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ULTRAMICRO ANALYSIS OF EXPLOSIVES IN SEA WATER

By
John C. Hoffsommer
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12 AUGUST 1971

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NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MARYLAND

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ULTRAMICRO ANALYSIS OF EXPLOSIVES IN SEA WATER

The instrumentation and techniques described in this report have been used successfully to analyze sea water samples for explosive contaminants at concentration levels in the range of parts per trillion. The work was supported by Naval Ordnance Systems Command work request WR-1-6091.

ROBERT ENNIS
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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INTRODUCTION

For many years obsolete munitions have been disposed of by dumping in deep water. In 1963, the United States Navy initiated a program in which obsolete Maritime Administration hulks were used. These old liberty ships were loaded with munitions and scuttled at sea (1). Because of the possibility of pollution of sea water near these areas, sites were selected and sea water samples near these sites were analyzed for the presence of explosive contaminants.

Since TNT (2,4,6-trinitrotoluene), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and tetryl (methyl-2,4,6-trinitrophenylnitramine) were the most common and abundant types of explosives dumped, methods were developed using these compounds as standards. This report describes the methods employed for the analyses of TNT, RDX, and tetryl in the part per billion to part per trillion range (1×10^{-9} to 1×10^{-12} g/ml), and the results obtained.

SAMPLES

Sea water samples were collected from two locations, one in the Atlantic Ocean and one in the Pacific. Sea water samples were collected in both Niskin and Nansen bottles and stored in 1.5 pt Mason Jars for the first area and in 200 ml all-glass pyrex bottles for the second area. However, it should be immediately pointed out that storage of sea water samples in Mason Jars is definitely not advised because material extracted from rubber or plastic components during storage contaminate the samples. This aspect is covered more completely in the results and discussion section. Analyses were performed within two weeks after the samples were taken.

PROCEDURE

Approximately 100 ml of the sea water sample was poured into a clean, dry 200 ml separatory flask, and 5.00 microliters (µl) of an internal standard (8.12×10^{-10} g/µl of 1,2-dinitrobenzene in acetone) was added by means of a #701, 10 µl Hamilton syringe. Forty to fifty ml of benzene (MCB, specially purified for work with electron capture detectors) was then added to the separatory flask, the flask stoppered, and the contents shaken vigorously for 2 to 3 min. and allowed to stand 5 to 10 min. for layer separation. The bottom (extracted sea water) layer was discarded while the benzene extract was poured through the top of the separatory flask into a clean, dry, 100 ml, round-bottom, flask containing a small, clean boiling chip. The benzene was then completely removed under reduced pressure with a water aspirator and a flask temperature maintained between 30 and 35°C. To the dry flask was added 0.20 to 0.25 ml of pure benzene. The benzene was swirled lightly on the sides of the flask and allowed to drain into a small pool on the bottom.

VAPOR PHASE CHROMATOGRAPHIC ANALYSIS

In all work connected with the nickel-63 electron capture detector, extreme caution must be exercised to avoid contamination (2) and overloading of this very sensitive detector. As little as one microgram of TNT will desensitize the detector.

An 8.0 to 9.0 µl portion of this benzene solution containing the extract was injected into an F & M model 5754A research gas chromatograph, equipped with a model 5763A electron capture nickel-63 detector and pulser kit together with a model 7128A Mosely dual channel recorder. One to two µl of pure benzene solvent was used as a "back flush" for all samples and standards injected. "Back flush" was accomplished by drawing approximately 2 µl of pure benzene into a 10 µl syringe, followed by about 0.2 µl air, and finally by 8.0 to 9.0 µl of benzene extract.

Samples were chromatographed on a 4' X 1/4" glass column packed with 2.92% Dexsil 300 GC (polycarboranesiloxane stationary phase with an average molecular weight of 16,000 to 20,000) on Chromosorb WAWDMCS 80/100 mesh; isothermally, 165°C; injection port temperature, 200°C; nickel-63 detector temperature, 295°C; carrier gas, Ar/CH_4: 95/5, v/v; flow rate, 217 ml/min.; pulse interval, 150 µsec; chart speed, 1"/min; attenuation, 40. Chromatograms of the benzene sea water samples were compared with standard chromatograms containing known concentrations of TNT, RDX and tetryl with 1,2-dinitrobenzene as internal standard.

RESULTS AND DISCUSSION

Table 1 shows typical retention times and peak height responses for the vapor phase chromatographic separation of a standard mixture of TNT, RDX, and tetryl with 1,2-dinitrobenzene as internal standard. Calculation of the concentrations for TNT, RDX, and tetryl that may be present in the concentrated benzene extract of the sea water sample may be made by normalizing standard and sample peak heights for TNT, RDX, and tetryl with internal standard peak heights. Since the same aliquot of internal standard is put into both the standard mixture and the sea water sample, an expression for the concentration of TNT in sea water is given by:

Table 1

RETENTION TIMES AND PEAK HEIGHT RESPONSES FOR A MIXTURE OF TNT, RDX, TETRYL AND 1,2-DINITROBENZENE

Component of Mixture	Concentration 10^{-12} g/µl	Peak Height Response mm (a)	Retention Time min. (b)
1,2-dinitrobenzene (c)	4.06	24.8	1.10
TNT	10.3	27.5	2.55
RDX	31.9	18.5	6.70
Tetryl	140	24.5	15.9

(a) 8 to 9 µl injection at attenuation, 40.
(b) Measured from solvent pressure peak.
(c) Internal standard.

$$g_{TNT}/ml = \left[\left(V_{std}\right)/\left(V_{sea\ sample}\right)\right]\left[\left(h_{IS\ std}\right)/\left(h_{IS\,x}\right)\right]\left[\left(h_{TNT\,x}\right)/\left(h_{TNT\ std}\right)\right]\left(C_{TNT\ std}\right)$$

where V represents the volume for the vapor phase chromatographic standard (1.00 ml benzene), and the sea sample (100 ml); h, the chromatographic peak height maximum for the internal standard (IS), in both standard (std) and benzene extract (x), and also the peak heights of TNT in standard and sample extract; and C, the concentration of TNT in the chromatographic standard, expressed in grams per milliliter. Similar expressions involving $(C_{RDX})_{std}$ or $(C_{tetryl})_{std}$ may be used to calculate the concentrations of RDX and tetryl in sea water.

This procedure works well only in those cases where there are no interfering peaks with the 1,2-dinitrobenzene, internal standard. Sea samples stored in all-glass bottles with glass stoppers gave relatively clean vapor phase chromatograms with 4 to 5 peaks on the average. None of these peaks interfered with the peak for 1,2-dinitrobenzene, or peaks that would correspond to TNT, RDX or tetryl. On the other hand, the benzene extracts of sea water samples stored in glass Mason jars with screw caps containing rubber seals and plastic liners gave chromatograms containing anywhere from 10 to 15 peaks, some of which interfered with 1,2-dinitrobenzene. Presumably, various plasticizers from the rubber seals and plastic liners were leached out by the sea water (3). All-glass containers are obviously preferred.

The efficiency of the combined extraction and evaporation procedure for the determination of TNT, RDX or tetryl in sea water at levels of 103, 320, and 1,400 parts per trillion (10^{-12} g/ml sea water), respectively, has been found experimentally to be 70 ± 10%. Efficiency was not determined at other concentrations. Similar (70% efficiency) results were obtained when the internal standard was added after the extraction and concentration procedure. The limits of vapor phase chromatographic detection for TNT, RDX, and tetryl by the present method are estimated to be in the order of 2,5, and 20 parts per trillion, respectively.

WATER ANALYSIS

We were not able to observe any peaks on the chromatographic traces corresponding to TNT, RDX, and tetryl in any of the samples taken in either the Pacific or Atlantic ocean areas. By intentional, low-level introduction of TNT, RDX, and tetryl into sea water which was analyzed, we have estimated these materials may be detected at levels of 2,5 and 20 parts per trillion, respectively. If explosives were present in the sea water samples, they must be at concentrations below those stated above.

Samples from the Atlantic area were taken from five stations; at each station, a bottom sample was taken (average depth of 2660 meters) and a sample vertically above at levels of 40, 70, 200, 400 and 600 meters from the bottom. Only the bottom and the 40 meter level samples were analyzed. Other levels were sampled to attain a vertical distribution of the explosive contaminant, and were to be analyzed only if explosives were detected in the bottom area.

Samples from the Pacific area were taken at two stations. Only the two samples taken at the greatest depth (5 meters above the bottom) and the two corresponding samples taken 40 meters vertically above the bottom were analyzed. Other samples taken at 20 and 60 meters above the bottom from these two stations were not analyzed.

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