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Federal Facilities Forum Issue

Field Sampling And Selecting On-site Analytical Methods For Explosives In Water

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The Federal Facilities Forum is a group of U.S. Environmental Protection Agency (EPA) scientists and engineers who represent EPA regional offices and are committed to the identification and resolution of issues affecting the characterization and remediation of federal facility Superfund, Resource Conservation and Recovery Act, and Base Realignment and Closure sites. Current forum members are identified at the end of this paper. The forum members identified a need to provide remedial project managers and other federal, state, and private personnel working on hazardous waste sites with a technical issue paper that identifies screening procedures for characterizing groundwater and surface water contaminated with explosive and propellant compounds. Some Forum members provided technical guidance and direction in the development of this issue paper, and other members provided comments.

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It is imperative that any persons working on sites believed to be contaminated with explosive residues thoroughly familiarize themselves with the physical and toxic properties of the materials potentially present and take all measures as may be prudent and/or prescribed by law to protect life, health, and property. This publication is not intended to include discussions of the safety issues associated with sites contaminated with explosive residues. Examples of safety issues to be considered include but are not limited to geophysical detection methods, explosion (detonation) hazards, toxicity of secondary explosives, and personal protective equipment. Information pertaining to toxicity concerns can be found in Roberts and Hartley (1992) and Yinon (1990). Specifically, this paper is not intended to serve as a guide for sampling and analysis of unexploded ordnance (UXO), bulk high explosives, or secondary explosives in soil where concentrations exceed 100,000 mg/kg (10%). **These conditions present a potential detonation hazard; therefore, explosive safety procedures and safety precautions should be identified before initiating site characterization activities in such environments.** It also does not serve as a guide to installation of groundwater wells in areas in which such hazards exist.

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Purpose and Scope

This issue paper provides guidance to remedial project managers on field sampling and selecting on-site analytical methods for detecting and quantifying secondary explosive compounds in water (see Table 1). A similar issue paper was previously prepared on explosives in soils (Crockett et al. 1996), and updated as a U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) report (Crockett et al. 1998). The paper also includes a brief discussion of the reference analytical method for the determination of 14 explosives and co-contaminants in water, soil, and sediments, EPA Method 8330 (EPA 1998).

Table 1. Analytical Methods for Commonly Occurring Explosives, Propellants, and Impurities/Degradation Products.

Acronym	Compound Name	Field Method	Laboratory Method
Nitroaromatics		Cs	N
TNT	2,4,6-trinitrotoluene	Cp, Ip, CFIp, FOBp	N
TNB	1,3,5-trinitrobenzene	Cs, Is, CFIs	N
DNB	1,3-dinitrobenzene	Cs	N
2,4-DNT	2,4-dinitrotoluene	Cs	N
2,6-DNT	2,6-dinitrotoluene	Cs, Is	N
Tetryl	Methyl-2,4,6-trinitrophenylnitramine	Cs	N
2AmDNT	2-amino-4,6-dinitrotoluene		N
4AmDNT	4-amino-2,6-dinitrotoluene	Is	N
NT	Nitrotoluene (three isomers)		N
NB	Nitrobenzene		N
Nitramines		Cs	N
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine	Cp, Ip, CFIp, FOBp	N
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	Cp	N
NQ	Nitroguanidine	Cs	Q
Nitrate Esters		Cs	
NC	Nitrocellulose	Cs	*L
NG	Nitroglycerin	Cs	G,*P
PETN	Pentaerythritol tetranitrate	Cs	*P
Ammonium Picrate/Picric Acid			
AP/PA	Ammonium 2,4,6-trinitrophenoxide/2,4,6-trinitrophenol	Cp, Is	A

A = Ammonium Picrate/Picric Acid (Thorne and Jenkins 1995a)
C = Colorimetric field method(s)
CFI = Continuous flow immunosensor
FOB = Fiber-optic biosensor
Q = Nitroguanidine (Walsh 1989)
I = Immunoassay field method(s)
L = Nitrocellulose (Walsh unpublished CRREL method)
N = EPA SW-846, Nitroaromatics and Nitramines by HPLC, Method 8330 (EPA 1998)
G = EPA SW-846, Nitroglycerin by HPLC, Method 8332 (EPA 1998)
P = PETN and NG (Walsh unpublished CRREL method)
p = Primary target analyte
s = Secondary target analyte

* The performance of a number of field methods has not been assessed using “approved” laboratory methods. It is recommended that verification of the performance of any analytical method be an integral part of a sampling/analysis projects quality assurance program.

This issue paper is divided into the following major sections: (1) purpose and scope, (2) background, (3) objectives of water sampling and monitoring water, (4) an overview of sampling and analysis for explosives in water, (5) procedures for statistically comparing on-site and reference analytical methods, (6) a summary of on-site analytical methods for explosives in water, and (7) a summary of the EPA reference method for explosive compounds in water, Method 8330. While some sections may be used independently, joint use of the field sampling and on-site analytical methods sections is recommended to develop a sampling and analytical approach that achieves project objectives.

Many of the explosives listed in Table 1 are not specific target compounds of on-site methods, yet they may be detected by one or more on-site methods because of their similar chemical structure. The explosive and propellant compounds targeted by high-performance liquid chromatography (HPLC) methods such as EPA Method 8330 also are listed in the table.

Background

Evaluating sites potentially contaminated with explosives is necessary to carry out EPA, U.S. Department of Defense, and U.S. Department of Energy policies for site characterization and remediation under the Superfund, Resource Conservation and Recovery Act, Installation Restoration, Base Realignment and Closure, and Formerly Used Defense Site environmental programs. Facilities that may be contaminated with explosives include, for example, active and former manufacturing plants, ordnance works, Army ammunition plants, Naval ordnance plants, Army depots, Naval ammunition depots, and Army and Naval proving grounds, burning grounds, artillery impact ranges, explosive ordnance disposal sites, bombing ranges, firing ranges, and ordnance test and evaluation facilities.

Historical disposal practices from manufacturing, spills, ordnance demilitarization, lagoon disposal of explosives-contaminated wastewater, and open burn and/or open detonation (OB/OD) of explosive sludge, waste explosives, excess propellants, and unexploded ordnance often resulted in soil and groundwater contamination. Common munitions fillers and their associated secondary explosives (indicated in parentheses [see Table 1 for definitions of acronyms used in the following paragraphs]) include Amatol (ammonium nitrate/TNT), Baratol (barium nitrate/TNT), Cyclonite or Hexogen (RDX), Cyclotols (RDX/TNT), Composition A-3 (RDX), Composition B (TNT/RDX), Composition C-4 (RDX), Explosive D or Yellow D (AP/PA), Octogen (HMX), Octols (HMX/TNT), Pentolite (PETN/TNT), Picratol (AP/TNT), tritonal (TNT), tetrytols (tetryl/TNT), and Torpex (RDX/TNT).

Propellant compounds include DNTs and single-base (NC), double-base (NC/NG), and triple-base (NC/NG/NQ) smokeless powders. In addition, NC is frequently spiked with other compounds (e.g., TNT, DNT, and DNB) to increase its explosive properties. Explosive D or Yellow D is used primarily in Naval munitions such as mines, depth charges, and medium to large caliber projectiles. Tetryl is used primarily as a booster charge, and PETN is used in detonation cord.

Although on-site waste disposal of munitions-related compounds was discontinued 20 to 50 years ago, a number of munitions facilities have high levels of soil and groundwater contamination. Under ambient environmental conditions, explosives are highly persistent in groundwater and soil, exhibiting a resistance to naturally occurring volatilization, biodegradation, and hydrolysis. Talmage et al. (1999) reviewed the environmental fate of several explosive compounds as discussed below. Data indicate that explosives in weathered, contaminated soils exhibit slower degradation and desorption kinetics than explosive residues in spiked soil samples (Grant et al. 1995). Desorption of explosives from soil depends on environmental factors including soil chemistry, contaminant concentration, and the number of pore volumes leached through the soil (Pennington et al. 1995; EPA 1995).

Biological degradation products of TNT in water, soil, or sediments include 2AmDNT; 4AmDNT; and 2,6-diamino-4-nitrotoluene; and 2,4-diamino-6-nitrotoluene. Photolysis of TNT in water results in formation of 1,3,5-trinitrobenzene (TNB) and several other compounds. The compound TNB biologically degrades into 3,5-dinitroanaline, which has been recommended as an additional analyte for EPA Method 8330 (Grant et al. 1993). In surface waters, TNT is degraded by photolysis and has a half-life of 0.5 to many hours. The biological half-life of TNT is much longer, ranging from several weeks to 6 months. Spanggord et al. (1980) reviewed studies on the sorption of TNT by soils and sediments and reported the soil-water partitioning coefficients (K_p) to range from 5.5 to 19.3 ([µg chemical in soil/g of soil]/[µg chemical in water/g of water]). Recent data show that irreversible binding may be a significant long-term fate of TNT that has sometimes not been considered in older studies (Brannon and Myers 1997; Comfort et al. 1995). Studies of compost residues (Thorne and Leggett 1997) and C-14 labeled TNT spiked into soil (Comfort et al. 1995; Hundal et al. 1997) show that, over time, solvent-extractable TNT and metabolic products decrease, but not all of the original TNT can be accounted for. As the solvent-extractable TNT decreases, the concentration of hydrolyzable TNT degradation products increases. Acid hydrolysis is able to break some chemical bonds between TNT degradation products and humus or soils. However, over time, those bonds seem to become even stronger and cannot be chemically broken to recover TNT degradation products (Hundal et al. 1997).

Although the water solubility of RDX is only low to moderate, the compound is moderately to highly mobile in the environment. When released to the environment, RDX can be expected to leach to and persist in groundwater (Talmage et al. 1999). In surface water, RDX is degraded by photolysis to formaldehyde, nitrate and nitrite ions, and nitroso compounds, for which the half-lives range from hours to many days, depending on the environmental conditions. As shown by measured soil-water K_p ranging from 0.80 to 4.15 for sandy loam, clay loam, and organic clay, RDX does not strongly partition to sediments. In soils, RDX is quite persistent and is biodegraded very slowly aerobically, and about an order of magnitude faster anaerobically (Brannon and Myers 1997). The limited biodegradation of RDX in water has been accompanied with the identification of hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX), which are RDX intermediates formed by sequential reductions of the nitro groups to nitroso groups (McCormick et al. 1981; Kitts et al. 1994; Sikora et al. 1997). These mono-, di-, and trinitroso intermediates of RDX are environmentally undesirable. Additional products formed were hydrazine, 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, formaldehyde, and methanol.

The compound HMX has a low to moderate affinity for soil and suspended material, which accounts for the ready migration of HMX to groundwater. However, the low solubility of HMX limits migration of HMX to groundwater. The primary mechanism of removal of HMX from surface water is through photolysis. The photolysis half-life of HMX is from 2 to 17 days and adsorption to suspended material and biosorption is not significant. While aerobic and anaerobic degradation of HMX to 1,1-dimethyl-hydrazine has been demonstrated in enriched media, biodegradation is not expected to contribute significantly to the loss of HMX under ambient conditions. While HMX contamination is not detected as commonly as TNT or RDX, military-grade RDX contains approximately 10% HMX as a manufacturing impurity (Army 1984).

Tetryl is primarily degraded by hydrolysis in groundwater in which it is sometimes detected and by photolysis in surface water in which it is seldom detected. Photolysis is about an order of magnitude faster than hydrolysis, and the latter rate has been estimated at about 300 days at 20°C with a pH of 6.8. The solubility of tetryl in water is 75 ppm at 20°C, which may impede leaching to groundwater. The primary hydrolysis product, picric acid, has a solubility of 11,000 mg/L and may leach to groundwater.

The frequency of occurrence of specific explosives in groundwater was assessed by Walsh et al. (1993), who compiled analytical data on water samples collected from 32 military installations. Of the 812 samples analyzed by EPA Method 8330 (EPA 1998), a total of 114 samples (14%) contained detectable levels of explosives. The frequency of occurrence and the maximum concentrations detected are shown in Table 2. The most commonly occurring compound in contaminated samples, RDX, was detected in 61% of the contaminated samples. The compound TNT was detected in 56% of the contaminated samples. Overall, RDX or TNT or both were detected in 94% of the samples containing explosive residues. Thus, by analyzing for RDX and TNT at the facilities sampled, 94% of the contaminated samples could have been identified. This demonstrates the feasibility of screening for one or two compounds or classes of compounds to identify the extent of groundwater and surface water contamination at munitions sites assuming that the method detection limits are adequate. At locations in which RDX-contaminated wastewater has been disposed of in lagoons or in which spills have occurred, there is a significant likelihood that the groundwater has been contaminated with explosives.

The U.S. Army conducted a study from 1984 to 1985 to evaluate the impact of selected open burn and/or open detonation facilities on groundwater quality under various site-specific conditions (AEHA 1986). A total of 109 wells were sampled at 17 individual facilities. The facilities were selected to represent a reasonably large cross-section of OB/OD sites with fairly diverse environmental settings. Samples were analyzed for TNT, 2,4-DNT, 2,6-DNT, RDX, HMX, and tetryl. The results (see Table 3) show that explosives were detected in groundwater at 9 of 19 (47%) sites. The compound most frequently detected was TNT, but RDX was detected at considerably higher levels. Detected in just two wells, HMX was detected at high concentration, and tetryl was never detected. The study examined factors potentially contributing to groundwater contamination including soil permeability, depth to groundwater, temperature, the level of surface soil contamination, the size and age of the facility, and annual precipitation and evaporation rates. The conclusions were that (1) in the eastern half of the country, the "predominant factor precluding significant contamination is low soil permeability" and (2) in the West, the major factor that precludes groundwater contamination is "apparently the significant excess of evaporation over precipitation". With the exception of the level of surface soil contamination, the other factors showed little or no association with resultant groundwater quality. Recent studies by AEHA (1994) and Jenkins et al. (1997) also have identified explosives groundwater contamination at OB/OD and target impact areas resulting from active firing range activities.

Other recent studies have shown that explosives in surface water may migrate considerable distances from moderate to highly contaminated disposal areas (LANL 1996; Murphy and Wade 1998). Elevated levels of explosives in surface waters and sediments have been detected from 1.0 to 1.5 mi downstream from source areas. Moderately to highly contaminated soils often leach explosives into groundwater, and contaminated groundwater may re-emerge into surface water, particularly for nitramines such as RDX and HMX. Contaminated sediments also may serve as a source of recontamination to surface water because of the low affinity of most explosives to sediments.

Table 2. Occurrence of Analytes Detected in Groundwater Contaminated with Explosives.

Compound	Samples with Analyte Present (%)	Maximum and (Median Levels) (μg/L)	
Nitroaromatics			
TNT	56	981	(3.5)
1,3,5-TNB	28	46	(1.5)
2-AmDNT	23	218	(11)
2,4-DNT	21	6.7	(1.2)
4-AmDNT	15	217	(4.6)
DNB	13	8.7	(0.78)
Tetryl	13	12	(0.92)
2,6-DNT	9	29	(0.10)
Nitramines			
RDX	61	1400	(3.0)
HMX	14	673	(76)
TNT and/or RDX	94		

Derived from Walsh et al. (1993).

Table 3. Occurrence and Concentration of Explosive Residues in Groundwater at Open Burning Open Detonation Sites.

Type Explosive	Facilities (%)	Wells (%)	Maximum (µg/L)	Geometric Mean (µg/L)
TNT	41	12	306	32
RDX	35	10	1195	168
2,4-DNT	35	6	1788	14
2,6-DNT	18	4	651	13
HMX	12	2	583	365
Tetryl	0	0	NA	NA

Derived from AEHA (1986)
17 facilities, 109 wells total

Objectives of Sampling and Monitoring Water

Data Quality Objectives

The EPA data quality objective (DQO) process is designed to facilitate the planning of environmental data collection activities by specifying the intended use of the data (i.e., the decision that is to be made), the decision criteria (i.e., the action level), and the tolerable error rates (EPA 1994a; ASTM D 5792, "Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives"). Integrated use of on-site and laboratory methods for explosives in water facilitates achieving objectives such as determining the horizontal and vertical extent of contamination, obtaining data to conduct a risk assessment, identifying candidate waste for treatability studies and pumping tests, identifying the amount of groundwater or surface water to be remediated, monitoring and optimizing treatment systems, and determining whether remedial actions have met cleanup criteria.

Objectives in Sampling Water

The frequency of occurrence and the coefficient of variation of a contaminant determine the number of samples required to adequately characterize exposure pathways, and both are essential in designing sampling plans. Low frequencies of occurrence and high coefficients of variation, such as with explosives, require more samples to characterize the exposure pathways of interest. Sampling variability typically contributes much more to total error than analytical variability. Under these conditions, the major effort should be to reduce sampling variability by taking more samples using less expensive methods (EPA 1992).

Environmental data such as the rates of occurrence, average concentrations, and coefficients of variation are typically highly variable for contaminants associated with explosive sites. Solid at ambient temperatures, explosives dissolve slowly and sparingly in aqueous solutions and have low vapor pressures. These chemical properties limit the modes of mobility compared to other contaminants such as fuels or solvents. The differences between explosives and most other organic contaminants are a function of contaminant fate and transport properties, occurrence in different media, interactions with other chemicals, and use and disposal practices. Areas of high concentrations that serve as sources for contamination of groundwater remain at or near the surface where deposited, unless the soils themselves are moved (Jenkins et al. 1996a).

The EPA guidance for data usability in risk assessment (EPA 1992) indicates that on-site methods can produce legally defensible data if appropriate method quality control is available and if documentation is adequate. Field analyses can be used to decrease cost and analytical time as long as supplemental data are available from an analytical method capable of quantifying multiple explosive analytes (e.g., Method 8330) (EPA 1992). Significant quality assurance oversight of field analysis is recommended to ensure data usability. The accuracy (i.e., the correctness of the concentration value and a combination of both systematic error [bias] and random error [precision]) of on-site measurements may not be as high as in fixed laboratories, but the quicker turnaround and the possibility of analyzing a larger number of samples more than compensates for this potential lack in accuracy. Remedial project managers, in consultation with chemists and quality assurance personnel, should set accuracy levels for each method and proficiency standards for the on-site analyst.

Drinking Water Health Advisories and Water Quality Criteria for Explosives

In 1985, the EPA and the Department of the Army established a Memorandum of Understanding (MOU) to develop EPA Drinking Water Health Advisories for Army environmental contaminants (Roberts and Hartley 1992). The (MOU) memo resulted in a review of the toxicological database for selected munitions chemicals and the development of recommended exposure limits for specific durations (1 day, 10 days, longer term [7 years], and lifetime [70

years]) (Roberts and Hartley 1992; Roberts et al. 1993; EPA 1996b). Both cancer and noncancer toxicity endpoints were considered in the assessment. The EPA Drinking Water Health Advisories values for lifetime exposure to selected explosives or 1E-04 lifetime excess cancer risk levels for EPA Group B (probable human) carcinogens are presented in Table 4.

The EPA has not established water quality criteria for munitions compounds, but a series of unpublished reports by Oak Ridge National Laboratory have been compiled (Talmage et al. 1999) in which acute and chronic water quality criteria were calculated for TNT in accordance with EPA guidelines (Stephan et al. 1985). However, the available data on other explosive compounds were not sufficient to meet these guidelines so Tier II or secondary values were calculated in accordance with EPA guidance for the Great Lakes System (EPA 1993c). These water quality criteria are summarized in Table 4 along with sediment quality criteria (Talmage et al. 1999) normalized to organic carbon (milligram explosive/kilogram organic carbon).

Table 4. Water Quality Criteria for Munitions-Related Chemicals

	Drinking Water	Water and Sediment Quality Criteria/Screening Benchmarks[a]		
Compound	Health Advisories (µg/L)	Acute[b] (µg/L)	Chronic[b] (µg/L)	Sediment[c] (mg/kg$_{oc}$)
TNT	2[d]	570	90	9.2
RDX	2[d]	700	190	1.3
HMX	400[d]	1880	330	0.47
1,3-DNB	1[d]	110	20	0.67
1,3,5-TNB		30	10	0.24
2,4-DNT	5[e]			
2,6-DNT	5[e]			
NC	Nontoxic			
NG	5[d]			
NQ	700[d]			

[a] Talmage et al. (1999)

[b] Calculated in accordance with EPA Tier I (TNT) or Tier II guidelines (other chemicals) (EPA 1993c)

[c] Milligrams chemical/kg organic carbon in the sediment; calculated in accordance with EPA guidelines (Stephan et al. 1985)

[d] Lifetime exposure (EPA 1996b)

[e] Lifetime excess carcinogenic risk of 1E-04 (EPA 1996b).

Advantages of On-Site Analytical Methods

On-site methods may be useful for analysis of water treatment processes for explosives, such as granular activated carbon (GAC) or chemical and ultraviolet (UV) oxidation treatment systems (EPA 1993a, 1996a; AEC 1997). However, on-site methods should be evaluated against laboratory methods on a site and matrix-specific basis because of the possibility of matrix interferences. Treatability studies may be used to evaluate the potential of different treatment technologies to remove and degrade target and intermediate explosive compounds and to evaluate whether clean-up levels can be achieved for site remediation. Treatability study waste for explosives-contaminated waters should be of higher than average concentration to evaluate removal rates for target and intermediate compounds. The potential effects from compounds related to treatment processes, such as TNB from chemical and UV oxidation systems (AEC 1997) and MNX, DNX, and TNX from biological and phytoremediation systems (Sikora et al. 1997), also should be evaluated.

On-site analytical methods are a valuable, cost-effective tool to assess the nature and extent of contamination (EPA 1997b). Because costs per sample are lower, more samples can be analyzed. In addition, the availability of near-real-time results permits redesign of the sampling scheme while in the field. On-site analysis also facilitates more effective use of off-site laboratories using more robust analytical methods. Even if on-site methods are only used to determine the presence or absence of contamination and the contaminated samples are sent off-site for laboratory analysis, total analytical costs can be reduced considerably, provided that the on-site methods have low enough detection limits to meet site DQOs. Because on-site methods provide near-real-time feedback, they can be used to focus additional sampling on areas of known contamination, thus possibly saving additional mobilization and sampling efforts.

Monitoring Remediation Measures

During site remediation, such as Superfund remedial actions, data may be needed on a near-real-time basis to assess the progress of pump-and-treat remedial actions (EPA 1994b; Craig et al. 1996). These treatment systems are often estimated to operate for a period of 10 to 30 years. On-site methods can be used during remediation to monitor individual extraction wells and combined influent explosives concentrations, as well as to evaluate GAC breakthrough and determine when to replace the GAC bed. Final attainment of groundwater or surface water clean-up levels should be determined by an approved method, such as EPA Method 8330 (EPA 1998).

Figure 1 shows the time series extraction well concentrations of TNT and RDX for a GAC treatment system for a 110-acre groundwater plume at the U.S. Naval Submarine Base in Bangor, Washington. The influent for a typical single-stage fixed bed GAC system enters the top of the carbon column, and the explosives are adsorbed as the waste stream flows through the column. The treated liquid stream (effluent) exits the bottom of the column. Once the effluent no longer meets the treatment criterion, the spent carbon is reactivated, regenerated, or replaced. As the GAC system continues to operate, the mass-transfer zone moves down the column. Figure 2 shows the adsorption pattern and the corresponding effluent breakthrough curve. The breakthrough curve is a plot of the ratio of effluent concentration (C_e) to influent concentration (C_o) as a function of the water volume treated per unit time. When a predetermined concentration appears in the effluent (C_B), breakthrough has occurred. At this point, the effluent quality no longer meets treatment objectives. When the carbon becomes so saturated with explosives that they can no longer be adsorbed, the carbon is said to be spent ($C_e = C_o$). Alternate design arrangements may allow individual adsorbers in multi-adsorber systems to be operated beyond the breakpoint as far as complete exhaustion. This condition of operation is defined as the operating limit ($C_e = C_L$).

On-site colorimetric methods for system monitoring and determination of breakthrough curves are being used at a Superfund remedial action for an explosives washout lagoon groundwater GAC pump-and-treat system (ACOE 1998). Figure 3 shows the RDX breakthrough curve for between bed samples in a two-bed GAC system in series for a 350-acre groundwater plume at the Umatilla Chemical Depot in Hermiston, Oregon. Influent concentrations into the system are 97 µg/L of TNT, 29 µg/L of TNB, 710 µg/L RDX, and 63 µg/L of HMX. Final effluent concentrations also are monitored using the on-site colorimetric methods. The only compound detected in the between bed samples and final effluent samples was RDX. The GAC system exhibits preferential adsorption for explosives compounds (TNT > TNB > HMX > RDX) in the same waste stream. Other explosives compounds are progressively displaced in favor of TNT adsorption. The presence of multiple explosives will reduce the carbon bed life in relation to single compound isotherms, particularly for the breakthrough of RDX (Vlahakis 1974; Lee and Stenstrom 1996). Typical loading rates achieve 1 to 4% total explosives loading onto the lead GAC bed before breakthrough occurs.

Overview of Sampling and Analysis for Explosives in Water

Explosive Hazards During Well Installation

The explosives safety procedures necessary for geophysical detection, handling, and disposal of UXO and geotechnical operations such as well installation in areas that potentially contain high levels of explosives in soil are beyond the scope of this document. These conditions present a potential detonation hazard; therefore, explosive safety procedures and safety precautions should be identified before initiating site characterization activities in these environments (EPA 1993a). A qualified explosives safety expert should be consulted in preparing field sampling procedures for operations under these conditions (ACOE 1996a, 1996b).

Water Sampling

Except for the significant hazards of installing wells and working in areas that may contain UXO, bulk high explosives, or highly contaminated surface soils such as explosives washout lagoons, procedures for sampling groundwater and surface water for explosive residues are similar to sampling for other semivolatile organic compounds. The EPA guidance on groundwater sampling can be found in Subsurface Characterization and Monitoring Techniques, Volume 1: Solids and Ground Water (EPA 1993b, Chapter 5). The American Society for Testing and Materials (ASTM) provides guidance for sampling surface and groundwater: "Guide for Sampling Groundwater Monitoring Wells," Standard D 4448; "Guide for Planning and Implementing a Groundwater Monitoring Program," Standard D 5851; "Practice for Sampling Wastes from Pipes and Other Discharge Points," Standard D 5013; and "Practice for Sampling with a Dipper or Pond Sampler," Standard D 5358. Other standard procedures can be located on the ASTM World Wide Web site, http://www.astm.org.

Well Screens and Casing Materials

Parker and Ranney (1993) and Parker et al. (1989) demonstrated that none of the explosives evaluated sorb to well casings. There were no significant differences among polytetrafluoroethylene, rigid polyvinyl chloride, and stainless steel used as well casing materials for RDX, TNT, HMX, TNB, DNB, NB, 2AmDNT, DNT, or NTs.

Containers, Holding Times, and Preservation Methods

The EPA guidance (EPA 1998) on sampling containers for semivolatile organic compounds specifies 1-gal, two 0.5-gal, or four 1-L amber glass containers with Teflon-lined lids. These containers and volumes were designed for laboratory procedures such as Method 8330 for which significant sample concentration may be required. Similar bottles, of adequate volume for the method, should be satisfactory for on-site analytical methods.

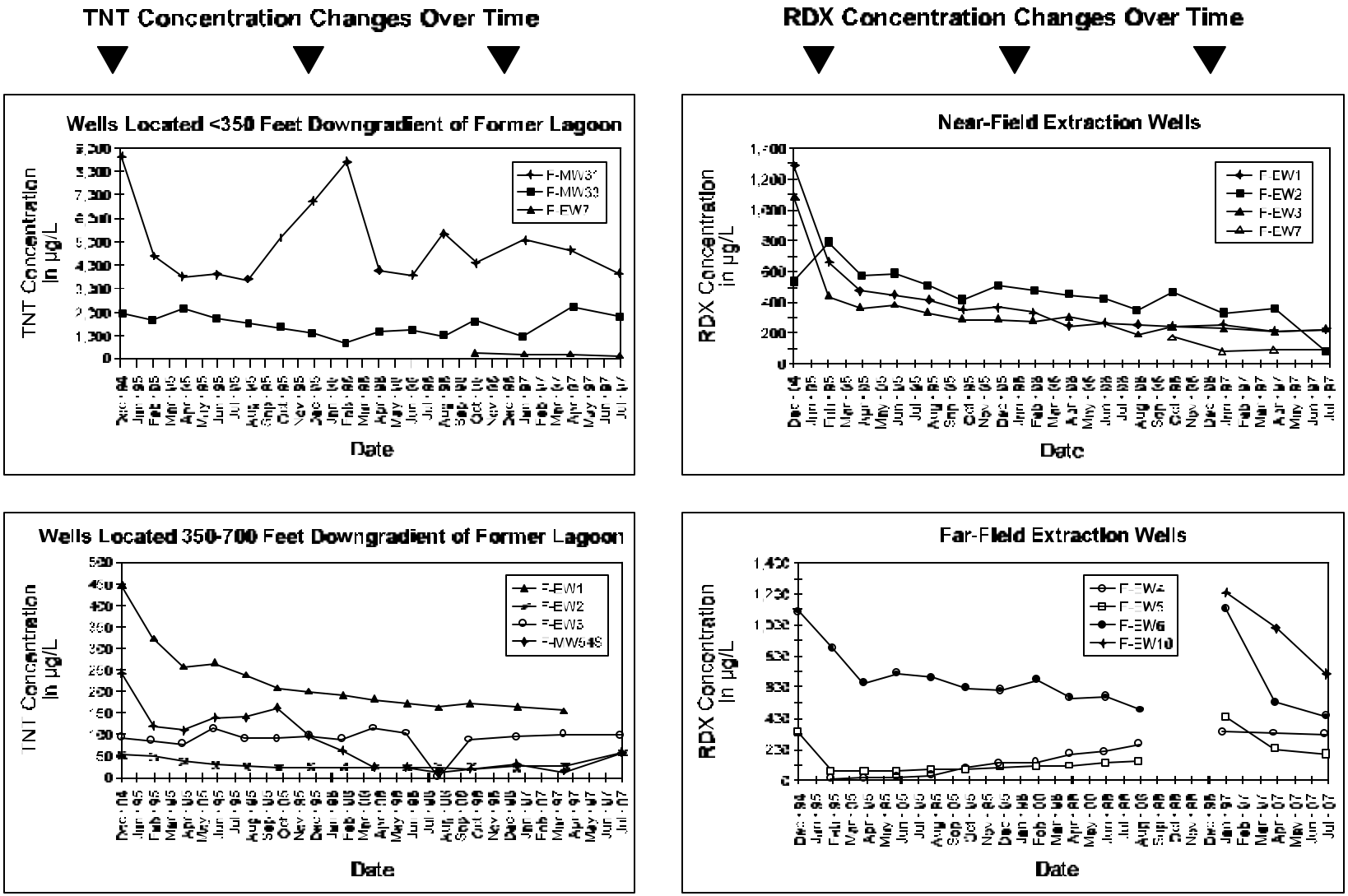

Figure 1. Extraction Well Concentrations of TNT and RDX for a GAC Treatment System for a 110-acre Groundwater Plume at the U.S. Naval Submarine Base in Bangor, Washington.

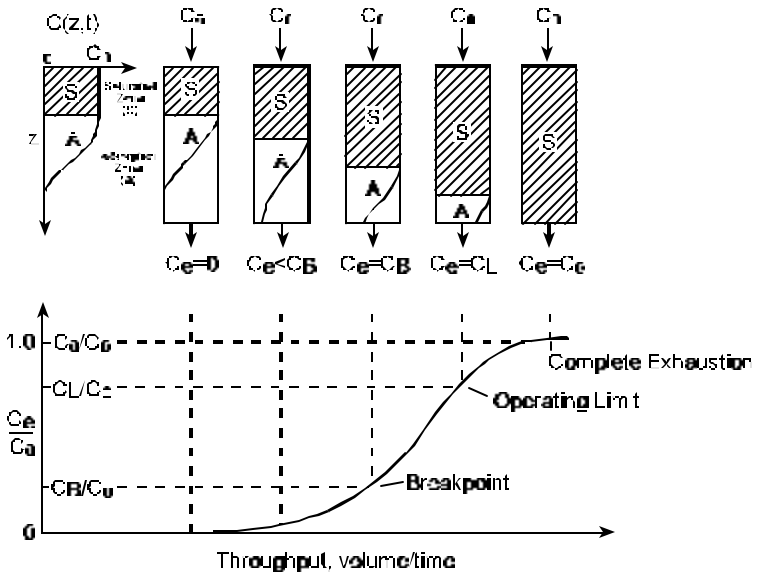

Figure 2. Breakthrough Characteristics of Fixed-Bed GAC Adsorper [3].

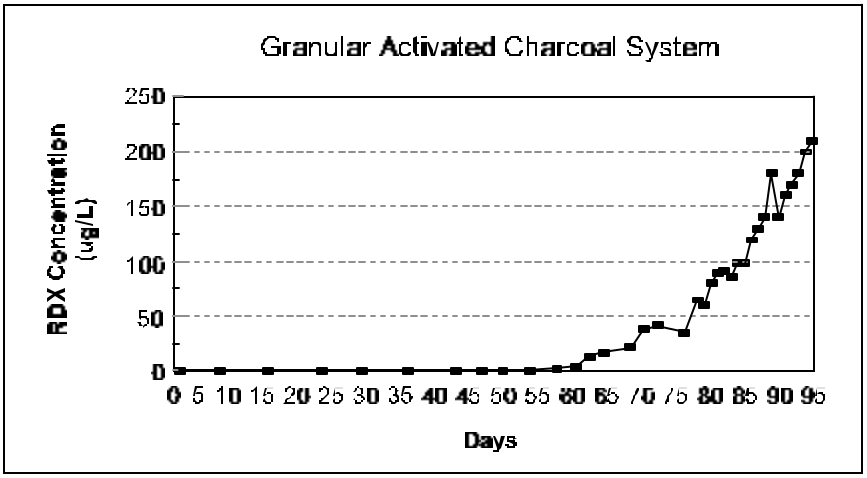

Figure 3. RDX Breakthrough Curve

The EPA-specified holding time for nitroaromatic compounds in water is 7 days until extraction, and extracts must be analyzed within the following 40 days (EPA 1998). The specified sample preservation procedure is cooling to 4EC. This criterion was based on professional judgment rather than experimental data. While recent, scientifically based data have been generated on improved preservation procedures for explosives in water (see below), the ramifications of using such procedures for legally defensible data should be considered during the DQO process. Deviation from EPA procedures may require the user to justify such changes and might result in the data being deemed unfit for the intended use.

Because of the short holding times between sample collection and analysis using on-site

analytical methods, sample preservation is typically not a concern. However, if samples will be held before analysis, sample preservation may need to be considered. For split samples sent to an off-site analytical laboratory, sample holding times and improved preservation methods become an important consideration.

Two recent studies, by Maskarinec et al. (1991) and Grant et al. (1993), have shown that nitramines are stable in water, without any form of preservation for 30 and 50 days. However, both studies also demonstrated that nitroaromatics can undergo significant degradation within days. Maskarinec recommended a maximum holding time of 4 days for DNT in groundwater while Grant found DNT relatively stable and recommended a holding time of 30 days for surface water. Grant's work on TNB and TNT showed losses of 55% and 35%, respectively, in 7 days for spiked surface water samples stored under refrigeration. Jenkins et al. (1995a) showed that tetryl also can degrade rapidly in surface waters with 73% being lost in 7 days despite refrigeration. Degradation was much faster in surface water than it was in groundwater or reagent water.

Because nitroaromatics can degrade rapidly in water samples, Jenkins et al. (1995a) evaluated possible sample preservation procedures. Sample acidification to a pH of 2 with sodium bisulfate was demonstrated to retard microbiological and chemical transformations, is relatively easy to conduct in the field, and does not interfere with solid phase extraction preconcentration procedures in Method 3535A (EPA 1998). Acidification of spiked surface water samples eliminated losses of TNT and TNB for 64 days and at least 28 days for tetryl. Nitramines (RDX and HMX) were stable in spiked, refrigerated surface water, with or without preservation, for at least 64 days. Small losses of aminodinitro-toluenes were observed for both acidified and unacidified samples, and the loss rate was initially higher for acidified samples. Acidified samples must be neutralized if the samples will be concentrated using the salting-out procedure in Method 8330.

Procedures For Statistically Comparing On-site And Reference Analytical Methods

When on-site methods are used, their performance needs to be evaluated, which is commonly done by analyzing the splits of some water samples by both the on-site method and a reference method (commonly Method 8330). The performance of the on-site method is then statistically compared to the reference method using a variety of criteria, depending upon the objective and the characteristics of the data. In most cases, measures of precision and bias are determined. Precision refers to the agreement among a set of replicate measurements and is commonly reported as the relative standard deviation (standard deviation divided by the mean and expressed as a percent), the coefficient of variation (standard deviation divided by the mean), or the relative percent difference (sample value minus the reference method value divided by the mean and expressed as a percent). Bias refers to systematic deviation from the true value.

The following discussion of statistical methods applies to comparisons of analytical results based on paired sample data (e.g., duplicate or split water samples are analyzed by both an on-site method and a reference method or water sample extracts are analyzed by a reference and on-site method).

Precision and Bias Tests for Measurements of Relatively Homogenous Material—When multiple splits of well-homogenized samples are analyzed using different analytical methods, statistical procedures summarized in Grubbs (1973), Blackwood and Bradley (1991), and Christensen and Blackwood (1993) can be used to compare the precision and bias of the methods. Grubbs described a statistical approach appropriate for comparing the precision of two methods that takes into account the high correlation between the measurements from each method. An advantage of Grubbs' approach is that it provides unbiased estimates of the precision of each method by partitioning the variance of the measurement results

into its component parts (e.g., variance caused by subsampling and by the analytical method). Blackwood and Bradley (1991) extended Grubbs' approach to a simultaneous test for equal precision and bias of two methods. Similar tests are provided in Christensen and Blackwood (1993) for evaluating more than two methods.

For comparisons involving bias alone, t-tests or analysis of variance may be performed. For comparing two methods, paired t-tests are appropriate for assessing relative bias in normally distributed data (otherwise data are transformed to achieve normality or nonparametric tests are used). A paired t-test can be used to test whether the concentration as determined by an on-site method is significantly different from Method 8330 or any other reference method. For comparing multiple methods, a randomized complete block analysis of variance can be used in which the methods are the treatments and each set of split samples constitutes a block.

These tests are best applied when the concentrations of explosives are all of approximately the same magnitude. As the variability in the sample concentration increases, the capability of these tests for detecting differences in precision or bias decreases. The variability in the true quantities in the samples is of concern, and high variability in sample results caused by poor precision rather than variability in the true concentration is handled well by these methods.

Precision and Bias Tests for Measurements over Large Value Ranges—When the concentrations of explosives cover a large range of values, regression methods for assessing precision and accuracy become appropriate. Regression analysis is useful because it allows characterization of nonconstant precision and bias effects and predicts intervals for new measurements (e.g., the results of an on-site method can be used to predict the concentration if the samples were analyzed by a reference method).

In a regression analysis, the less precise on-site method is generally treated as the dependent variable and the more precise reference analytical method (e.g., Method 8330) as the independent variable. A linear relationship and a slope that differs from a value of 1.0 indicates a constant relative bias in the on-site method (i.e., the two methods differ by a fixed percentage). Similarly, an intercept value significantly different from zero indicates a constant absolute bias (i.e., the two methods differ by a fixed absolute quantity). Of course, both fixed and relative bias components may be present.

When uncertainty is associated with the concentration of an explosive as measured by the reference method, standard least squares regression analysis can produce misleading results. Standard least squares regression incorporates the assumption that the independent variable values are known exactly as in standard reference material. When the reference method results contain appre-ciable error compared to the on-site method, regression and variability estimates are biased. Furthermore, the interpretation of R-squared and uncertainty intervals are affected, which is known as an errors-in-variables problem.

Because of the errors-in-variables problem, the slope coefficient in the regression of the on-site data on the reference data generally will be biased low. Hence, a standard regression test to determine whether the slope is significantly different from 1 can result in rejection of the null hypothesis even when there is no difference in the true bias of the two methods. A similar argument applies to tests of the intercept value being equal to zero.

To perform a proper errors-in-variables regression requires consideration of the measurement errors in both the dependent and independent variables. The appropriate methods for performing the regression (including some guidance about how large the error in the reference analytical method can be before a problem is encountered) are outlined in Mandel (1984). These methods require estimating the ratio of the random error variance for the on-site method to that of the reference analytical method. With split sample data, suitable estimates of the variance ratio generally can be obtained by using variance

estimates from Grubbs' test or the related tests mentioned above.

If the variance ratio is not constant over the range under study, more complicated models than those analyzed in Mandel (1984) must be employed. Alternatively, transformations of the data could stabilize the variance ratio. Note that it is the variance ratio, not the individual variances, that must remain constant. For example, the ratio of variances for two methods with nonconstant absolute variances but constant relative variances will still have a constant variance ratio.

It should be noted that performing regressions on data sets in which samples with concentrations below the detection limit (for one or both methods) have been eliminated also may result in biased regression estimates, regardless of the regression analysis method that is used.

Comparison to Regulatory Thresholds and Action Limits—When the purpose of sampling is to make a decision based on the comparison of results to a specific value such as an action level for cleanup, on-site and reference analytical method results may be compared simply on the basis of the degree of agreement between the two methods. The appropriate statistical tests are based on the binomial distribution and include tests of equality of proportions and chi-square tests comparing the sensitivity and specificity (i.e., false positive and false negative rates) of the on-site method relative to the reference analytical method. Note that any measure of consistency between the two methods is affected by how close the true values in the samples are to the action level. The closer the true values are to the action level, the less the two methods will agree, even if they are of equal accuracy. For example, if the action level is 2 Fg/L and most samples have levels of above 100 Fg/L, the agreement between the on-site method and reference should be very good. If, however, the concentration in most samples is 0.5 to 10 Fg/L, the two methods will be much more likely to disagree. This must be kept in mind when interpreting results, especially when comparing across different studies for which samples may have been collected at considerably different analyte levels.

Summary of On-site Analytical Methods for Explosives in Water

There is significant interest in field methods for rapidly and economically determining the presence and concentration of secondary explosives in groundwater and the influent and effluent to groundwater remediation facilities. Such procedures allow much greater flexibility in mapping the extent of contamination, designing pumping strategies based on near-real-time data, accruing more detailed characterization for a fixed cost, and guiding continuous remedial actions. Ideally, on-site analytical methods would provide high-quality data on a near-real-time basis at low cost and of sufficient quality to meet all intended uses including risk assessments and final remedial action objectives without the need for more rigorous procedures. While the currently available on-site methods are not ideal (i.e., they are not capable of providing compound-specific concentrations of multiple compounds simultaneously as might be desired in risk assessment), they have proved to be very valuable during the characterization and remediation monitoring of some sites. Currently available field methods that have been evaluated against standard analytical methods and demonstrated in the field include colorimetric, immunoassay, and biosensor methods (see Table 5). Each method has relative advantages and disadvantages, so that no method is optimal for all applications. To assist in the selection of one or more screening methods for various users needs, Table 6 (modified and expanded from EPA 1997a) provides information on on-site test methods for detecting explosives in water. The selection criteria are discussed in the following sections.

The three types of on-site methods, colorimetric, immunoassay, and biosensor, are fundamen-tally quite different. The CRREL colorimetric methods were developed by Jenkins for TNT (Jenkins 1990)

and RDX (Walsh and Jenkins 1991) in soils. Later Jenkins et al. (1994a, 1995b) developed a solid-phase extraction method for TNT and RDX in water in which the extraction disks could be extracted with acetone and analyzed by the soil analytical procedures. The same methods are now used in the Strategic Diagnostics, Inc., EnSys procedure for extraction of TNT and RDX + HMX from groundwater, and the EnSys TNT and RDX soil test kits are used to complete the analysis (see below). (Note that the EnSys procedure refers to the RDX + HMX kit as simply the RDX kit while the draft EPA Method 8510 refers to it as RDX + HMX. The latter designation is used throughout this document.) The commercial versions of the methods are the most commonly used. Therefore, the tables and the text refer only to the EnSys procedures for TNT and RDX + HMX but the CRREL methods can provide equivalent results.

Researchers at CRREL also developed a colorimetric analytical procedure for quantifying ammonium picrate and picric acid in soil and water (Thorne and Jenkins 1995a, 1995b). In the procedure, 2 L of water are drawn through an anion extraction disk under vacuum and the disk is washed to remove interferences. Picrate ions are converted to picric acid and are eluted from the disk, and absorbance measurements are made before and after conversion to the yellow picrate ion.

In the EnSys colorimetric method for water, solid-phase extraction is used to remove and concentrate analytes from water. A 2-L water sample is passed through a stack of two membranes to preconcentrate TNT on the top membrane and RDX on the bottom membrane. Acetone is used to elute RDX + HMX from the bottom disk, and a chemical reaction is induced that causes a color change indicative of RDX in the solution. The RDX + HMX concentration is estimated from the absorbance at 510 nm on a portable spectrophotometer. The top disk is eluted with acetone, and a different chemical reaction is induced causing a color change indicative of TNT. The TNT concentration is estimated from the absorbance at 540 nm.

Table 5. Available On-Site Analytical Methods for Explosives in Water.

Analyte(s)	Type Test	Developer/Test Kit
Nitroaromatics	Colorimetric	EnSys - TNT
1. TNT	Colorimetric	EnSys - TNT
	Immunoassay	D TECH - TNT
		RaPID Assay
	Biosensor	Continuous Flow Immunosensor - TNT
		Fiber-Optic Biosensor - TNT
2. TNB	Colorimetric	CRREL, EnSys - TNT
	Immunoassay	RaPID Assay
	Biosensor	Continuous Flow Immunosensor - TNT
3. DNT	Colorimetric	EnSys - TNT
4. Tetryl	Colorimetric	EnSys - TNT
Nitramines	Colorimetric	EnSys - RDX + HMX
1. RDX	Colorimetric	EnSys - RDX + HMX
	Immunoassay	D TECH - RDX
	Biosensor	Continuous Flow Immunosensor - RDX Fiber-Optic Biosensor - RDX
2. HMX	Colorimetric	EnSys - RDX + HMX
3. NQ	Colorimetric	EnSys - RDX + HMX
Nitrate Esters	Colorimetric	EnSys - RDX + HMX
1. NC	Colorimetric	EnSys - RDX + HMX
2. NG	Colorimetric	EnSys - RDX + HMX
3. PETN	Colorimetric	EnSys - RDX + HMX
AP/PA	Colorimetric	CRREL [1]

[1] U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory

Table 6. Comparative Data for Selecting On-Site Analytical Methods for Explosives in Water.[a]

Method/Kit	Criteria						
	Method Type, Analytes, and EPA Method #	**Detection Range and Range Factor**	**Type of Results**	**Samples per Batch**	**Water Sample Size**	**Sample Preparation and Extraction**	**Analysis Time/ Production Rate (one person)**
CRREL	Colorimetric Ammonium Picrate /Picric Acid	AP/PA: 3.6 to 200 Fg/L (56 X)	Quantitative	AP/PA: Single or batched	2 L	Filtration if the sample is cloudy, solid-phase extraction using anion extraction disk, eluted with methanol and sulfuric acid.	20 minutes to hours to filter, faster per sample if batched; recommended only for low turbidity waters. 20 mins./ sample to analyze.
EnSys (Commercial version CRREL, TNT and RDX methods)	Colorimetric TNT RDX + HMX Draft Method 8510	TNT: 1 to 30 Fg/L (30 X) RDX: 5 to 200 Fg/L (40 X) HMX: 15 to 300 Fg/L (20 X)	Quantitative	Single	2 L	Solid-phase extraction using two membranes filters, elution of filters with acetone.	20 minutes to a few hours for filtering, recommended only for low turbidity waters. TNT : 35 mins./10 samples RDX: 50 mins./10 samples
D TECH	Immunoassay - ELISA TNT RDX	TNT & RDX: 5 to 45 Fg/L (9 X) with DETECHTOR	Semiquantitative (concentration range)	Four (single or batch)	1 mL	None	40 minutes for eight samples for TNT and RDX. 10 to 15 mins. for single sample
RaPID Assay	Immunoassay - ELISA Magnetic particle/tube kit TNT	TNT: 0.07 to 5 Fg/L (71 X)	Quantitative	Batch up to 51 samples	100 µL	Filter (0.2Fm) if gross particulates are present	70 minutes for 51 samples
Continuous Flow Immunosensor	Immunosensor TNT RDX Proposed Method 4655	TNT and RDX: 10 to 1,000 Fg/L (100 X)	Quantitative	Sequential	150 µL	To 955 µL sample, add 25 µL ethanol and 20 µL of 50X buffer	3 to 4 minutes per sample, plus 3 to 4 minutes for internal standard, plus 1 minute peak analysis. Total time < 20 minutes for typical 2-3 analyses/sample
Fiber-Optic Biosensor with Fluidics Unit	Immunosensor TNT RDX Proposed Method 4656	TNT: 10 to 150 Fg/L (15 X) RDX: 10 to 100 Fg/L (10 X)	Quantitative	Single up to a batch of four	1.7 mL for four fiber analyses	To 1.7 mL of sample, add 200 µL buffer and 100 µL acetone.	TNT: 8 minutes per quadruplicate sample or batch of four. RDX: 16 minutes per quadruplicate sample or batch of four. Double times to run reference analysis. Typically each sample is analyzed 2 to 4 times.

[a] Expanded and modified from EPA 1997a

Table 6. (Continued)

Method/Kit	Criteria			
	Interferences and Cross-reactivities > 1% based on IC50	**Supplier Recommended QA/QC** [1]	**Storage Conditions and Shelf Life of Kit or Reagents**	**Skill Level**
CRREL	Relatively free of humic and nitroaromatic interferences.	Blank and spiked water samples analyzed daily.	Store at room temperature.	Medium high
EnSys	TNT = TNT + TNB + DNB + DNTs + tetryl; RDX + HMX = RDX + HMX + PETN + NQ + NC + NG Humics interfere with TNT and RDX; nitrate and nitrite interfere with RDX. TNT interferes with RDX method only when both are present.	Method and water blanks and a control sample daily, one duplicate/20 samples. Some positive field results (1:10) should be confirmed.	Store at room temperature. Shelf life: TNT = 2 to 24 months at 27EC RDX = 2 to 12 months at 27EC	Medium
D TECH	Cross-reactivity: TNT: tetryl = 35%; TNB = 23%; 2AmDNT = 11%; 2,4-DNT = 4%; AP/PA unknown but ~100% at lower limit of detection RDX: HMX = 3%	Samples testing positive should be confirmed using standard methods.	Store at room temperature or refrigerate; do not freeze or exceed 37EC for prolonged period. Shelf life: 9 months at room temperature.	Low
RaPID Assay	Cross-reactivity: TNB = 65%; 2,4-Dinitroaniline = 6%; tetryl = 5%; 2,4-DNT = 4%; 2AmDNT = 3%; DNB = 2%	Duplicate standard curves; positive control sample supplied. Positive results requiring action may need confirmation by another method.	Refrigerate reagents 2 to 8EC. Do not freeze. Shelf life 3 to 12 months.	Med-high, initial training recommended
Continuous Flow Immunosensor	TNT Method: TNB = 600%, tetryl = 38%, 2-AmDNT = 21 %, 2,4-DNT= 20%, NB = 16%, 2-NT = 9%, HMX = 5%, 2,6-DNT = 4% RDX: 1,2-dinitroglycerin = 18%, HMX = 5%, TNB = 4%, 2,4-DNT = 3%, 1,3-DNB = 3%	Internal standards used for quantification, blank matrix sample for background subtraction.	Store activated membranes moist at 4EC and away from light. Shelf life ~ 1 month	Medium
Fiber-Optic Biosensor with Fluidics unit	TNT Method: TNB = 9%. All other tested explosives <4% RDX Method: no explosive related interferences, (<3%) no nitrate/nitrite interference	Reference analysis every other sample, run blank once per set of fiber probes.	Fiber probes: Shelf life > 1 year when stored < 27EC	Medium

[a] Expanded and modified from EPA 1997a
[1] Site specific DQOs should always be used to select appropriate QA/QC

Table 6. (Continued)

Method or Kit	Criteria					
	Training Availability	Costs (not including labor)	Comparisons to Method 8330 References	Other References	Developer Information	Additional Considerations
CRREL	None Applicable video on CRREL soil method available only, address in text.	$15/sample plus $1,500 for Hach spectrometer. Vacuum filtration apparatus needed.	Thorne and Jenkins 1995a	Thorne and Jenkins 1995b	Tom Jenkins CRREL 72 Lyme Road Hanover, NH 03755-1290 (603) 646-4385	Large work area (two large desks); requires the most setup; electricity required; deionized, methanol, and sulfuric acid required; must assemble materials; glassware must be rinsed between analyses; vacuum filtration apparatus needed.
EnSys	Training available. Applicable video on CRREL soil and groundwater methods are available, addresses in text.	$21/sample for TNT, $25/sample for RDX plus $175/day or $450/wk, $800/mo for lab station. Lab station cost = $1,950. Vacuum filtration apparatus needed.	Craig et al. 1996; EPA 1997a; Jenkins and Schumacher 1990; Jenkins et al 1994b	Jenkins et al. 1995b USACE 1999	Strategic Diagnostics 111 Pencader Dr. Newark, DE 19702-3322 (800) 544-8881 www.sdix.com	Large work area (desk size) power supply required to charge Hach spectrometer; possible TNB interference; color indication of other compounds; requires acetone and deionized water; cuvettes must be rinsed between analyses. Nitrate and nitrite interferences with RDX kit can be corrected using alumin-a-cartridges. Vacuum filtration apparatus needed.
D TECH	Training available	$32.50/sample for TNT or RDX plus $300 for DTECHTOR (optional).	Craig et al. 1996; EPA 1997a; Teaney and Hudak 1994 Thorne and Myers 1997	Calif. EPA 1996a, 1996b	Strategic Diagnostics 111 Pencader Dr. Newark, DE 19702-3322 (800) 544-8881 www.sdix.com	Small working area; few setup requirements; no electricity or refrigeration required; temperature dependent development time (effect can be reduced by changing DTECHTOR setting); significant amount of packing; relatively narrow range; no check on test; easy to transport or carry; kits can be customized. Out-of- range reruns require use of another kit.
RaPID Assay	Training available	$13 to $20/sample plus $4,000 for equip. (purchase), 175/day, $450/wk or $800 for first month, $400 each additional month (rental).	Craig et al. 1996; EPA 1997a; Rubio et al. 1996	Calif. EPA 1996c	Strategic Diagnostics 111 Pencader Dr. Newark, DE 19702-3322 (800) 544-8881 www.sdix.com	Large work area (desk); requires setup time, electricity and refrigeration; less temperature dependent; low detection limit; all reagents supplied; reagents and kit need refrigeration. Out-of-range reruns require dilution and full reanalysis.
Continuous Flow Immunosensor	No formalized training available at this time.	$50/coupon which lasts for ~20 to 30 samples plus $21,000 for instrument (FAST 2000).	Craig et al. 1996; EPA 1997a; Bart et al. 1997 a, 1997b; ESTCP 1998	Narang et al 1998, Whelan et al. 1993	Anne Kusterbeck Naval Research Lab. 4555 Overlook Ave. SW Washington, D.C. 20375 (202) 404-6042	Desk size work area. Less packaging waste, requires electricity and refrigeration. Instrumentation available from: Research International, 18706 142nd Ave. NE, Woodinville, WA 98072, (206) 486-7831
Fiber-Optic Biosensor with Fluidics unit	No formalized training available at this time.	$3 to 5/sample plus $18,000 for instrument (Analyte 2000 from Research International) and $~8,000 for Fluidics unit.	Craig et al. 1996; EPA 1997a; Shriver-Lake et al. 1995, 1997; ESTCP 1998	Shriver-Lake et al. 1998, Golden et al. 1997	Lisa Shriver-Lake Naval Research Lab. 4555 Overlook Ave. SW Washington, D.C. 20375 (202) 404-6045	Desk size work area, can be operated without fuidics unit, requires electricity, refrigeration recommended. Less packaging waste. Quantification requires sample dilution when percent inhibition is >60% for TNT or > 80% for RDX

[a] Expanded and modified from EPA 1997a

The steps of the various immunoassay methods differ considerably. The simplest of the methods is the D TECH method. In the D TECH kit, antibodies specific for TNT and closely related compounds are linked to solid particles. The TNT molecules in water samples are captured by the solid particles and collected on the membrane of a cup assembly. A color-developing solution is added to the cup assembly, and the presence (or absence) of TNT is determined by comparing the solution in the assembly cup to a color card or by using the simple field test meter. The color is inversely proportional to the concentration of TNT.

The continuous flow immunosensor (CFI) and the fiber-optic biosensor (FOB) methods were developed by the Naval Research Laboratory (NRL). The CFI method (Bart et al. 1997a, 1997b; EPA 1997a) is an antibody-based biosensor capable of detecting low molecular weight molecules in aqueous solutions. With the CFI method, TNT or RDX antibodies are immobilized onto a solid phase (beads, membrane or glass capillary) saturated with a fluorescent-dye labeled antigen. The solid phase is placed in a support and an aqueous buffer solution is pumped through the support to establish flow. Samples are prepared in the buffer solution and injected upstream of the support. When a sample containing TNT or RDX is introduced, the TNT or RDX binds to the immobilized antibody, displacing some of the labeled antigen, which is subsequently detected by a fluorometer. The concentration is proportional to the fluorometer signal. A portable version of the CFI (FAST 2000) has been engineered by Research International, Inc. which incorporates the solid phase, sample injection, pump, fluidics control, and a fluorometer into a single instru-ment, with associa ted software for data acquisition and analysis using a lap top computer.

The FOB method (Shriver-Lake et al. 1995, 1997; EPA 1997a) is based on a competitive immunoassay using a fluorescent dye as the reporter molecule. Fluorescent-dye labeled TNB is used as the competitor on the surface of an optical probe. The labeled TNB is exposed to an antibody-coated optical fiber for 4 minutes, generating a specific signal that corresponds to the 100% signal. The reference signal is defined as the signal change associated with the labeled TNB alone. Inhibition of this signal is observed when TNT is present in a sample. The percent inhibition observed is proportional to the TNT concentration in the sample. The reference signal is determined both before and after running the sample to normalize for the gradual decrease in antibody activity. A portable version of the FOB (Analyte 2000) has been engineered by Research International, Inc. Originally developed only for TNT, the FOB method has been modified and is now available for RDX as well.

Method Type, Analytes, and EPA Method Number

The first column of the criteria listed in Table 6 identifies the type of water screening method, the analytes it detects, and the EPA draft method number.

The CRREL colorimetric method for Explosive D or Yellow D (AP/PA) has been formally documented (Thorne and Jenkins 1995a) but it is not under consideration for incorporation into SW-846 (EPA 1998), nor is it being evaluated by any method certification organization.

Commercially available colorimetric kits marketed under the EnSys trade name and manufactured by Strategic Diagnostics, Inc., are available for determining nitroaromatics (TNT) and nitramines (RDX + HMX) in soils. The same analytical methods can be used to analyze acetone extracts of filter disks that have extracted nitroaromatics and nitramines from 2 L of water via vacuum filtration. The water-extraction step requires at least a small field laboratory. Therefore, Strategic Diagnostics has not promoted the EnSys TNT and RDX + HMX procedures for analysis of water although the company will provide procedures upon request. The EnSys TNT colorimetric method detects nitroaromatics (i.e., TNT, TNB, DNB, DNTs, and tetryl), and the RDX + HMX method detects nitramines (RDX, HMX, and NQ), and nitrate esters (NC, NG, and PETN). While NC is detected by the actual analytical method, it is not clear that acetone will elute NC from the membrane filter disks with the

other explosives. The EnSys RDX + HMX method is draft EPA Method 8510 and is designed for soil and water. The EPA Method 8515 is the EnSys TNT method specific to soil (summarized in soils issue paper [Crockett et al. 1996, 1998]). However, the water extraction step of the RDX + HMX method (draft Method 8510) extracts TNT on the first filter of a two-filter stack, and the first filter can be extracted with acetone and analyzed using the TNT soils method (Method 8515). The EPA currently has no plans to revise Method 8515 to include analysis of water samples.

Strategic Diagnostics, Inc., also manufacturers commercial enzyme-linked immunosorbent assay (ELISA) kits, including the D TECH and RaPID Assay kits to detect TNT in water. D TECH immunoassay kits also are available for RDX. Other explosives compounds can sometimes be detected using immunoassay kits because of their cross-reactivity (see the Interferences and Cross-Reactivity section). The California Environmental Protection Agency has certified the D TECH kits for TNT (California EPA 1996a) and RDX (California EPA 1996b) for both water and soil. The California EPA also has certified the RaPID Assay kit for TNT (California EPA 1996c) for water and soil.

The Naval Research Laboratory's two biosensor-based methods have been evaluated although they are not yet fully commercially available. The FAST 2000 and Analyte 2000 instruments are commercially available but the coated membranes and optical fibers are not. However, the draft EPA methods describe how to prepare membranes and fibers. Both the CFI and FOB methods are capable of determining TNT and RDX. A recent report on both methods (ESTCP 1998) has been submitted to EPA with the intent of establishing new methods to be incorporated into SW-846 (EPA 1998) and EPA has assigned draft method numbers, Method 4655 for the CFI and 4656 for the FOB method. The draft methods are written for both TNT and RDX in water only but a soils method may follow.

Detection Range and Range Factor

The lower detection limits of the on-site methods for water range considerably, from 0.07 µg/L to 15 µg/L. The detection range of a test kit can be important and a broad range is generally more desirable. The importance of the range of the test kit depends on the range of concentrations expected in samples, the ability to estimate the approximate concentration from the sample extract, the amount of effort required to dilute and rerun a sample, and the sampling and analytical objective. Some test kits have a range factor (upper limit of range /lower limit) of just one order of magnitude (10X), while other methods span two orders of magnitude (100X). Because the concentration of explosives may range widely, reanalysis of many out-of-range samples may be necessary if the objective is to determine the concentration of an explosive in water. The D TECH immunoassay methods require an additional complete analysis for each sample dilution. Other immunoassay methods can run multiple dilutions in the same analytical run, but the dilutions must be prepared without knowing whether they are needed. The EnSys colorimetric procedure for RDX provides sufficient reagent to allow running several dilutions at no additional cost. For the EnSys kits, the analyzed sample can simply be diluted and reread in the spectrophotometer. Research results indicate that dilution ratios of as high as 1 to 10,000 may be necessary to keep concentrations in the linear range of the tests, and these dilutions can be conveniently made in one step using glass microliter syringes (Jenkins et al 1996b). The procedures that the test methods use for sample dilution should be considered during method selection.

The detection range of a kit becomes much less relevant when the objective is to determine whether a sample is above or below a single action limit because the same dilution can be used for all samples. In some cases, changing the range of a kit may be desirable to facilitate decision making. Cleanup levels for explosives in water vary considerably depending on, for example, the site conditions, compounds present and their relative concentration, use of the water, results of risk assessments, and the selected remedial technology (EPA 1993a, 1996a; Craig et al. 1996). Typical remediation goals for water are less than one microgram/liter for DNTs; low micrograms/liter for RDX, TNT, TNB, DNB, and NG; and hundreds of micrograms/liter for HMX and NQ (EPA 1996a).

Type of Results

The type of results provided by the various screening methods are, depending on the concentration range, quantitative or semiquantitative. The CRREL 2,4-DNT, EnSys, RaPID Assay, the CFI, and the FOB are quantitative methods that provide a numerical result. The D TECH kits are semiquantitative and indicate that the concentration level of an analyte is within one of several ranges. For example, the D TECH RDX water kit, without dilution, indicates a concentration within one of the following ranges: less than 5, 5 to 15, 15 to 25, 25 to 45, 45 to 60, and greater than 60 µg/L.

Samples per Batch

Several of the available test kits are designed to run batches of samples, single samples, or both. However, using a test kit designed for analyzing a large batch to analyze one or two samples may not be cost-effective or efficient. For methods requiring filtration to concentrate the analyte, multiple samples can be simultaneously extracted using a filtration manifold.

Water Sample Size

The test methods use samples of either 1 mL or less of water, or 2 L of water.

Sample Preparation and Extraction

Sample preparation and extraction only applies to the colorimetric methods, which require filtration and extraction of a 2-L water sample.

Analysis Time

The filtration and extraction step associated with both the CRREL and EnSys methods requires a minimum of 20 minutes exclusive of extracting the filter and may take well over an hour depending on the amount of particulate matter in the sample. For this reason, these methods are not recommended for turbid waters.

Actual sample analysis time for a single sample ranges from 3 minutes to about 70 minutes although as many as 10 samples can be batched and analyzed in the same 70 minutes. For the NRL methods, eight or more subsamples from each sample were analyzed and the results were averaged for the recent method validation study (ESTCP 1998). However, for routine use, it is expected that two to four subsamples would typically be analyzed from each sample. The effective production rate also depends on the number of reruns required for samples out of the detection range.

Interferences and Cross-Reactivity

One of the major differences among the field methods is interference for colorimetric methods and cross-reactivity for the immunoassay and biosensor methods. The colorimetric methods for TNT and RDX are broadly class sensitive—that is, they are not only able to detect the presence of the target analyte but also respond to many other similar compounds (nitroaromatics, and nitra-mines and nitrate esters, respectively). For colorimetric methods, interference is defined as the positive response of the method to secondary target analytes or co-contaminants similar to the primary target analyte. The immunoassay and biosensor methods are relatively specific for the primary target analytes that they are designed to detect. For the immunoassay and biosensor meth-ods, cross-reactivity is defined as the positive response of the method to secondary target analytes or co-contaminants similar to the primary target analyte.

Depending on the sampling objectives, broad sensitivity or specificity can be an advantage or a disadvantage. If the objective is to determine whether explosive compounds are present, then broad sensitivity is an advantage. Another advantage of the broad response of colorimetric methods is that they may be used to detect compounds other than the primary target analyte. For example, the colorimetric RDX + HMX method may be used to determine PETN when RDX + HMX levels are relatively low or absent. If a secondary target analyte is present at only low concentrations in a sample, the effect on the analytical result is minimal. If the objective is to determine the concentration of TNT when relatively high levels of other nitroaromatics or RDX when

elevated levels of other nitramines or nitrate esters are present, other methods may be more appropriate.

Extremes of temperature and pH can interfere with on-site analytical methods. According to the California Military Environmental Coordination Committee, physical conditions comprising temperatures outside the range of 4 to 32EC and pH levels less than 3 or greater than 11 (CMECC 1996) are generally not recommended for both colorimetric and immunoassay methods. Specific product literature should be consulted for more information.

Colorimetric Methods—For TNT methods, the primary target analyte is TNT and the secondary target analytes are other nitroaromatics such as TNB, DNB, 2,4-DNT, 2,6-DNT, and tetryl. For RDX methods, the primary target analyte is RDX + HMX, and the secondary target analytes include PETN, NG, and NQ. If the primary target analyte is the only compound present, the colorimetric methods measure the concentration of that compound. If multiple analytes are present, the field methods measure the primary target analyte plus the secondary target analytes. The response of colorimetric methods to the secondary target analytes is similar to the response of the primary target analyte and remains constant throughout the concentration range of the methods although the observed colors may be different.

If multiple analytes are present in water, colorimetric field results can be roughly compared with EPA Method 8330 results (EPA 1998). For example, if a water sample (as analyzed by Method 8330) contains 100 µg/L each of TNT, TNB, RDX, and HMX, the EnSys colorimetric methods for TNT would measure approximately 200 µg/L (100 TNT + 100 TNB), and the RDX test kit would measure approximately 200 µg/L (100 RDX + 100 HMX). This example is somewhat simplistic because each compound has a somewhat different response factor.

While colorimetric kits are not compound specific, the color development of the extracts often can provide an indication of the types of compounds that may be present. For example, with the TNT kit, TNT and TNB turn red; DNB turns purple; 2,4-DNT turns blue; and 2,6-DNT turns pink and tetryl turns orange. For the EnSys RDX + HMX kit, RDX and HMX turn pink as do nitroglycerine, PETN, and nitrocellulose. An orange color indicates a mixture of TNT and nitramines or nitrate esters.

Immunoassay Methods—For TNT immunoassay kits, the primary target analyte is TNT, and the secondary target analytes are nitroaromatics TNB, DNTs, AmDNTs, and tetryl. For the RDX kit, the primary target analyte is RDX, and there is but little cross-reactivity with HMX (3%). If the primary target analyte is the only compound present in water, the immunoassay methods measure the concentration of that compound.

If multiple analytes are present in water, the immunoassay kits measure the primary target analyte plus some percentage of the cross-reactive secondary target analytes. The response of immunoassay kits to the secondary target analytes is not equivalent to that of the primary target analyte and does not remain constant throughout the concentration range of the kits. In addition, different immunoassay kits have different cross-reactivities to secondary target analytes based on the antibodies used to develop each method. Cross-reactivities for immunoassay kits are usually reported at the 50% response level (IC_{50}), typically the midpoint of the concentration range of the kits.

Table 7 shows the reported cross-reactivities at IC_{50} for the immunoassay kits. A complete cross-reactivity curve for the entire concentration range should be obtained from the manufacturers for the immunoassay kits being considered. Where multiple analytes exist in water samples, immunoassay results may not directly compare with EPA Method 8330 (EPA 1998) results. For example, an immunoassay kit may have cross-reactivities of 23% for TNB for the TNT test kit and 3% HMX cross-reactivity for the RDX test kit. The following simple example illustrates cross-reactivity; however, in practice, it is not practical to calculate contaminant concentrations in this manner because of synergistic effects and cross-reactivity is nonlinear. Using the same sample as the

colorimetric example above, if a water sample (as analyzed by Method 8330) contains 100 µg/L each of TNT, TNB, RDX, and HMX, the TNT field immunoassay kit would measure approximately 123 µg/L (100 TNT + 23 TNB), and the RDX field method would measure approximately 103 µg/L (100 RDX + 3 HMX).

Biosensor Methods—For the CFI method, relative to TNT at 100%, the cross-reactivities of other explosive compounds are TNB 600%; tetryl 38%; 2-AmDNT 21%; 2,4-DNT 20%; NB 16%; 2-NT 9%; HMX 5%; 2,6-DNT 4%; 4-AmDNT 1%; and RDX 1%. The RDX method is much more compound specific with 18% cross-reactivity for 1,2-dinitroglycerin, 5% for HMX, 4% for TNB, and about 3% for DNB, 3-NT, and 2-NT.

For the FOB TNT method, TNB is 9% cross-reactive, and for the RDX method, all of the 17 explosive-related compounds tested are less than 3% cross-reactive.

Matrix Interferences—Colorimetric, immunoassay, and biosensor methods may be subject to positive or negative matrix interferences from organic and inorganic substances in water. For colorimetric methods, through careful visual analysis noted by a positive red or pink color change in the sample before colorimetric analysis, these interferences can be evaluated. Inorganic nitrate and nitrite in water samples interfere with colorimetric methods unless special procedures are used to remove these compounds during analysis. It is important to note that high levels of humic organics can impart a yellowish coloration to the acetone extracts. An increase in the intensity of the yellow color upon reaction with the reagent is not a positive response for the TNT test, and the development of a reddish hue to the solution is necessary before a detection is claimed. Analysis of a field matrix blank may be useful in identifying such interference.

Many of the immunoassay methods use a reverse-coloration process, and nontarget analyte organic matrix interference results in less color development. Therefore, on-site method results are biased high compared to laboratory results.

Both the CFI and FOB NRL methods have been used at several different sites, but interferents other than other explosives have not been determined.

Supplier Recommended Quality Assurance/Quality Control

The manufacturers or developers recommended quality assurance/quality control (QA/QC) procedures vary considerably with the on-site method. Some test methods do not specify QA/QC procedures and leave to the investigator the determination of the numbers of blanks, duplicates, replicates, and standards that are run. During field application of these methods, it is common to send at least 10 to 20% of the positive samples to an off-site laboratory for analysis by EPA Method 8330. A smaller fraction of the nondetect samples also may be verified. In some cases, field methods are used to identify samples containing explosive residues, and all such samples are sent to an off-site laboratory for analysis. In any case, the QC samples recommended by the method developer should be used. However, it is up to the user to determine how much and what types of QA/QC are needed to achieve the DQOs.

While it is essential to ensure that field methods perform as intended, requiring laboratory type QC may be inappropriate for on-site analytical methods. Because site characterization efforts may be cost constrained, excess QC samples reduce the number of field samples that can be analyzed. Good sample handling procedures and correlation of the field methods with the laboratory HPLC method over the concentration range of interest should be the primary performance criteria. Documentation of procedures and results must be emphasized.

During the initial evaluation of on-site and off-site analytical methods, it may be desirable to analyze a variety of QC samples to determine sources of error. The methods can then be modified to minimize error as efficiently as practical to include, for example, the collection and analysis of duplicates, replicates, splits of samples, and splits of extracts.

Table 7. On-Site Analytical Methods for Explosives in Water, Percent Interference, or Cross-Reactivity.

	Nitroaromatics								Nitramines		Other
Test Method	**TNT**	**TNB**	**DNB**	**2,4-DNT**	**2,6-DNT**	**2AmDNT**	**4AmDNT**	**Tetryl**	**RDX**	**HMX**	**PETN**
TNT											
EnSys [a]	100	100	100	100	100	NC	NC	100	NC	NC	-
D TECH [a]	100	23	-[b]	4	-	11	<1	35	<1	<1	-
RaPID Assay [a]	100	65	2	4	<1	3	1	5	<1	<1	-
Flow Immunosensor	100	600	-	20	4	21	1	38	1	5	-
Fiber Optic Biosensor [a]	100	9	<3	<3	<3	<3	<3	<4	<1	<4	-
RDX											
EnSys [a]	NC	NC	NC	NC	NC	NC	NC	NC	100	100	100
D TECH [a]	<1	<1	<1	<1	<1	<1	<1	<1	100	3	<1
Flow Immunosensor	2	4	3	3	1	1	2	1	100	5	-
Fiber Optic Biosensor [a]	<3	<3	<3	<3	<3	<3	<3	<3	100	<3	-

[a] Interference for colorimetric methods, cross-reactivity for immunoassay methods at 50% response (IC_{50})

[b] No data

NC No Color Development

Storage Conditions and Shelf Life of Kit or Reagents

Storage conditions and the shelf life of immunoassay kits are more critical than with colorimetric methods. The reagents for some immunoassay kits should be refrigerated but not frozen or exposed to high temperatures. Their shelf life can vary from 3 months to more than 1 year. Colorimetric reagents can be stored at room temperature. The EnSys colorimetric kits have shelf lives of at least 2 months and up to 1 or 2 years. Before ordering test kits, it is important to know when they will be used to ensure that they will be used before the expiration date.

For immunoassay kits, D TECH may be stored at room temperature while the RaPID Assay reagents should be refrigerated. Neither kit should be subjected to freezing.

The CFI membranes need to be stored moist at 4EC, and away from light. They have a shelf life of about 1 month. It is recommended that the FOB be operated out of direct sunlight and recommended but not required, that stock solutions be refrigerated. Stock solutions can be freeze dried for storage up to a year and rehydrated and held for up to a month unrefrigerated. The antibody-coated fibers may be preserved and stored for more than a year at room temperature if freeze dried or be placed in a buffer solution at 4EC. These procedures may become simplified if the CFI and FOB methods become commercialized.

Skill Level

The skill level necessary or required to run these tests varies from low to high (Table 6), requiring a few hours to a day of training. The manufacturer of the commercial kits generally provides on-site training. A free training videotape on the CRREL version of the TNT and RDX procedures (which also is useful for the EnSys colorimetric kits) is available by submitting a written request to:

Commander U.S. Army Environmental Center
Attn: SFIM-AEC-ETT/Martin H. Stutz
Aberdeen Proving Ground
MD 21010
E-mail: mstutz@aec2.apgea.army.mil.

A training video on the USACE Standard Operating Procedures for Analysis of TNT and RDX (USACE 1999) will be available from:

Kira Lynch
Seattle District Corps
PO Box 3755 (EN-TB-ET)
Seattle WA 98124-2255
E-mail: Kira.P.Lynch@usace.army.mil.

Training videos are also available for some kits.

Cost

As shown in Table 6, routine sample costs vary by method. The cost per sample is affected by the costs of consumable items, analytical instruments, and reusable apparatuses required to run the method. In figuring the cost per sample, it is important to estimate the costs of possible reruns for out-of-range analyses. With the EnSys colorimetric kits, or the CRREL AP/PA method, the color-developed extracts may be simply diluted and reread with the spectrophotometer. It should also be noted that the CRREL TNT and RDX + HMX methods should become more economical than the EnSys kits as the number of samples increases. With the other methods, the original water sample must be diluted and reanalyzed, which for immunoassay methods requires the use of an additional kit. Colorimetric methods typically have sufficient extra acetone for dilution to rerun samples with no increase in material cost. It should be noted that the per-sample costs shown in Table 6 are only for supplies plus equipment. Labor, data management, data review and data reporting are not included.

In contrast to the previous methods which have relatively low initial costs and higher per sample costs, the two NRL biosensor-based methods, have high initial capital costs and low per sample costs. Eventually there is a break-even point at which, with high numbers of samples, the NRL methods become more economical than colorimetric and immunoassay methods.

Comparisons to Laboratory Method 8330

The objectives of the study or investigation, the site-specific contaminants of concern, the concentration ranges encountered or expected, and their relative concentration ratios affect the selection of

a particular on-site method. The accuracy of an on-site method is another selection criterion but care must be used in interpreting accuracy results from comparisons between reference analytical methods and on-site methods.

Colorimetric methods actually measure classes of compounds (i.e., nitroaromatics or nitramines) and immunoassay methods are more compound specific. Therefore, the reported accuracy of a method may depend on the mix of explosives compounds present in the water sample and the reference method data used for the comparison (i.e., data on specific compounds or total nitroaromatics or nitramines).

The precision and bias of the screening methods are most appropriately assessed by comparison to established laboratory methods such as EPA Method 8330. Methods of comparison that have been used include relative percent difference (RPD), linear regression, correlation, and percent of false positive and false negative results. If precision and bias are of critical importance, it is recommended that the reports referenced in this section be consulted directly. Statistical results can be misleading when outliers or extreme values are present. For example, in one linear regression comparing field and laboratory methods, the slope reported was 11 (i.e., measured against an ideal slope of 1) while the correlation coefficient was 0.99 (i.e., measured against an ideal of 1.0) all because of one very high concentration value being included with the remaining low values. It also should be remembered that the contribution of analytical error may be small compared to total error. Field error is usually the major contributor to total error. In comparing results, it should be noted that all CFI and FOB statistical results are usually based on the means of several analyses per sample whereas the regression lines and RPD for the other on-site methods are based on single measurements.

Several studies have been conducted comparing the performance of two or more on-site methods with Method 8330. Thorne and Myers (1997) evaluated several immunoassay methods including the D TECH TNT and RDX kits, and the RaPID Assay TNT kit. Craig et al. (1996) and EPA (1997) evaluated (1) the EnSys TNT and RDX + HMX colorimetric kits, (2) D TECH TNT and RDX immunoassay kits, (3) the RaPID Assay TNT immunoassay kit, (4) the CFI methods for TNT and RDX, and (5) the FOB for TNT. The results presented include estimates of method bias as determined by calculated RPDs and linear regression analysis. Another study was conducted by NRL to obtain more comprehensive data on the FOB and CFI methods (ESTCP 1998). The Army Corps of Engineers compared the EnSys TNT and RDX + HMX method with Method 8330 during monitoring at the Umatilla Groundwater site (ACOE 1998). The results from each of these studies are summarized below and in Tables 8 and 9.

The Thorne and Myers (1997) study investigated TNT and RDX levels in 44 groundwater wells from three sites: the Umatilla Army Depot in Hermiston, Oregon; the Naval Submarine Base in Bangor, Washington; and the Naval Surface Warfare Center in Crane, Indiana. The capability of immunoassay kits was evaluated to determine whether groundwater samples exceeded the EPA lifetime health advisory of 2 µg/L (Roberts and Hartley 1992; Roberts et al. 1993) and whether the RPDs (the difference between the field and reference method concentration divided by the mean value and expressed as a percent) were within ± 50% of Method 8330 results. The results "were disappointing" and "none of the test kits performed as well as advertised," Thorne and Myers (1997) reported. "The quantitative assays were neither accurate nor precise enough to replace Method 8330 although they could be used adequately as screening tools". The D TECH RDX test "failed badly" by producing 24% false negative and 18% false positive results relative to the drinking water advisory limit of 2 µg/L. The D TECH TNT kit produced 30% false positive and no false negatives. The detection limit of both D TECH kits are above the 2 µg/L drinking water advisory limits. The RaPID Assay method for TNT demonstrated no false positive or false negative results. Thorne and Myers also looked at the percent of sample results within ± 50% of the Method 8330 results. For D TECH TNT and RDX kits, 32% and 58% of the results,

respectively, were within acceptable limits. For the RaPID Assay method, 85% of the results were acceptable. Finally they conducted regression analyses comparing the RaPID Assay TNT kit performance with Method 8330 results on groundwater samples. The ideal regression line would be $Y = mX + b$ where the slope, m, would equal 1 and the intercept, b, would equal 0. The dependent variable is Y (on-site method estimate), and the independent variable is X (Method 8330 result). A correlation coefficient (r) is typically calculated that shows the degree of association between the on-site method and Method 8330 and can range between -1 and +1. For a perfect positive correlation r = 1. The Thorne and Myers RaPID Assay results were $Y = 1.48X + 0.0$ with a correlation coefficient of r = 0.93, which is highly significant (99% probability level).

Results from the EPA study (Craig et al. 1996; EPA 1997a) are summarized in Tables 8 and 9 for the groundwater samples from the Umatilla Chemical Depot in Hermiston, Oregon, and the Naval Submarine Base in Bangor, Washington. Groundwater at Umatilla has high nitrates and low turbidity while groundwater and leachate at Bangor has relatively high organic carbon and higher turbidity. Tables 8 and 9 includes the slope of regression lines for TNT and RDX data respectively, the correlation coefficient (r), the mean and median of the absolute RPD values (indication of precision), and mean of the RPDs (indication of bias). The mean RPD closest to 0 shows the greatest average agreement with the reference laboratory method. The study concluded that no on-site analytical method out performed the other methods in all comparisons. For the TNT methods, the EnSys and CFI had the highest accuracy followed by the FOB, RaPID Assay, and D TECH methods. All TNT method results were biased high based on the net RPDs at both sites and were generally biased slightly low for RDX. For RDX, the EnSys and CFI methods showed the highest accuracy followed by D TECH. In general, the RDX on-site analytical methods performed better than the TNT method. The performance may have resulted from the higher levels of RDX, which necessitated sample dilution and, thereby, also reduced matrix interferences.

The EnSys TNT kit accuracies were similar for both sites and for the RDX kit, results were slightly more accurate at the Bangor site. Using an RPD acceptance criterion of ± 50% of the Method 8330 result, 89% of the EnSys TNT results were acceptable and 78% of the RDX results were acceptable. Overall accuracy of the TNT and RDX EnSys colorimetric methods were acceptable.

The D-TECH methods were more accurate at Umatilla than Bangor because of lower interference from organics and particulate matter. The majority of the TNT RPD values were positive and linear regression slopes were greater than 1.0, thereby indicating a high bias for the on-site methods, possibly resulting from TNB interference or cross-reactivity. Using an RPD acceptance criterion of ± 50% of the Method 8330 result, 70% of the D TECH results were acceptable while 56% of the RDX results were acceptable.

The CFI TNT method performed about the same at both sites while the FOB method performed better at the Umatilla site. For RDX, the CFI performed well at both sites and was similar in accuracy to the EnSys method.

A recent report (ESTCP 1998) documented the performance of the NRL CFI and FOB methods at the Umatilla Army Depot, the Bangor Naval Submarine Base, and the Crane, Naval Surface Weapons Center. Both methods were modified significantly between the Craig et al.(1995) study and the ESTCP (1998) study. For the CFI, the instrument was changed and the small columns were replaced by membranes. The FOB TNT antibody was changed as well as the fiber geometry. The statistics provided in Table 8 and discussed below were calculated after the analytical results below 10 µg/L, or listed as below the detection limit, were replaced with 5 µg/L (one-half of the method detection limit). However, data were not included if both the NRL and Method 8330 data would have been replaced with 5 µg/L. This approach was taken to permit more data to be included in the analyses yet avoid producing extreme RPDs near the detection limit. Because a few very high or low values relative to

most of the data can have a misleading impact on linear regression data, some regression equations were recalculated with high or low samples deleted based on the Method 8330 concentration. The recalculated results are discussed in the text below.

The CFI data for TNT showed highly significant correlations with Method 8330 data at the Umatilla and Bangor sites; however, the mean and median RPDs were high (Table 8). This apparent contradiction results from several high concentration samples. If the three samples at Umatilla with Method 8330 results greater than 200 µg/L are deleted (367, 846, and 1160 µg/L), the regression equation changes to $Y = 0.61X + 9$ and the correlation coefficient drops to 0.51, which is not significant (95% probability level). For the Bangor site, two of the seven sample results showed concentrations greater than 200 µg/L and most of the remaining Method 8330 values were below 5 µg/L. Only four samples from the Crane facility were analyzed by the CFI method; therefore, no regression line was calculated. The mean and median RPDs were about 100.

The FOB results for TNT showed regression slopes of 0.41 and 0.35 for the Umatilla and Bangor sites, respectively. The corresponding correlation coefficients were 0.52 and 0.70, which were significant and not significant, respectively. For all of the TNT samples analyzed by the FOB method, the TNT levels were below 200 µg/L. No Crane samples were analyzed for TNT using the FOB method.

For RDX, the CFI method showed highly significant and significant regressions with Method 8330 data collected at Umatilla and Bangor, respectively (ESTCP 1998). Net RPDs demonstrated a low bias at both sites (-63 and -42), and the means and medians of the absolute RPDs ranged from 68 to 78. At Crane, the CFI method showed a highly significant regression, mean and median absolute RPDs of 64 and 42 with a net RPD of -6. If the one especially high or low 8330 value is deleted from the Bangor and Crane data sets, the resulting regression lines are still significant, as is the regression for Umatilla when the three samples with 8330 values greater than 200 µg/L are deleted.

The FOB results on RDX at Umatilla and Bangor showed highly significant regressions, mean and median RPDs generally below 50, and low net RPDs. All of the Umatilla 8330 results were below 200 µg/L, and if two high samples (356 and 562 µg/L) at Bangor are deleted, the regression is still significant although the slope of the regression line changes to 2.5.

The Army Corps of Engineers collected numerous groundwater samples at Umatilla that were analyzed for multiple compounds during an effort to document the conditions in groundwater wells and the effectiveness of the granular activated carbon treatment system (ACOE 1998). After eliminating nonrepresentative data, EnSys and Method 8330 data were available for 40 RDX and 36 TNT samples (Table 8). These regression results for these data show $Y = 0.69X + 132$ with $r = 0.90$ for RDX and $Y = 1.3X - 15$ with $r = 0.97$ for the TNT data. The averages of the absolute value of the RPDs were 31 for RDX and 44 for TNT. For these data sets, the net RPDs (average when sign is considered) were -6.1 for RDX and 22 for TNT and are relatively unbiased compared with other study results presented in Table 9. Ideally, the net RPD should balance out to zero indicating no bias.

Several projects comparing Method 8330 results with on-site analytical methods are underway so additional published data will become available from EPA and the Corps of Engineers. Also, see the section on emerging technologies about a planned demonstration for the summer of 1999 on current and emerging on-site methods for explosives in water and soil.

Table 8. Comparison of On-Site Analytical Methods for TNT to EPA Method 8330

Method	TNT						
	Regression Umatilla	**Regression Bangor**	**Correlation Coefficient (r) Umatilla/Bangor**	**Mean RPD (absolute value) Umatilla/Bangor**	**Median RPD (absolute value) Umatilla/Bangor**	**Net RPD Umatilla/Bangor**	**Number of Samples Umatilla/ Bangor**
EnSys[1]	Y = 1.4X + 191	Y = 1.1X + 51	0.98**/1.0**	66/58	45/63	66/58	15/9
D TECH[1]	Y = 2.0X + 73	Y = 11X - 558	0.88**/1.0**	64/143	48/152	58/143	15/7
RaPID Assay[1]	Y = 1.0 X + 140		0.99**combined	78 combined	87 combined	78 combined	7 combined
Flow Immunosensor[1]	Y = 1.2 + 46	Y = 1.2 X + 242	0.70*/0.84*	47/52	47/38	32/51	11/7
Fiber-Optic Biosensor[1]	Y = 1.7X -267	Y = 0.71X + 285	0.91**/0.76*	33/107	25/116	30/100	12/8
Flow Immunosensor[2,4]	Y = 0.71X - 18	Y = 1.6X - 7	0.92**/0.98**	114/100	147/89	-41/87	14/7
Fiber-Optic Biosensor[2,4]	Y = 0.41X + 24	Y = 0.35X + 10	0.52*/0.70	85/55	74/52	67/40	16/6
EnSys[3]	Y = 1.3X - 15		0.97**	44	30	22	36
Method	**Regression Crane**		**Correlation Coefficient (r)**	**Mean RPD (absolute value)**	**Median RPD (absolute value)**	**Net RPD**	**Number of Samples**
Flow Immunosensor[2,4]	NA		NA	103	103	36	4

[1] EPA 1997a

[2] ESTCP 1998

[3] ACOE 1998

[4] Statistics based on means of usually eight or more analyses of each sample.

* Statistically significant at the 95% probability level.

** Statistically significant at the 99% probability level.

Table 9. Comparison of On-Site Analytical Methods for RDX to EPA Method 8330

Method	RDX						
	Regression Umatilla	Regression Bangor	Correlation Coefficient (r) Umatilla/Bangor	Mean RPD (absolute value) Umatilla/Bangor	Median RPD (absolute value) Umatilla/Bangor	Net RPD Umatilla/Bangor	Number of Samples Umatilla/Bangor
EnSys[1]	Y = 0.81X + 135	Y = 0.96X + 6	0.86**/0.92**	33/21	27/21	-11/-7.7	23/12
D TECH[1]	Y = 1.3X -269	Y = 1.7X + 172	0.96**/0.61*	53/67	32/56	-36/61	23/12
Flow Immunosensor[1]	Y = 0.92X + 203	Y = 0.72X + 1.1	0.72**/0.92**	26/30	19/23	-11/-30	20/12
Flow Immunosensor[2,4]	Y = 0.72 X - 30	Y = 0.67X - 3	0.91**/0.69*	78/76	78/68	-63/-42	20/11
Fiber-Optic Biosensor[2,4]	Y = 0.53X + 13	Y = 0.61X + 38	0.64**/0.82**	37/56	33/40	10/14	20/10
EnSys[3]	Y = 0.69X + 132		0.90**	31	32	-6.1	40
Method	**Regression Crane**		**Correlation Coefficient (r)**	**Mean RPD (absolute value)**	**Median RPD (absolute value)**	**Net RPD**	**Number of Samples**
Flow Immunosensor[2,3]	Y = 0.75X + 40		0.77**	64	42	-6	13
Fiber-Optic Biosensor[2,3]	Y = 0.44X - 5		0.94**	100	104	-100	11

[1] EPA 1997a

[2] ESTCP 1998

[3] ACOE 1998

[4] Statistics based on means of usually eight or more analyses of each sample.

* Statistically significant at the 95% probability level.

** Statistically significant at the 99% probability level.

Additional Considerations

Other important factors in the selection of an on-site method include, for example, the size and type of working area required, the temperature of the working area, the need for electricity and refrigeration, the amount of waste produced, the need to transport solvents, and the degree of portability. Immunoassay methods are more sensitive than colorimetric methods to freezing and elevated temperatures, and the ambient temperature affects the speed at which color development takes place on some immunoassay methods. Most tests are best run protected from the weather, for example, in a van, field trailer, or nearby building.

Emerging Methods

A GC-nitrogen phosphorus detector method currently under development at CRREL appears to offer the ability to provide on-site analysis for the common suite of nitroaromatics and nitramines in water (Hewitt and Jenkins in press). In this method, the analytes of interest are preconcentrated by passing 1 L of water through Empore SDB-RPS extraction membranes and eluting the retained compounds with 5 mL of acetone. An aliquot of the acetone extract is then determined on a field portable gas chromatograph equipped with a nitrogen-phosphorus detector. Method detection limits were demonstrated to be below 1 ppb for TNT, RDX, 4-amino-DNT, 2-amino-DNT, and 2,4-DNT.

Two German companies are now manufacturing immunoassay kits for explosives in water but no literature was found comparing on-site results to standard methods. The TNT kit by Coring System uses a 96 well microplate to which TNT conjugate is bound. Samples, or TNT standards and a TNT specific antibody (rabbit) are pipetted into wells and the plate is incubated for an hour. After rinsing, a rabbit specific antibody is added, the plate is incubated for an hour, rinsed, and substrate is added to the wells. After 20 minutes of incubation, blue color development is stopped and the resulting yellow color is read at 450 nm using a photometer. The TNT concentration is inversely proportional to the color. The method detection limit is reported to be 0.5 µg/L for water. The method is cross reactive with 1,3-DNT (650%), and 2,4-DNT (60%). For more information send e-mail to: info@coring.de.

Coring currently has no plans to market their kit in the U.S. No information was provided by Bio-Genes on their immunoassay procedure.

In December, 1998, EPA issued a Notice of an Intention to Conduct a Demonstration and Performance Verification Study of Explosives Field Analytical Devices as part of the Environmental Testing and Verification program. The demonstration is planned for the summer of 1999 and will include analysis of both water and soils. For further information on the demonstration, contact:

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Summary of the EPA Reference Methods for Explosive Compounds in Water

Properties of Secondary Explosives

The two secondary explosives used to the greatest extent by the U.S. military over the past 70 years are TNT and RDX. With their manufacturing impurities and environmental transformation products, the two compounds account for a large part of the explosives contamination at active and former U.S. military installations. While all explosive compounds can all be classified as semivolatile organic chemicals, their physical and chemical properties require different analytical approaches than normally is used for other semivolatiles.

Table 10 presents some of the important physical and chemical properties for TNT and

RDX, and some of their commonly encountered manufacturing impurities and environmental transformation products. The unique properties that differentiate these chemicals from other semivolatiles such as polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PNAs) are their thermal lability and polarity. Many of these compounds thermally degrade or explode at temperatures below 300EC. Thus, methods based on gas chromatography (GC) have not gained wide acceptance. However, methods developed by Hable et al. (1991) and Walsh and Ranney (1998a, 1998b) have shown that the gas-chromatography electron-capture detector (GC-ECD) method can be used successfully for nitro-aromatics and nitramines in water. In addition, log K_{ow} values range from 0.06 to 2.01 compared with values of 4 to 5 for PCBs and PNAs, indicating that these compounds are quite polar and that the nonpolar solvents used for other semi-volatile organics are not the best choice for extraction of nitroaromatics and nitramines from water. For most routine analyses, environmental water samples are extracted with either salting-out solvent extraction with acetonitrile or using solid-phase extraction with a styrene-divinyl-benzene-based solid phase (Method 3535A [EPA 1998]). The sample extracts are analyzed using reversed-phase high-performance liquid chromatography (RP-HPLC), often using Method 8330 (EPA 1998) or a recently adopted GC-ECD method, Method 8095 (EPA 1998).

Water Extraction

High concentration water samples have generally been analyzed by diluting an aliquot of the water 1:1 with methanol, then filtering the sample through a 0.45 to 0.50-µm filter, and analyzing a 100-µL aliquot of the filtrate by RP-HPLC-UV. Quantitation limits for this direct water method (Method 8330) range from 5.7 µg/L for 2,4-DNT to 14 µg/L for RDX.

Often detection limits that can be obtained using the direct water method are not sufficient for project-specific DQOs. In these cases, the target analytes must be extracted from the water and preconcentrated before either RP-HPLC-UV (Method 8330) or GC-ECD (Method 8095) determination. Extraction is accomplished using either salting-out solvent extraction (Leggett et al. 1990) followed by nonevaporative preconcentration (Jenkins and Miyares 1991), or by solid-phase extraction, EPA Method 3535A (Jenkins et al. 1995b, 1995c; EPA 1998).

A direct comparison of salting-out solvent extraction and solid-phase extraction with RP-HPLC-UV was conducted by Jenkins et al. (1994a, 1995b, 1995c) using groundwater samples from the Crane, Indiana, Naval Surface Warfare Center. The results indicate that excellent extraction efficiency was achieved using both procedures (recoveries were generally greater than 90%). Quantitation limits using these approaches were similar and ranged from less than 0.1 µg/L for some target analytes to 0.84 µg/L for RDX. The authors cautioned, however, that carefully cleaned solid phases must be used or interferences will be released from the solid phases by some water matrices (Jenkins et al. 1994a, 1995b, 1995c). A small residual peak that interfered with RDX was found even with highly cleaned solid-phase materials. The GC-ECD method, which was recently given preliminary approval by the EPA (Method 8095, [EPA 1998]), specifies that solid-phase extraction should be used when samples are to be analyzed by GC-ECD. The salting-out solvent extraction method was not evaluated for use with GC-ECD. Method detection limits (MDLs) for the GC-ECD method range from 0.04 µg/L to 0.4 µg/L for the various target analytes when a 500-mL sample is used and preconcentrated into 5 mL of acetonitrile.

Reversed-Phase High-Performance Liquid Chromatography Determination

Generally, detection of the analyte within the proper retention time window on two columns with different retention orders is required for confirmation of the presence of these explosives. Method 8330 specifies primary analysis on an LC-18 (octadecylsilane) column with confirmation on a cyanopropylsilane (LC-CN) column (Jenkins et al. 1989).

Table 10. Physical and Chemical Properties of Predominant Nitroaromatics and Nitramines.

Compound	Molecular Weight	Melting Point (EC)	Boiling Point (EC)	Water Solubility (mg/L at 20E)	Vapor Pressure (torr at 20E)	log K_{ow}
TNT	227	80.1 to 81.6	240 (explodes)	130	4.4E-06	1.86
TNB	213	122.5	315	385	2.2E-04	1.18
2,4-DNT	182	69.5 to 70.5	300 (decomposes)	270	1.1E-04	2.01
Tetryl	287	129.5	(decomposes)	80	5.7E-09	1.65
RDX	222	204.1	(decomposes)	42	4.1E-09	0.86
HMX	296	286	(decomposes)	5 at 25E	3.3E-14	0.061

Walsh, Chalk, and Merritt (1973) were the first to report on the use of RP-HPLC for the analysis of nitroaromatics in munitions waste. Most subsequent HPLC methods for these compounds rely on UV detection because of its sensitivity and ruggedness. Initially, determination was specified at 254 nm because of the availability of fixed wavelength detectors at this wavelength based on the mercury vapor lamps and a significant absorbance of all target analytes. Current instruments are generally equipped with either variable wavelength detectors or diode array detectors, and wavelengths of maximum absorption can be selected to optimize detection. However, 254 nm is still often used because it is specified in Method 8330 and because of the low incidence of interference at this wavelength.

Gas-Chromatography Electron-Capture Detector Determination

The earliest use of gas chromatography to determine nitroaromatics dates from the early 1960s (Parsons et al. 1961). The early methods used the relatively insensitive flame ionization detector, and it was not until the early 1970s that the selectivity and sensitivity of the ECD for nitroaromatics was realized (Murrmann et al. 1971). The first GC-ECD method for nitroaromatics and nitramines in water was developed by Hoffsommer and Rosen (1972). The introduction of fused silica columns in the early 1980s reduced the problems with thermal degradation of these thermally labile compounds and permitted routine determination of nitramines by GC. Routine analytical methods were developed for nitroaromatics by Belkin et al. (1985) and for nitroaromatic and nitramines by Hable et al. (1991) at the Army Environmental Hygiene Agency. Hable's method used solvent extraction to extract and preconcentrate the target analytes and GC-ECD for determination. Unfortunately, two separate extractions were needed, one for nitroaromatics using toluene and a second for nitramines using isoamylacetate. More recently, Walsh and Ranney (1998b) combined solid-phase extraction with GC-ECD, and the results were used to establish EPA Method 8095 (EPA 1988). One advantage of Method 8095 compared with Method 8330 is the ability to quantify nitroglycerine and PETN in the same determination as the nitroaromatics and nitramines.

Method 8095 specifies that detection of peaks from the ECD within the proper retention time window on two columns with different polarity is required for confirmation of the presence of the target analytes. Method 8095 specifies DB1 as the primary analytical column (although DB5 provides better resolution for target analytes) and either RTX200 or RTX225 as the confirmation column (Walsh and Ranney 1998a, 1998b).

It is important that the injector and oven temperatures, column lengths, and linear velocities specified in Method 8095 are used for GC-ECD analysis. Otherwise, poor recovery, particularly for HMX, will result. The injection port liner must be thoroughly deactivated and changed frequently, or performance will be degraded for HMX, RDX, and the aminodinitrotoluenes. Particular attention also must be given to thorough drying of the solid phase used for solid-phase extraction before elution with acetonitrile.

A comparison of the performance of GC-ECD with RP-HPLC-UV for these target analytes in water is presented by Walsh and Ranney (1998a, 1998b). Analysis of extracts by both RP-HPLC-UV and GC-ECD results in excellent analytical confirmation, particularly when target analytes are present at very low concentrations.

Method Specifications and Validation

Based on the research described above, EPA Method 8330 (EPA 1998) and Method 8095 (EPA 1998) specify the following:

A. Salting-out the Solvent Extraction

1. Place 251.3 g of sodium chloride in a 1-L (round) volumetric flask. Add a 770-mL aliquot of the water sample, and stir the flask with a stirring bar until the salt is dissolved.
2. While stirring the solution, add 164 mL of acetonitrile to the flask. Stir for at least 15 minutes (30 minutes is safer) to dissolve as much acetonitrile as possible. Turn off the

stirring bar, and allow the phases to separate for at least 10 minutes.

3. Remove the upper acetonitrile layer (about 8 mL) with a Pasteur pipette and transfer it to a 100-mL (round) volumetric flask. Add 10 mL of fresh acetonitrile to the water sample in the 1-L flask and stir for an additional 15 minutes, followed by 10 minutes to allow the phases to separate. Remove the upper acetonitrile layer and combine with the initial acetonitrile extract in the 100-mL flask.

4. Add 84 mL of salt water (325 g of NaCl per 1,000 mL of reagent-grade water) to the 100-mL flask, and stir for 15 minutes, followed by 10 minutes for phase separation. Carefully transfer the top acetonitrile layer to a 10-mL graduated cylinder using a Pasteur pipette. Add an additional 1.0 mL of acetonitrile to the 100-mL flask and stir for 15 minutes followed by 10 minutes for phase separation. Combine the second extract with the first in the 10-mL graduated cylinder. Record the volume of extract and then dilute it 1:1 with reagent grade water. This extract is analyzed using RP-HPLC.

B. Cartridge Solid-Phase Extraction

1. Obtain prepacked solid-phase extraction cartridges (Porapak RDX or Sep-Pak, 6 cc, 500 mg, or equivalent). Clean the cartridges by placing them on a solid-phase extraction manifold and passing 15 mL of acetonitrile through each using gravity flow. Then flush the acetonitrile from the cartridges using 30 mL of reagent-grade water. Ensure that the cartridges are never allowed to dry after the initial cleaning.

2. Place a connector on the top of each cartridge and fit the connector with a length of one-eighth-in.-diameter Teflon tubing. Place the other end of the tubing in a 1-L beaker containing 500 mL of sample. Turn on the vacuum and set the flow rate through each cartridge at about 10 mL per minute. Adjust the flow rate if it declines significantly because of partial plugging from the suspended material. After extracting the sample, remove the top plug containing the fitted tubing from each cartridge and pass 10 mL of reagent-grade water through the cartridge using gravity flow unless the cartridges are sufficiently plugged to require a vacuum. Use a 5-mL aliquot of acetonitrile to elute the retained analytes from the cartridges under gravity flow. Measure the volume of the recovered acetonitrile, and either use directly for GC-ECD determination (Method 8095) or dilute 1:1 with reagent-grade water for RP-HPLC-UV determination.

C. Membrane Solid-Phase Extraction

1. Preclean styrene-divinylbenzene membranes (47 mm, Empore or equivalent) by centering on a 47-mm vacuum filter apparatus and add several milliliters of acetonitrile to swell the membrane before clamping the reservoir in place. Add a 15-mL aliquot of acetonitrile to soak into the membrane for 3 minutes. Then turn on the vacuum and pull most (but not all) of the solvent through the membrane.

2. Add a 30-mL aliquot of reagent-grade water and resume the vacuum. Just before the last of the water is pulled through the membrane, remove the vacuum, fill the reservoir with a 500-mL sample, and resume the vacuum. The sample extraction will take from 5 minutes to an hour depending on the amount of suspended matter present. Once the water is eluted, draw air through the membrane for 1 minute to remove excess water. Place a 40-mL vial below the outlet of the membrane, and add a 5-mL aliquot of acetonitrile on top of the membrane. Allow the acetonitrile to soak into the membrane for 3 minutes. Then apply the vacuum to pull the acetonitrile through the membranes into the vials. Remove each resulting extract with a Pasteur pipette, and measure the volume in a 10-mL graduated cylinder. Measure the volume of the recovered acetonitrile, and either use directly for GC-ECD determination (Method 8095) or diluted 1:1 with reagent-grade water for RP-HPLC-UV determination.

Summary

A number of defense-related sites are contaminated with elevated levels of secondary explosives in groundwater and surface water. Levels of contamination range from barely detectable (approximately 1 µg/L) to more than 10,000 µg/L. On-site analytical methods are essential to more economical and improved characterization and remediation. What they lack in accuracy and multi-compound specificity, they more than make up for in the increased number of samples that can be analyzed and the utility of near-real-time data for making decisions on-site. While verification using a standard laboratory analytical method such as EPA Method 8330 or 8095 should be part of any quality assurance program, reducing the number of samples analyzed by more expensive methodology can result in reduced costs and more efficient use of limited resources while still achieving the DQOs.

Two basic types of on-site analytical methods are in use for explosives in water: colorimetric and immunoassay. Colorimetric methods generally detect broad classes of compounds such as nitroaromatics or nitramines while immun assay methods are more compound specific. Prototype biosensor methods for TNT and RDX have been field tested and are emerging methods for explosives analysis in water (Rogers and Gerlach 1996). Because TNT or RDX is usually present in explosive-contaminated groundwater or surface water, the use of field procedures designed to detect these or similar compounds can be very effective.

Selection of an on-site analytical method involves evaluation of many factors including the specific objectives of the study and DQOs, compounds of interest, explosives present at the site, the number of samples to be run, the sample analysis rate, interferences or cross-reactivity of the method, the skill required, the analytical cost per sample, and the need for and availability of support facilities or services. Other factors that should be considered are the precision and accuracy of the on-site analytical method and the required detection limits. It should be remembered that analytical error may be small compared to field error and that the precision and bias of a method is dependent on the site-specific conditions (compounds present and relative concentration) as well as the skill of the analyst.

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