Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Chemosphere 71 (2008) 1701–1708
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Optimized microwave extraction for trace detection of 2,4,6-trinitrotoluene in soil samples

Ann Kjellström [1], Mona Brantlind, Carina Eldsäter *

FOI Swedish Defence Research Agency, Grindsjön, SE 147 25 Tumba, Sweden

Received 23 August 2007; received in revised form 2 January 2008; accepted 2 January 2008
Available online 4 March 2008

Abstract

An optimized microwave assisted extraction method for determination of trinitrotoluene (TNT) and related compounds in soil is presented. The new enhanced method exhibits improved extraction recovery and precision as well as sample handling time. For the separation and detection gas chromatography coupled to a thermoionic probe was used achieving TNT and dinitrotoluene detection limits per injection at the femtogram level. The generated extraction recovery and precision data are given for spiked and certified soil. Determined TNT and related compounds residues in soil collected from different parts of the world are presented.

Keywords: Microwave assisted extraction; TNT; DNT; Soil

1. Introduction

Huge efforts are taken in mine affected countries to clear land mines and unexploded ordnances in order to reclaim land (MacDonald et al., 2003). One of the most widely used military high explosives is 2,4,6-trinitrotoluene (TNT). It is also the most common explosive found in buried land mines. Today reliable and instantaneous explosive detection is utilized in the field by mine detection dogs (MDDs) (Furton and Myers, 2001; MacDonald et al., 2003). Surveys of scent patterns is becoming important for use within development of MDD training (Harper et al., 2005) and for the development of explosive and land mine detection devices.

Military grade TNT contains impurities, such as different isomers of dinitrotoluene, trinitrobenzene and dinitrobenzenes (Zhao and Yinon, 2002). Trace amounts of the explosive and its manufacturing by-products migrate from buried objects to the surrounding soil (Jenkins et al., 2001). Adsorption to soil particles occurs and since these compounds are moderately to weakly soluble in water (Phelan and Barnett, 2001a,b), dissolution into the water phase of the soil takes place. Besides TNT the most prevalent signatures near buried TNT-filled land mines in mine fields (Kjellström and Sarholm, 2000) and test fields (Jenkins et al., 2001) are the manufacturing by-product 2,4-dinitrotoluene (2,4-DNT) and the degradation products 2-amino-4,6-dinitrotoluene (2-A-4,6-DNT) and 4-amino-2,6-dinitrotoluene (4-A-2,6-DNT). The frequency of detection and the concentrations may vary tremendously from one type of land mine to another (Jenkins et al., 2000; Desilets et al., 2001).

Currently most methods for trace analysis of TNT and related compounds in soil are based on the sample work-up protocol described in the US Environmental Protection Agency method 8330 (EPA 8330) (USEPA, 1994). Detection limits of 1 ng g^{-1} for di- and trinitroaromatics from spiked soils have been reported (Walsh, 2001) using GC–ECD analysis as described in US EPA 8095 (USEPA, 2000). Other attempts have been made with solvent extraction, e.g. acetone, followed by GC equipped with a nitrogen–phosphorus detector (GC–NPD), reporting detection limits of 0.10 and 0.11 $\mu g\ g^{-1}$ for TNT and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), respectively (Hewitt and Jenkins, 1999).

---

* Corresponding author. Tel.: +46 8 55503988; fax: +46 8 55503949.
E-mail address: carina.eldsater@foi.se (C. Eldsäter).

[1] Present address: Swedish Customs, P.O. Box 128 54, SE 112 98 Stockholm, Sweden.

0045-6535/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2008.01.004

Supercritical fluid extraction (SFE) of nitroaromatic compounds from soil (Batlle et al., 2005) together with GC–ECD and GC–chemical ionization-MS has reported detection limits comparable to the EPA 8330 method and shorter analysis time.

The use of solid phase micro extraction (SPME) fibers exposed to TNT contaminated soils and sediments via direct burial resulted in detection limits of 20–500 μg g^{-1} dry weight (Conder et al., 2003). Other attempts with SPME used extraction in methanol, water/methanol mixtures (Darrach et al., 1998; Stahl and Tilotta, 2001) or acetonitrile (Darrach et al., 1998; Monteil-Rivera et al., 2005) before application of the SPME fibers. A detection limit of 1–9 ng g^{-1} dry sediment for TNT was achieved using acetonitrile and GC–ECD (Monteil-Rivera et al., 2005).

Desorption electrospray ionization mass spectrometry utilizing MS/MS in negative ion mode has been used to detect TNT from plastic surfaces with detection limits of 10–100 fg (Takáts et al., 2005). A GC–NPD equipped with a nitrogen specific type bead (Batlle et al., 2003; Sanchez et al., 2003) have reported detection limits at the femtogram level of TNT in air samples.

Microwave assisted extraction (MAE) as soil sample preparation technique has been found to compare favorably with Soxhlet, sonication, supercritical and pressurized fluid extraction techniques (Lopez-Avila et al., 1995; Dean and Xiong, 2000; Cortazar et al., 2005) and has been developed into a valuable alternative to traditional extraction methods in environmental analysis (Dean and Xiong, 2000; Shen and Lee, 2003; Cortazar et al., 2005). MAE has also proven to be an efficient extraction method for thermolabile compounds (Font et al., 1998; Proestos et al., 2006). This prompted us to analyze the potential of the technique for the extraction of explosives in soil and a method with a buffer solution was developed (Kjellström, 2002). A very similar method has recently been published by Holmgren et al. (2005).

This study describes the optimization of our original microwave extraction method accompanied by GC and thermoionic detection for the analysis of the extracts. Recovery of spiked samples and certified reference material are given. Samples collected during 4 years from mined areas and test fields in different parts of the world and subsequently analyzed using the optimized method are presented. We have also evaluated the method of Holmgren et al. (2005) and compared the performance with our optimized method.

2. Experimental

Sodium phosphate buffer (0.1 M, pH 8) was prepared from sodium phosphate, monobasic monohydrate ($NaH_2PO_4 \cdot H_2O$) p.a. grade, deionized water and adjusted to pH 8 with sodium hydroxide. Toluene (Merck Suprasolv), methyl-tertbuthyl-ether (MTBE) (Merck residual analysis grade) and acetone (Merck Lichrosolv) were purchased from VWR International, Sweden.

The reference substances 2,6-dinitroluene (2,6-DNT), 2,5-dinitroluene (2,5-DNT), 2,4-DNT, 2,3-dinitroluene (2,3-DNT), 3,4-dinitroluene (3,4-DNT), 3,5-dinitroluene (3,5-DNT), 1,3,5-trinitrobenzene (TNB), 2-A-4,6-DNT, 4-A-2,6-DNT, 2,4-diamino-6-nitrotoluene (2,4-DA-6-NT) and 2,6-diamino-4-nitrotoluene (2,6-DA-4-NT) were purchased from LGC Promochem AB (Borås, Sweden), except TNT and RDX which were provided by FOI Swedish Defence Research Agency (Weapons and Protection, Tumba, Sweden). The surrogate standard 2,4-dinitroanisole (2,4-DNA) was from Dr Ehrensdorfer GmbH (Augsburg, Germany) and the volumetric standard 5-nitroindoline (5-NI) was from Sigma Aldrich (Milw. WI, USA). MTBE was used for the preparation of all standard stock solutions (0.1–0.8 mg ml^{-1}). Standard mixtures (0.01 and 0.16 mg ml^{-1}) were prepared from stock solutions every two weeks. Solutions were kept in amber glass vials and stored in the freezer.

A certified homogenous blank soil matrix, Semivolatile blank soil #056 from Environmental Resource Associates (ERA) (LGC Promochem, Borås, Sweden) and blank sand (<300 μm) from Rådasand AB (Lidköping, Sweden) were used as spiking matrices. Validation was performed using certified soils from LGC Promochem (Borås, Sweden): Nitroaromatics, ketones and nitrosamines in soil #920 from ERA and CRM 117-100 from Resource Technology Corporation.

Field samples from Afghanistan, Laos, Croatia and Tanzania were obtained from the Geneva International Centre for Humanitarian Demining and field samples from Sweden were obtained from Swedish Armed Forces. The soil was sampled into amber glass vials shut tight with teflon septa caps and stored in the freezer. Blank samples were stored and analyzed parallel to field samples to ensure that no contamination of samples occurred during handling and analysis.

Blank soil and sand samples were spiked with 5–175 ng of the target compounds in a 50 μl volume of MTBE. Standards were prepared with the same amount of target compounds. The spiked samples were shaken and left 2 h for the solvent to evaporate before covered with aluminum foil and left in the freezer over night.

MAE was performed using an ETHOS E microwave system from Milestone Srl (Italy) equipped with a 36-piece rotor and 50 ml glass extraction vessels. Magnetic stirring was applied and a reference vessel was used for automatic temperature control. All soil samples were grinded with a mortar and pestle and 1 g was used for analysis. The dry substance was determined by gravimetric analysis (24 h at 105 °C). The surrogate standard (2.4 μg) was added in 50 μl of MTBE.

The samples were extracted in 25 ml of aqueous sodium phosphate buffer (0.1 M, pH 8). The MAE was ramped to 80 °C for 5 min (maximum 500 W), the temperature was then held for 5 min (maximum 900 W) followed by 10 min (maximum 500 W). A minimum of 10 samples and a maximum of 30 samples were extracted at the same