

ON-SITE CHARACTERIZATION OF EXPLOSIVE RESIDUES IN SOILS AND ON RANGE SCRAP USING GC-TID ANALYSIS

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ABSTRACT

An economical on-site method has been developed for rapid identification and quantification of frequently detected nitroaromatic, nitramine, and nitrate ester explosives (e.g., TNT, TNB, RDX, HMX, NG, 2,4-DNT, 2,6-DNT, PETN, 2Am-DNT, 4Am-DNT, Tetryl, 1,3-DNB) in soil and on range scrap. The method combines quick and simple sample preparation procedures, colorimetric wet chemical pre-screening, and gas chromatographic (GC) analysis. The final analysis step uses a GC equipped with a thermionic ionization detector (TID) that is selective for compounds containing nitro (NO₂) functional groups. Quantitative results using the GC-TID method were in good agreement with results from HPLC (Method 8330) or GC electron capture (Method 8095) for the analysis of the same sample extract and for sample splits.

INTRODUCTION

The ability to quickly characterize the spatial distribution of contamination over a large area and to minimize the number of non-detect samples sent off-site for analysis are two common incentives for using on-site methods. On-site rapid colorimetric screening and subsequent analysis by gas chromatography–thermionic ionization detection (GC-TID) meets these objectives for the suite of explosives that often coexist in soils and on range scrap at military training facilities and other defense-related sites. Moreover, this assay fills an existing gap between the capabilities of the current EPA-approved on-site methods (4050, 4051, 8510, and 8515) and laboratory-based methods (8330 and 8095), is field rugged, and requires minimal auxiliary support. This paper describes a procedure that uses a simple colorimetric analysis to estimate the proper dilution and GC-TID detection for contaminant identification and quantification. In addition, information will be provided on comparisons between GC-TID analysis and Methods 8330 and 8095.

MATERIALS AND METHODS

A qualitative and semi-quantitative visual colorimetric test to screen on-site for explosive residues can be performed using the Expray kit (Plexus Scientific, Silver Spring, MD). The Expray kit comes in a small, lightweight (less than 1.4 kg) case that contains several sheets of test paper and three aerosol cans for dispensing chemical reagents. The first aerosol can tests for the presence of polynitroaromatics, the second for nitramines, and the third for inorganic nitrates.

The GC used was the Model 8610C (SRI Instruments, Torrance, CA) equipped with a heated (250°C) TID detector, a heated (225°C) on-column injection port, and an internal air compressor. This instrument currently sells for less than \$9K and requires a personal computer (\$1K) for controlling oven temperature programs and for collecting and handling data. Separations were performed on either a metal or glass Crossbond 100% dimethyl polysiloxane column (DB-1), 15 m × 0.53-mm i.d., 0.5 μm film thickness. Injections of 1 μL were made manually with a 10-μL glass syringe (SGE). The carrier gas was high-purity nitrogen flowing at 37 mL/min, and the TID potential was set at –3.40 V. In addition, air was supplied to the detector from the onboard compressor at a rate of approximately 15 mL/min. Using an oven temperature program of 95°C ramped at 10°C/min to 105°C, then ramped from 105° to 240°C at 40°C/min, there was baseline resolution between many of the explosives analytes listed in Method 8330. Sample injections can be made about every 7.0 min (Hewitt et al., 2001).

Calibration Standards

Analytical standards of the 14 explosives-related analytes listed in Method 8330, as well as nitroglycerine and PETN, were purchased either as a mixed stock standard (each analyte at 1.00 mg/mL) or individually from AccuStandard, Inc. (New Haven, CT). These stock standards were specially prepared using acetone as the solvent. The preparation and handling of mixed-analyte working standards was reported elsewhere (Hewitt and Jenkins 1999).

Sample Preparation

To screen surfaces of range scrap, either the entire piece was submersed in acetone or the exposed surface was wiped (rubbed) with an acetone-moistened cotton swab held with metal tweezers (Hewitt 2001). To estimate the surface concentration, the surface area of the piece submersed or swabbed should be measured. Moreover, the swab should be air-dried prior to extraction with 5 mL (or more) of acetone. For qualitative information, an area estimate is not necessary, and if a cotton swab is used, it can be placed directly into the barrel of a 5-mL disposable plastic syringe, followed by 1 mL of acetone.

Soil samples were prepared by extracting 1.0 to 40 g of field-moist soil with a one-to-five-fold greater volume of acetone (i.e., 1:1 to 1:5). Extractions were performed in either glass or plastic bottles by manually shaking the soil / solvent slurry several times for 30 seconds over a 30-minute period.

Following extraction, an aliquot of the acetone was passed through a 25-mm Millex FH (0.45- μ m) filter that was attached, via a Luer-LokTM fitting, to a disposable 3-mL plastic syringe. The filtered extract was directly transferred to a 2-mL amber deactivated glass vial.

Colorimetric screening was performed by transferring a 5- μ L aliquot of solvent extract to a test sheet. Several (6 to 12) sample extracts can be screened simultaneously by pre-marking the test paper and carefully placing each aliquot. After allowing the acetone to evaporate, the surface of the test sheet was sprayed per kit instructions. If color appears following application of the first aerosol, then polynitroaromatics (e.g. TNT, TNB, DNT, picric acid, tetryl, etc.) were likely present. Some of the colors that may appear upon the application of this first aerosol are blue, red, or orange. A bluish color appears when 2,4-DNT or 2,6-DNT is the dominant compound, a reddish-brown color appears for TNT and TNB, and an orange color for tetryl and picric acid. After application of spray from the second aerosol can, the formation of a pink color indicated the presence of nitramines or nitrate esters (e.g., RDX, HMX, NG, PETN, NC, NQ, and/or tetryl). Application of the first two aerosol cans allowed for the sequential detection of both polynitroaromatic and nitramines. If there was no color development, then the sample was sprayed with the third aerosol can. The development of a pink color after applying the third aerosol indicated the presence of an inorganic nitrate (ammonium, potassium, sodium, barium, strontium nitrate, or black powder).

Visual and Instrument Calibration

A visual scale for the colorimetric screening test was prepared by spraying (see above) 5- μ L aliquots of 10-, 100-, and 1000-mg/L standards of TNT and RDX after they had been placed on test sheets. All six aliquots were placed on the same sheet; however, the TNT standards had to be covered when applying the second aerosol. This screening method can detect the presence of 0.05 μ g of explosive analyte when concentrated in a discrete location on a white surface. In general, the color intensity changes from a very light shade for 0.05 μ g to a distinct light color for 0.5 μ g and to a dark color for 5 μ g.

For GC-TID, a five-point calibration curve is recommended for each analyte of concern. This number of standards allows non-linear models to be used when necessary. A non-linear model (quadratic through the origin) should be chosen when the linear regression through the origin fails to establish a correlation coefficient (r) of greater than 0.990. Calibration checks should be made after every five samples by randomly running one of the four highest working standards. When the calibration model fails to establish a concentration within $\pm 20\%$ of the expected value for a standard, re-calibration should be performed. The concentrations of the working standards ranged anywhere from 0.01 to 50 μ g/L, depending on the analysis objectives. Table 1 shows MDLs obtained for spiked Ottawa sand. Typical chromatograms are available elsewhere (Hewitt et al., 2001).

Table 1. Method detection limits (MDLs) based on matrix (Ottawa sand) spike samples.

<u>Compound</u>	<u>MDL (mg/kg)</u>
NG	0.10
1,3-DNB	0.012
2,6-DNT	0.0054
2,4-DNT	0.0016
TNB	0.0024
TNT	0.0016
RDX	0.0094
4AmDNT	0.010
2AmDNT	0.0068
Tetryl	0.0017
HMX	0.027

Column: DB-1, 15 m, 0.5- μ m film.

EXPERIMENTS

Three experiments were conducted: a) a quantitative assessment of explosives residues on a fragment removed from a hand grenade that had not properly detonated (“low order”) and on quality assurance coupons (explosives-spiked metal plates [Hewitt 2001]), b) a qualitative assessment of explosives residues on the fins of two 120-mm mortar rounds after being fired, and c) an analysis of several soil sample extracts and soil sample splits. The colorimetric screening step was only used with the soil samples since analyte concentrations were either known or were expected to be low on the other materials.

Two of four metal coupons (1.5- × 1.5-cm rusted steel plate) spiked with approximately 1 mg of TNT, RDX, and HMX (Hewitt 2001) and a 2.8-cm² fragment of a hand grenade casing were each wiped with an acetone-moistened cotton swab. The remaining two coupons, two wiped coupons, the hand grenade fragment, and the three air-dried cotton swabs were then submersed in acetone. Table 2 compares the GC-TID and Method 8330 concentration estimates obtained for the acetone extracts of these samples.

Table 2. Comparison between GC-TID and Method 8330 for extracts of sample wipes and solvent immersion samples.

	<i>Solvent extract (mg/L)</i>					
	<i>TNT</i>		<i>RDX</i>		<i>HMX</i>	
	<i>TID*</i>	<i>HPLC**</i>	<i>TID</i>	<i>HPLC</i>	<i>TID</i>	<i>HPLC</i>
Hand grenade fragment						
Cotton swab	600	630	610	690	88	120
Swiped fragment	190	200	250	310	23	34
Coupons						
Unswiped coupon	850	940	760	920	890	910
Unswiped coupon	890	950	860	930	1000	920
Cotton swab	780	820	620	730	690	720
Swiped coupon	79	78	180	150	140	140
Cotton swab	800	820	700	790	710	710
Swiped coupon	50	51	51	58	60	54

* GC-TID

** Method 8330

Two mortar fins that had been recovered from impact craters following proper detonation were each wiped several times with acetone moistened cotton balls. In each case an area of approximately 16 cm² was wiped at various locations (inside and outside of the stem, between one set of tail fins, and inside the bottom of the stem) on each of the two fins. After air-drying, each swab was placed in the barrel of a 5-mL plastic syringe, a filter was attached, and 1 mL of acetone was placed on the swab. The plunger was then inserted and the swab was depressed to release the solvent. Table 3 compares the GC-TID and Method 8095 concentration estimates obtained for NG, the only explosive detected, in the acetone extracts.

Fourteen soil sample extracts were screened using the visual colorimetric method described above, then diluted as needed to achieve analyte concentrations below 50 mg/L prior to GC-TID analysis. Six of the samples were taken from archived soil stored at the Cold Regions Research and Engineering Laboratory, and the remainder were samples (sample splits) that had been used as part of the U.S. Environmental Protection Agency’s Environmental Technology Verification (ETV) Program (www.epa.gov/etv). All of these samples were handled so that the colorimetric screening and subsequent GC-TID analysis were blind (sample identity was masked). Table 4 shows the dilutions made based on the colorimetric screening and a comparison between GC-TID and Method 8330 concentration estimates.

Table 3. Comparison between GC-TID and Method 8095 for NG in extracts of wipe samples of 120-mm mortar fins.

<i>Sample location</i>	<i>NG (mg/L)</i>	
	<i>GC-TID</i>	<i>Method 8095</i>
Fin A		
Stem exterior	0.29	0.26
Stem interior	2.3	2.0
Between tail fins	0.12	0.19
Bottom interior	1.2	0.92
Fin B		
Stem exterior	10	11
Stem interior	3.7	2.5
Between tail fins	7.2	4.3
Bottom interior	2.0	1.7
Method blank	0.00	0.0035

Table 4. Sample extract dilutions based on colorimetric screening and comparison between GC-TID and Method 8330 results for the analysis of soil extracts and soil sample replicates. The GC-TID was calibrated over a range of 0.5 to 50 mg/L. Only those analytes with the highest concentrations are presented in the table. Several of these samples also contained 2,4-DNT and TNB, and one contained tetryl.

	<i>Colorimetric screening dilutions</i>		<i>TNT (mg/kg)</i>		<i>RDX (mg/kg)</i>		<i>HMX (mg/kg)</i>	
	<i>1st Spray</i>	<i>2nd Spray</i>	<i>TID</i>	<i>HPLC</i>	<i>TID</i>	<i>HPLC</i>	<i>TID</i>	<i>HPLC</i>
Soil sample extracts								
1.	1:10*	1:100	690	640	480	517	<120	<30
2.	ND**	1:10	<0.5	<0.5	<0.5	<0.5	71	77.9
3.	ND	ND	52	51.5	<0.5	0.18	<2.0	<1.5
4.	ND	ND	<0.5	0.12	<0.5	0.052	<2.0	<1.0
5.	1:10	1:10	630	642	73	53.4	23	37
6.	1:1000	1:10	12000	11700	<10	<60	<100	<300
Soil sample splits†								
7.	ND	1:10	<0.5	<0.5	<0.5	<0.5	250	180
8.	ND	1:10	<0.5	<0.5	<0.5	<0.5	220	210
9.	1:1000	ND	18000	23000	<50	<50	<200	<2
10.	1:10	1:100	110	120	2100	2300	260	260
11.	1:10	1:100	76	76	1000	1100	200	180
12.	1:10	ND	81	84	11	7.1	<20	<2
13.	ND	ND	1.0	0.9	100	110	20	15
14.	1:10	1:100	170	300	3500	4100	280	400

* Dilution made based on colorimetric screening

**ND – no dilution necessary

† Samples from the Environmental Technology Verification Program. HPLC analysis of sample splits were performed by a reference laboratory.

RESULTS AND DISCUSSION

Tables 2–4 show that there was good agreement between the concentration estimates that were established by the GC-TID method and those determined with either Method 8330 or Method 8095. Past participation in the EPA's Environmental Technology Verification Program (www.epa.gov/etv) and work in a land mine field (Hewitt et al., 2001) were also very successful. For example, the on-site method of analysis established more accurate explosives concentrations for reference samples than those obtained by the reference laboratory for the ETV program and allowed us to delineate the surface boundaries of explosives residues above buried land mines. These two activities highlight the reliability and flexibility of this analytical method.

The recoveries of explosives using a cotton swab moistened with acetone (>70%) from the hand grenade fragment and spiked coupons also agreed with previous trials (Hewitt 2001). Furthermore, the ratio of RDX to HMX, 7.74, for the Comp B filled hand grenade was in good agreement with a previously established value (7.61) using Method 8330 (Jenkins et al., in press). Although the surface wipes of the 120-mm mortar fin failed to detect a distinct distribution of NG, its presence is consistent with earlier efforts. For example, testing of mortar fins for NG when this explosive was present in the igniter has shown that this analyte can remain on surfaces for several years, regardless of its environmental settings (M. Walsh, personal communication, CRREL).

The novelty of this effort involved the coupling of a quick and simple colorimetric screening test with a GC-TID analysis. Pre-screening is advisable for any GC analysis of unknown samples. Indeed, the ability to perform timely on-site GC analyses can easily be confounded by inadvertently introducing a high-concentration sample because of the time involved to return the analytical system response to baseline conditions (i.e., to avoid false positives for subsequent analyses). The findings in Table 4 show that this colorimetric screening test can identify high concentrations of both nitroaromatic and nitramine explosives independently of each other or in the same sample extract. The success of this preliminary study has encouraged us to recommend this technique for use in range characterization activities involving on-site sample analysis.

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REFERENCES

Hewitt, A.D., and T.F. Jenkins (1999) On-site method for measuring nitroaromatic and nitramine explosives in soil and groundwater using GC-NPD: Feasibility Study. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, Special Report 99-9. < http://www.crrel.usace.army.mil/techpub/CRREL_Reports/ >

Hewitt A.D., T.F. Jenkins, and T.A. Ranney (2001) Field gas chromatography / thermionic detector system for the analysis of explosives in soils. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, ERDC/CRREL TR-01-9. < http://www.crrel.usace.army.mil/techpub/CRREL_Reports/ >

Hewitt A.D. (2001) Characterization of range scrap and development of quality assurance coupons for hot gas treatment. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, ERDC/CRREL TR-01-7. < http://www.crrel.usace.army.mil/techpub/CRREL_Reports/ >

Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, L.V. Parker, C.A. Hayes, and E. Wahlgren (in press) Characterization of explosives contamination at military firing ranges. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, ERDC/CRREL TR.