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Pre-Screening for Explosives Residues in Soil Prior to HPLC Analysis Utilizing Expray

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ABSTRACT

The characterization of Department of Defense (DoD) training lands for explosives residues involves sampling and analyzing soil samples collected at firing points and impact areas. Laboratory instruments used for this analysis are susceptible to accumulating high concentrations of these compounds, thus possibly requiring reanalyzing. By using the Expray Explosives Detection Kit to determine the approximate concentration of explosives compounds prior to analysis, soil extracts can be diluted to a concentration that will not interfere with analysis results. This report describes the method used to develop the visual index for concentration determination of explosives in soil extracts, and also the use of the Expray Kit.

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PREFACE

This report was prepared by Kevin L. Bjella, Physical Science Technician, Environmental Sciences Branch (ESB), Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory (ERDC-CRREL), Hanover, New Hampshire. The author gratefully acknowledges Dr. Thomas F. Jenkins and Nathan D. Mulherin for their review of this manuscript. The author also gratefully acknowledges the technical assistance provided by Alan D. Hewitt and Marianne E. Walsh, ESB.

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KEVIN L. BJELLA

1 INTRODUCTION

Characterization of the presence and amount of energetic residues on military training ranges involves the sampling and analyzing of the surface and near-surface soils. The concentration of energetic residues in samples collected at firing points and impact locations can range from below instrumental detection limits in parts per billion (ppb) to percent levels. Reverse-Phase High-Performance Liquid Chromatography (RP-HPLC) is typically used for analysis of these energetic residues. Extract concentrations of 10 parts per million (ppm) TNT and 20 ppm RDX/HMX/NG are considered safe upper limits for RP-HPLC. Higher analyte concentrations may carry over to subsequent samples, elevating responses and yielding false positives. This requires reanalysis of the samples possibly affected, and may require that corrective measures be taken to address instrumental performance. To avoid interruptions to the analytical runs, a simple screening technique was developed using a commercially available colorimetric explosives detection kit.

Pre-screening utilizing the Expray Explosives Detection Kit prior to analysis has proven to be useful for coarse determination of concentration values within a factor of 10. Dilution can then be carried out to bring the sample concentration down to an analytically acceptable level, and/or the placement within the analyzing sequence can be designed to minimize the effects of the carryover. This report describes the testing of the Expray Explosives Detection Kit for this screening process.

2 BACKGROUND

Explosives are classified as “primary” or “secondary” based on their susceptibility to initiation. Primary explosives, which include lead azide, lead styphnate, and mercury fulminate, are highly susceptible to ignition and are often used to ignite secondary explosives. Secondary explosives are much more prevalent on military sites than primary explosives. They include trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). These are used as the main destructive explosive in ammunition (Thiboutot et al. 2002). TNT is the most commonly used, either independently or in varying compositions where Composition B contains TNT and RDX, and octol contains TNT and HMX. HMX is also found as a manufacturing by-product of RDX.

The most commonly used organic chemicals for rocket, artillery, and mortar propellants are nitroglycerin (NG) and nitrocellulose (NC). The residues most often detected at the firing points are NG and dinitrotoluene (DNT) (Jenkins et al. 2003). These compounds also can be found downrange in rocket impact areas because there often is unburned propellant remaining when the rockets detonate.

Characterization of impact areas and firing points consists of collecting surface soil samples from a location of interest and placing these into a container, either a bag or jar (Pennington et al. 2002). These samples may be either discrete (one sample unit for the given area) or composite (multiple sample units from a given area), and can range in weight from 50 to 5000 grams. Discrete samples are generally small (50–100g) and can be directly extracted with solvent without pre-processing. Composite samples are generally much larger and require extensive processing (i.e., sieving and grinding) to more evenly distribute the explosives residue particle(s) throughout the sample. The composites are then subsampled to obtain a representative fraction that can be extracted with solvent prior to instrumental analysis.

During sampling there are few indicators that an area may have high concentrations of explosives residues. Munition fragments, non-detonated munitions, discolored soil, discolored ponded water, or unburned propellant lying in the vicinity of an impact area or firing point may indicate relative concentrations. Yet with these indicators it is impossible to determine whether dilution of extracts will be necessary prior to analysis. To quickly determine the approximate concentration of either a nitramine or nitroaromatic residue in a soil or water sample, we have employed the use of an Expray Explosives Detection Kit (Fig. 1). The cost of the full kit is approximately \$U.S. 270 and it takes approxi-

mately 15 minutes to screen 50 samples. The major benefit is the prevention of instrumental problems from overloading and having analyte concentrations within the linear range of the method.



Figure 1. Expray Explosives Detection Kit.

3 METHOD AND MATERIALS

Equipment

The Expray kit is composed of three aerosol cans, each of which contains reagents that will react with explosives residues and give an easily discernable color change. The first can is designed for the colorimetric detection of polynitroaromatics (TNT, tetryl, trinitrobenzene). The second can is for nitramines and nitrate esters (RDX, HMX, NG, and NC). The third can is for the detection of nitrate-based explosives, ammonium-nitrate and fuel oil (ANFO), and black powder. The complete kit comes with a special collector test paper that has an impervious backing and raised coarse areas that aid in sample retention and swiping. It also contains tests strips to determine whether the reagents are still reactive, and a reference card for quick identification of possible indicators. The manufacturer states that a single can will perform a maximum of 110 tests, using the included test paper. Our tests have indicated that approximately 20 batches of samples with up to 50 samples on an 8.5- × 11.0-inch sheet of paper can be screened from one can. The determination of the type of explosive and relative concentration is dependant on the sequence of the application. Expray 1 must be applied first, followed by Expray 2, followed by Expray 3.

Expray 1 contains an alkali that reacts with polynitroaromatics and forms Meisenheimer complexes, which are highly colored compounds. The alkali is tetrabutylammonium hydroxide, and the colors range from dark brown for TNT to orange for tetryl. A blue-green color indicates the presence of DNT (Plexus Scientific, Silver Spring, Maryland).

Expray 2 contains compounds that produce a Griess reaction with the nitrate ions from the reaction with Expray 1, and this yields an azo dye, giving a color change. For nitramines (RDX, HMX), sulfanilamide and N-ethylenediamine are used to produce the dye. For nitrate esters (NG, NC, PETN), sulfanilic acid is used to produce diazonium ions, which are complexed with an aromatic nucleophile to produce the dye. Dimethyl sulfoxide is also added as a solvent to accelerate the reaction for nitramines. The color produced is pink for any nitramine and nitrate ester.

Expray 3 is used for the detection of inorganic nitrates (ANFO, gun powder, black powder). Zinc dust is used to reduce the nitrates to nitrite ions, which then react with the Griess reagent. This will also yield a pink color with the presence of nitrates. There is no way to distinguish between innocent fertilizers and nitrate-based explosives.

Expray claims this product can detect a minimum of 20 nanograms of RDX and 5 nanograms of TNT. In our tests, application of 1 μ L of 20 ppm RDX (20 ng) and 1 μ L of 5 ppm TNT (5 ng) onto the test paper failed to yield a visually detectable color change. A granular sample tested at these masses may very well produce a color change; however, we did not perform those tests.

Method

TNT, RDX, HMX, and NG are the analytes most commonly found in soils at DoD training ranges and therefore these four were selected for this study. The TNT, RDX, and HMX standards were made from Standard Analytical Reference Material (SARM) obtained from the U.S. Army Environmental Center and were prepared in acetonitrile (ACN) at 1 g/L, and NG is obtained in solution form. Dilutions were prepared from these standards with ACN and concentrations were confirmed by HPLC analysis using a system consisting of a Spectra System P1000 pump, AS3000 autosampler, and UV 2000 dual wavelength detector. Eluent consisted of 85:15 MilliQ filtered water:2-propanol. The column was a Waters NovaPak C8, 150 mm $\times$ 3.9 mm at 28°C.

Eight types of paper were chosen for this study to determine whether screening results were dependent on the type of paper used. The eight are

1. Expray sample paper. Unknown composition, appears to be a more robust form of glass fiber with an impervious backing and raised fluffed areas.
2. Boise Aspen. White/20 lb/10.0 M copy paper, 30% post-consumer fiber.
3. Whatman's Filter Paper #1. Qualitative cellulose filters.
4. Whatman's Filter Paper #2. Qualitative cellulose filters.
5. Fisher Filter Paper #09-803-5, P2. Unknown composition, most likely cellulose.
6. Baroid Filter Paper #988. Unknown composition, most likely cellulose.
7. Reeve Angel Filter Paper #934 AH. 100% borosilicate glass fiber, chemically inert.
8. VWR Scientific Filter Paper Grade 417. Qualitative cellulose filter.

The test paper was prepared by placing a Pasteur pipette into the standard, drawing approximately 8–10 μ L of liquid into it, and then touching the tip briefly to the test paper, which drew the liquid out. Because it was found that some of the paper drew differing amounts of solution, all tests were performed by placing the total volume (8–10 μ L) drawn into the pipette onto each type of paper and therefore holding the testing volume constant (see Fig. 2).



Figure 2. Blotting the test paper.

The area was allowed to dry thoroughly before applying the Expray solutions. Drying time during this study was short (one minute) due to the use of the high-vapor-pressure solvent ACN. The cans were shaken for 10 seconds, held approximately 15 cm from the paper, and swept across the blotted area at an approximate velocity of 8 cm/s while in a fume hood (respiratory precautions were taken due to the solvents in this product). Expray 2 was then applied in the same manner after Expray 1 was allowed to dry (approximately 30 seconds). Expray 3 was not used in this experiment as it was not applicable to the nitro-aromatic, nitramine, and nitrate esters in question.

Three phases of testing were conducted to study the four analytes. The first phase was designed to establish an approximate operating range for the Expray kit using 25, 50, 75, 100, 125, 150, 200, and 250 ppm of each of the four standards. Using the eight different types of paper, five sequences were performed to test repeatability.

The second phase was designed to establish detection limits to ± 10 ppm. Ten standards were made for each of the four analytes, ranging from 10 ppm to 100 ppm in 10-ppm increments. Having established the general repeatability of the

testing, only three sequences were performed during this phase. The eight different types of paper were used, and the same technique was conducted as before.

The third phase was designed to identify three distinct color intensities that could be quantitatively matched to “order-of-magnitude” dilutions of tenfold, hundredfold, and thousandfold. Standards of 20, 30, 40, 50, 100, 250, 500, 750, and 1000 ppm were made to cover the realistic concentrations found at training ranges and also the dynamic range of the color intensities. Having eliminated most of the differing types of paper (see results), two sequences were tested using only the Whatman’s #1 filter paper. The same technique was conducted as before.

4 RESULTS

Expray 1: The presence of nitroaromatics (TNT) immediately exhibited a dark brown color and was discernable by a distinct boundary that was coincident with the wetted perimeter immediately after blotting.

Expray 2: The application of the second spray is slower to indicate than Expray 1. In the presence of a nitramine (RDX or HMX) or nitrate-ester (NG), the color change resolved in 5 to 10 seconds where time was dependent on concentration. The color change was pink and varied in intensity according to the concentration. In both cases there was a distinct boundary coincident with blotting.

TNT is detectable down to 20 ppm and very intense at 750 ppm. The color gradation from 20 ppm to 100 ppm is not dramatic, and there is a distinct jump in intensity with the 500-ppm concentration. The color gradation between 500 ppm and 1000 ppm is not dramatic as well. The faint color intensity, 20 to 100 ppm, would suggest a tenfold dilution. The medium intensity from 100 to 500 ppm would suggest a hundredfold dilution. Finally, the brightest color intensity, from 500 to 1000 ppm, would suggest a thousandfold dilution (Fig. 3a, Table 1).

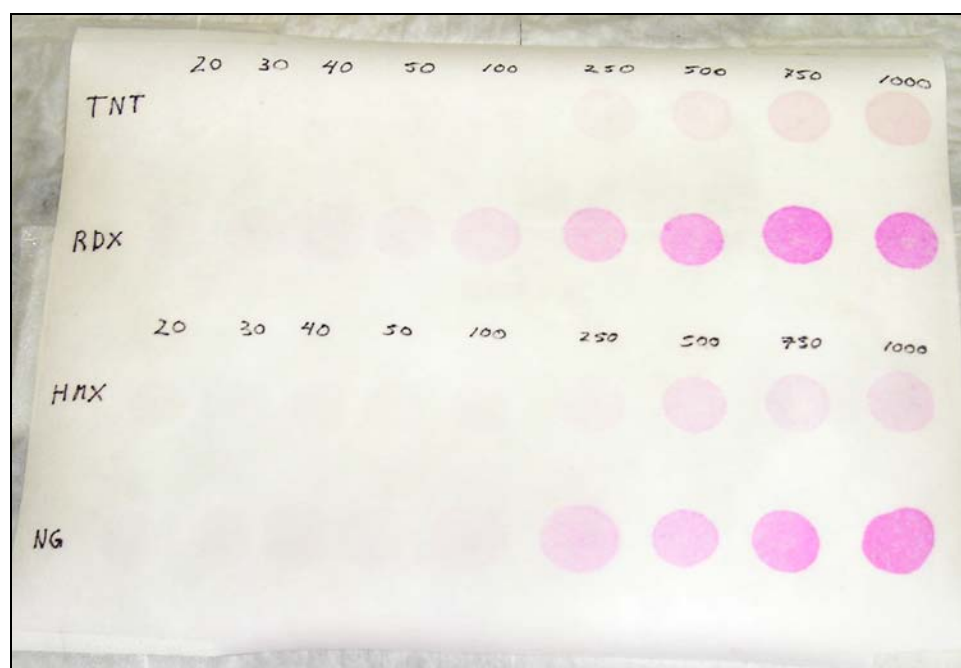
RDX was discernable down to 30 ppm and very intense at 500 ppm. The color gradation from 30 to 100 ppm was not dramatic and would suggest a tenfold dilution. The medium intensity color occurred at 250 ppm so 100 ppm to 500 ppm would require a hundredfold dilution. The color intensity from 500 to 1000 ppm was dramatic; however, the gradation was not very discernable. This would require a thousandfold dilution (Fig. 3b, Table 1).

HMX was discernable down to 100 ppm with only a slight gradation to 1000 ppm. Great care would need to be taken if it were known that the samples were to contain only HMX. The first indication would immediately require a hundredfold dilution with the brightest intensity requiring a thousandfold dilution. The brightest intensity was very faint in comparison with RDX (Fig. 3b, Table 1).

NG was discernable down to 40 to 50 ppm with only a slight gradation up to 100 ppm. A tenfold dilution would be required for this intensity range. From 100 to 1000 ppm is the medium color intensity with little gradation, where a hundredfold dilution would be required. The color intensity was greatest at 1000 ppm; however, not as intense as RDX, but greater than HMX, and this would require a thousandfold dilution (Fig. 3b, Table 1).



a. Can #1.



b. Can #2.

Figure 3. Application results.

Table 1. Detectability results.			
Explosive	Faint color Tenfold dilution	Medium color Hundredfold dilution	Brightest color Thousandfold dilution
TNT	20 to 100 ppm	100 to 500 ppm	500 to 1000 ppm
RDX	30 to 100 ppm	100 to 500 ppm	500 to 1000 ppm
HMX	—	100 to 500 ppm	500 to 1000 ppm
NG	50 to 100 ppm	100 to 750 ppm	750 to 1000 ppm

The results indicate that there is a dramatic difference in the detectability between the differing types of paper. The copy paper provided the worst detectability and it is believed that chemicals introduced in the manufacturing process may be adversely affecting the reaction. This paper is relatively smooth and glossy in comparison to the filter papers and therefore may have an effect on the absorption of the sample, yielding poor results. Experience has shown that on a few occasions false negatives were reported from field samples blotted on copy paper, when in fact the concentration of RDX and/or TNT was significantly high enough that it should have yielded some color indication. Retesting with either Expray test paper, cellulose, or glass fiber paper produced an indication consistent with the concentration. Copy paper was thus eliminated from the study.

The glass fiber paper had the best detectability, giving a more intense indication relative to the other papers. This enhanced detectability may be due to the paper being very absorptive, not allowing the aliquot of standard to spread laterally, thereby concentrating the sample in a smaller area. However, this paper is very easily torn, and so does not allow for writing upon in order to identify the sample. This was a significant drawback and hence this paper was eliminated from the study. The Expray test paper at the time of study was available only in the testing coupons (size 6×4.4 cm), and because of this extremely small size it was eliminated from the study. However, 8.5- $\times$ 11-inch sheets, which are desirable for large-scale blotting, are now available.

The remaining cellulose fiber papers all performed similarly. The cellulose papers do have some ash content, and the Whatman's has resin with an unknown quantity of nitrogen. It is felt these additives were not a detriment to the study and the cellulose filter papers performed as well as the Expray test paper. Whatman's #1 is familiar and easily obtainable, therefore all further testing was completed using this paper.

As mentioned earlier, false negatives have been observed, and this we attribute to the testing paper used in the procedure. However, we cannot discount the possibility of other interferences resulting in poor results, such as the soil matrix and/or organics masking the colorimetric results. Some false positives have been

observed when analyzing samples from anti-tank firing points where high concentrations of propellant are present. It is hypothesized that these samples contained high concentrations of nitrocellulose, which is not detectable with the methods used for HPLC or GC analysis. These samples did contain concentrations of NG and 2,4 DNT, but less than the level of concentration suggested by the Expray indication, thus causing redilution and reanalyzing of the samples.

5 CONCLUSIONS

The Expray Explosives Detection Kit can be used to not only give a qualitative measurement, but will also provide a semi-quantitative measurement prior to HPLC or GC analysis. TNT and RDX gave the best color intensities and gradation, yielding a much clearer definition for performing orders-of-magnitude dilutions. HMX was discernable at a concentration much higher than the other three and with little color gradation through the range of concentrations. NG showed little color gradation through its dynamic range. Throughout the testing it was noted that the results were variable (± 20 ppm) at concentrations lower than 500 ppm with all analytes.

These experiments have shown that after the analyte in question reached the upper limit of color intensity (brightest color), it was impossible to determine the relative sample concentration. Therefore it is recommended to dilute and repeat spraying when these high concentration extracts are encountered to ensure safe analyzing.

Experience indicates that care should be taken when evaluating the soil extracts, as some field samples may not react fully with the Expray solution, yielding false negatives. Also, false positives may be encountered when analyzing firing point samples due to the presence of nitrocellulose, which also reacts to form a pink color with Expray 2. The location in which the sample was taken should be scrutinized along with the results of the spraying to determine whether an error possibly occurred. The sequence of samples should be scrutinized to minimize the effects of carryover, i.e., they should be analyzed in order of increasing concentration. The recent availability of the Expray test paper in 8.5- × 11-inch sheets allows it to be used for large-scale pre-screening and is recommended; however, other cellulose filter papers can be used.

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