

# Enhanced Extraction of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in the Presence of Sodium Dodecyl Sulphate and its Application to Environmental Samples

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## Abstract

A method for enhanced extraction of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) from environmental samples is developed with the assistance of sodium dodecyl sulphate (SDS) surfactant. In this study, the concentration of SDS surfactant and other analytical parameters are optimized on a high-performance liquid chromatography–UV system. An isocratic flow of 1.0 mL/min with mobile phase acetonitrile–water; 70:30 (v/v) at 230 nm wavelength on a reverse-phase amide column is used for baseline separation of explosives and making calibration curves. The amount of recovered explosives from spiked soil and water samples are calculated. The limits of detection obtained for HMX and RDX standards are 1.5 and 3.8 ppb (S/N = 3), respectively, which are much better than obtained by the Environmental Protection Agency method 8330. The recoveries are found to be enhanced by 1.7 and 1.6-fold with SDS solution as compared to water for HMX and RDX, respectively, from soil samples.

## Introduction

Cyclic nitramine explosives such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (Figure 1) are commonly used high explosives in armed forces munitions. These high explosives are usually dumped into the sea, burned, or detonated in remote areas, constituting potentially serious and hazardous contamination problems (1). Both RDX and HMX have low values of octanol/water partition coefficients ( $K_{ow}$ ), and  $\log K_{ow}$  values for RDX and HMX are 0.90 and 0.16, respectively (2), indicating their high affinity towards aqueous phase. For soil samples, this affinity is represented in terms of organic-carbon/

water partition coefficients ( $K_{oc}$ ), which can be determined directly from  $K_{ow}$  values depending on the type of sorbate (3,4). The  $K_{oc}$  is used as a chemical specific measure of the tendency for organics to be adsorbed by soil. It is largely independent of soil properties (e.g., the type and amount of clay, soil pH, cation exchange capacity, and hydrous oxide contents). For RDX and HMX, the values of  $\log K_{oc}$  lies in the range from 0.89–2.4 and 0.54–2.8, respectively (5). Broadly, the value of sorption or distribution coefficient ( $K_d$ ), which is a measure of how tightly the analyte binds or sticks to soil particles (including organic matter, clays or iron and manganese oxides), is less than unity (i.e.,  $K_d < 1$ ) for both nitramine high explosives, indicating their high mobility in soil (6). Therefore, RDX and HMX can migrate through subsurface soil very rapidly even though both are moderately to weakly soluble in water (i.e., 40.2 and 6.6  $\mu\text{g/mL}$ , respectively, at 25°C [7]), causing groundwater contamination very swiftly and as a consequence can travel distances from the contamination site. It has also been shown that explosives are modestly toxic to aquatic organisms, earthworms, and indigenous soil microorganisms (8,9). Many explosives are known toxins and carcinogens (10). RDX has been used as a potential rat poison (11). Also, the discharge of contaminated manufacturing waste streams into rivers or groundwater, burial of obsolete munitions, and

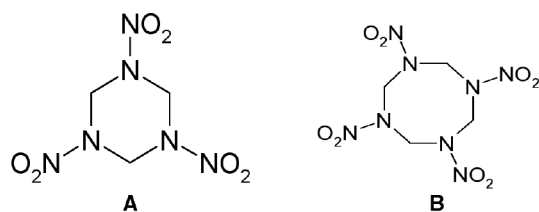


Figure 1. Chemical structure of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (A) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (B).

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training exercises increase the availability of explosives for migration into water supplies (12), so they pose a threat to living species as they find their way into the food chain.

Therefore, the ecological fates of HMX, RDX, and their degradation products are the subject of intensive study nowadays (13,14). For example, there is a growing requirement for the analysis of matrices such as soil and water in order to address environmental problems related to improper handling procedures, either in storage or in disposal of explosive products (15–17). For analytical issues, high-performance liquid chromatography–UV (HPLC–UV) has become a widespread and powerful method which belongs among the basic tools in each modern laboratory nowadays, and is recommended by US Environmental Protection Agency (EPA) method 8330 (18) for the analysis of explosives. Due to the high thermal stability and low vapor pressure of nitro explosives, HPLC is an instrument of choice for the analysis of explosives. The application of an HPLC–UV technique for the analysis of organic high explosives has been reviewed (19).

EPA Method 8330 (18) provides a salting-out extraction procedure for low concentrations (parts per trillion; i.e., nanograms per liter) of explosive residues present in surface or groundwater with acetonitrile; it allows direct injection of aqueous samples containing high concentrations of explosives after dilution with methanol–acetonitrile. In this method, large volumes of water sample (770 mL) and acetonitrile (aprox. 175 mL) were used for the salting-out extraction process, which is inconvenient. Both organic solvents are hazardous to health and the environment, being toxic (20–25). Also, the method is very cumbersome, time consuming, and requires much expertise, high levels of accuracy, and precision during analysis. This method is applicable only on miniaturized scale in the laboratory, not on a large scale in the field. The developed method with the assistance of surfactants can be used on a laboratory as well as on a field scale. On the field scale, the method can be applied for soil washing and determination of levels of contamination. Soil washing is the process in which contaminants sorbed onto fine soil particles are separated from bulk soil in an aqueous-based system on the basis of particle size. Wash water may be augmented with a basic leaching agent, surfactant, pH adjustment, or chelating agent to remove organics and heavy metals. The greatest advantage of soil washing with aqueous solution of surfactant is that it reduces the amount of soil needing further cleanup. This reduction lowers the cost of clean up and the cost of disposing of polluted material. This also works when the soil is heavily polluted. At the present time, soil washing is used extensively in Europe and has been progressively increasing use in the USA. Hence, the technique provides a cost-effective and environmentally proactive alternative to stabilization and land filling applicable on a macro scale, which is not recommended with organic solvents. Much work has been published on the soil washing with surfactant-based aqueous solutions (26–31). Surfactants are particularly attractive for such applications as they potentially have lower toxicity and more favorable biodegradability in the environment than many organic-solvent based systems. Washing fluid can be regenerated back, which increases the importance of soil washing with surfactants. The presence of

SDS in either water sample or aqueous extract of soil enhances the peak area of HMX during chromatographic analysis, which ultimately affects the limit of detection of HMX; the peak area for RDX remains almost the same during experimental concentration ranges of SDS. Because the two main nitramines are present in numerous explosive compositions, this paper investigates the potential use of aqueous solution of SDS to enhance the extraction of both explosives from complex soil environment and subsequent analysis by HPLC–UV. The method could be applied successfully on other aqueous samples obtained from the environmental media.

However, Hawari et al. (32) have reported the enhanced recovery of RDX from soil (2.0 g) with the help of anionic surfactants like SDS, Ligniste 458, and Lignosol, as well as cyclodextrins, but at very high concentration of explosive (1000 ppm). With 1% (w/v) solution (34.7mM) of SDS, 1.2-fold recovery was obtained as compared to water on a C<sub>18</sub> column, and this concentration of SDS was much higher than its own critical micelle concentration (8.2mM). The extracted RDX was accompanied with its own hydrolyzed product (i.e., 3,5-dinitro-1,3,5-triazacyclohex-1-ene [ca. 5%]) when extracted with anionic surfactants, while no RDX hydrolyzed product was obtained with the cyclodextrin-assisted extraction. The recovery was much better with cyclodextrins, so major emphasis was given to them, and no extraction and analytical conditions were optimized in the presence of SDS. The use of very high concentrations of anionic surfactant for extraction and the methoxide anion present in solvent phase (aqueous methanol) may be the causes of the removal of acidic proton alpha to nitro group in RDX (32). In our study, a reduced concentration of SDS (0.14mM) was used for recovery of explosives, and aprotic solvents were used instead as mobile phase, which accounts for the higher stability of RDX and HMX during the analytical process.

Limits of detection and other parameters were determined in the presence of SDS, which were not reported earlier. So this study can be used to monitor the concentration of explosives present in soil and water samples obtained from munitions manufacturing sites or other military-related activities, and in soil washing processes used for the bioremediation of explosives in soil.

## Experimental

### Reagents

Standard solutions of HMX and RDX in acetonitrile (1000 µg/mL) were purchased from Supelco (Bellefonte, PA). Acetonitrile (HPLC grade; UV cut-off 190 nm) was purchased from J.T. Baker chemicals (Xalostoc, Mexico). Triple distilled water was used as one of the solvents for chromatographic separation. Sodium dodecyl sulphate (Qualigens Fine Chemicals, Bombay, India) was used as an extracting surfactant. A stock solution containing a mixture of HMX and RDX, each at a concentration of 10 µg/mL, was prepared in acetonitrile from the standards. Samples were wrapped in aluminum foil to prevent photodecomposition and stored at –4°C in deep freezers. All the solvents were degassed on an ultrasonic bath prior to use.

## Instrumentation

The HPLC system consisted of a pump (Dionex P680, Dionex Softron GmbH, Germering, Germany) with four solvent chambers, a Supelco Ascentis RP-amide 150 × 4.6 mm; 5 μm reversed-phase analytical column, a Dionex UVD170U detector operated at a wavelength 230 nm connected to a computer loaded with Chromeleon software for data acquisition. Separations were carried out at room temperature maintained at 20–22°C. The sample was injected directly using a rheodyne's 20 μL loop on the valve for analysis. Aqueous and non-aqueous solvents were filtered with 0.45 μm Nylon 6,6 membrane filters (Pall Life Sciences, Mumbai, India) and 0.40 μm syringe filter (Rankem, New Delhi, India). ELICO (India) double beam UV-visible spectrophotometer SL-164 was used for obtaining the absorption spectra of both explosive components.

## Procedures

### Optimization of separation conditions

Solution of a mixture of HMX and RDX was prepared (100 ppb) in triply distilled water by adding 50 μL of 10,000 ppb mixture to 5 mL water. Conditions for baseline separation of HMX and RDX were optimized with respect to mobile phase and wavelength. The final optimized conditions were: isocratic flow of acetonitrile–water, 70:30 (v/v), at a flow rate of 1.0 mL/min, with detection at wavelength 230 nm, on a reverse-phase amide column.

A series of aqueous samples containing SDS concentrations between 0.07 and 0.21 mM were analyzed under the optimized conditions of analysis. It was found that peak area for HMX increases in the presence of surfactant, and was highest at a concentration 0.14 mM of SDS, and was almost constant for RDX within this concentration range of SDS (Figure 2). The enhancement in peak area for HMX may be due to a change in matrix properties in presence of SDS, which consequently increases the sensitivity for HMX. Therefore, the optimum concentration of SDS was kept constant at 0.14 mM for the extraction of explosives from soil and as an additive in ground water sample during analysis. Calibration curves were prepared by varying the concentration from 10 to 400 ppb in the presence of SDS (0.14 mM). The regression coefficients ( $r^2$ ) for HMX and RDX were found to be 0.996 and 0.997, respectively. The calculated limits of detection are 1.5 and 3.8 ppb ( $S/N = 3$ ) for HMX and RDX standards, respectively.

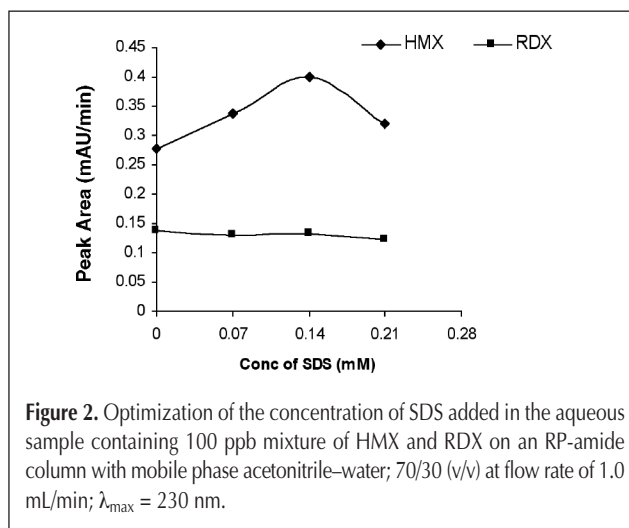
### Application to surface soil sample

Alluvial surface soil having high cation exchange capacity and rich in exchangeable cations such as  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$  was taken as a sample up to 20 cm depth. The soil was taken from agriculture land which was used for floriculture and contains high contents of minerals, humic substances, and moisture. The soil sample was dried at 45–50°C in an oven for two to three days to remove the moisture, and was finely ground in a mortar and pestle to 30-mesh (0.6 mm) sieve. A 500 ppb

mixture of explosives in 1.0 mL acetone was added to 1.0 g of soil and mixed thoroughly. The solvent was allowed to evaporate at room temperature followed by thorough mixing of dry soil to evenly distribute HMX and RDX. Soil was equilibrated for 2 h thoroughly for better deposition of pollutants before extraction. Similarly, another soil sample was prepared by adding 200 ppb of explosive mixture in the same amount of soil following the same procedural steps. Both soil samples were stirred constantly with teflon coated magnetic beads in the presence of 10 mL of aqueous solution of SDS (0.14 mM) for 1 h. Each extract was filtered on 0.45 μm Nylon 6,6 membrane filter. The filtrates obtained were clear, but to remove any particulate matter of size less than 0.45 μm, each extract was filtered with 0.4 μm syringe filtration, so that the extract was completely free from all types of suspended impurities. Blank samples were also prepared and purified following the same steps. Extracts were injected directly into the injector of the HPLC and were analyzed under optimized chromatographic conditions. Each experiment was repeated three times and the results are summarized in Table I.

### Application to groundwater sample

Ground water sample was collected from a tube well located



**Figure 2.** Optimization of the concentration of SDS added in the aqueous sample containing 100 ppb mixture of HMX and RDX on an RP-amide column with mobile phase acetonitrile–water; 70/30 (v/v) at flow rate of 1.0 mL/min;  $\lambda_{max} = 230$  nm.

**Table I. Recovery of HMX and RDX from 500 and 200 ppb Soil Samples**

Sr. no.	Explosive	Original concentration (ppb)	Solvent	Extracted (ppb)	Recovery (%)	Recovery factor	% RSD*
1	HMX	200	Water	39.4	19.8	1.0	3.0
			SDS (0.14mM)	57.5	28.7	1.4	3.5
		500	Water	109.0	21.8	1.0	3.2
			SDS (0.14mM)	176.0	35.2	1.6	5.0
2	RDX	200	Water	87.5	43.5	1.0	2.5
			SDS (0.14mM)	148.8	74.3	1.7	2.2
		500	Water	185.0	37.1	1.0	4.8
			SDS (0.14mM)	325.0	65.0	1.7	7.2

\* Each experiment is repeated three times.

nearby an explosives testing site. A small portion of this water sample was spiked with explosive mixture, SDS solution was added, and the final volume made up to 5.0 mL with water, so that the final concentration of explosive mixture was 100 ppb and that of SDS surfactant was 0.14mM in the final volume. The sample was analyzed under optimized chromatographic conditions. The experiment was repeated three times and average value was recorded. The same experiment was repeated for 50 ppb spiked sample. Blank samples were also analyzed and no traces of explosives were found.

## Results and Discussion

The retention times for HMX and RDX on the reverse-phase amide column were 1.9 and 2.1 min, respectively, which were less than reported in EPA method 8330 (i.e., 2.4 and 3.7 min, respectively on reverse phase C<sub>18</sub> column), even at a lower flow rate of 1.0 mL/min as compared to the EPA method (1.5 mL/min). Baseline separation of both explosives was achieved with an acetonitrile–water mobile phase on an RP-amide column, which is not achievable on a C<sub>18</sub> column with the same mobile phase. In EPA method 8330, the HPLC–UV chromatogram for HMX and RDX with other nitro explosives was taken at a wavelength of 254 nm, which is very far away from the absorption maxima for both these nitramine explosives (i.e., ~234 nm [33–38]). So in this developed method, the chromatogram was taken at  $\lambda_{\max}$  230 nm. Recoveries were calculated for HMX and RDX from calibration curves for 500 and 200 ppb extracted samples of soil. For comparison purposes, the amount of explosives recovered from the soil sample with the help of water is assumed to be an integrated value 1.0 and the amount of explosives recovered with the assistance of surfactant were compared accordingly. From 500 ppb sample of spiked soil, 176 ppb (35.2%) of HMX and 325 ppb (65%) of RDX were recovered from a single extraction with aqueous solution of surfactant, which is approximately 1.6- and 1.7-fold higher than water. Similarly, 57.5 ppb (28.7%) of HMX and 148.8 ppb (74.3%) of RDX were extracted from 200 ppb spiked soil sample, which is 1.4 and 1.7 times higher than recovery with water. Relative standard deviation (RSD) was calculated for each explosive (Table I). It was observed from the extraction results that the recovery of HMX is comparatively lesser than RDX, which may be accounted to the lower aqueous solubility of HMX than RDX (3). Cho et al. have reported the association of an ion pair of anionic surfactant like SDS with humic acid in the aqueous environment resulting in lowering of its hydrophobic interaction with polycyclic aromatic hydrocarbons (39) well below its critical micelle concentration. Therefore, we may consider that an aqueous solution of SDS causes the lowering of intermolecular association between explosives and humic acid of contaminated soil, resulting in fast release of contaminants to the aqueous media. Also, in the HPLC–UV chromatogram, no peak for added SDS is observed, which absorbs in UV region;  $\lambda_{\max}$  222 nm (3.45mM SDS solution, reference water) clearly proves the phenomenon. But the incorporation of a higher concentration of surfactant for the

extraction from soil samples causes the distortion of the chromatogram instead of increasing the peak area for explosives, which may be due its effect on the surface of the packing and

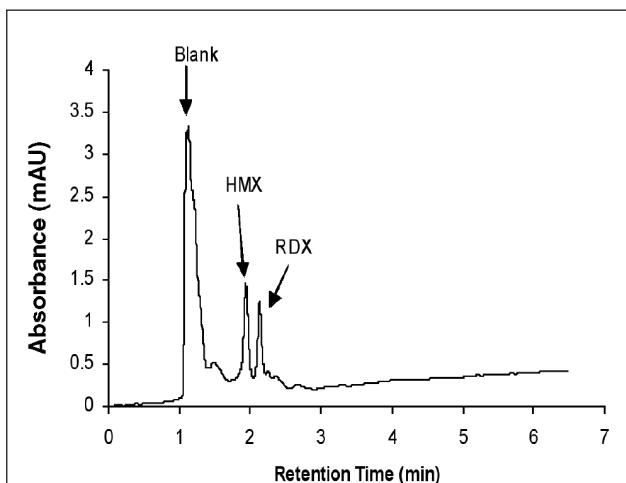


Figure 3. HPLC–UV chromatogram of spiked soil (500 ppb) washed with aqueous solution of SDS (0.14mM) under optimized chromatographic conditions as shown in Figure 2.

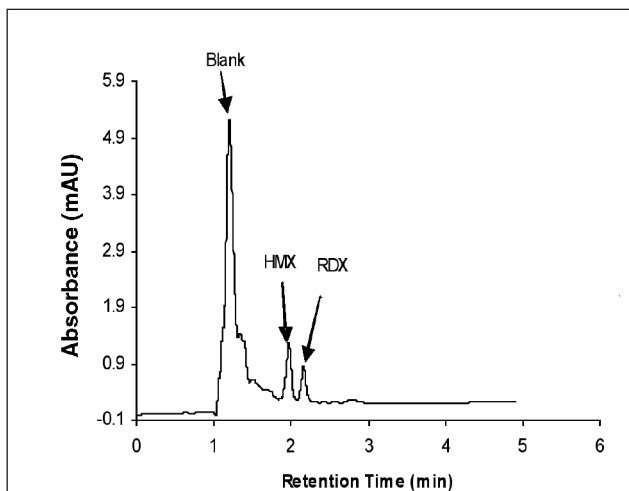


Figure 4. HPLC–UV chromatogram of spiked groundwater with explosive mixture (50 ppb) containing 0.14mM SDS in the sample under optimized chromatographic conditions as shown in Figure 2.

Table II. Recovery of Explosives from Groundwater Samples

Sr. No.	Explosive	Original concentration (ppb)	Concentration obtained (ppb)	% RSD*
1	HMX	100	86.0	2.9
		50	42.5	3.1
2	RDX	100	110.0	3.4
		50	55.2	3.5

\* Each experiment is repeated three times.

change of the characteristics of the reverse-phase column (40). Similarly, no extra peak is observed in the chromatogram for the hydrolyzed product of RDX (32), clearly demonstrate the advantage of using a lower concentration of anionic surfactant and water–acetonitrile as mobile phase. Three to four washing cycles were needed for HMX, while two to three washing cycles were needed for the complete recovery of RDX from the soil sample. The HPLC–UV chromatogram (Figure 3) is shown for the extract of washed soil spiked with 500 ppb concentration of these explosives.

Similarly, the HPLC–UV chromatogram after analysis of spiked groundwater at 50 ppb concentration is shown (Figure 4). The method gave satisfactory results up to 10 ppb concentration level. Experiments were repeated three times and the results of determinations are summarized in Table II. Variation in the recovered concentration of explosives from spiked groundwater may be due to the interaction of SDS with ions or other constituents present in water (41), consequently decreasing its availability for explosive components. The detection limits for spiked groundwater samples were found to be 1.9 and 3.4 ppb (S/N = 3) for HMX and RDX, respectively. The detection limits for spiked soil samples were found to be 3.0 and 5.6 ppb (S/N = 3) for HMX and RDX, respectively, for the first step of extraction. The calculated quantitation limits (3 × limit of detection) for HMX and RDX extracted from soil were calculated to be 9.0 and 16.8 ppb after the first extraction, which were much better than those reported in EPA method 8330 (i.e., 2.2 and 1.0 ppm, respectively).

## Conclusion

The RP-amide column has advantages over the C<sub>18</sub> column because of its fast and baseline separation of explosives. The incorporation of SDS in aqueous samples has dual advantages (viz., increase in sensitivity for HMX as well as enhancement in extraction of both nitramine explosives). The optimized concentration of SDS can be used for the enhanced recovery of explosives present in ppb range from soil samples. Limits of detection for groundwater samples and limit of quantitation for soil extract samples were found to be much better than those reported in EPA method 8330. Hence, a sensitive and simple method has been developed, avoiding the use of hazardous solvents like acetonitrile–methanol, for the analysis of explosives present at sub ppb level in groundwater and soil samples.

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## References

1. J. Yinon and S. Zitrin. *Modern Methods and Applications in Analysis of Explosives*. Wiley, New York, NY, 1993, pp. 212.
2. F.M.-Rivera, L. Paquet, S. Deschamps, V.K. Balakrishnan, C. Beaulieu, J. Hawari, and A. Malik. Physico-chemical measurements of CL-20 for environmental applications comparison with RDX and HMX. *J. Chromatogr. A* **1025**: 125–132 (2004).
3. M.N. Sara. *Site Assessment and Remediation Handbook*. CRC Press, Boca Raton, FL, 2003, pp. 737–740.
4. R.S. Boethling and D. Mackay. *Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences*. CRC Press, Boca Raton, FL, 2000, pp.151–153.
5. I. Boyer, J.K. Miller, R.E. Watson, J. DeSesso II, and C.M. Vogel. *Noblis Technical Report, Comparison of the Relative Risks of CL-20 and RDX*. Noblis Center for Science and Technology Falls Church, Virginia, July 2007, pp. 1–2.
6. S.S. Suthersan and F.C. Payne. *In situ Remediation Engineering*. CRC Press, Boca Raton, FL, 2005, pp. 206.
7. J. Hawari and A. Halasz. Biodegradation of explosives. In *Encyclopedia of Environmental Microbiology*. G. Bitton, Ed. Wiley, New York, NY, 2000, pp. 1.
8. W.D. Won, L.H. Di Salvo, and J.Ng. Toxicity and mutagenicity of 2,4,6-trinitrotoluene and its microbial metabolites. *Appl. Environ. Microbiol.* **31**: 576–580 (1976).
9. S. Rocheleau, R. Cimpoaia, L. Paquet, I. van Koppen, S. Guiot, J. Hawari, S.Thiboutot, G. Ampleman, and G.I. Sunahara. Ecotoxicological evaluation of a bench-scale bioslurry treating explosives-spiked soil. *Biorem. J.* **3**: 233–246 (1999).
10. J. Yinon. *Toxicity and Metabolism of Explosives*. CRC Press, Boca Raton, FL, 1990.
11. J.L. Osmon and R.E. Klausmeier. The microbial degradation of explosives. *Dev. Ind. Microbiol.* **14**: 247–252 (1972).
12. W.E. Pereira, D.L. Short, D.B. Manigold, and P.K. Roscio. Isolation and characterization of TNT and its metabolites in groundwater by gas chromatograph–mass spectrometer–computer techniques. *Bull. Environ. Contam. Toxicol.* **21**: 554–562 (1979).
13. P.-Y. Robidoux, J. Hawari, S. Thiboutot, S. Guiot, G. Ampleman, and G.I. Sunahara. Chronic toxicity of octahydro-1,3,5,7-tetrahydro-1,3,5,7-tetrazocine (HMX) in soil determined using the earthworm (*Eisenia andrei*) reproduction test. *Environ. Pollut.* **111**: 283–292 (2001).
14. T.S. Sheremata, A. Halasz, L. Paquet, S. Thiboutot, G. Ampleman, and J. Hawari. The fate of the cyclic nitramine explosive RDX in natural soil. *Environ. Sci. Technol.* **35**: 1037–1040 (2001).
15. S.D. Harvey, R.J. Fellows, D.A. Cataldo, and R.M. Bean. Analysis of the explosive 2,4,6-trinitrophenylmethyl nitramine (tetryl) in bush bean plants. *J. Chromatogr.* **630**: 167–177 (1993).
16. J.P. Whelan, A.W. Kusterbeck, G.A. Wemhoff, R. Bredehorst, and F.S. Ligler. Continuous-flow immunosensor for detection of explosives. *Anal. Chem.* **65**: 3561–3565 (1993).
17. W. Kleibohmer, K. Cammann, J. Robert, and E. Clussenbrock. Determination of explosives residues in soils by micellar electrokinetic capillary chromatography and high-performance liquid chromatography: A comparative study. *J. Chromatogr.* **638**: 349–356 (1993).
18. Method 8330, Nitroaromatics and nitramines by high performance liquid chromatography (HPLC) available online at [www.epa.gov/sw-846/pdfs/8330.pdf](http://www.epa.gov/sw-846/pdfs/8330.pdf), pp. 8330(1)–8330(21).
19. D. Gaurav, A.K. Malik, and P.K. Rai. High-performance liquid chromatographic methods for the analysis of explosives. *Crit. Rev. Anal. Chem.* **37**: 227–268 (2007).
20. A.E. Ahmed, J.P. Loh, B. Ghanayem, and G.I. Hussein. Studies on the mechanism of acetonitrile toxicity. I: Whole body autoradiographic distribution and macromolecular interaction of 2-14C-acetonitrile in mice. *Pharmacol. Toxicol.* **70**: 322–30 (1992).
21. T. Zhang and H. Jin. Aquatic toxicity of acetonitrile and its water quality criteria for the protection of aquatic life in China. *Int. J. Environ. Pollut.* **15**: 568–575 (2001).

22. U.C. Pozzani, C.P. Carpenter, P.E. Palm, C.S. Weil, and J.H. Nair. An investigation of the mammalian toxicity of acetonitrile. *J. Occup. Med.* **1**: 634–42 (1959).
23. K. Katz, A. Ruha, and S. Curry. Aniline and methanol toxicity after shoe dye ingestion. *J. Emerg. Med.* **27**: 367–369 (2004).
24. A. Helmstetter, A.P. Gamberdinger, and R.J. Pruell. Acute toxicity of methanol to *Mytilus edulis*. *Bull. Environ. Contam. Toxicol.* **57**: 675–681 (1996).
25. B. Urbanyi, B. Baranyai, I. Magyary, and A. Dinnyes. Toxicity of methanol, DMSO and glycerol on carp (*Cyprinus carpio*) embryos in different developmental stages. *Theriogenology*. **47**: 408–408(1) (1997).
26. W. Chu and K.H. Chan. The mechanism of the surfactant-aided soil washing system for hydrophobic and partial hydrophobic organics. *Sci. Total Environ.* **307**: 83–92 (2003).
27. M.R. Taha, I.H. Soewarto, Y.B. Acar, R.J. Gale, and M.E. Zappi. Surfactant enhanced desorption of TNT from soil. *Water, Air, Soil Pollut.* **100**: 33–48 (1997).
28. M.C. Morley and G.E. Speitel, Jr. Biodegradation of high explosives on granular activated carbon: Enhanced desorption of high explosives from GAC—Batch studies. *ANRC Environmental Program*, in press.
29. K.Urum, T. Pekdemir, and M. Çopur. Surfactants treatment of crude oil contaminated soils. *J. Colloid Interface Sci.* **276**: 456–464 (2004).
30. S. Deshpande, B.J. Shiau, D. Wade, D.A. Sabatini, and J.H. Harwell. Surfactant selection for enhancing ex situ soil washing. *Water Res.* **33**: 351–360 (1999).
31. W. Chu. Remediation of contaminated soils by surfactant-aided soil washing. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management* **7**: 19–24 (2003).
32. J. Hawari, L. Paquet, E. Zhou, A. Halasz, and B. Zilber. Enhanced recovery of the explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) from soil: cyclodextrin versus anionic surfactants. *Chemosphere* **32**: 1929–1936 (1996).
33. U.S. Department of Labor, Occupational Safety & Health Administration, Method no., PV2135, <http://www.osha.gov/dts/sltc/methods/partial/pv2135/pv2135.html>.
34. U.S. Department of Labor, Occupational Safety & Health Administration, Method no. PV2032, <http://www.osha.gov/dts/sltc/methods/partial/pv2032/2032.html>.
35. E.C. Mattos, E.D. Moreira, R.C.L. Dutra, M.F. Diniz, A.P. Ribeiro, and K. Iha. Determination of the HMX and RDX content in synthesized energetic material by HPLC, FT-MIR, and FT-NIR spectroscopies. *Quím. Nova.* **27**: 540–544 (2004).
36. C.A. Groom, S. Beaudet, A. Halasz, L. Paquet, and J. Hawari. Detection of the cyclic nitramine explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX) and their degradation products in soil environments. *J. Chromatogr. A* **909**: 53–60 (2001).
37. A. Hilmi, J.H.T. Luong, and A.-L. Nguyen. Determination of explosives in soil and ground water by liquid chromatography amperometric detection. *J. Chromatogr. A* **844**: 97–110 (1999).
38. I. Aims and G.I. Baram. Portable liquid chromatograph for mobile laboratories. *J. Chromatogr. A* **728**: 387–399 (1996).
39. H.-H. Cho, J. Choi, M.N. Goltz, and J.-W. Park. Combined effect of natural organic matter and surfactants on the apparent solubility of polycyclic aromatic hydrocarbons. *J. Environ. Qual.* **31**: 275–289 (2002).
40. R.E. Majors. Column watch: The cleaning and regeneration of reversed phase HPLC columns. *LC-GC Europe* **July**: 4 (2003).
41. L.V. Jianoxiao, W. Dong, and Z. Jioti. Interaction mechanisms between anionic surfactant micelles and different metal ions in aqueous solutions. *J. Dispersion Sci. Technol.* **27**: 1073–1077 (2006).

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