

Trace Explosives Signatures from World War II Unexploded Undersea Ordnance

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Trace explosives signatures of TNT and DNT have been extracted from multiple sediment samples adjacent to unexploded undersea ordnance at Halifax Harbor, Canada. The ordnance was hurled into the harbor during a massive explosion some 50 years earlier, in 1945 after World War II had ended. Laboratory sediment extractions were made using the solid-phase microextraction (SPME) method in seawater and detection using the Reversal Electron Attachment Detection (READ) technique and, in the case of DNT, a commercial gas chromatograph/mass spectrometer (GC/MS). Results show that, after more than 50 years in the environment, ordnance that appeared to be physically intact gave good explosives signatures at the parts per billion level, whereas ordnance that had been cracked open during the explosion gave no signatures at the 10 parts per trillion sensitivity level. These measurements appear to provide the first reported data of explosives signatures from undersea unexploded ordnance.

Introduction

The detection of undersea unexploded ordnance (UXO) is a matter of vital concern to several United States agencies, including the Department of Defense (U.S. Navy, Army Corps of Engineers), and the Environmental Protection Agency. This issue has been highlighted as a result of the Base Realignment and Closure (BRAC) Act in which formerly used defense sites (FUDS) will be returned to the civilian sector.

Central to the problem of undersea UXOs is their detection, by both physical means (e.g., forward- and side-scanning sonars, magnetic field gradiometers, electrooptical sensors) and chemical means (e.g., seawater and/or sediment sampling and detection). A suite of these physical and chemical sensors has been incorporated into the so-called Mobile Undersea Debris Survey System (MUDSS) (1). The present study is aimed at testing the hypothesis that sediment sampling near a UXO, followed by chemical extraction and detection, can be a viable method of verifying an active target. To our knowledge, this is the first chemical evaluation under actual environmental conditions of sediment adjacent to old, live UXOs (2).

The site chosen for the sediment sampling was offshore of Rent Point in Halifax Harbor, Canada. On a historical note Halifax, NS, was a nexus for convoys destined for Europe during the Second World War. When the war ended, ships returning from Europe unloaded live ordnance of every type. The relatively small munitions bunker complex quickly

became filled. A minor fire in 1945 caused detonation of the entire complex, and for 10 days explosions scattered large quantities of UXOs. After the explosions subsided, a modest cleanup was pursued on land but no effort was made to clean up the floor of Halifax Harbor or the Bedford Basin. The bunkers were later rebuilt and used by the Canadian Armed Forces. The nearby shoreline was restricted to military personnel, and the decision was made to leave the underwater UXOs undisturbed. Hence all of the ordnance at Halifax could be expected to be live, with few if any inert rounds. This fact removed a large source of uncertainty in this study, namely, that a negative detection result could almost certainly be ascribed to a deteriorated round rather than to the presence of an inert one (such as used in target practice). Also, since the UXOs had lain undisturbed for over 50 years, this was an ideal location for testing the durability of explosives signatures.

The group of Canadian Navy divers at Halifax (3) were extremely capable, cooperative, and unstinting in their willingness to provide sediment samples in this extremely hazardous environment. The divers proceeded by (a) exploring the local harbor bottom, (b) reporting on their findings, (c) conferring on the sediment-collection scenario, (d) sampling the sediment adjacent to the selected UXOs, and (e) documenting via underwater camera the collection procedure. In total, 12 separate live targets were involved. Four samples from each target were collected, one from each of four cardinal points about the target. A freeze-frame image from the videotape of one of the live rounds studied (target no. 3) is shown in Figure 1.

The samples were brought back to the laboratory, and any explosives materials were extracted using solid-phase microextraction (SPME). The extracted species were detected using the Reversal Electron Attachment Detection (READ) technique and, for verification in some cases, a commercial gas chromatograph/mass spectrometer (GC/MS). The READ system uses the fact that explosives have an extremely large cross section for attachment of zero-energy electrons, via the so-called *s*-wave attachment phenomenon. The SPME/READ technique is highly selective toward those molecules that adsorb to the SPME fiber and have large electron attachment cross sections at ultralow electron energies. Its use as opposed to, for example, the use of more accessible GC/MS or HPLC/MS methods, offers the possibility of good selectivity, free of interferences from other chemical species present in seawater. Details of the SPME/READ sampling, extraction, and detecting methods are given in the following sections.

Experimental Section

Materials. All standards of 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (2,4-DNT) were prepared from standard analytic reference materials obtained from Pantex, Inc., through Sandia National Laboratory. Methanol and acetonitrile used as extractants were reagent grade materials obtained from Baker Chemicals. Distilled, deionized water was used to make up the standard dilutions of TNT. All glassware was passivated through the use of silanization, the standard silanization solution obtained from Supelco, Inc.

Sediment Acquisition Procedure. Through discussions with Canadian Armed Forces personnel (3), a site off Rent Point in the Bedford Basin adjacent to the ammunition storage bunkers used by the Canadian Armed Forces was chosen for collection of the samples. The services of the Harbor Inspection Dive Team of the Canadian Armed Forces

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FIGURE 1. Freeze-frame image from the undersea videotape of target no. 3, a 5 in. intact artillery shell. Sediment collected at two locations about this UXO tested positive for TNT in the low ppb range (see Table 1). The shiny object in the upper left-hand corner is a diver's knife for reference.

Reserves were generously provided for the hazardous task of UXO sediment collection. The collection scenario was as follows:

(a) The dive team surveyed a portion of the seabed, locating, marking, and videotaping the target UXOs.

(b) The dive team returned to shore, and the videotape was reviewed to identify which UXOs should be sampled. This judgment was based on whether the UXO was intact or was broken open.

(c) The dive team returned to each targeted UXO and acquired sediment samples at distances of between 6 and 12 in. from the UXO. One sample was taken from each of four cardinal points around each UXO. This process was also videotaped. The total sample collected was 250 mL of a sediment-water slurry for each target.

(d) The samples were returned to the surface and labeled. Samples obtained the first day remained at ambient temperature for no longer than 6 h before being placed in a commercial freezer after the day's collection was completed.

During the second day of sampling, the dive teams were sufficiently experienced, and a return-to-dock to review the videotape prior to sampling was not needed. Videotaping of each target on the second day was done before and during sample acquisition. On both days, considerable amounts of bottom silt were disturbed and made water-borne during the operations. This made it impossible to ascertain where the samples were taken from each target, but the dive team confirmed that samples were taken in the four cardinal directions. Sample collection was identical in all other aspects to the first day's collection.

Before shipping the samples to JPL (Pasadena, CA), it was verified that all samples were frozen. The bottles were placed in large boxes, and packing foam was injected to protect and insulate the samples. Shipping was as checked baggage on a commercial airline. Samples arrived frozen at JPL where they were immediately placed in a freezer. The holding times of nitroaromatic and nitramine explosives in water have been studied extensively (4–6), and it is found that trace explosives can be up to 90 days provided the samples are stored in silanized containers and frozen immediately after collection (6).

Explosives–Sediment Extraction Procedure. Considerable work has been carried out at several laboratories on characterizing the dissolution and extraction of explosives in seawater and ground soil (6–10). On the basis of earlier results (10), the extraction procedure was started by removing from the freezer the four samples corresponding to one particular UXO target and allowing them to thaw. Where there was less than 100 g of sediment in each of the four samples, the sediments were pairwise combined into two silanized glass beakers and separately analyzed. A quantity of 100 mL of methanol or acetonitrile was added to each of the samples, and the slurry was placed in a sonic bath for a period of at least 1 h. Samples were sonicated by the direct method: the sample beakers were placed in a larger perforated metal basket that was suspended in the sonic bath. Soil motion was visible during the entire sonication period. At the end of sediment sonication, soil and liquid layers were allowed to separate, and the liquid layer was pipetted into a separate, clean silanized glass beaker. The

glass beakers containing the pipetted water/solvent mixture were then desiccated inside a vacuum bell jar connected to a dry ice cooled cold trap. After desiccation was complete, 250 mL of water was added to each sample, and the sample was sonicated for an additional 1 h.

Results indicate that three methods are effective in extracting explosives from solutions in water (11, 12). These methods are (a) solid-phase extraction (SPE), (b) salting-out solvent extraction (SOE), and (c) membrane SPE. For this investigation the extraction of explosives from the aqueous solution was effected by solid-phase microextraction (SPME) (12). SPME has been successfully integrated to various sensor technologies, such as gas chromatography (GC) and high-performance liquid chromatography (HPLC) (13–15). The poly(dimethylsiloxane) divinylbenzene (PS–DVB) fiber used in the SPME has been found to have the highest relative efficiency of the commercially available fibers for TNT extraction (16).

The addition of salt or the adjustment of the solution pH can increase the ionic strength of the solution, thereby reducing the solubility of some analytes. In this study no increase in extraction efficiency was found when salt was added: extractions from spiked samples made from seawater or distilled water yielded the same efficiencies. With the advice of the fiber manufacturer (16), aqueous samples were adjusted to pH 8 before SPME extractions were performed. A bubble aeration scheme was used to agitate the sample during SPME extraction. This both enhanced extraction efficiencies, and hence reduced extraction time, and eliminated losses through adsorption of trace explosives to a stir bar. A 10 mL pipet tube was silanized, cleaned with methanol, and connected to a source of pure N₂ (99.99%). With the bottom 2–3 mm of the pipet tip inside the solution, the gas flow was adjusted until a gentle bubbling of the liquid was observed. To minimize cross-contamination of extractions, the pipet was either discarded and replaced with a freshly silanized one or cleaned thoroughly with methanol when samples were changed.

Equilibrium times for the adsorption of explosives to the SPME fiber were found to be approximately 5 min. To ensure consistent results, all extractions were performed for 15 min. Since even small amounts of water are detrimental to the cathode of the READ electron gun (see below), after each extraction the SPME fiber was dried in a vacuum desiccator for at least 15 min before injection of the fiber into the desorption oven. Samples were prepared, extracted, and analyzed within 3 h of being first removed from the freezer and thawed. Aqueous redilutions were not allowed to remain at room temperature for longer than 1 h to minimize loss from photodegradation. Typically with aqueous solutions bearing parts per billion TNT concentrations, five or six extractions could be performed before depletion of the samples was detected.

Since RDX explosives charges had been used in Halifax Harbor to effect an initial cleanup of the UXOs, it was decided not to test the samples for trace RDX: positive results for RDX could almost certainly be ascribed to residues of the cleanup. Also, present within the collected sediment were numerous fragments of cordite. Cordite was commonly used during World War II as the propellant charge in artillery rounds. It was typically composed of a mixture of nitrocellulose, nitroglycerin, and lubricants. Because of the high selectivity of the READ detection system to TNT, RDX, PETN, etc. (see below), no false positive results were expected or found due to the cordite in the sediment. To test that this propellant could not yield false positives, a 2-g piece of cordite was placed in a passivated beaker with 250 mL of water. The beaker was placed in a sonic bath for about 1 h, and an SPME extraction from the aqueous solution was performed. No

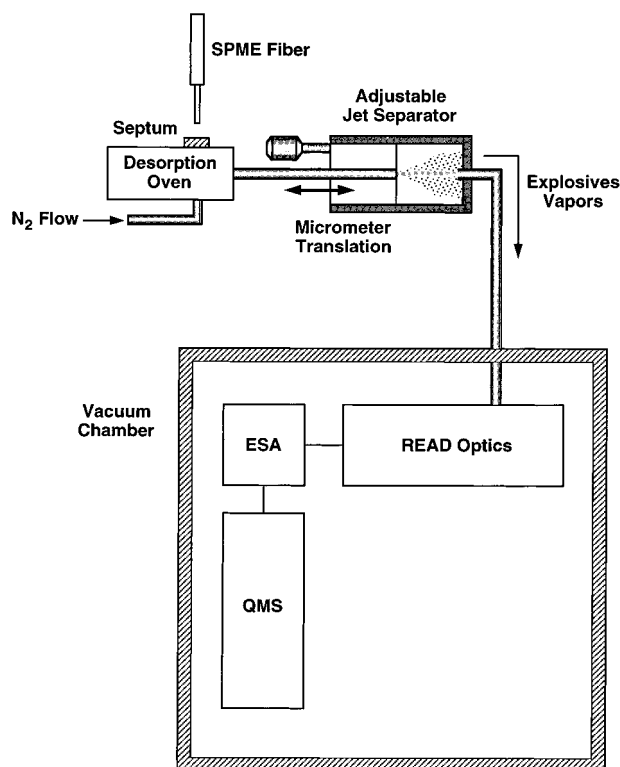


FIGURE 2. Schematic diagram of the SPME/READ system used in this study. Electron reversal and attachment and ion extraction take place within the READ optics. The electrostatic analyzer (ESA) ensures the sign of charge by deflecting the negative ions after attachment in the READ optics to the quadrupole mass spectrometer (QMS). Details of the READ system have been reported (17–19).

mass peaks that would interfere with identification of TNT or DNT were observed.

The READ System Used with SPME. Details of the operation of the READ have been given elsewhere (17, 18), and its operation with explosives discussed (19). Briefly, the READ system uses the fact that the explosives molecules have an extremely large cross section for attaching zero-energy electrons. This cross section varies as (electron velocity)⁻¹. Hence, the attachment rate (or ionization efficiency) is favored for slow electrons. Referring to the block diagram in Figure 2, the READ system provides a large density of electrons with zero and near-zero velocities by stopping and reversing, using a shaped electrostatic mirror, the current from an electron gun column. The analyte is introduced to this stopping region, and upon attachment each explosives type forms a characteristic negative-ion fragmentation pattern. Using a quadrupole mass spectrometer, the READ monitors one or more fragment peaks to detect the species and with calibration to provide concentration levels.

The explosives molecules are thermally desorbed from the SPME fiber by injection into an oven connected to the READ. The vapors pass through the gas line into an adjustable jet separator. Pure nitrogen at approximately 1 psia flows through the oven. Mass separation in a jet separator requires supersonic expansion from the source orifice. The nitrogen flow both transports the explosives into the READ and applies sufficient pressure to the source orifice of the jet separator to effect a supersonic expansion and on-line concentration of the heavier analytes (20). The spacing between the source and skimmer orifice was empirically adjusted for maximum signal at a mass peak corresponding to electron dissociative attachment to TNT.

TABLE 1. Summary of the SPME/READ Explosives Tests on Samples Collected at Halifax, Nova Scotia, Canada

target no.	target description	sample identification	results
1	5 in. shell, poor condition, broken open	A, B, C, D	no explosives detected
2	5 in. shell, very poor condition, broken open	E, F, G, H	no explosives detected
3	5 in. shell, good condition, intact	I, J	no explosives detected (confirmed by GC/MS)
4	9 in. shell, semi-buried, appeared intact	W, X	TNT detected at low ppb concn
		K, L	DNT detected at high ppbtr concn
5	two 5 in. shells, very poor condition, broken open	M, N	no explosives detected
		O, P, Q, R	no explosives detected (confirmed by GC/MS)
6	5 in. shell, semi-buried, intact	T	DNT detected at low ppb concn (confirmed by GC/MS)
7	background sediment sample	S, U, V	no explosives detected (confirmed by GC/MS)
		17, 20	no explosives detected

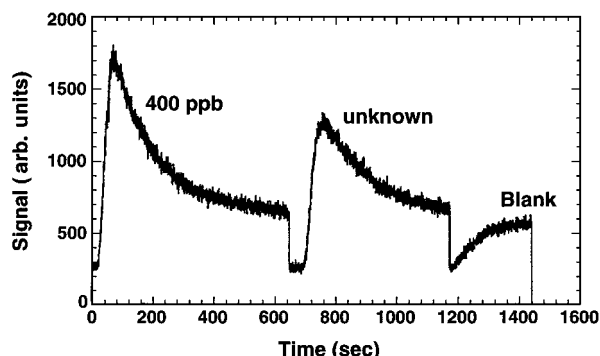


FIGURE 3. Display of the SPME/READ TNT negative-ion fragment signal at $m/e = 167$ u. Time is shown after injection of extractions from a 400 ppb standard TNT solution, a sediment-extraction sample of unknown concentration, and a blank.

For example, theory predicts from the ratio of TNT to N_2 molecular weights a factor of 8 enhancement in signal with a 0.5 mm spacing, relative to the 2.0 mm spacing supplied with the fixed-distance, commercial separators (20). The desorption oven, gas line, and jet separator are constructed of stainless steel, with silica-lined stainless steel tubing used in all three components. Tube unions were either Swagelok Chromographic or SGE Chromographic zero dead-volume fittings. The desorption oven and gas line are typically maintained at 190 °C, and the jet separator was at 140 °C during operation. No evidence for deterioration of the explosives at these temperatures was found. The lower temperature in the jet separator was necessary to protect the single Viton O-ring used to isolate the translation stage from the atmosphere.

Results and Discussion

Thermal desorption of explosives from the SPME fiber should be performed at a high temperature, suggested to be slightly above the boiling point of the analyte (10). Shown in Figure 3 is the time evolution of the fiber desorption. The mass peak $m/e = 167$ u of TNT is monitored. At this oven temperature (approximately 190 °C), the desorption process takes from 1 to 2 min. Result with a blank extraction is also shown in Figure 3. The slow rise in background level after injection of the blank sample is due to the rise in the READ chamber pressure from 8×10^{-6} to 1.4×10^{-5} Torr. Its integrated signal was subtracted from measurements of the standard and unknown. Typically, an SPME extraction of a sediment sample was sequentially analyzed with SPME extractions of a spiked sample of known concentration and then a seawater blank. This technique enabled an accurate determination of the trace explosives yields with no effects due to possible instrumental drifts.

During the 1–2 min the explosives were desorbing from the fiber, the quadrupole mass spectrometer could be tuned to various mass peaks of the fragmentation pattern, mapping

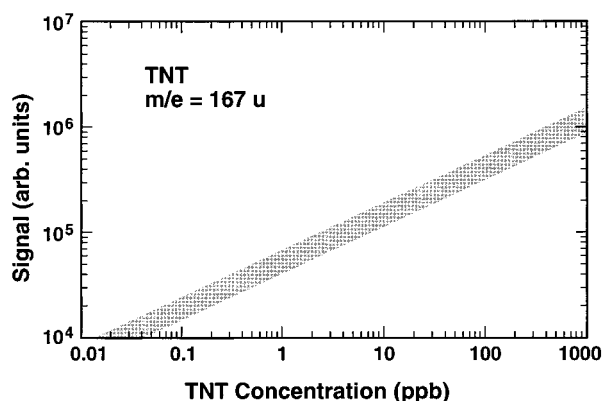


FIGURE 4. Sensitivity curve of the SPME/READ system to TNT concentration in water ($m/e = 167$ u monitored). The shaded region represents the sensitivity, and its error, in determining the TNT concentration corresponding to the indicated signals.

out the characteristic signature of the dissociative attachment signal. If ions with $m/e = 227$ and 197 u were detected (19), it would indicate that TNT was present in the SPME extraction. If these ions were absent, but ions with $m/e = 182$, 167 , and 151 u were detected, then an isomer of DNT was present. The SPME results for the sediments collected near the Halifax UXOs are summarized in Table 1. SPME extractions were performed at least three times for those sediments that yielded positive assays for TNT or DNT. The negative-ion signal detected by the SPME/READ system as a function of calibrated samples of TNT in water is shown in Figure 4.

As an independent test of the SPME/READ analysis, the solvent-extracted material from three different sediment samples were split and analyzed by GC/MS for the presence of trace TNT or DNT. The samples were chosen before any READ testing was done. Also, samples were chosen solely on the basis of their color. Typically, the solvent extractions had varying hues of yellow, and the samples chosen for GC/MS analysis were both nearly colorless or a strong yellow. The methanol/water mixture was extracted using 25 mL of methylene chloride, pipetted, dried over sodium sulfate, and then evaporated to 1.5 mL under a stream of dry nitrogen. An injection of a 4 μ L sample into a Finnigan Incos XL GC/MS was used for analysis. The colorless samples were evaporated to dryness and then rediluted in a smaller amount of methylene chloride for analysis. This was done to lower the detection limit since these samples were not as dark-yellow in color. In evaporating the samples, some of the early eluting peaks in the GC/MS analysis were unavoidably lost due to their higher volatility. The GC/MS results obtained from analysis of the sediment near target no. 6 (5 in. shell, semi-buried, intact) are summarized in Table 2. The sediment sample from target 5 (two 5 in. shells, broken open) yielded no detectable DNT or TNT at the 200 ng detection limits. By way of comparison, it is estimated that the

TABLE 2. Summary of Some Compounds Identified in the GC/MS Analysis of Sediment Collected near Target No. 6

compound	scan number	yield (μg)
trimethylhexene isomers	388–426	590
3-ethyl-1-octene	537	390
tetramethylpentane	597	25
DNT	928	1.1
TNT	1022	not detected (<200 ng)
tetradecanoic acid	1033	18
hexadecanoic acid	1067	31
benzopyranone compounds	1105	250
fluoranthene	1194	5
pyrene	1219	12

detection limit for the READ system is considerably less than 100 pg of TNT (21).

In general, the results herein indicate that sediment collected near UXOs that appeared (through visual inspection) to be broken open showed no evidence for TNT. Ultimate detection sensitivities of 10 ppt were observed for TNT in water. Samples near targets that appeared intact showed trace explosives up to parts per billion concentration levels. For the intact rounds, positive results were found at only two of the four cardinal points, indicating a directionality to the source. Intact munitions appear to be releasing their contents as a slow leak, very likely through pinholes in the eroded casing, or through the screw threads linking the fuse assembly to the main charge. Presumably, the signal strength is strongest near the point of emission, hence the directionality within the sediment samples. This directionality could be assisted by a prevalent, directed bottom current. One may also presume from the detection results that in the 50 years since the Halifax explosion broken munitions have had their contents dissolved, reacted, biodegraded, or even photodegraded. One may also conclude that trace explosives can very likely be detected at even further distances from a UXO, certainly with diminished concentration levels but well within present SPME/READ detection limits.

It is clear that in any UXO disposal strategy one would gain further information about a UXO site from chemical examination of the sea-bottom sediments. This additional information can be expected to yield positive results. Hence the chemical information offers another diagnostic dimension that is quite orthogonal to that from optical, magnetometer, and sonar instruments that are presently being deployed for UXO detection and classification. Chemistry will be an important tool in any explosives—ordnance disposal strategy.

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