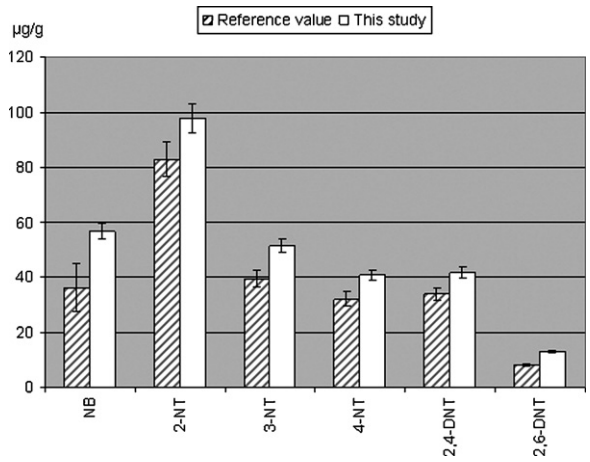

Fig. 1. Soil 1. Hatched: reference values according to EPA 8330. White: values according to our method. The error bars show ±1 standard deviation.

is recommended after 50 injections according to the mentioned method. To our mind, it is simpler to cut a column than to exchange a liner. The ECD detector recommended in EPA 8095 is less selective than a mass spectrometer, mainly because of interferences from halogenated and oxygenated compounds and occasional non-linearity. The LOD of the analytes has a greater spread in an ECD detector, compared to an MS detector. Another benefit of our method is its very low consumption of carrier gas, compared to EPA 8095, which also requires two different columns and two different analytical runs to achieve full separation and identification of all analytes.

Also the method published by Collin et al. [24] used a split-splitless injector. In our case, the aim was to extract and analyze soils with low levels of the analytes with available equipment at high throughput. A simple way to increase the sensitivity is to introduce the whole injection into the column, *i.e.* splitless injection. Given the nature of our analytes, thermal decomposition had to be minimized. Therefore, cool on-column injection was the method of choice. Collin et al. [24] used two different column diameters in their long and their short method, respectively. Our choice was to use the same diameter in both cases, since this facilitated the switch between the two methods.

The Achilles heel of on-column injections is the deterioration of the column, which can result in markedly lower responses. To avoid such problems, a standard solution was injected and the response controlled frequently, *e.g.* one out of six samples. If the area of any of the analytes decreased more than 10%, the column was cut to expose new surface at the injection site. In extreme cases, where the extract contain large quantities of non-volatile materials, only one or two injections can be made between the standards to ascertain that the column is still performing. The other extreme is sandy soils, where 20–30 samples can be analyzed without any trimming of the column. Such samples can be obtained in Afghanistan and other arid war zones. It is difficult to give any general instructions on the number of injections that can be performed between the standard runs. It depends on the extract being analyzed and all extracts are unique. Thus, the performance of the system must be monitored continuously. For most soils, 20 soil samples can be analyzed without any trimming of the column. This can be contrasted to the 50 injections without changing of the split-splitless liner possible according to EPA 8095. Since the system used for cool on-column injection cools down between every injection, no extra time for cooling is required when the column has to be cut. A split-splitless system, on the other hand, must cool down from over 200 °C to room temperature to allow the change of liner to take place. The time required to cut a column or change the liner depends on the experience of the analytical chemist. In our case, ten minutes is enough to cut the column and reinitiate the system. If time is the important factor, split-splitless injectors will be more efficient if four to fives times as many samples can be run at such as system on the same liner, compared to on our system without cutting of the column. The main advantage of a split-splitless injector is that it saves the column from degradation. In our system, a long column (30 m) can be cut six times (20 cm per time) with maintained separation. This corresponds to 120 soil samples. A short column (6 m) can be cut three times, which results in 60 soil samples per column. The approximately 28 m of column remaining from the long column were used for four short columns. This adds another 240 samples to the life span of one column. Since the concentrations of explosives in contaminated soils are often very low, the thermal decomposition of the analytes must be minimized. Therefore, our choice still remains the use of cold on-column injection, even though it cannot be excluded that splitless injection using a split-splitless injector could be more efficient in certain cases.

Running the MS in the SIM mode allowed us to analyze our extracts with no other pre-treatment than filtration. One risk with this method is that the extract could contain other compounds with the same m/z as the desired analytes. This could lead to false

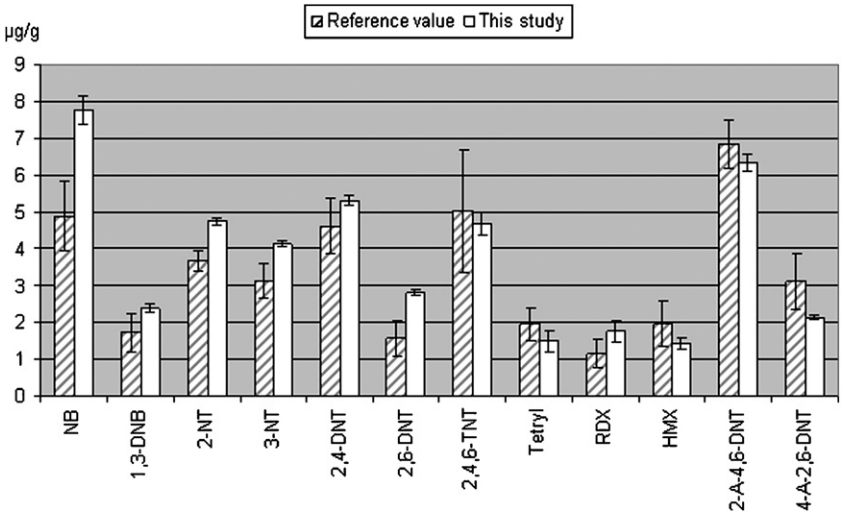

Fig. 2. Soil 2. Hatched: reference values according to EPA 8330. White: values according to our method. The error bars show ±1 standard deviation.

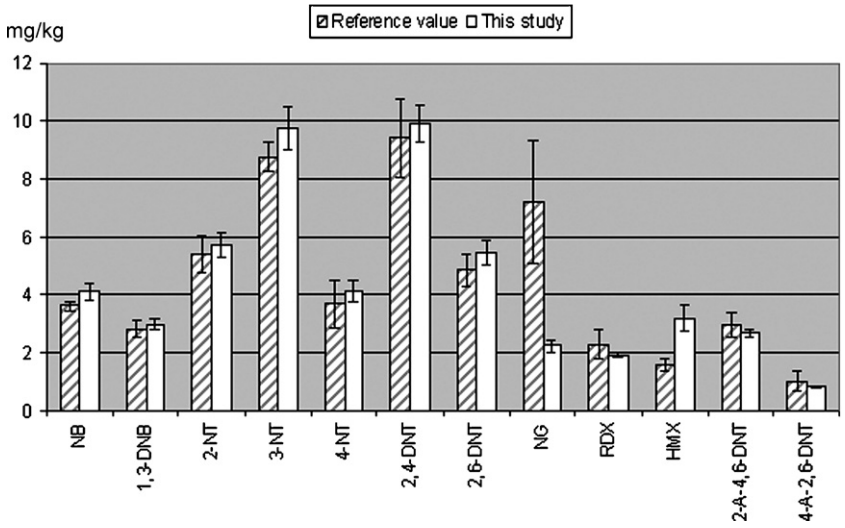

Fig. 3. Soil 3. Hatched: reference values according to EPA 8330. White: values according to our method. The error bars show ±1 standard deviation.

positives or, if the concentration of the contaminant is much higher than that of the analyte, false negatives due to ion-quenching. A first way to eliminate false positives is comparison of the retention time of the peaks to those of a standard sample and exclude all peaks that deviate. A second way is to look at more than one fragment, since the fragmentation pattern is one way to identify a compound. The use of more fragments will also prevent ion quenching, which is unlikely to occur for all fragments analyte at the same time.

The use of a retention gap to reduce the consumption of column was attempted, but the retention gaps evaluated deteriorated quicker than the column itself.

The results of Tables 5–7 (Supplementary material) show that the present method yields higher recoveries for most of the energetic compounds in all tested samples with a few exceptions.

In the case of soil 1, Fig. 1, all compounds were significantly better recovered with the present method compared to the certified values, which could be explained by minimized losses as described above, *vide supra*.

The same trend for the relatively volatile mono- and dinitroaromatics can be seen in the case of soil 2, Fig. 2. Seven out of twelve compounds had higher recoveries with our method than with EPA 8330. The mono- and dinitroaromatics represent six out of these. The only other compound with the same behavior is RDX. This is in contrast with the other five compounds, whose lower recoveries could be a consequence of their lower solubility in the mixture of acetonitrile and dichloromethane, in comparison with pure acetonitrile. RDX was also the only analyte to fall outside of the prediction interval of the certified soil. All differences are significant due to the large number of analyses being performed.

In soil 3, Fig. 3, eight out of 12 compounds gave significantly better recoveries with our method compared to the certified values. Once again, the results of the more volatile mono- and dinitroaromatics could explain all but one. In this case, HMX contrasted with the other compounds, whose lower solubility could be expected to result in reduced recoveries. HMX was the only compound to fall outside of the confidence interval of the certified soil. It remains unclear whether this is an effect of the different soil types or any other factor. That is the subject of a future study.

Our seemingly low recovery of nitroglycerine (NG) could be explained in the following manner: In the analysis of the samples containing nitrate esters, there were two compounds with lower retention times than NG. They both had higher retention times than ethylene glycol dinitrate when compared to a standard containing

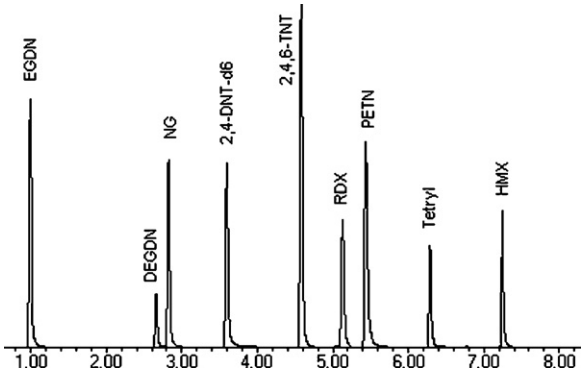

Fig. 4. Method 1 applied on a mixture of nitrate esters, TNT and nitramines. EGDN and DEGDN are included in the mixture to allow for analysis of these components, which are common in dynamite. They were not present in the reference soils.

that substance. It is our belief that these peaks arise from decomposition products of NG, where the parent compound has lost one or two of its nitro groups. The ionization pattern was the same as for other nitrate esters, *i.e.* only the nitrate ion at −62 *m*/*z*. Such products are difficult to separate on C18 columns with isocratic LC systems. Thus, co-elution of NG and its decomposition product is likely in such LC systems. The decomposition products absorb UV light at the same wavelength as NG. The combination of co-elution

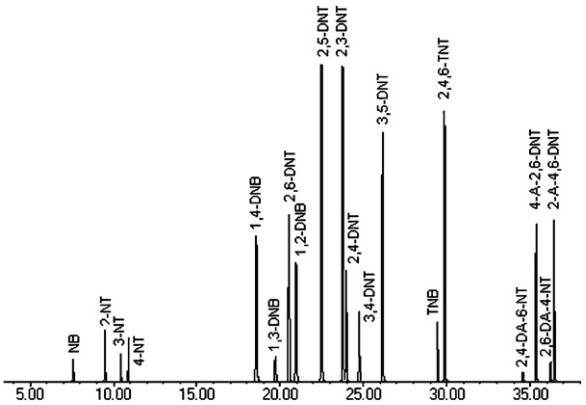

Fig. 5. Method 2 applied on a mixture of TNT and related compounds.

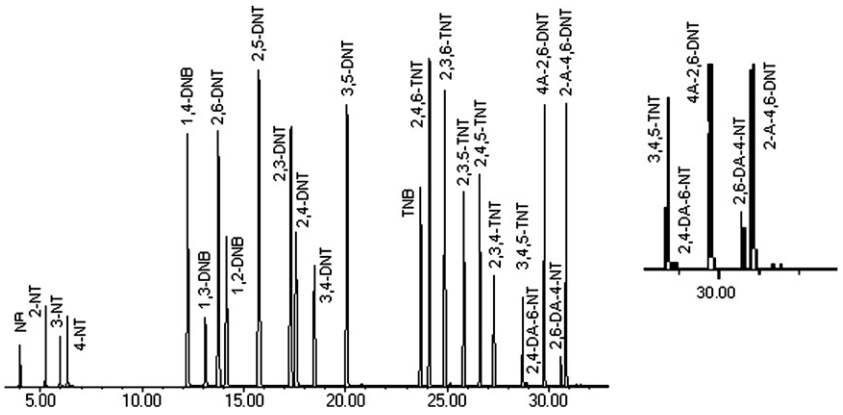

Fig. 6. Method 2 with a slightly modified temperature profile to yield full separation of all TNT isomers.

and increased UV absorption could then result in too high a result for NG. In the GC, all peaks separate and such problems are avoided. This discussion is only relevant for the detailed quantification of NG as such in soil, since there is no natural source of its decomposition products. The latter were not quantified, since no reference materials were available at the time of the study. Fig. 4 illustrates method 1, which is the shorter of our methods.

The example of NG is an illustration of the problems caused by co-elution of very similar products. In our longer method 2, all analytes have baseline separation. This is illustrated by Fig. 5 that shows method 2 applied to a mixture of TNT and related compounds and Fig. 6 demonstrating that all TNT isomers can be separated by the use of this method. The only two analytes that cannot be analyzed with method 2, *i.e.* HMX and PETN, have full baseline separation from any other analyte in our shorter method 1. This is illustrated in Fig. 4. Consequently, a combination of our two methods will allow facile and accurate quantification of all analytes.

Though, slightly lower recoveries for some of the less volatile compounds are more than compensated by the high sensitivity of our chosen analysis method. For the analytes in this study, the sensitivity of a LC–UV system ranges from 0.7 to 141 ng per injection [21]. The latter extreme case is PETN, but most of the analytes have an LOD between 1 and 10 ng per injection. The LODs in this study varied between 0.09 and 23.9 pg per injection for the different analytes, which is 1000 times lower. This allows for smaller samples to be used or lower levels of the analytes in the soils to be analyzed. The LODs were evaluated from standard solutions in pure acetonitrile, whereas the samples from the extracts consisted of a 50:50 mixture of acetonitrile and dichloromethane. The reason for this difference was that earlier result showed little or no influence of the solvents – either pure acetonitrile or the 50:50 mixture of acetonitrile and dichloromethane – on the response factors and the spread in the latter.

The parameters optimized in the GC–MS method were carrier gas flow, temperature gradient, column length, and ionization temperature. The first two were varied until satisfactory separation was obtained. The column length has the biggest influence on the two following parameters. The reason to use two different column lengths was the thermal lability of some analytes. A shorter column was required to reduce the time at elevated temperatures, in particular for HMX and PETN. The optimum column length was 6 m. The temperature in the ion source was varied between 120 °C and 250 °C. Sufficient ionization of all analytes was obtained at 180 °C. Lower temperatures resulted in insufficient ionization and higher temperatures in decomposition.

There was no PETN in the certified soils, but the compound was included in the GC–MS method, since it is a common explosive in certain areas. For instance, it is the main explosive in the plastic explosive used by the Swedish Armed Forces. EGDN and DEGDN were included for the same reason, since they are common in different types of civilian dynamite. The product sheets of the certified soils only stated the content of two dinitrotoluenes and one trinitrotoluene. All isomers were included in the GC–MS method to allow for analysis of these compounds if the need would arise. The same is true for the diaminonitrotoluenes, which are degradation products of TNT.

4. Conclusions

A new extraction method for soils contaminated with explosives was developed. The extracts were analyzed with GC–MS. The extraction method worked well for the three certified soils, on which it was validated. The more volatile analytes ranging from nitrobenzene to dinitrotoluenes had higher recovery in our method than in EPA 8330. The less volatile components, besides the cyclic nitramines RDX and HMX, had a lower recovery than the certified values. Nonetheless, they were all at least within the prediction range and in many cases within the confidence interval of the certified soils. RDX and HMX showed contradicting trends in the two soils, where they were present. Further studies are needed to ascertain whether this depended on the type of soil use or any other factor.

The GC–MS analysis method was validated in terms of linearity and LOD. The MS was not perfectly linear, but the curvature of correlation was small. This method had considerably lower LODs than the LC–UV method used in EPA 8330. This allows for either the use of smaller samples or lower levels to be detected.

The most important benefit of the new extraction method is that it is time-saving and simple. This in combination with the highly sensitive analysis method will allow a higher throughput of samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.12.014.

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