

**TRACE EXPLOSIVES SIGNATURES
FROM
WORLD WAR II UNEXPLODED UNDERSEA ORDNANCE**

M. R. Darrach, A. Chutjian* and G. A. Plett

Jet Propulsion Laboratory, California Institute of Technology

4800 Oak Grove Drive

Pasadena, CA 91109 USA

Abstract

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 fifty 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-chromatography /mass spectrometer (*GC/MS*). Results show that, after more than 50 years in the environment, ordnance which appeared to be physically intact gave good explosives signatures at the parts-per-billion level, whereas ordnance which 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 UXOs.

key words: undersea ordnance, explosives detection, electron attachment, mass spectroscopy

Introduction

The detection of undersea unexploded ordnance (UXO) is a matter of vital concern to several United States agencies, including the Department of Defence (US 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, electro-optical 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, Nova Scotia 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 ten 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 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, twelve 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 Fig. 1.

The samples were brought back to the laboratory, and any explosives materials 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-chromatography/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. Details of the sampling, extraction, and detecting methods are given in the following sections.

EXPERIMENTAL

Materials

All standards for 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 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 judgement 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 6-12" 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 from each target the samples were taken, 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 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]. Based on the results of Ref. 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 sediment in each of the four samples, the sediment was aggregated into two separate samples in two silanized glass beakers. A quantity of 100 ml methanol or acetonitrile was added to each of the samples and the slurry placed in a sonic bath for a period of at least 1 hour, Samples were sonicated by the direct method: the sample beakers were placed in a larger perforated metal basket which 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 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 water was added to each sample, and the sample sonicated for an additional 1 hour.

Results indicate that three methods are effective in extracting explosives from solutions in water [1 1,12]. 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 (*SPA-E*) [1 21]. *SPME* has been successfully integrated to various sensor technologies, such as gas chromatography (*GC*) and high-performance liquid chromatography (*HPLC*) [1 3-1 5]. 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 [1 6].

The addition of salt, or adjustment of the solution pH can increase the ionic strength of the solution, thereby reducing the volatility 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 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 pipette tube was silanized, cleaned with methanol, and connected to a source of pure N₂ (99.99%). With the bottom 2-3 mm of the pipette 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 pipette 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 hours of being first removed from the freezer and thawed. Aqueous redilutions were not allowed to remain at room temperature for longer than 1 hour 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 two-gram 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 hour and an *SPME* extraction from the aqueous solution performed. No mass peaks which 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 Fig. 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. For example, theory predicts from the ratio of TNT to N₂ molecular weights a factor of eight 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 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 [16]. Shown in Fig. 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 1-2 min. Result with a blank extraction is also shown in Fig. 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, 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 quadruple mass spectrometer could be tuned to various mass peaks of the fragmentation pattern, mapping out the characteristic signature of the dissociative attachment signal. If ions with $m/e = 227$ u 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 $m/e = 182$ u, 167 u 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 which 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 Fig 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 $\mu\ell$ sample into a Finnigan Incos XL *GC/MS* was used for analysis. The colorless samples were evaporated to dryness, 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" shell, semi-buried, intact) are summarized in Table 2. The sediment sample from Target 5 (two 5" shells, broken open) yielded no detectable DNT or TNT at the 200 ng detection limits.

Conclusions

A solid-phase microextraction (*SPME*) method was successfully developed and optimized for extracting trace explosives from seawater and sediment. This technique was interfaced to the *READ* explosives-detection system, and standard tests carried out to determine sensitivities to TNT as a function of analyte concentration. Ultimate detection sensitivities of 10 pptr were observed for TNT in water.

A detailed study of sediments present near live undersea ordnance was made at Halifax Harbor, Canada. Analysis showed that sediment collected near UXOS that appeared (through visible inspection) to be broken open showed *no* evidence for TNT at the 10 pptr level, 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 fifty 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 be expected to yield positive results. Hence the chemical information offers another diagnostic dimension which is quite orthogonal to that from optical, magnetometer, and sonar instruments which are presently being deployed for UXO detection and classification. Chemistry will be an important tool in any explosives-ordnance disposal strategy.

Acknowledgements

The authors would like to acknowledge the excellent cooperation and assistance of LCDR J. Hewitt, Commanding Officer of the Fleet Diving Unit/Atlantic; and of the Harbor Inspection Dive Team of CFB Shearwater, Nova Scotia, Canada. This work was performed at the Jet Propulsion Laboratory, California Institute of Technology, and was supported by the Office of Naval Research, and the Department of Defense/Strategic Environmental Research and Development Program through agreement with the National Aeronautics and Space Administration,

Literature Cited

- [1] The MUDSS is a JPL-USN Coastal Systems Station collaboration sponsored under the Department of Defense/Strategic Environmental Research and Development Program (SERDP).
- [21] See also, for example, Fauth, M. 1. *Determination of the Fate of Fragmented or Unexploded Munitions and Munitions Ingredients in the Environment — a Literature Search*, DTIC AD-B120489(L) C.1 (1988).
- [31] Petty Officer 2nd Class J. Walsh, Center Chief, EOD Center No. 1, Fleet Diving Unit Atlantic, CFB Shearwater, Nova Scotia, Canada (private communication).
- [4] Jenkins, T. F.; Leggett, D. C.; Grant, C. L.; C. F. Bauer, C. F. *Anal. Chem.* 1986, 58, 170.
- [5] Bauer, C. F.; Grant, C. L.; Jenkins, T. F. *Anal. Chem.* 1986 58, 176.
- [6] Grant, C. L.; Jenkins, T. F.; Meyers, K. F.; McCormick, E. F. *Env. Toxic. Chem.* 1995, 14, 1865.
- [7] Leggett, D. C.; Jenkins, T. F.; Miyares, P. H. *Anal. Chem.* 1990, 62, 1355.
- [8] Jenkins, T. F.; Miyares, P. H. *Anal. Chem.* 1991, 63, 1341.
- [9] Anspach, G. L.; Jones, W.E. III; Kitchens, J. F. *Evaluation of Solid Sorbents for Sampling and Analysis of Explosives from Seawater (Atlantic Research Corp. Report ARC-49-5028, Alexandria, VA 1982) unpublished.*
- [101] Bruggemann, E. E. *HPLC Analysis of SEX, HMX, TAX, RDX and TN Tin Waste water (Army Medical Bioengineering Research and Development Laboratory, Report USA MBRDL-TR-8206, Fort Detrick, MD 1983) unpublished.*
- [11] Jenkins, T. F.; Grant, C. L. *Anal. Chem.* 1987, 59, 1326.
- [12] Jenkins, T. F.; Miyares, P. H.; Meyers, K. F.; McCormick, E. F. *Anal. Chim. Acts*

1994, 289, 69.

- [13] Arthur, C. L.; Pawliszyn, J. *Anal. Chem.* 1990, 62, 2145.
- [14] Rivasseau, D.; Caude, M *Chrom.* 1995, 41, 462.
- [15] Arthur, C. L.; Potter, D. W.; Bucholz, K. D.; Motlag, S.; Pawliszyn, J. *LC-GC* 1992, 70, 656.
- [16] Shirey, R. *Supelco, Inc.*, private communication.
- [17] Bernius, M. T.; Chutjian, A. *Anal. Chem.* 1990, 62, 1345.
- [18] Boumsellek, S.; Chutjian, A. *Anal. Chem.* 1992, 64, 2096.
- [19] Boumsellek, S.; Alajajian, S. H.; Chutjian, A. *J. Am. Soc. Mass Spectrom.* 1992, 3, 243.
- [20] Fernandez de la Mora, J.; Rosell-Llompart, J. *J. Chem. Phys.* 1989, 97, 2603.

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

Target Number	Target Description	Sample Identification	Results
1	5" shell poor condition broken open	A, B, C, D	no explosives detected
2	5" shell very poor condition broken open	E, F, G, H	no explosives detected
3	5" shell good condition intact	1, J W, X	no explosives detected (confirmed by <i>GC/MS</i>) TNT detected at low ppb concentrations
4	9" shell semi-buried appeared intact	K, L M, N	DNT detected at high ppb concentrations no explosives detected
5	two 5" shells very poor condition broken open	O, P, Q, R	no explosives detected (confirmed by <i>GC/MS</i>)
6	5" shell semi-buried, intact	T S, U, V	DNT detected at low ppb concentrations (confirmed by <i>GC/MS</i>) no explosives detected (confirmed by <i>GC/MS</i>)
7	background sediment sample	17, 20	no explosives detected

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

Figure Cap tions

Figure 1. Freeze-frame image from the undersea videotape of Target No. 3, a 5" 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.

Figure 2. Schematic diagram of the *SPME/READ* system used in this study [17-19]. 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 quadruple mass spectrometer (*QMS*). Details of the *READ* system are given in Refs. 17-19.

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.

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.







