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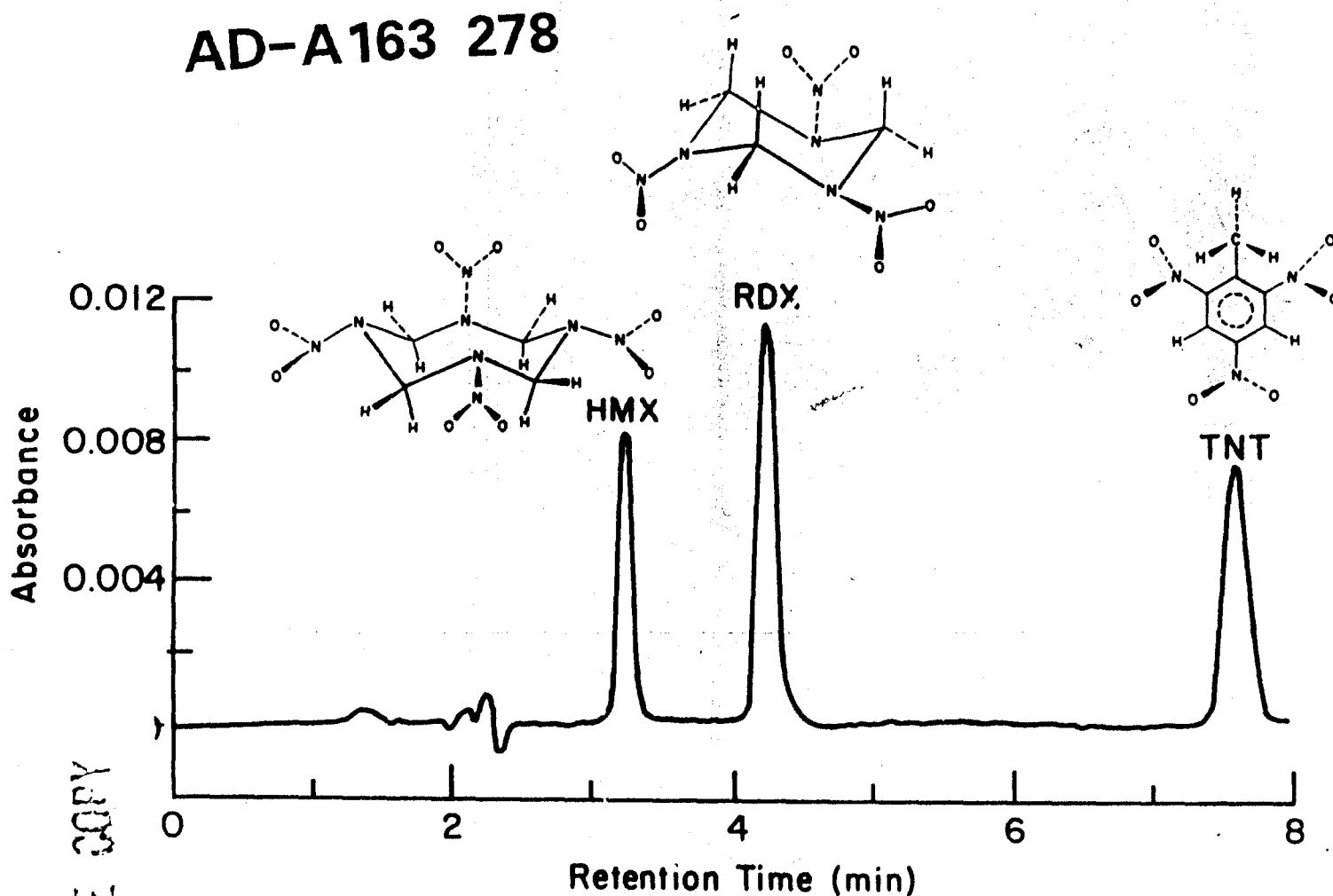
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TNT, RDX and HMX explosives in soils and sediments

Analysis techniques and drying losses

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Cover: Liquid chromatogram, using a 254-nm UV detector, of a mixed standard of TNT (336 $\mu\text{g/L}$), RDX (834 $\mu\text{g/L}$) and HMX (800 $\mu\text{g/L}$) in the ternary solvent system (50% H_2O /38% methanol/12% acetonitrile). A conformational drawing of each explosive molecule is shown above its chromatographic peak.

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TNT, RDX and HMX explosives in soils and sediments

Analysis techniques and drying losses

J.H. Cragin, D.C. Leggett, B.T. Foley and P.W. Schumacher

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Drying	HMX	Sorption												
Drying losses	RDX	TNT												
Explosives	Sediment	Volatilization												
Freeze drying														
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A method for the analysis of TNT, RDX and HMX explosives in soils and sediments has been developed. It consists of methanol extraction followed by reversed-phase high performance liquid chromatography using 10% acetonitrile/40% methanol/50% water as the eluant. This method was used to study the effect of various drying techniques upon the recovery of TNT, RDX and HMX from soil and sediment samples contaminated with high (%) and low (µg/g) levels of these explosives. For highly contaminated samples, complete recovery of TNT and RDX was obtained using freeze drying while air drying at room temperature resulted in greater than 90% recovery for both explosives. Other techniques, such														

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20. Abstract (cont'd)

as oven drying at 105°C, oven drying at 45°C, microwave oven drying, and drying under infrared lamps, all resulted in greater losses, with TNT and RDX recoveries ranging from 76 to 90%. Drying losses were not due to simple volatilization but rather to chemical reaction and/or sorption. For soil and sediment samples containing low levels of TNT, RDX and HMX, recoveries of all three explosives were quantitative for all of the above drying techniques.

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PREFACE

This report was prepared by J.H. Cragin, Research Chemist, Snow and Ice Branch, and D.C. Leggett, Research Chemist, B.T. Foley and P.W. Schumacher, Physical Science Technicians, Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Financial support for this work was provided by U.S. Army Toxic and Hazardous Materials Agency (USA THAMA) under project "R99-Analytical Systems Technology." This report was technically reviewed by T.F. Jenkins and Dr. J.L. Oliphant of CRREL, and by M.H. Stutz of USA THAMA.

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TNT, RDX AND HMX EXPLOSIVES IN SOILS AND SEDIMENTS

Analysis Techniques and Drying Losses

J.H. Cragin, D.C. Leggett, B.T. Foley
and P.W. Schumacher

INTRODUCTION

The Army has been disposing of expired munitions in appreciable quantities for the last 20 years. Most of this disposal involves direct combustion (detonation or incineration), which effectively removes these toxic explosives from the environment. However, a significant amount of wastewater (red and pink water) results from munitions manufacture and load-and-pack operations. This wastewater is stored in lagoons where the munitions concentrate by water evaporation and settle to the bottom, becoming incorporated into the sediments. The munitions can then migrate to the underlying groundwater and contaminate the surrounding soil. Two major objectives of the Army's Installation Restoration Program (Renard 1981) are cleanup of these contaminated soils and lagoons and protection of the surrounding land.

Support of this cleanup effort requires environmental monitoring of soil and lagoon sediment, which necessitates development of a fast and accurate analytical method. Accurate analysis of these samples also depends on sample collection and pretreatment. Since soil and sediment samples contain varying amounts of water, a common pre-analysis procedure is sample drying. Dry samples are easier to homogenize and results can be reported on the usual dry weight basis, but volatile organic compounds can be lost during the drying process. The objectives of this study were to develop an extraction and analysis procedure for the determination of TNT (2,4,6-trinitrotoluene), RDX (2,3,5-trinitro-1,3,5-triazine) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazine) in soils and sediments and to assess losses of these explosives for various drying techniques.

MATERIALS AND METHODS

Samples

Spiking and drying studies were first conducted with uncontaminated soil and sediment samples. The soil was a Charlton silty loam (0-15 cm) from the Connecticut River valley of New Hampshire. For standard addition recovery tests, we used two types of uncontaminated sediments: one from West Point Reservoir, Georgia, and the other from Kewaunee River Harbor of Lake Michigan. Relevant physical and chemical characteristics of these samples are given in Table 1. Of the two sediments, the West Point sample was coarse and sandy while the Kewaunee sample was fine textured and contained more organic matter. These samples were spiked with various amounts of TNT for the drying study.

A sludge sample taken from an old disposal lagoon at the Louisiana Army Ammunition Plant, in Shreveport, contained high levels of TNT and

Table 1. Physical and chemical characteristics of soil, sediment and sludge samples.

Sample	Moisture content (%) ^{a†}	Organic carbon (%) ^a	Fe (%) ^a
Charlton soil	2.5	1.8	1.4
West Point sediment	45.0	1.6	5.1
Kewaunee sediment	59.0	4.1	—
Louisiana Lagoon sludge	94.0	—	—

^a Percentages are on a dry weight basis.

[†] All reported moisture contents and dry weights were determined by drying samples overnight in an oven at 105 °C.

Table 2. Soil and sediment samples containing low ($\mu\text{g/g}$) concentrations of explosives.

Sample	Location and type	Moisture content (%)	Preliminary concentration ($\mu\text{g/g}$)		
			TNT	RDX	HMX
1	Louisiana sediment A, pond 9	24	1800	1000	300
2	Louisiana sediment B, pond 9	25	15	700	150
3	Louisiana soil, adjacent to pond 9	23	200	200	14
4	Milan soil A, O-Line pond	22	< 1	< 1	< 1
5	Milan soil B, O-Line pond	—	< 1	< 1	< 1
6	Milan soil C, O-Line pond	14	< 1	< 1	< 1
7	Milan soil A, burning area, 0–10 cm	4.5	10	200	100
8	Milan soil B, burning area, 0–10 cm	8.9	20	3000	1000
9	Milan soil A, burning area, 10–15 cm	24	10	100	30
10	Milan soil B, burning area, 10–15 cm	22	50	500	50

RDX. These high levels of TNT and RDX prompted us to collect a second set of 10 samples containing lower concentrations of explosives to bracket the range of contaminants found in the environment. These samples, including sediments A and B, were collected from both the Louisiana Army Ammunition Plant and the Milan Army Ammunition Plant (Table 2). Although taken from the same lagoon (pond 9) as the highly contaminated sludge sample, sediment samples A and B were deeper fine clay deposits, consisting of the original site material that had been contaminated with explosives by percolating pond water. The lagoon sludge sample consisted primarily of highly organic surface sediments and explosives that had precipitated since the lagoon was constructed. The Milan samples were all sandy or loamy soils collected either adjacent to a settling lagoon (O-Line Pond) or in an area where explosives were disposed of by open-air burning.

The moisture contents (Table 2) of the low-level samples range from 4.5 to 25%. The agreement between duplicates from the same areas is good except for the Milan soil from the top 10 cm of the burning area. This variability may be due to the low absolute amount of moisture present in these two samples.

Sample preparation and extraction

All laboratory glassware used to contain, dry, or extract samples was first cleaned by thoroughly rinsing with Resi-Analyzed acetone (Baker). Because of the different types of samples and their varying moisture and organic matter contents, preparative techniques were not identical for all samples. The basic method involved solvent extraction of explosives from the soil or sediment sample and subsequent measurements by gas chro-

matography (GC) or high performance liquid chromatography (HPLC). Initially acetone was used as the extracting solvent for the samples shown in Table 1. Extractions on samples with low explosive levels (Table 2) were performed using methanol. Specific procedures for each of the different samples are given below.

1. *Charlton soil.* For the TNT loss studies a 1.03-g wet sample (equivalent to 1.00 g dry weight) was weighed into a 20-mL glass scintillation vial and spiked with the appropriate amount of TNT to give 0, 1, 5, 10, 50, or 100 μg TNT/g dry sample. Samples were mixed with a stainless steel spatula and allowed to sit for time periods of 0, 1, 2 or 7 days. The zero time sample was extracted immediately after spiking. Extraction was done by adding 15.0 mL Resi-Analyzed acetone (Baker), shaking the mixture for 1 hr on a wrist-action shaker, decanting and diluting the solution before analysis by GC. Blank (unspiked) samples for each storage time were treated similarly. Duplicate samples were prepared and analyzed for each TNT concentration and storage time.

2. *West Point sediment.* One of the first experimental undertakings was checking the recovery of TNT from dried samples. Sediments from West Point reservoir were used for this purpose since they were sandy and had low organic matter content. One-gram dried samples were spiked with 0, 0.5, 1.0, 2.0, 5.0, and 10.0 μg of TNT (in acetone) and 20.0 mL of acetone was added. The suspension was shaken briefly, allowed to sit for 1 hr and then extracted as described above. A similar extraction was also carried out using Baker Resi-Analyzed hexane instead of acetone.

3. *Kewaunee sediment.* For the TNT loss studies the Kewaunee sediments were treated in a manner similar to that used for the Charlton soil. Because

of its higher moisture content (59 vs 2.5% for the soil), a larger wet sample (2.41 g) was needed for a 1.00-g equivalent dry weight.

4. *Louisiana lagoon sludge.* This sample (94% moisture content) was homogenized by vigorous shaking for 5 minutes. Individual subsamples of 1.30-g wet weight (0.67-g dry weight) were taken from this slurry for drying and analysis. The high TNT concentration present required the use of a greater amount (60 mL) of acetone per sample for extraction. Multiple 60-mL extractions recovered little additional TNT, indicating that one extraction was sufficient. Extraction using 60 mL of acetone and twice as much sludge (2.60-g wet weight) also gave complete recovery.

5. *Moderately contaminated samples.* The samples containing low levels of explosives (Table 2) were treated quite similarly. Initial extractions used methanol and 0.6 g (wet weight) of sample. Although recoveries of TNT, RDX and HMX were all greater than 80%, it was not possible to claim complete recovery because of the poor analytical precision ($\pm 13\%$ rsd). To improve precision a larger sample (4.00-g dry weight) was extracted with 60 mL of HPLC grade methanol. Extraction involved ultrasonically agitating the samples in methanol for 30 min., allowing the suspension to settle, and then centrifuging a 5-mL aliquot at 7500 rpm for 1 hr. The supernatant was analyzed directly by HPLC.

Part of the analytical imprecision for these low-level samples was due to sample inhomogeneity, especially for the Louisiana sediment samples. These sediments were composed of a very fine sticky clay that was difficult to disaggregate and mix when wet. Several attempts were made to homogenize the wet sediment by either mixing with a spatula or by rolling in a jar mill, but none proved completely satisfactory because of the sediment's cohesive nature. Dried samples were much easier to homogenize. Soil and sediment samples are notoriously inhomogeneous for trace constituents, and sample drying greatly simplified the homogenization process. Consequently, for the low-level analyses, 30-g samples were first dried and then homogenized by rolling and shaking in a glass container. Multiple 4.00-g subsamples were then extracted as described above.

Analytical techniques

When the drying study was started, a validated literature method for analysis of TNT, RDX, or HMX in soils and sediments was not available. Consequently, an analytical technique had to be developed. Initial analyses were done using GC,

which worked well for TNT in the soil samples. However, the high organic matter content of the sediment and Louisiana lagoon sludge samples caused interference for both TNT and RDX, so that later analyses were done using HPLC.

Gas chromatographic analyses for TNT were conducted on a Perkin-Elmer Sigma 3 gas chromatograph. Specific analytical conditions were 10% Dexsil 300 on Analabs ABS 100/120 mesh; column temperature 220°C; column length 1.8 m; injector temperature 190°C, electron capture detector (^{63}Ni) at 190°C with standing current of 2 nanoamps, and 25 mL/min of 5% methane in argon carrier gas. Under these conditions the response for TNT was 7.8×10^{11} mV s g $^{-1}$.

For HPLC analyses, a Perkin-Elmer LC-65T detector was used in combination with a Perkin-Elmer Series 3-pump system. The variable wavelength UV detector was set at 230 nm for best overall sensitivity. Initially a silica gel column was used for the separation with 0.5% isopropanol/hexane eluant, but this required a time-consuming solvent exchange with hexane using Kuderna-Danish evaporators. Later a 5- μm C8 (Supelco) reversed-phase column (250- $\times$ 4.6-mm o.d.) was used for high level analyses with either 35% isopropanol/water or 60% methanol/water as the mobile phase at a flow rate of 1.3 mL/min. This permitted direct injection of the acetone extracts. For low level analyses an HPLC solvent system of 50% H $_2$ O/40% methanol/10% acetonitrile gave the best separation of TNT, RDX and HMX.

Sample drying

Drying tests were conducted on the highly contaminated Louisiana lagoon sludge, and on a low level Louisiana sediment and a Milan soil sample. Samples were dried in cleaned glass containers (petri dishes, beakers or scintillation vials) which presented a large open surface area to speed the drying process. Six different drying methods were employed: air drying at room temperature, oven drying at 45°C, oven drying at 105°C, drying in a microwave oven, infrared drying using IR lamps, and freeze drying. Oven drying was done in a Precision mechanical convection oven for various lengths of time until the sample was dry; this required 30 min at 105°C, 5.5 hr at 45°C and 6 hr at room temperature ($\approx 25^\circ\text{C}$). Microwave oven drying (≈ 20 min) and infrared drying (40 min) were done at low power settings to eliminate boiling or spattering and to prevent localized hot spots. For freeze-drying, the samples were frozen overnight and then the water vapor was removed over a 2-hr period by sublimation under vacuum

using a Virtis model 10-147BR freeze dryer. The different drying methods gave very consistent results: final dry weights of 36 subsamples of Louisiana lagoon sludge dried by the above methods were all between 0.66 and 0.72 g.

The above oven-drying periods are shorter than the customary method of heating the samples at 105°C overnight or for 24 hours because we did not want to volatilize excess organics from the sludge and mistakenly attribute the weight loss to water. The rate of weight loss was much slower at 105°C after the initial 30 minutes, suggesting that the subsequent slower loss may be due volatilization of organics or higher-order (more strongly bound) water.

RESULTS AND DISCUSSION

Analytical method development

In developing an analytical technique, TNT was used because it was the expected predominant explosive in soils and sediment. The first test was to determine if GC, which showed a linear response to TNT standards, could be used to reliably measure TNT extracted from dried sediments. Dried West Point sediment samples were spiked with TNT and extracted with acetone (selected because of its high solvating ability for TNT) or with hexane. Recoveries were complete with acetone (Table 3) but poor with hexane. So acetone was used for all subsequent GC extractions. This test also showed that spiked TNT can be quantitatively recovered from dried sediments.

The next step was to determine effectiveness of the extraction technique for wet samples. Since preliminary extractions on spiked Kewaunee sediments gave low recoveries, we decided to determine how recovery varied with storage time. Samples of wet (2.5% moisture content) Charlton soil and wet (59% moisture content) Kewaunee sedi-

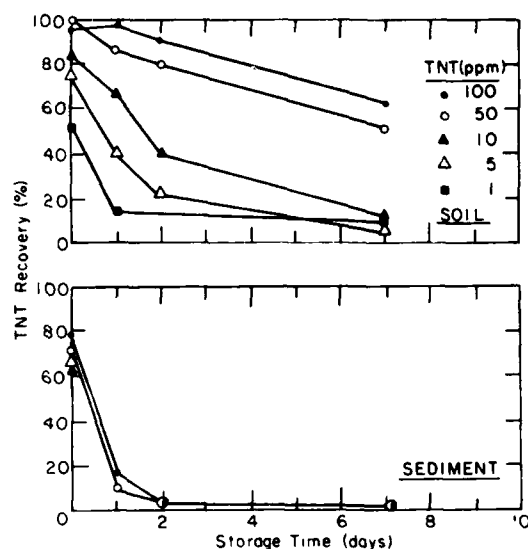


Figure 1. Time variation of recoveries of TNT from spiked Charlton soil and Kewanee sediment samples.

ment were spiked with various amounts of TNT and allowed to sit for up to 7 days before extraction. The decrease in extraction efficiency with time is shown in Figure 1. For the soil samples, recoveries decreased appreciably with time, being 50 to 60% for the 50- and 100- g TNT/g spikes and less than 20% for the 1-, 5-, and 10- μ g TNT/g spikes after 7 days. Recoveries for the spiked sediment samples dropped even more markedly than those for the soil samples, with less than 5% of all spikes recoverable after 2 days. For both soils and sediments, the percentage recovery was lower for lower level spikes. The sediment sample, with its greater surface area per unit weight and its higher organic carbon content, lost TNT at a much faster rate than did the soil. Similar losses have been obtained in sorption studies where TNT in water was equilibrated with sediment (Sikka et al. 1980, Spanggard et al. 1980). The above findings imply that analyses of samples for native TNT probably err on the low side once TNT has been in contact with soil or sediment for some length of time.

Some difficulty was experienced with GC analysis of TNT in sediments. Reproducibility was poor for the lower concentrations, which we believe to be caused by interference from other organic compounds extracted from the sediments. These compounds sorb on the GC column and may interact with TNT in subsequent analyses, preventing normal TNT elution.

Because of these interferences with GC, an analysis technique with HPLC was next investigated.

Table 3. Recovery of 2,4,6-TNT from dry sediment.

TNT added (μ g)	Conc. TNT in sediment (ppm)	TNT found (μ g)	Recovery (%)
0.00	0.00	0.00	—
0.50	0.50	0.75	150
1.00	1.00	1.17	117
2.00	2.00	2.37	118
5.00	5.00	4.86	97
10.00	10.00	10.52	105

Using standards of TNT in hexane, we found that TNT could be successfully eluted from a silica gel column with 0.5% isopropanol in hexane. However, direct injection of TNT in acetone did not give good separation, probably because of the high polarity of the acetone relative to the eluting solvent. Other solvents, such as acetonitrile, methylene chloride, or isopropanol, gave similar results.

So the best TNT-extracting solvent, acetone, could not be analyzed directly on the LC, while the desired analytical solvent, hexane, did not extract TNT efficiently. This dilemma was resolved by conducting a solvent exchange of acetone with hexane using Kuderna-Danish evaporators. Samples (in hexane) were then filtered and dried with anhydrous Na_2SO_4 and dinitrotoluene (DNT) added as an internal standard. Samples analyzed by this HPLC technique agreed well (within 10%) with previous GC analyses.

Although the above acetone-extraction, solvent-exchange procedure worked well for TNT analysis, it was fairly time consuming. A more rapid method was attempted using reversed-phase HPLC, in which the mobile eluting phase is more polar than the stationary adsorbent column material. A C8 column was used, and after some experimentation, we found that an eluant of 35% isopropanol/water gave good separation of TNT, RDX, and HMX for the contaminated sludge sample (HMX appeared as a shoulder on the side of a peak from an unidentified compound). An eluant of 60% methanol/water gave similar results and was also used.

This method worked very well and was used for all subsequent sludge analyses. It eliminates the lengthy solvent exchange, filtering, and drying steps and permits direct analysis of the acetone extracts. Most importantly, the reversed-phase HPLC method allows wet samples to be analyzed without the need for initial sample drying. This was especially advantageous for the sludge drying studies because analysis of an undried sample gave a baseline against which to evaluate losses of the explosives resulting from various drying techniques.

Drying of highly contaminated samples

The contaminated Louisiana lagoon sludge sample was used for drying tests because it contained a known, stable (with time) amount of TNT. The other uncontaminated soil and sediment samples were not suitable for this purpose because TNT recovery decreased with time after they were spiked, as discussed previously. With

the other samples, it would have been difficult to distinguish between losses of TNT caused by sample drying and those due to sorption.

Recoveries of TNT and RDX for the six drying methods are shown in Figures 2 and 3 for the highly contaminated Louisiana sludge sample. Drying techniques are plotted on the abscissa in order of decreasing recovery, with the average recovery for the undried (wet) samples set equal to 100%. Thirteen TNT analyses of this wet sample over a time period of several weeks showed that it contained $15.2 \pm 1.0\%$ TNT and $8.6 \pm 0.8\%$ RDX on a dry weight basis. Recoveries for both explosives were essentially complete for freeze drying. For the other drying methods, recoveries were inversely related to the drying temperature. TNT recoveries show this relationship rather clearly with recoveries decreasing in the following order: air drying > oven drying at 45°C = microwave oven drying

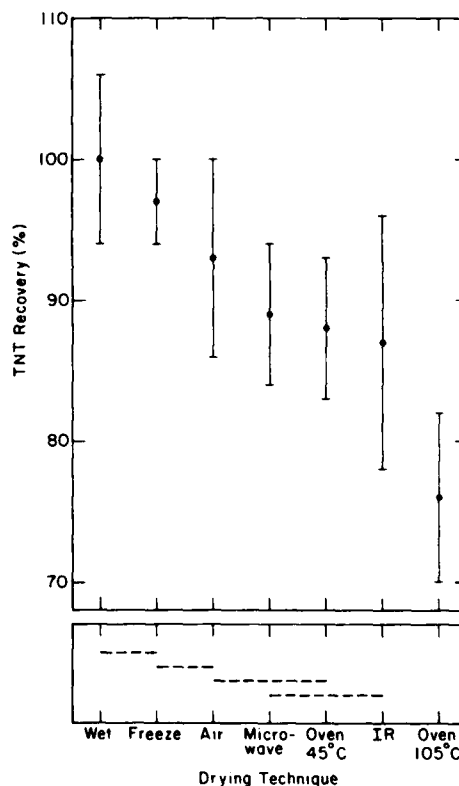


Figure 2. Drying losses of TNT from Louisiana lagoon sludge. Recoveries are given as a percentage of the recovery from undried samples. Lower section of figure shows results of Duncan's multiple range test (see text). Dashed lines connect drying techniques whose recovery differences are statistically not significant.

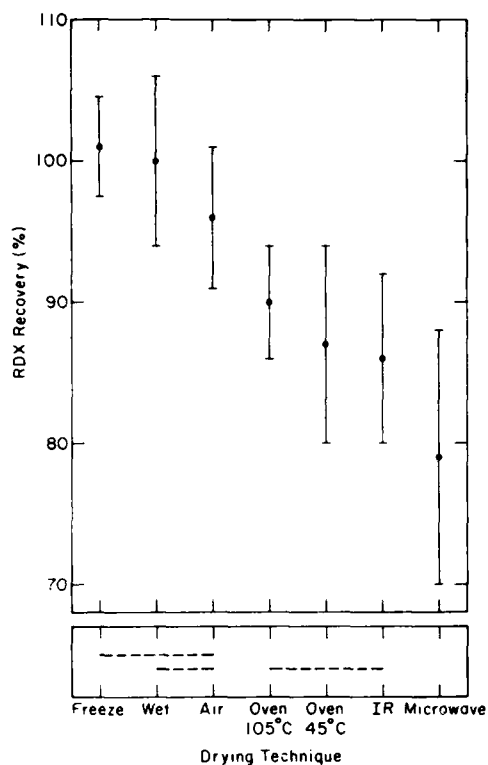


Figure 3. Drying losses of RDX from Louisiana lagoon sludge. Recoveries are given as a percentage of the recovery from undried samples. Lower section of figure shows results of Duncan's multiple range test (see text). Dashed lines connect drying techniques whose recovery differences are statistically not significant.

= drying under infrared lamps > oven drying at 105°C. Oven drying at 45°C, microwave oven drying, and drying under infrared lamps gave similar recoveries for TNT. Of these three methods, oven drying is preferable because all samples are heated to the same temperature and drying can be unattended; microwave oven drying and IR lamp drying required constant attention to prevent overheating. In addition, the energy density is not uniform within the microwave oven so that some samples dry faster than others when several are dried simultaneously. This lack of uniform temperature control may be responsible for greater variability in recovery for TNT in the IR and microwave-dried samples. Poor temperature control may also have caused the low RDX recovery for the microwave-dried sample.

An analysis of variance of the raw TNT and RDX data indicated that recovery differences due to drying technique were significant for both explosives at the 95% confidence level relative to the

sampling analysis error. Calculated F values resulting from the analysis of variance show only that the mean explosive recovery of one or more drying techniques is significantly different from others; the analysis of variance does not give any indication of which drying techniques differ from which. In order to determine which mean recovery values are significantly different we used Duncan's multiple-range test. This test involves comparison of the shortest significant differences, D , for all possible explosive recovery means when they are arrayed according to their magnitude (lowest to highest). The value for D is calculated $D = R$ (LSD). R ranges between 1.0 and 1.3 depending upon the number of degrees of freedom for error, the level of significance (95% in this case) and the position of the mean in the array; LSD, the least significant difference, is equal to $t(2 s^2/r)^{1/2}$ where s^2 is the mean square for error, r is the number of replications and t is the "Student's" t statistic.

Results of Duncan's multiple-range test comparing each individual drying technique with other techniques are shown as horizontal dashed lines in the lower portion of Figures 2 and 3. A line between two or more drying techniques means that differences in recoveries by these techniques were not significant at the 95% level. For example, for TNT (Fig. 2) the recovery after freeze drying was not statistically different from that of the wet sample. Recoveries after air drying, although significantly different from those for the wet sample, were not significantly different from those for freeze drying. Similarly, TNT recoveries after microwave oven drying, oven drying at 45°C and drying under infrared lamps can be grouped as having no statistically significant differences in TNT recovery. Oven drying at 105°C, which gave the lowest TNT recovery, was significantly different from all other drying techniques.

RDX recoveries (Fig. 3), although similar to those for TNT, do not follow exactly the same trend with drying technique. There was no significant difference between recoveries of the freeze-dried, air-dried and wet samples. The slightly higher recovery for the freeze-dried samples than for the wet reference samples is not statistically significant and is probably due to random error. Oven drying at both 45° and 105°C and drying under infrared lamps gave significantly lower recoveries than freeze- and air-drying. Microwave oven drying gave the lowest and most variable recovery of RDX of all drying techniques.

An interesting feature shown in Figures 1 and 2 is the relatively good precision of recoveries obtained after freeze drying. Standard deviations are

the lowest of any drying technique and are even lower than those of the wet samples. Thus, in addition to giving complete recovery, freeze drying actually improves analysis precision.

Solvent extraction

An important part of the analysis procedure is the extraction of explosives from the soil or sediment. One problem encountered with HPLC analyses of acetone extracts was that the solvent obscured the HMX peak and sometimes overlapped the RDX peak. Therefore, several other solvents were compared as possible substitutes for acetone. Extraction solvents selected were methanol, acetonitrile and tetrahydrofuran (THF), which are also commonly used as HPLC eluants. Two samples were used for extraction: a sediment (Louisiana sediment A) containing high $\mu\text{g/g}$ concentrations of explosives and a soil (Louisiana soil next to pond 9) containing low $\mu\text{g/g}$ explosive levels. Table 4 shows the amount of TNT, RDX and HMX in these samples based on single extractions with each solvent.

Results of Duncan's multiple-range test are shown in this table as lower-case letters appearing after the recovery concentration for each solvent. For a given sample and explosive, solvents with similar postscript letters had recoveries that were not statistically different. As an example, for TNT extracted from Louisiana sediment A, acetone was significantly superior to the other three solvents which, in turn, were statistically indistinguishable in their extraction efficiencies. For TNT and RDX in both samples, acetone was generally the super-

ior extracting solvent but its superiority was not always statistically significant. Of the other three solvents, methanol was superior in extracting TNT from the Louisiana soil while tetrahydrofuran was better in extracting RDX from the Louisiana sediment. None of the solvents showed significant differences in extracting RDX or HMX from the Louisiana soil sample. Thus, although methanol and tetrahydrofuran performed about equally well overall, methanol was selected for all future extractions because of its lower toxicity.

The values given in Table 4 are listed as relative concentrations because they are based on single extractions. Tests showed that a single 60-mL extraction did not quantitatively remove explosives from the low-level samples, as it did for the highly contaminated Louisiana lagoon sludge sample. A second extraction was then performed to calculate the extraction efficiency for methanol. If we let:

- W_1 = weight of initial sample used for 1st extraction
- M_1 = weight of explosive in initial sample
- W_2 = weight of sample used for 2nd extraction
- M_2 = weight of explosive from 1st extraction
- M_3 = weight of explosive from 2nd extraction
- R = fraction recovered,

then

$$\frac{M_1}{W_1} \cdot R = \frac{M_2}{W_2} \quad (1)$$

Table 4. Comparison of solvent efficiencies for extraction of TNT, RDX and HMX from sediment and soil samples. Different lower case letters after concentrations within columns for each sample designate concentrations that are significantly (85%) different (see text.)

Sample	Solvent	Relative concentration* ($\mu\text{g/g}$ dry weight)		
		TNT	RDX	HMX
Louisiana sediment A	Acetone	370 $\pm$ 100 a	1350 $\pm$ 160 a	†
	Methanol	2910 $\pm$ 200 b	1080 $\pm$ 60 b	**
	Acetonitrile	2640 $\pm$ 300 b	1180 $\pm$ 50 b	360 $\pm$ 10 a
	Tetrahydrofuran	2670 $\pm$ 150 b	1400 $\pm$ 70 a	470 $\pm$ 30 b
Louisiana soil next to pond 9	Acetone	59 $\pm$ 7 ab	74 $\pm$ 12 a	†
	Methanol	62 $\pm$ 11 a	72 $\pm$ 8 a	21 $\pm$ 2 a
	Acetonitrile	49 $\pm$ 3 bc	79 $\pm$ 3 a	22 $\pm$ 5 a
	Tetrahydrofuran	39 $\pm$ 2 c	75 $\pm$ 3 a	**

* Precision listed represents the total instrumental and extraction variability for triplicate determinations of each of three extracts.

† Extraction solvent masked the HMX chromatographic peak.

** Insufficient sample for analysis.

Table 5. Drying recoveries of TNT, RDX and HMX from sediment and soil samples containing low ($\mu\text{g/g}$) concentrations of explosives.

Drying method	Louisiana sediment recovery (%)			Milan soil recovery (%)		
	TNT	RDX	HMX	TNT	RDX	HMX
Freeze dryer	97	99	99	98	104	104
Air at 25 °C	103	91*	92*	101	99	104
Desiccator	100	101	98	101	104	103
Oven at 105 °C, 1 hr	95	98	112*	102	102	103
Oven at 105 °C, overnight	89*	60*	111*	93*	62*	103
Explosive concentration ($\mu\text{g/g}$ dry weight)	1460	1070	340	50	6600	910

* Denotes recovery difference that was statistically significant.

$$(1 - R) \cdot R \cdot \frac{M_1}{W_1} = \frac{M_2}{W_2} \quad (2)$$

Dividing eq 2 by 1

$$1 - R = \frac{M_2/W_2}{M_1/W_1} \quad (3)$$

or

$$R = 1 - \frac{M_2/W_2}{M_1/W_1} \quad (4)$$

Since W_1 , W_2 , M_2 and M_1 are all known quantities, the percentage recovery, $100R$, or extraction efficiency, can be calculated from eq 4. Extraction efficiencies for the low level Louisiana sediment and soil samples were near 100% for TNT but only 50% for RDX and 58% for HMX. Extraction efficiencies were essentially the same for all wet and dried samples and for samples of different explosive concentrations. Using the above extraction efficiencies, we found the explosive concentration in the original sample with eq 1. Recoveries reported in Table 5 are based on actual concentrations in the original samples.

Drying of low level samples

Before drying, all 10 wet samples containing expected low concentrations of explosives were analyzed using acetone extraction and 60% methanol/water as the HPLC eluant. Samples were not homogenized and the resulting preliminary concentrations, given in Table 2, are thus approximate values (within a factor of two). But Table 2 does permit a rough comparison of the levels of explosives present in these samples. The three Milan soil samples adjacent to O-Line Pond clearly contain

negligible amounts ($< 1 \mu\text{g/g}$) of explosives and thus are not suitable for studying drying losses. Of the six remaining samples, two were selected for drying: Louisiana sediment A from pond 9 and Milan soil B from the burning area. These two samples have very different physical characteristics: the sediment is a wet, fine, high-consistency clay and the soil is relatively dry and sandy. They cover the low end of explosive concentrations from about $20 \mu\text{g/g}$ to about 0.3% but still have enough explosive present to permit reliable detection after drying losses.

Drying techniques used for these two low-level samples were similar to those for the highly contaminated Louisiana lagoon sludge sample. Because of the poor recovery and precision observed for the Louisiana lagoon sludge, microwave oven drying and infrared lamp drying were not used. Also the marginally successful method of oven drying at 45°C was replaced with drying at room temperature in a desiccator. This method was tried as a possibly speedier alternative to air drying.

Drying recoveries for the low-level samples are shown in Table 5. Values with asterisks were found to be statistically different at the 95% level using Duncan's multiple range test. Reasons are not known for the high recovery (112%) of HMX after oven drying at 105°C for 1 hr or for the low recoveries of RDX and HMX after air drying. No other drying techniques resulted in statistically significant losses except oven drying overnight. Weight measurements after oven drying for periods of $\frac{1}{2}$, 1, 2, 4, 24 and 48 hr showed that the samples were essentially dry with no further weight loss after 1 hr. Thus, heating at 105°C overnight, although a commonly used drying technique, is not only unnecessary but detrimental for samples containing low levels of explosives.

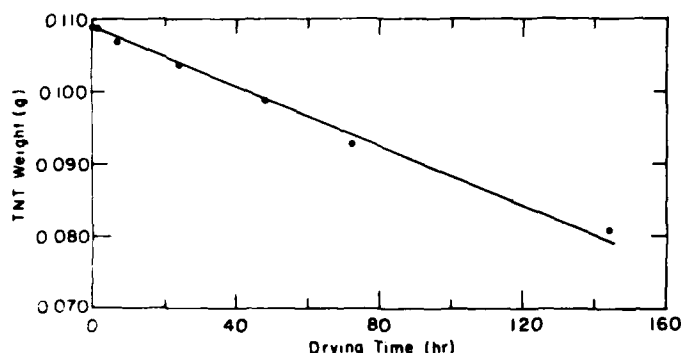


Figure 4. TNT volatilization loss in oven at 105°C. Initial sample weight was 0.1092 g.

The question of the mechanism of explosive loss during drying was next addressed. Initially, the loss was attributed to simple volatilization but calculations suggested that the vapor pressure of TNT was too low to account for the observed loss. To verify this, an amount (0.109 g) of pure TNT equivalent to that in the sample was heated in an oven at 105°C (Fig. 4). No measurable loss occurred in 30 minutes, the time used to dry the sludge sample. Almost six days (144 hr) of heating at 105°C was required to volatilize as much TNT (= 30 mg) as the sludge sample lost in 30 minutes.

Since we felt that the above drying test may not have been an adequate simulation of sediment drying because pure TNT melts at this temperature, drastically reducing the surface area available for volatilization, we performed an additional experiment in which an equivalent amount of TNT was mixed with 30–70 mesh silica gel and placed in an oven at 105° for 4 hr. Negligible weight loss occurred after correction for moisture. However, when the silica gel was removed from the oven and extracted with methanol only 129 mg, or 86%, of the 150 mg added initially was recovered. The methanol solution had a brown color, but no additional peaks for degradation products were observed in the HPLC chromatogram. A second methanol extraction recovered no additional TNT, but revealed that the silica gel retained a brown coloration, indicating a sorbed component.

Clearly volatilization was not responsible for the TNT loss observed during sludge drying. Biological degradation can be ruled out because of the drying temperature (105°C). Neither does simple degradation appear to be responsible for TNT or RDX loss since no breakdown products were observed in the chromatograms for the sludge sample or the silica gel. The above suggests that loss

during drying is caused either by chemical reaction or by irreversible sorption of explosives and/or degradation products onto the sample. Irreversible losses of TNT have been found to occur in the presence of wet sediments (Sikka et al. 1980, Spanggord et al. 1980) and clay minerals (Leggett and Foley, in prep.). These losses could only be partially attributed to biotransformation (Spanggord et al. 1980), and chemical reaction with the sediment has been suggested as another loss mechanism (Sikka et al. 1980).

Chemical reaction could also be responsible for the losses of explosives that we observed after spiking and drying. Higher drying temperatures would increase losses because of increased rates of chemical reaction. Removal of tightly bound water may also have activated potentially reactive sites within the sediments, causing additional loss. The complete recoveries observed after freeze drying may be the result of the low temperature, but probably more important is the immobilization that results from not having liquid water present as a reaction medium during drying. Once frozen, molecules are locked within the sample matrix and remain fixed during dehydration, unable to react. Thus, when a freeze-dried sample is extracted, the solvent removes TNT, RDX and HMX as efficiently as from a wet sample, resulting in 100% recovery.

Irreversible sorption of organic contaminants on sediments has been reported by others (Peck et al. 1980, Wildish et al. 1980, Sullivan et al. 1982, Di Toro and Horzempa 1982). Humic polymers are also known to interfere with extraction of organic contaminants by organic solvents (Ogner and Schnitzer 1970, Hassett and Anderson 1979, Gjessing and Berglund 1981, Carlberg and Martinsen 1982). The apparently irreversible nature of this type of sorption is thought to be related to the

three-dimensional conformation or gel-like properties of natural humic polymers (Freeman and Cheung 1981, Carlberg and Martinsen 1982). The extent of apparent irreversibility is related to the particular solvent used for extraction and may be due to very slow desorption kinetics rather than true irreversibility (Freeman and Cheung 1981).

It may be that drying of sediment containing a large amount of organic matter causes collapse of the gel network, which on subsequent solvent extraction is not re-expanded completely by the particular solvent (methanol in this study) chosen for extraction. Again this effect may not occur with freeze drying where the original open structure is more likely to be maintained during drying.

SUMMARY AND CONCLUSIONS

TNT, RDX and HMX can be determined in sediments, soils and sludge by extracting samples with methanol and subsequent analysis using HPLC with 60% methanol/water or 10% acetonitrile/40% methanol/50% water as the eluant. An advantage of this method is that analysis can be performed directly on wet samples without the time delay or possible losses associated with drying. However, drying is advisable for samples containing low ($\mu\text{g/g}$) concentrations of explosives to facilitate homogenization and improve analysis reproducibility. Because of the large inherent concentration variability of trace constituents in soils and sediments, sample size and efficient homogenization are very important for good precision with a recommended minimum sample weight of 4.0 g per extraction.

No loss of explosives occurred during drying of low level soils and sediments. For highly contaminated lagoon sludge only freeze drying gave complete recovery; air drying resulted in greater than 90% recovery while recoveries using other drying methods were appreciably lower.

Drying losses of explosives are thus dependent upon sample type and explosive concentration. Without a priori knowledge of sample composition, freeze drying is the recommended technique since it resulted in complete recovery for all samples. Air drying at room temperature would be an acceptable alternative if a freeze-drying apparatus is not available. In no case was oven drying overnight at 105°C necessary. Thirty minutes was sufficient and longer times should be avoided.

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