

Use of solid-phase microextraction/gas chromatography–electron capture detection for the determination of energetic chemicals in marine samples

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Abstract

Gas chromatography with electron capture detection (GC–ECD) is a highly explosive–sensitive analytical technique. However, its application to the analysis of sediment extracts is hampered by the presence of numerous endogenous interferences. In the present study, solid-phase microextraction (SPME) was used both as a purification technique for sediment extracts and as an extraction technique for water samples prior to analysis by GC–ECD. SPME/GC–ECD coupling was optimized and applied to the trace analysis of nine explosives including nitroaromatics and RDX in real seawater and marine sediment samples. Addition of a high concentration of salt (30%, w/v) in the aqueous medium and use of a carbowax/divinylbenzene (CW/DVB) coating led to optimal extraction efficiencies. Method detection limits (MDLs) ranged from 0.05 to 0.81 $\mu\text{g/L}$ in water and from 1 to 9 $\mu\text{g/kg}$ in dry sediment. Except for RDX, spike recoveries in seawater were satisfactory (89–147%) when samples were fortified at 2 $\mu\text{g/L}$ of each analyte. Spike recoveries from dry sediment fortified at 10 $\mu\text{g/kg}$ of each analyte gave lower recoveries but these could also be due to degradation in the matrix. With a smaller volume of aqueous sample required compared to solid-phase extraction (SPE), SPME is an attractive method for the analysis of limited volumes of sediment pore-water. Moreover, the use of SPME eliminated interferences present in sediment extracts thus allowing the detection of the target analytes that were otherwise difficult to detect by direct injection.

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1. Introduction

Military training and wartime activities, including dumping of ammunition and sinking of warships have resulted in the undersea deposition of large amounts of unexploded ordnances (UXO). Since most explosives are toxic [1,2], their potential leakage from UXO and the subsequent contamination of various bodies of water are presently a subject of concern to several federal agencies including the Canadian and U.S. Navy. Due to the lack of effective tools to survey underwater areas and map the location of undersea UXO, the detection of the latter by both physical and chemical means

is of prime importance. In a marine environment where natural attenuation (biodegradation, photolysis and hydrolysis) of explosives occurs and therefore leads to trace levels, sensitive analytical methods that are able to suppress matrix effects are required.

Water and soil samples collected at military installations are generally analyzed by U.S. Environmental Protection Agency SW-846 Method 8330 [3]. This method involves the extraction of water samples by either salting-out or solid-phase extraction (SPE) [4], the extraction of solid by sonication with acetonitrile, and the analysis of the acetonitrile extract using high-performance liquid chromatography with an ultraviolet detector (HPLC–UV). An alternative gas chromatography method involving an electron capture detector (GC–ECD) has also been developed to complement the SW-

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846 Method 8330 [5–8]. The advantages of the GC–ECD method include lower detection limits and improved chromatographic resolution [5].

SPE is a robust method for extracting explosives from water [4,9–12]. However, the numerous steps that SPE method involves including conditioning, retention, rinse and elution make the technique a lengthy and time-consuming technique. Moreover, in the case of marine samples where the volume of sediments and consequently the volume of pore water may be limited, application of SPE, which generally requires large volumes of water (~500 mL), may not be possible. An extraction technique that could be applied to smaller volumes of water would thus be profitable. As for the solid fraction of sediments, extraction by sonication with acetonitrile often gives rise to organic-rich extracts that interfere with explosives during GC analysis. A purification technique that allows analyzing traces of explosives in an extract that contains numerous interferences would therefore be beneficial.

Solid-phase microextraction (SPME) that was developed by Pawliszyn is a rapid, simple, sensitive and solvent-free extraction technique [13,14]. Compared with SPE, SPME uses a miniature cylindrical coated fused-silica fiber that allows rapid mass transfers during the adsorption and desorption processes, and therefore requires smaller volumes of samples. SPME extraction has been applied in combination with GC/MS for the determination of TNT and the amino metabolites in seawater [15]. It has also been used by Darrach et al. [16] to purify a water/solvent extract from marine sediment collected near an UXO before applying reversal electron attachment detection (READ) or GC/MS for TNT and DNT analysis, respectively. Furton et al. investigated the use of SPME/GC–ECD and SPME/HPLC–UV for the recovery of explosives from aqueous solutions and demonstrated that both couplings could be used for detecting traces of explosives [17].

The aim of this study was to develop a reproducible method to quantify energetic chemicals (nitroaromatics and nitramines) in seawater and marine sediments while using commercially available and commonly used instrumentation. We used SPME as both a purification technique for sediment extracts and an extraction technique for water samples, and coupled it with GC–ECD, a highly explosive-sensitive detection technique. The method was optimized and accuracy, precision and limits of detection were determined. The applicability of the method to natural samples was evaluated with natural water and sediment samples from Hawaii.

2. Experimental section

2.1. Chemicals

The target analytes were in the form of an acetonitrile solution (8095 calibration mix A) purchased

from Restek Corp (Bellefonte, PA). Mix A contained 2-amino-4,6-dinitrotoluene (2-ADNT); 4-amino-2,6-dinitrotoluene (4-ADNT); 1,3-dinitrobenzene (1,3-DNB); 2,4-dinitrotoluene (2,4-DNT); 2,6-dinitrotoluene (2,6-DNT); 1,3,5-trinitro-1,3,5-triazine (RDX); 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX); tetryl; 1,3,5-trinitrobenzene (TNB); 2,4,6-trinitrotoluene (TNT); each at a concentration of 1 mg/mL. 3,4-Dinitrotoluene (3,4-DNT), which was used as an internal standard, was purchased as 1 mg/mL solution in methanol (8330 internal standard) from Restek Corp. (Bellefonte, PA). The solvent used, acetonitrile, was of HPLC grade (Fisher, Nepean, Ont.). Deionized water was obtained with a Milli-Q^{UV} plus (Millipore) system.

2.2. Sediments and seawater sampling

Four areas located offshore near the Hawaiian Islands were selected for collection of marine sediment and water samples. Samples UXO-1 and UXO-3 were collected from WWII-ERA UXO disposal site, sample UXO-5 was collected at a subsurface detonation site and sample REF-7 came from a reference site with no ordnance field nearby. At each labeled site, water was collected about 0.5 m below the surface, in polyethylene 4L bottles, and samples were immediately transferred into 1L amber glass bottles containing 1.5 g of sodium bisulphate for acidification. A 4L sample was also collected in the reference site and stored without acidification. Sediment samples were scooped into 4L plastic cores. At the end of the 6.5 h campaign, all samples were immediately placed on ice in a commercial cooler and processed for shipping. Upon arrival at BRI-CNRC (Montreal, Que.), samples were immediately stored at 4 °C, and analyzed 3 days later.

Samples were identified as follows: the above site names were used followed by letters “w” or “s” for water or sediment samples, respectively (for instance UXO-1w and UXO-1s correspond to water and sediment samples, respectively, taken at the first site visited). The non-acidified water sample from the reference site was denoted REF-7wna where “na” stands for non-acidified.

2.3. Solid-phase microextraction

Water samples were extracted by immersing a fused-silica fiber coated with the sorbent phase of interest (Supelco) in the aqueous solution (35 mL) that was stirred continuously at room temperature and 990 rpm with a Variomag magnetic stirrer (ColeParmer Instrument, Anjou, Que.). Three different fibers were tested for their ability to extract explosives: a 65 µm film of carbowax/divinylbenzene (CW/DVB); a 65 µm film of polydimethylsiloxane/divinylbenzene (PDMS/DVB); and an 85 µm film of polyacrylate (PA). The three fibers were conditioned in a GC injector port prior to use, according to the

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