

Alexander Kamyshny,¹ Ph.D.; Shlomo Magdassi,¹ Ph.D.; Yaniv Avissar,² B.S.;
and Joseph Almog,¹ Ph.D.

Water-Soaked Evidence: Detectability of Explosive Traces After Immersion in Water

ABSTRACT: Various factors governing the detectability of explosive traces after being soaked in water were studied. The variables are: the type of the surface (surfaces liable to be found in aircraft were chosen), the type of explosive, the type of water (tap or seawater), and movement of the immersed surface in the water. The maximal immersion times (t_{max}) after which explosive detection was possible were evaluated. This datum was found to depend on the type of explosive (one of the important factors is solubility in water), the surface material and the environmental conditions (tap or seawater movement). Detection of PETN on high-density polyethylene, linoleum, glass and aluminum, by the chemical Explosive Testing Kit (ETK), was possible even after a month of soaking in seawater. In addition, it has been found that movement of bulk water around the samples with deposited explosives considerably decreases t_{max} values. It is, therefore, recommended to retrieve samples for explosive analysis as soon as possible and in areas where the currents of water is minimal.

KEYWORDS: forensic science, explosives, explosive traces, PETN, RDX, Semtex, TNT, water-soaked evidence

Detection of explosive traces in the debris after an explosion can be crucial to the investigation. It can indicate the criminal use of explosives, as opposed to the possibility that the explosion occurred by accident, e.g., the ignition of a mixture of combustible vapors with air. Thus, forensic scientists played a key role in determining that a bomb containing the plastic explosive Semtex had caused the 1988 crash of Pan Am flight 103 in Lockerbie, Scotland. Detection of post-detonation explosive traces, however, is often difficult, particularly after an aircraft crash, and specifically, if the aircraft had fallen into the sea.

In July 1996, a TWA Boeing 747 mysteriously exploded in mid-flight and fell into the Atlantic Ocean, off the U.S. coast. Parts of the aircraft were found floating in the water a few hours after the explosion. Others could be retrieved only months later. Exhaustive tests indicated minute traces of explosives. Model experiments with Semtex and C4 explosives deposited onto aluminum sheets, which were immersed then in seawater, showed that after only an hour, it was no longer possible to detect any traces (1,2). Several factors could possibly be responsible for the analysis failure. Explosives can be dissolved or mechanically removed by the water; they can be consumed by microbes, modified, or decomposed by light (2).

This explosion and the uncertainty regarding the source of the explosive traces prompted us to study some of the factors governing the rate of disappearance of explosive traces from items immersed in water.

The study tried to determine the detectability of several types of explosives (TNT, PETN, RDX, and Semtex) deposited onto various supports, which are liable to be found in aircraft (glass,

polyethylene, aluminum, seat fabric, and linoleum) after soaking in fresh and seawater.

There are at present some extremely sensitive methods for the analysis of explosive traces, which combine chromatography with mass spectrometric, photoluminescence, chemiluminescence and electrochemical detection (3–8). Highly specific and sensitive immunosensors have also been reported recently (9,10). It was decided, nevertheless, that to study the disappearance rate of explosive traces, a somewhat less sensitive, but simpler and less expensive analytical technique could be applied. To follow the traces of various explosives, we used a simple colorimetric kit, ETK (Explosives Testing Kit), which is a compact field device extensively used by the Israel Police and some other law enforcement agencies for the detection of traces of explosives on hands of suspects (11). In spite of lower sensitivity compared with instrumental analytical techniques, this kit allows the evaluation of the maximal immersion times (t_{max}), after which explosive detection is not possible and to compare the persistence of explosives on various surfaces.

Experimental

ETK Method

The ETK technique is based on the formation of colored compounds upon reaction of polynitroaromatic compounds, such as TNT, with an alkali. Under the same conditions, nitrate esters such as nitroglycerin (NG), ethylene glycol dinitrate (EGDN), pentaerythritol tetranitrate (PETN), and nitrocellulose (NC) undergo alkaline hydrolysis producing nitrite ions, which are readily detected by the well-known Griess reaction (11–13).

Estimation of ETK Detection Limit

ETK method is based on visual detection of color reaction. In this respect, the detection limit is the smallest amount of explosive

¹ Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, 91904, Israel.

² Israel Police Counter-Terrorist Unit, Israel.

Received 25 Jan. 2002; and in revised form 20 Aug. 2002; accepted 19 Oct. 2002; published 3 Feb. 2003.

that could be visually observed by the ETK method. For estimation of ETK detection limit, solutions of TNT, PETN, RDX, and Semtex in acetone were pipetted onto *N* 1 Whatman filter paper. The diameter of the spot was ~ 1.6 cm (area of the spot ~ 2 cm²). Explosive amounts in the pipette drop ranged from 50 000 to 5 ng. Thus, the surface concentration was 250–0.025 ng/mm². Pipetting of ETK reagents directly onto dried explosive spots performed the analysis. In all cases, control experiments without dissolved explosive (only acetone) were carried out. It was found that the optimal time of color development was 10 min. After this time coloration of the control samples started to develop, i.e., a false effect can be observed.

The obtained data indicated that the limit of the visual detection after reaction with the ETK reagent for TNT was 500 ng per spot; for PETN, 100 ng per spot; for RDX, 5 ng per spot; and for Semtex, 20 ng per spot.

Examination of Surfaces Contaminated with Explosives after Soaking in Tap and Seawater

Glass (Gls) slides ($\sim 40 \times 25 \times 1$ mm), polyethylene (PE) films ($\sim 15 \times 15 \times 1.5$ mm), aluminum (Al) slides ($\sim 8 \times 20 \times 1$ mm), linoleum (Ln) pieces ($\sim 25 \times 25 \times 1$ mm) and airplane seat fabric (SF) strips (1.5×1.5 cm) were used as target surfaces.

For the study of the explosive stability in tap or seawater, one drop of an explosive solution in acetone (0.0125 mL) of concentration 80 $\mu\text{g/mL}$ was pipetted onto a surface, and a total amount of explosive deposited onto a surface was 1 μg (area of spots was about 0.2 cm² for hydrophobic surfaces, such as polyethylene, and about 3 cm² for glass and Al). This amount was higher than the detection limits, but it was decided to start with relatively high amounts to be able to follow its disappearance in water. After drying at room temperature, the supports with deposited explosives were placed into polyethylene vials containing 250 mL of water, without stirring, and then periodically taken out (10 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h, 22 h, then every day during a week, then the periodicity was from a week to a month) dried and tested by pipetting the reagents 1 and 2 of ETK directly onto the spots (for each detection a separate sample was used). In the case of seat fabric, the explosive residues were extracted with 0.5 mL of acetone before detection (since the color of the fabric was dark brown) and tested by adding the ETK reagents to the acetone extract. All measurements were performed at least 3 times, and an average is presented in the figures.

Stability of RDX on Polyethylene and Al Immersed in the Mediterranean Sea

Drops of RDX solution in acetone, containing 1 μg of the explosive, were pipetted onto 4 cm² of polyethylene or Al pieces with 3 mm holes drilled in one corner, dried and wired onto cells on a metal rack. The racks were attached to a rope, which was anchored at one end and submerged in seawater 1.5 miles off the Tel Aviv coast at a depth of 10 m (water temperature 30°C). The samples were taken out periodically (10 min, 60 min, 90 min, 120 min, and 180 min) and tested for RDX presence with the use of HPLC.

Dried slides were washed with about 500 μL of boiling acetone (56°C). The acetone solutions were evaporated to about 50 μL followed by addition of 100 μL of TNT solution in acetone (10 $\mu\text{g/mL}$). The TNT solution was used as internal standard. The samples were evaporated again to about 100 μL and cooled to room temperature.

Quantitative analyses of 50 μL samples were performed with the use of Waters HPLC system. A 616 Waters pump, connected to a

717 Plus autosampler with temperature controller at 18°C coupled with a 996 UV-VIS photodiode array detector (PDA). A 100×3 mm column with MOS-Hypersil (C-8) 5 μm , under 30°C temperature-control oven was applied. The elution liquid was comprised of methanol:acetonitril:isopropanol:water with volume ratio of 5:5:10:80 (0.7 mL/min elution). Chromatograms were analyzed at 230 nm with resolution 1.2 nm. Absorption spectra for each peak were recorded in the range of 200–350 nm. Data were collected and processed using a Millennium v 2.1 software (Waters, Milford, MA). Because we used relatively small amounts of RDX and TNT, the relative standard deviations of peak areas were about 7% ($n = 10$).

Influence of Movement on Explosives Deposit Stability

To evaluate the effect of water movement on the detectability of explosive traces after soaking in seawater, several experiments were carried out with PETN deposited onto polyethylene and linoleum and RDX deposited onto polyethylene. Polyethylene and linoleum pieces labeled by 1 μg of explosive were inserted in the cells of a plastic rack and placed into a shaker filled with tap water. Shaken samples (60 strokes/min) were periodically taken out, dried and examined by ETK.

Results

Detectability of Explosives after Soaking in Tap and Seawater

From the data presented in Figs. 1–4, it is immediately apparent that the detectability of explosives (t_{max}) depended on the type of explosive, on the type of the surface as well as on the type of water (in all cases the initial amount of explosives deposited onto surfaces was 1 μg).

TNT, indeed, was the first to disappear from all the surfaces (t_{max} varies from 30 min to several hours depending on a type of surface). This means that the chances to detect TNT traces are the lowest. PETN, on the other hand, was the last to disappear indicating that the prospects of detecting its traces are the highest (t_{max} varies from 7 month on glass and polyethylene in tap water to 30 days on linoleum and only 2 h on SF in seawater). Semtex, which is a mixture of PETN and RDX, also displayed rather high persistence in tap and seawater, especially on polyethylene.

As seen from Figs. 3 and 4, for all explosives studied, the seat fabric surface was characterized by the lowest t_{max} (actually, a process of penetration between the fibers might be a reason of such a low stability; see “Discussion”). The “best” surface for the detection of explosive traces in seawater was polyethylene (t_{max} was 5 months for PETN, 3 months for Semtex, and 15 days for RDX). PETN on linoleum could be detected after 1 month of soaking in seawater.

Data presented in Figs. 1–4 indicated also the higher stability of explosives deposited onto various surfaces, to tap water compared with seawater with the exception of PETN on Al (t_{max} was 40 days in tap water and 3 months in seawater).

Detectability of RDX on Polyethylene and Al after Immersion in the Mediterranean Sea

At the next stage, the detectability of RDX on surfaces after immersion in the Mediterranean Sea was studied. The pieces of polyethylene or Al with deposited RDX (1 μg) were submerged in the sea, 1.5 miles off the Tel Aviv coast at a depth of 10 m, as described in “Experimental”. It was found that RDX on Al could not be detected at all even after a few minutes of immersion in the sea,

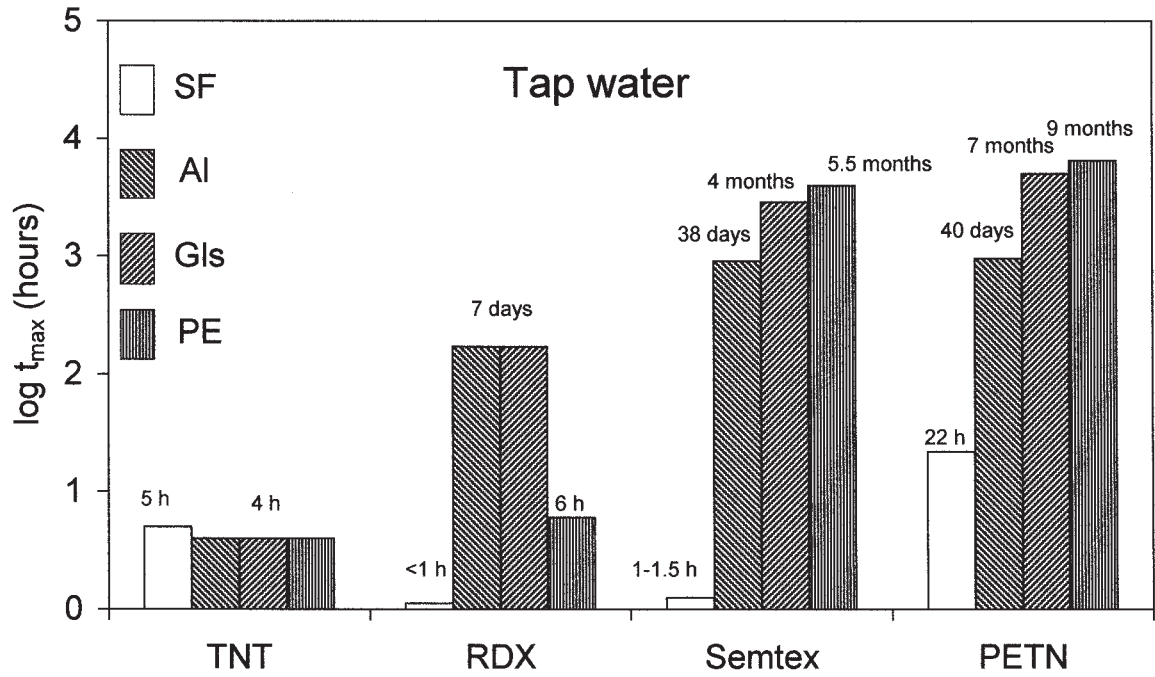


FIG. 1—Detectability of explosives after soaking in tap water as a function of the explosive type (SF - seat fabric, Al - aluminum, Gls - glass, PE - polyethylene).

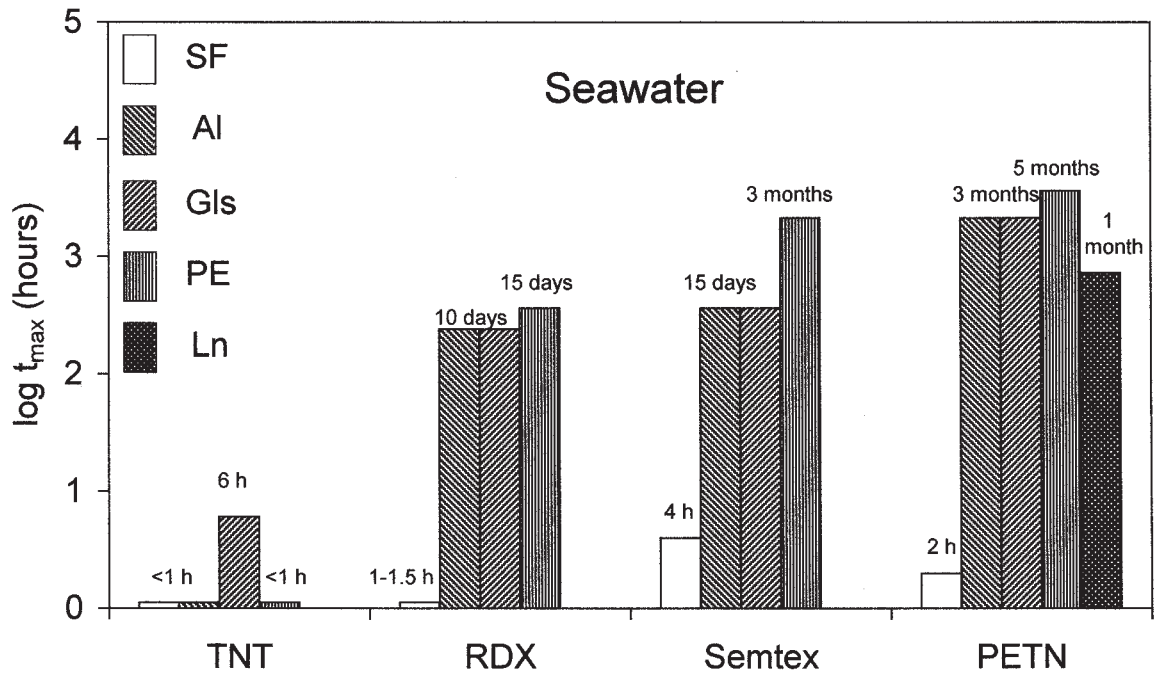


FIG. 2—Detectability of explosives after soaking in seawater as a function of the explosive type (SF - seat fabric, Al - aluminum, Gls - glass, PE - polyethylene, Ln - linoleum).

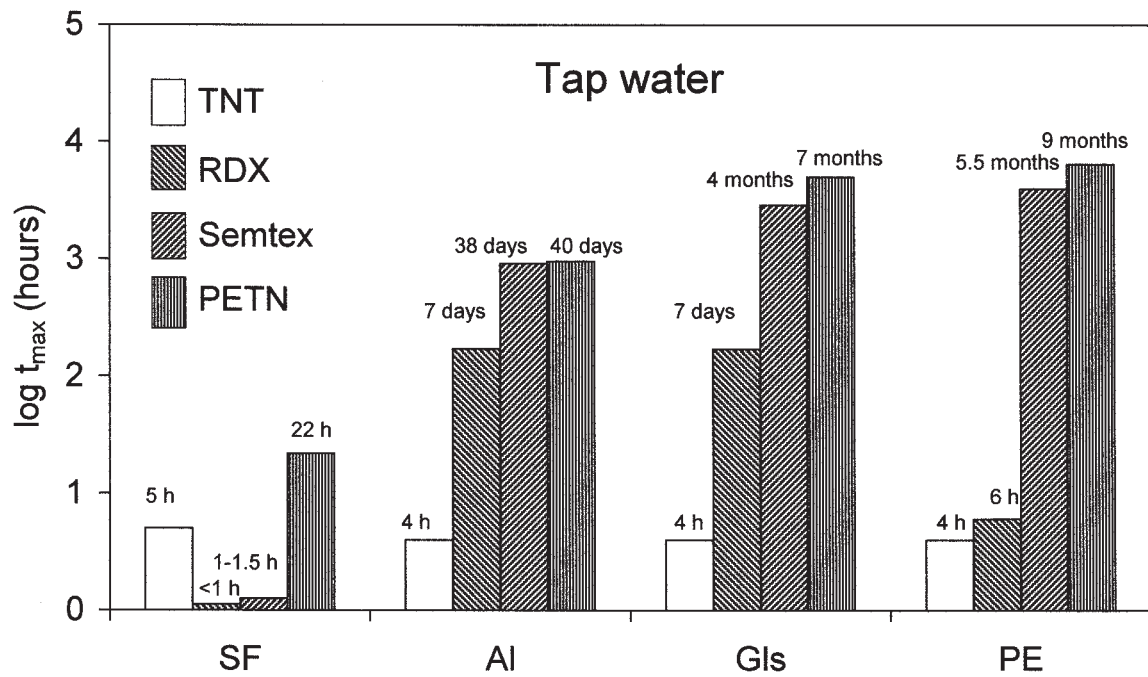


FIG. 3—Detectability of explosives after soaking in tap water as a function of the support (SF - seat fabric, Al - aluminum, Gls - glass, PE - polyethylene).

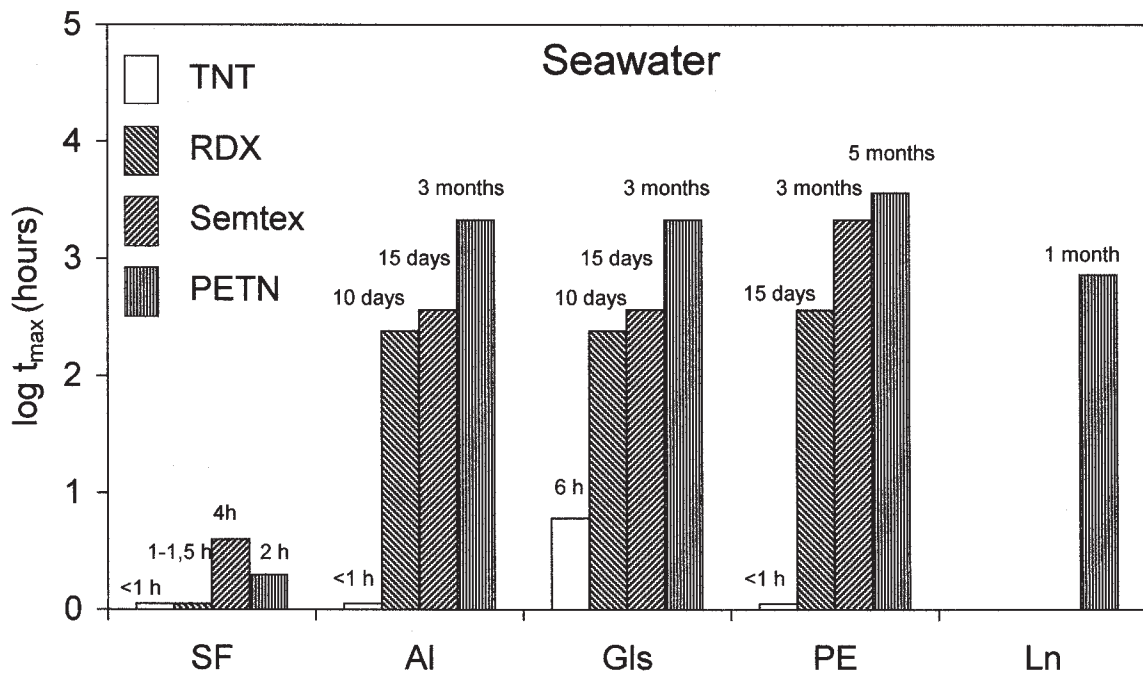


FIG. 4—Detectability of explosives after soaking in seawater as a function of the support (SF - seat fabric, Al - aluminum, Gls - glass, PE - polyethylene Ln - linoleum).

while on PE, it could be detected after 2 h (Fig. 5). Such disparity with the results of the static laboratory experiments might be explained by mechanical removal of the explosive traces by water movement in the sea.

Influence of Movement on Explosive Deposit Detectability

In order to evaluate the effect of movement, we studied its influence on the detectability of RDX and PETN deposited onto polyethylene and linoleum.

Water movement was found to decrease t_{max} for RDX on polyethylene in comparison to simple soaking (in our experiment, from 6 to 4 h). In spite of significant decrease in t_{max} for PETN

caused by movement, it could be detected on polyethylene and linoleum after 15 and 12 days, respectively (Fig. 6).

Discussion

The goal of this study was to gain some knowledge on the factors governing the disappearance of explosive traces from blown-up aircrafts that sink in the sea. The model chosen by us for this study is not very accurate, because it lacks the explosion factor. We assume, however, that for most analytical purposes, it does represent the actual situation, as it contains the main elements that play a role in the disappearance process, namely, the support materials (that are taken from an aircraft), the explosives, and the environ-

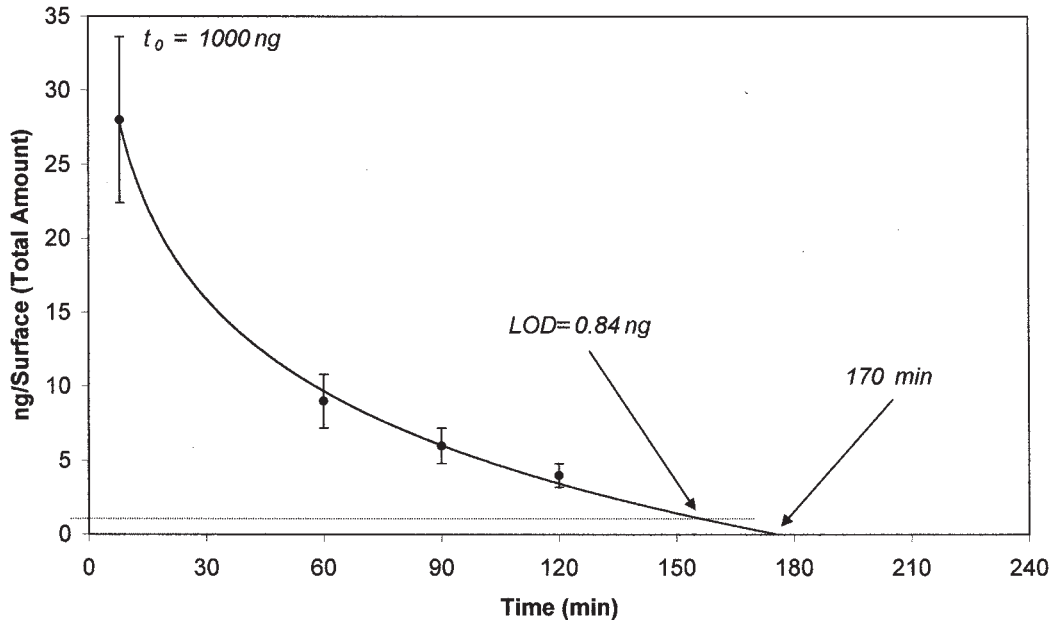


FIG. 5—Detectable amounts of RDX after immersion in the Mediterranean Sea as a function of immersion time.

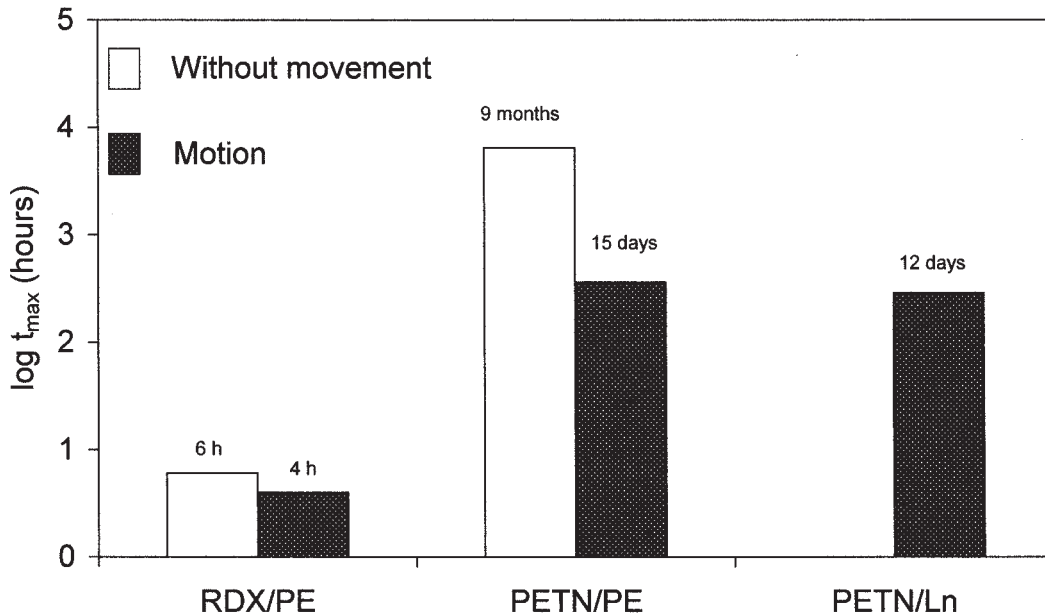


FIG. 6—Influence of longitudinal mechanical movement on explosive's deposit detectability in tap water (PE - polyethylene, Ln - linoleum).

ment. The main difference between our model and real situations is the extra clean-up step in the latter (14).

More specifically, this study provided semi-quantitative answers to the following questions:

1. Is it possible to detect explosive traces after immersion in water?
2. How long after the immersion can explosive traces still be found (t_{max})?
3. What is the connection between t_{max} and the type of explosive and support?
4. What is the effect of environmental factors (type of water, movement) on t_{max} ?

Explosive traces could be detected on various surfaces liable to be found in aircraft. In quiet water, traces of explosives could be detected even after extensive periods (up to three months for PETN-containing explosives). While polyethylene, linoleum, aluminum, and glass are surfaces that preserve the traces, the durability on seat fabric was considerably shorter. A plausible explanation for this difference could be the following: As opposed to the other surfaces, seat fabric is an absorbing material. In our experiment, the explosives have been applied in solution. Their molecules could, therefore, penetrate between the fibers and adhere to them, thus significantly increasing the area to which they are attached and hence, the susceptibility to water. Another probable explanation is that the explosive traces had to be extracted from the seat fabric prior to analysis, and the extraction factor could affect the detection efficiency.

As could be expected, a good correlation was found between the disappearance rate and the solubility of an explosive in water. For instance, the stability of the explosive deposits both in tap and seawater decreased, on the average, in the order PETN > Semtex > RDX > TNT (Figs. 1–4). The solubility of these explosives in water increases in the same order: PETN - $2 \cdot 10^{-4}$ %, RDX - 0.006%, TNT - 0.02%, Semtex is the mixture of PETN and RDX (9).

Immersion of samples with deposited explosives in the sea resulted in a drastic decrease in t_{max} . RDX deposited onto polyethylene pieces could be detected after 2 h of immersion in the sea, while the same explosive on Al surface could not be detected even after few minutes.

In order to understand the great difference in t_{max} between soaking in vials and immersion in the sea, we studied the influence of movement on the persistence of the explosive deposits. It was found that the longitudinal movement of polyethylene and linoleum pieces with deposited RDX and PETN in a shaker (60 strokes/min) caused a noticeable decrease in t_{max} . As in the case of quiet water, PETN showed the highest persistence (t_{max} = 12 days for linoleum and 15 days for polyethylene), while t_{max} for RDX on polyethylene was only 4 h (Fig. 6). The obvious conclusion is, that the best areas for searching explosive traces in the sea would be areas, which are less exposed to currents of water.

The t_{max} for RDX on polyethylene in a shaker is twice as long as t_{max} for RDX on the same support immersed in the sea. Therefore, other factors including the attack by marine life should be taken in account as well. For instance, the impossibility to detect RDX on Al even after a few minutes of immersion in the sea may be explained by strong corrosive action of seawater on such a reactive metallic substrate.

Conclusions

Under laboratory conditions, there is a reasonable prospect to detect explosive traces on aircraft parts after immersion in water for one to two weeks. Traces of PETN are consistently more persistent in water than the other explosives. If PETN is a part of the formulation, it may be possible to detect its traces even after a few months.

After immersion in the ocean, RDX residues last only minutes to hours, depending on the substrate. The main factors that govern the disappearance rate are the explosive type, the type of surface, and the immersion period. Water movement remarkably accelerates the disappearance of explosive traces. Items to be examined for explosive traces must be drawn out of the water as soon as possible.

References

1. Mullins J. Lost at sea. Seawater launders the evidence after a plane crash. *New Scientist* 1998;157:19.
2. Fox FT, Sisk S, DiBartolo R. Immersion studies of aircraft parts exposed to plastic explosives. Report (U.S. Department of Transportation. Federal Aviation Administration) 1998;13.
3. Yinon J, Zitrin S. Modern methods and applications in analysis of explosives. New York: John Wiley & Sons 1993;33–267.
4. Lewin U, Efer J, Engewald W. High-performance liquid chromatographic analysis with electrochemical detection for residues of explosives in water samples around a former ammunition plant. *J Chromatogr* 1996;730:161–7.
5. Welsch T, Block H. Separation and enrichment of traces of explosives and their by-products from water by multiple micro liquid extraction for their determination by capillary gas chromatography. *Fresenius J Anal Chem* 1997;357:904–8.
6. Proceedings of Workshop on explosives trace analysis methods. DERA, Fort Halstead, Sevenoaks, Kent, April 28–29, 1999. In: Science & Justice 1999;39:261–8.
7. Sigman ME, Ma C-Yu. In-injection port thermal desorption for explosives trace evidence analysis. *Anal Chem* 1999;71:4119–24.
8. Woltman SJ, Even WR, Sahlin E, Weber SG. Chromatographic detection of nitroaromatic and nitramine compounds by electrochemical reduction combined with photoluminescence following electron transfer. *Anal Chem* 2000;72:4928–33.
9. Donner DL, Shriver-Lake LC, McCollum A, Ligler FS. Transition from laboratory to on-site environmental monitoring of 2,4,6-trinitrotoluene using a portable fiber optic biosensor. In: Aga DS, Thurman EM, editors. Immunochemical technology for environmental applications. Washington, DC: American Chemical Society, Symposium Series 1997;657:198–209.
10. Bart JC, Judd LL, Hoffman KE, Wilkins AM, Charles PT, Kusterbeck AW. Detection and quantitation of the explosives 2,4,6-trinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine in groundwater using a continuous flow immunosensor. In: Aga DS, Thurman EM, editors. Immunochemical technology for environmental applications. Washington, DC: American Chemical Society, Symposium Series 1997;657:210–20.
11. Almog J, Kraus S, Glatstein B. ETK—an operational explosive testing kit. *J Energetic Mater* 1986;4:159–67.
12. Yinon J, Zitrin S. Modern methods and applications in analysis of explosives. New York: John Wiley & Sons 1993;1–32.
13. Advanced version of ETK, which detects also inorganic nitrates, chlorates and bromates, was developed by the Israel Institute for Biological Research: Margalit, Y. Kit for detecting explosives. US Patent 5,480,612 Jan. 2, 1996
14. Yinon J, Zitrin S. Modern methods and applications in analysis of explosives. New York: John Wiley & Sons 1993;170–90.

Additional information and reprint requests:

Joseph Almog, Ph.D.
Casali Institute of Applied Chemistry
The Hebrew University
Jerusalem, 91904, Israel