ANALYSIS OF RDX and RDX BREAKDOWN PRODUCTS in ENVIRONMENTAL SAMPLES

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Introduction

Hexahydro-1,3,5-trinitro-1,3,5-triazine, commonly known as RDX use in propellants and explosives have resulted in soil and groundwater contamination [1,2,3]. Concerns regarding the environmental fate of these nitramine compounds are arising because of their persistence in the environment. RDX remediation schemes have been proposed for specific treatment processes, and evidence has been presented indicating detection of postulated metabolites and breakdown products [3,4,5,6]. In order to make informed evaluations of RDX remediation technologies, the RDX metabolites and breakdown products must be identified and quantified. The determination of the nitramine metabolites and breakdown products produced in a range of remediation technologies will provide a means of assessing the feasibility of these techniques for explosive removal and insight into the RDX degradation pathways for specific treatment processes. The information gained from quantitative chromatography will also enable researchers to determine relative toxicities of these metabolites, which will provide additional criteria for remediation technology evaluation.

Analytical techniques for the detection of nitroaromatic breakdown products have been developed and refined over the years, but the determination of degradation products of nitramine compounds has not received extensive attention. High performance liquid chromatography (HPLC) equipment has been used in this study to separate RDX from its degradation products and from other common energetic compounds. Two analytical columns: a C18 and a CN bonded silica high performance liquid chromatographic column were used to eliminate common interferences from matrix elements and other metabolites. This technique yielded method detection limits for RDX and several metabolites that are comparable to limits for other energetic compounds using existing methods [7].

Materials and Methods

The HPLC system used in this study consisted of a Dionex Summit HPLC system (Dionex Corporation, Sunnyvale, CA) that was composed of pump model P580, ASI-100 automated sample injector, degasser model DG-1210, UVD 340U ultraviolet detector, and Chromeleon 6.4 Chromatography Software. A Supelco LC-18 reverse phase HPLC column 25 cm x 4.6 mm (5 µm), catalog # 5-8298, was used as the primary column and Supelco LC-CN reverse phase HPLC column 25 cm x 4.6 mm (5 µm), catalog # 5-8231, was the confirmation column. Mobile phase for the C-18 column was (1:1 (v/v) methanol/reagent

water) and 1:3 (v/v) methanol/reagent water was used for the CN column. Reagent grade chemicals were used in all tests. Run conditions for both columns included 1mL/min flow rates and 20 min run times.

Sample preparation. For high explosives concentrations in aqueous samples, water samples were prepared by adding 5 ml acetonitrile to 5 ml of sample. Samples were filtered using a 0.45 µm Millipore Millex-SR Teflon filter (catalog # SLSR025NB), pipetted into an autosampler vial, and analyzed using HPLC. For low-level explosives concentrations, water samples were concentrated onto solid phase cartridges (Waters SepPak Vac cc (500 mg) Porapak RDX, catalog # WAT047220) using a vacuum manifold and eluted off using a small volume of acetonitrile. The concentrated extracts were diluted 1:1 (v/v) with reagent grade water, pipetted into autosampler vials, and analyzed using HPLC.

Solid samples were thoroughly mixed to achieve maximum homogeneity prior to sub-sampling. For the analysis, approximately 5.0 grams ± 0.5 g of wet sample (weight was recorded) were weighed into a 20-mL glass vial with a Teflon-lined cap. Samples and associated QC samples were spiked with surrogate and matrix spike spiking solutions, as appropriate. Acetonitrile (10 ml) was added and, using a vortex mixer, the sample is swirled for one minute, then placed in a water-cooled ultrasonic bath for 18 hours. After sonication, samples were allowed to settle for 30 minutes. Aliquots (5-mL) of supernatant were removed using 5-mL pipets with disposable tip, and put in a 20-mL vial. A 5-mL portion of calcium chloride solution (5 percent by weight) was added to the 5-mL aliquot of supernatant to flocculate any remaining particulates. Samples were then filtered using a 0.45 µm Millipore Millex-SR Teflon filter (catalog # SLSR025NB). Representative aliquots of the filtrate were pipetted into autosampler vials and analyzed using HPLC.

Concentration ranges. The concentration range over which nitramine breakdown products can be determined is matrix dependent. For high explosive concentration levels in liquid phase samples, a concentration range of 0.02 to 20 µg/mL can be detected in mobile phase and natural waters spiked with standards. For low level explosives determinations using solid phase extraction procedures, natural waters spiked with standards can be determined over a concentration range of 0.20 ng/mL to 200 ng/mL. Clean soils spiked with explosives standards can be tested in the concentration range of 0.10 to 20 µg/g. Samples that contain high concentrations of other contaminants may have much higher backgrounds associated with them, giving considerably higher detection limits for the target analytes.

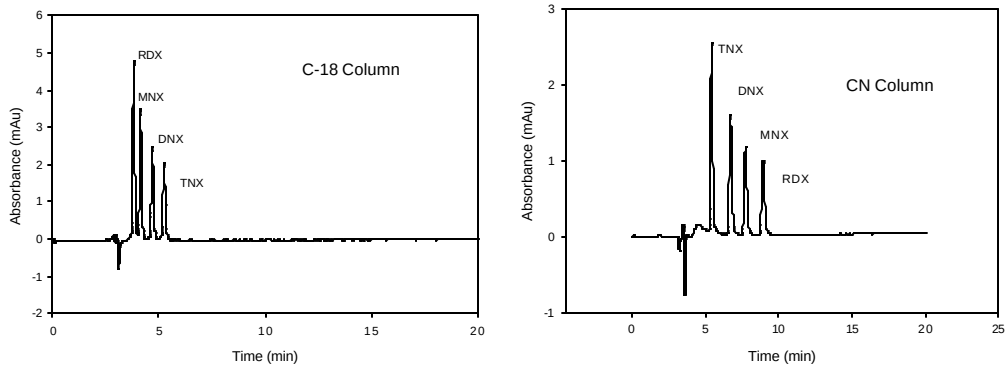
Results and Discussion

The nature of the metabolites and breakdown products depends on the treatment process or the weathering that the sample has undergone. A number of remediation products of the nitramines have been suggested. McCormick [4] identified hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) as products of sequential reduction of RDX. Other researchers have recently confirmed these products and attempted to identify specific degradation pathways [1,2,5,8]. The nitrosoamine products appeared under anaerobic conditions in biologically active systems, but not in sterile soils, indicating these compounds were formed through biotransformation of RDX. A method was needed to analyze for the reduction products of RDX that would eliminate the interferences caused by other known

energetic compounds and matrix elements when using standard methods.

Figure 1 shows chromatograms acquired with RDX, MNX, TNX, and DNX prepared using reference standards in 50 percent acetonitrile, 50 percent distilled water. Baseline separation was achieved on both columns. The two columns in this proposed method have dissimilar polarities, since CN columns contain silica coated by a more polar (relative to the C18) cyanide derivative. The first analytical aspect of using two dissimilar columns is to confirm the peak identified on the primary column by assuring the same compound is identified at the same concentration and distinctive retention time on the second column. The likelihood of an unknown interfering peak matching retention times on a single column is quite high, but a significantly different molecular compound is not likely to have identical retention characteristics on two columns with dissimilar solid phases. The second role this dual column technique serves is the removal of known interferences. Some of the common explosives and explosives degradation products interfere with MNX and TNX on a single column allowing only nominal identification, but the second column allows identification and quantification of the nitroso-nitramine analytes.

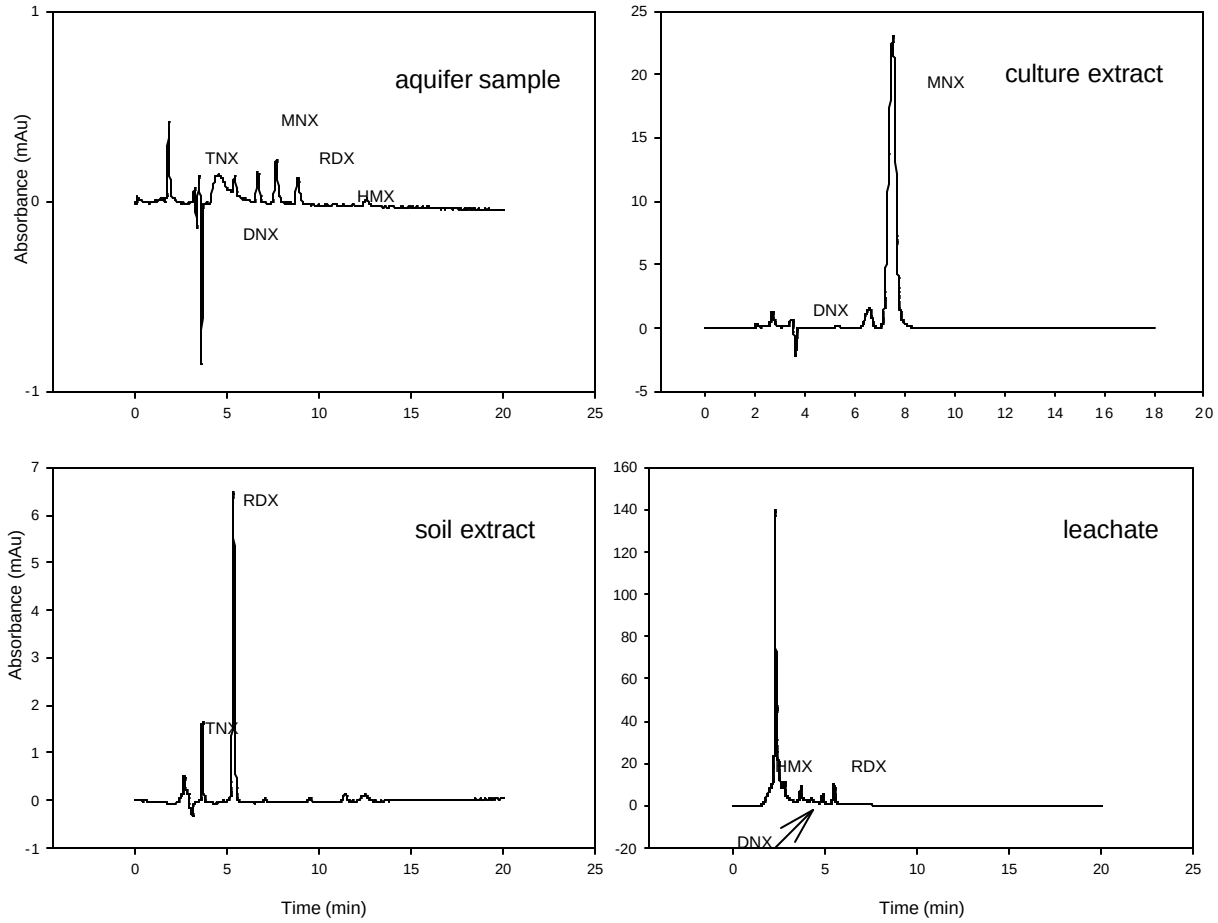
Figure 1. Chromatogram of RDX and RDX Degradation Products on C-18 and CN Columns.



Excellent linearity was achieved over three orders of magnitude of the concentration range for RDX, MNX, DNX, and TNX. This allows for quantitation of RDX and these three nitroso breakdown products over this range of concentrations. Retention times for RDX, MNX, DNX, and TNX were stable throughout the calibrated concentration range. Method detection limits and data reporting limits were determined for the nitrosylated RDX compounds and good precision was obtained for replicate analysis in both water and soil matrices. The USEPA SW846 method for determination of MDL and LRL was utilized to calculate the results.

Environmental Samples. The proposed method has been used to detect RDX and its nitroso degradation products in environmental and biological samples. Figure 2 illustrates the chromatograms obtained when analyzing a simulated aquifer, a bacterial culture extract, a leachate, and an aged, contaminated soil. Separation of the metabolites was good in all cases and matrix elements did not interfere with the analytes in any of the chromatograms.

Figure 2. Environmental Samples analyzed using the proposed method.



This method satisfies the need for analytical techniques to monitor the formation and subsequent degradation products of toxic and carcinogenic nitrosyl substituted nitramines, specifically those derived from RDX. The ability to detect and quantify these nitrosylated RDX degradation products makes the further evaluation of the effectiveness of innovative remediation techniques for nitramine degradation possible.

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