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Trace analysis of military high explosives (2,4,6-trinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine) in agricultural crops

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Abstract

This study implements procedural modifications to a previously described methodology with the goal of obtaining the lowest possible detection limits for the analysis of the military explosives in a wide variety of plant tissues. The modified methodology analyzes 1.0-g portions of lyophilized material rather than 1.0-g fresh plant tissue as specified by the previous protocol. The method was found to be applicable to a large diversity of agricultural crop species including tomato, corn kernels, corn stover, radish, lettuce, hot peppers, bell peppers, grapes, carrot, alfalfa, bush bean and soybean. In general, detection limits in the low-ng/g (parts-per-billion, w/w) range were achieved for both hexahydro-1,3,5-trinitro-1,3,5-triazine and 2,4,6-trinitrotoluene. © 1997 Elsevier Science B.V.

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1. Introduction

Past activities related to military explosives manufacturing and ordnance assembly have resulted in severely contaminated munitions production and packing plants [1]. During these operations, wastewater from the packing process was often directed to disposal trenches. At the time, it was believed the munitions residues would remain localized in the upper surface soil layers where disposal could be conveniently conducted at a later date. However, in some areas, explosives and their transformation products have leached from the contaminated surface into subsurface aquifers [1,2]. Aquifer pollution plumes continue to spread beyond military surface property boundaries and are threatening municipal water supplies [1,2]. Pollution plumes are also impacting agricultural irrigation wells, and possible food-chain implications must be carefully considered. Techniques that are capable of detecting explosives at low-ng/g concentrations in a wide variety of crop plants are needed for this assessment.

Several studies have addressed plant uptake and metabolism of munitions compounds. Palazzo and Leggett were the first to analyze plant tissue for parent 2,4,6-trinitrotoluene (TNT) residues [3]. Later, more detailed studies were conducted with radiolabeled analyte that combined plant uptake and metabolism studies with improved analytical methodology [4]. Analytical procedures developed for these studies were based on acid hydrolysis of tissue followed by solvent extraction of the hydrolysate. The solvent extract was then fractionated by normal-phase chromatography on a solid-phase extraction cartridge. High-performance liquid chromatography

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(HPLC) analysis was used for quantitative determination of explosive in the appropriate solid-phase extraction fraction. These studies allowed analysis of parent explosive without analytical interferences. Furthermore, use of radiolabeled analyte allowed characterization of plant metabolites and construction of a mass balance. The first of these studies examined TNT [4], whereas later investigations extended the analytical methodology to hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) [5] and 2,4,6-trinitrophenylmethylnitramine (tetryl) [6].

Metabolism studies determined that TNT was rapidly converted to polar metabolites by plants [4]. The initial metabolic intermediates, 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene, were found localized in relatively high concentration in root tissue. Analysis for the aminodinitrotoluene isomers was straightforward since these compounds were contained in the same solid-phase extraction fraction as TNT [4]. In contrast to TNT, plants grown in the presence of RDX were found to bioaccumulate this explosive in their aerial tissues [5]. The finding that RDX is bioaccumulated in plants grown either hydroponically or in soil has potentially serious consequences. It may be possible that certain crop species are capable of biomagnifying low-level RDX contamination in irrigation water drawn from munitions-contaminated aquifers.

Scientists at Pacific Northwest National Laboratory developed a methodology that was originally intended for the analysis of explosives in bush bean leaf foliage [4–6]. Solid-phase extraction proved extremely effective in separating explosives from the majority of plant pigments and other indigenous metabolites. The method was found equally applicable to the analysis of various plant structures, including the stem, pod, seed and root tissue. According to the established protocol, fractionation of 1.0 g fresh-mass tissue results in 1.0 ml of final extract that is analyzed by HPLC. The detection limit for this analysis (0.1 μg/g) is essentially equivalent to the chromatographic detection limit of approximately 0.1 μg/ml. The principal goal of this study was to evaluate the general applicability of the TNT and RDX methodology for a wide variety of crop species. A secondary goal was to explore simple procedural modifications that would improve detection limits.

2. Experimental

HPLC analyses utilized a Beckman (Fullerton, CA, USA) Ultrasphere reversed-phase column (24 cm×4.6 mm, d_p=5 μm). Binary water–acetonitrile gradients were delivered to the column at a flow-rate of 1.0 ml/min by a Waters (Milford, MA, USA) Model 600E system controller and pump. For TNT, a simple linear gradient from 40% to 100% acetonitrile within 20 min was used [4]. Pure acetonitrile was delivered to the column for an additional 15 min before recycling and equilibrating the column with the initial mobile phase composition. A more complex biphasic mobile phase delivery was used for analysis of RDX [5]. In this gradient, the acetonitrile composition was increased from 20% to 60% over 20 min. The gradient then continued from 60% to 100% within 10 min. This final mobile phase was delivered for a period of 10 min before recycling to the original composition. In one instance unique selectivity was obtained by substituting methanol for acetonitrile during the RDX gradient delivery. Samples were introduced to the column by use of a Waters WISP Model 710 automatic injector. Typically, 20-μl volumes were injected for analysis. As the column was developed, the eluting components were detected by a Waters 490E detector operated at 0.008 absorbance units full scale. TNT and RDX were detected at 254 and 234 nm, respectively. Integrated peak areas, provided by a Hewlett-Packard (Wilmington, DE, USA) Model 3390A integrator, formed the basis for quantitative measurements. Several chromatographic analyses utilized a Hewlett-Packard Model 1090 HPLC system with diode array detection to confirm compound identity.

With the exception of diethyl ether, organic solvents used for tissue extraction or HPLC analysis were HPLC grade obtained from J.T. Baker (Phillipsburg, NJ, USA). HPLC-grade water was also from J.T. Baker. Diethyl ether was purchased from Mallinckrodt (Chesterfield, MO, USA). RDX and TNT were Standard Analytical Reference Material (SARM) provided by the US Army Toxic and Hazardous Material Agency (Aberdeen Proving Ground, MD, USA). Dinitrodurene (1,4-dinitro-2,3,5,6-tetramethylbenzene) was obtained from Aldrich (Milwaukee, WI, USA). Florisil Sep-Pak cartridges were purchased from Waters Corporation.

Plant material for these studies came from various sources. Red oak tree leaf and natural grass cover (Johnson and Perennial Grasses) tissue samples were collected from areas of suspected munitions contamination and shipped on ice from the Milan Army Ammunition Plant in Milan, TN, USA. These tissues were analyzed for RDX by the previous methodology, which required 1.0 g of fresh tissue. The remaining studies used a modified procedure that required 1.0 g of freeze-dried tissue for analysis. These tissues were lyophilized immediately after harvest and stored at −20°C before chemical fractionation. Most tissues were from control plants grown in non-contaminated soil under laboratory conditions by the US Army Edgewood Research, Development and Engineering Center (ERDEC). Tissue analyses were performed on the edible portions of tomato, bush bean, radish, alfalfa, lettuce, soybean and corn stover. Additionally, edible portions of agricultural crop specimens grown in the vicinity of Cornhusker Army Ammunition Plant near Grand Island, NB, USA, were analyzed for RDX. These crops were irrigated with water known to contain low-ng/ml concentrations of TNT and RDX. Field-grown crops included tomato, hot pepper, carrot, green bell pepper, corn kernels and grapes. Finally, carrots and pressed alfalfa cubes were obtained from a local supermarket and a feed store, respectively. These tissues were used to generate the example chromatograms presented below. Previous data from our laboratory indicated a 67% water content for alfalfa tissue.

A modification of a previously described plant analysis method formed the basis for these studies. Analytical procedures were essentially the same as previously reported [4–6], with the exception that extractions were performed on 1.0 g of lyophilized material rather than 1.0 g of fresh tissue. Lyophilization removed free water, resulting in a stabilized tissue that was easier to store. Analysis of an equivalent mass of lyophilized tissue dramatically reduced detection limits due to the larger effective amount of tissue analyzed.

The procedures for TNT and RDX are summarized in Fig. 1 and are briefly described below. For both analyses, the flowchart is identical through the solvent extraction stages. After an acid hydrolysis step, the tissue is extracted with diethyl ether both

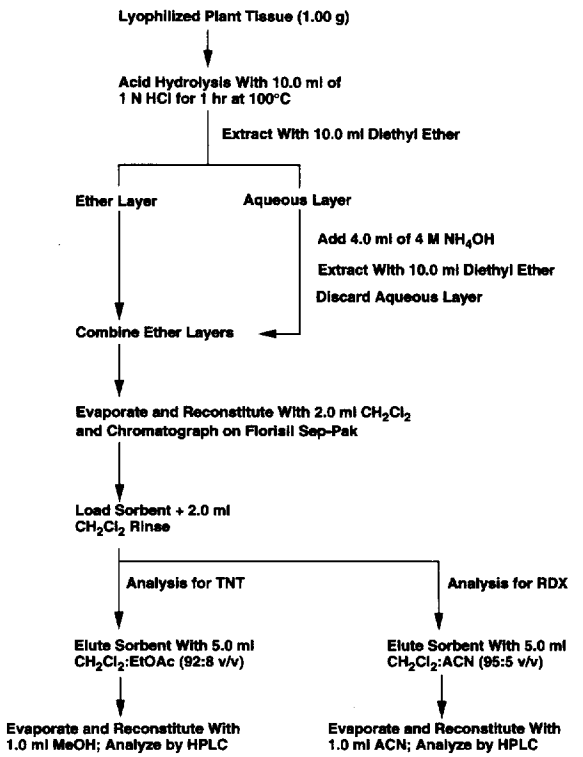

Fig. 1. Flowchart illustrating the fractionation and analysis of plant tissue for TNT or RDX. Choice of solid-phase adsorbent eluate forms a divergence in the analysis scheme between the explosives. Abbreviations used in the flowchart are as follows: ACN = acetonitrile; EtOAc = ethyl acetate; MeOH = methanol and CH_2Cl_2 = methylene chloride.

before and after pH adjustment with ammonium hydroxide. The combined organic extracts are evaporated to dryness. The remaining residue is reconstituted in methylene chloride and applied to a Florisil Sep-Pak cartridge. Elution of explosives from the Florisil adsorbent forms a divergent point in the analysis schemes for TNT and RDX. As indicated in Fig. 1, slightly different solvent mixtures were used to elute the explosive from the Florisil adsorbent. In each case, the explosive-containing fraction was reduced to dryness under a nitrogen stream and reconstituted with an appropriate solvent for reversed-phase HPLC analysis. Further Florisil elution fractions were collected during previous studies that examined plants grown with ^{14}C-radiolabeled munitions to allow characterization of plant metabolites. Creation of these additional fractions was not neces-

sary to quantitate the parent explosive and was omitted in the simplified procedure presented here.

Soil samples from the Milan Army Ammunition Plant were collected from areas immediately adjacent to plant tissue collection sites to verify contamination with muntions compounds. The soil analysis method was based on the sonic extraction method described by Majors et al. [7]. Deviations from the Majors procedure included use of dinitrodurene (1,4-dinitro-2,3,5,6-tetramethylbenzene) as an internal standard and a ten-fold concentration of the extract before HPLC analysis.

3. Results and discussion

3.1. Milan soil contamination

The internal standard soil analysis method was designed to quantitate munitions at concentrations around 5 μg/g and soil fortification studies at this level showed reasonable recoveries (>90%) for both TNT and RDX. However, analysis of Milan soil showed contamination with these explosives far below the 5 μg/g level. Calculations based on peak areas indicated that both TNT and RDX were present at roughly 100 ng/g. The actual soil contamination of these explosives may be somewhat higher since lower recoveries are associated with diminished analyte concentrations [8]. Chromatographic analysis of the soil extracts also verified the presence of the aminodinitrotoluene isomers. Although the exact concentrations of the explosives and TNT reduction products were not determined, these preliminary studies were sufficient to meet our objective of verifying trace TNT and RDX contamination in Milan soils.

3.2. Enhanced detectability demonstrated on a variety of tissue samples

Milan plant samples were analyzed in duplicate for RDX by the previous procedure that required 1.0 g of fresh tissue [5]. Chromatograms were relatively clean and displayed no interferences in the region of RDX elution. RDX was not present in grass or leaf samples at concentrations above the 0.1-μg/g chromatographic detection limit. For the remaining samples, detection limits were reduced by analyzing an equal mass of freeze-dried rather than fresh tissue. Detection limits achieved under these conditions were, in general, limited by the matrix background signal coincident with the expected retention window of the explosive. To determine detection limits, blank tissues were analyzed and the baseline signal fluctuations in the immediate vicinity of the anticipated explosive retention time were measured. Next, the detection limit was calculated as the quantity of explosive that would result in a signal equivalent to the background signal. This value was calculated by comparison to the peak height that resulted from analysis of 1.0-μg/ml standards that bracketed the blank tissue samples. Detection thresholds reported here are different from conventional limits calculated on a signal-to-noise basis and more accurately reflect a less than or equal value for tissue explosive concentrations. This method was judged to be more relevant for the present studies because detection limit values are, in general, matrix limited and the instrument was not operated at a sufficiently high sensitivity to visualize instrumental noise.

Table 1 summarizes the detection limits and recoveries obtained during this study. The last six rows in Table 1 are data from the Cornhusker Site field samples. These crops were known to be irrigated with contaminated aquifer water and, since possible bioaccumulation of RDX in field samples was of principal concern, the tissues were analyzed exclusively for this explosive. Analyte recoveries were based on analysis of desiccated tissue blanks that were fortified with 5.0 μg/g of explosive. Percentage recoveries were calculated from peak areas obtained from spike samples compared to 5.0-μg/ml explosive standards. Unless indicated differently, all detection limits and percentage recovery entries in Table 1 are based on quadruplicate tissue analyses. The corn stover and soybean sample tissues were harvested in the desiccated state and, therefore, detection limits for these two tissues were based on freeze-dried masses rather than fresh masses. Since these values do not account for water normally associated with the tissue, detection limit values are artificially inflated relative to the other table entries.

As expected, due to the desiccated state of the soybean and corn stover tissues at harvest, these samples yielded the highest detection limits for TNT;

Table 1
Average recoveries and detection limits along with the associated standard deviations (S.D.s) for TNT and RDX analyses of various tissues

Origin/ Crop	RDX		TNT	
	Detection limit (ng/g fresh mass ±S.D.)	Percent recovery[a] (average±S.D.)	Detection limit (ng/g fresh mass±S.D.)	Percent recovery[a] (average±S.D.)
Control tissues grown under laboratory conditions by Army ERDEC				
Tomato	5±1	90±4	3.4±0.4 (n=3)	80±10
Soybean[b]	50±28	70±3 (n=8)	26±7	66±2 (n=8)
Corn (stover)[b]	51±1	75±18	69±20	56±17
Bush Bean	8±1	68±11	6±2	85±6
Radish	3.2±0.3	103±38	2.7±0.3	73±1
Alfalfa	15±10	76±3	7±3	76±12
Lettuce	7±9	71±9	6±4	67±4
Field samples collected in vicinity of Cornhusker Army Ammunition Plant				
Tomato	17±8	–	–	–
Hot Pepper	28±9 (n=3)	–	–	–
Carrot[c]	39±11 (n=5)	–	–	–
Green Pepper[d]	20±10 (n=2)	–	–	–
Corn (kernel)[d]	13±2 (n=2)	–	–	–
Grapes	18 (n=1)	–	–	–

Values are listed in ng explosive per g fresh-mass tissue (ppb, w/w). Unless indicated differently, all values are based on quadruplicate analyses.

[a] Recoveries were determined from tissues spiked with 5 μg/g explosive (on a dry-mass basis).

[b] Values for these tissues are based on tissue dry masses.

[c] Analysis of these carrot tissues required substitution of methanol for acetonitrile in the HPLC gradient to avoid the co-elution of an interfering peak.

[d] Error value is the analysis range rather than a standard deviation.

26 and 69 ng/g, respectively (Table 1). TNT detection limits for the other tissues were in the low-ng/g concentration, ranging from a minimum of 3.4 ng/g for tomato to a high of 7 ng/g for alfalfa. All recovery averages were above 50% and ranged from 56% to 80% for corn stover and tomato, respectively. Analysis variability for TNT detection limits and recoveries was acceptable as evidenced by the reasonably low standard deviations (Table 1). As discussed below, analysis of soybeans for TNT required additional consideration due to the large quantities of oil contained in this tissue.

The detection limits for RDX in non-desiccated tissues were also in the low-ng/g range (Table 1). Detection limit values for these tissues ranged from 5 to 39 ng/g for tomato and carrots, respectively. Also consistent with the TNT analysis, the highest RDX detection limits were observed for dry corn stover (51 ng/g) and soybean (50 ng/g) tissues. As discussed below in more detail, a methanol–water HPLC gradient was used to analyze carrots for RDX to obviate chromatographic co-elution of an interfering component. Recovery of spikes tended to be slightly higher for RDX compared to TNT. RDX recoveries ranged from 103% to 70% for radish and soybean, respectively. Analysis of soybeans for RDX also required an additional sample preparation step due to the copious amounts of oil contained in these tissues (see below). RDX sample analysis variance was acceptable, as indicated by the low standard deviations for both the detection limits and the spike/recoveries presented in Table 1. Analysis of the field-grown samples from the Cornhusker and Milan Army Sites gave no indication of containing RDX at concentrations above the detection limits.

Chromatograms of many tissues were relatively free of interfering compounds, at least in the vicinity of the munitions elution ranges. This was particularly true for corn kernels, green bell peppers, grapes and tomatoes. For these tissues, where very little interference exists, it may be possible to further reduce the detection limits by increasing sample size to the

point where the matrix signal becomes prominent. However, there is a practical limit to the amount of tissue that can be effectively hydrolyzed by 10 ml of acid solution during the initial sample preparation step. Rehydration of tissue during the hydrolysis step results in the absorption of a large amount of the available acid solution. This was particularly evident with the corn stover samples and likely explains the lower recoveries and the higher detection limits and variances observed when analyzing this tissue.

Several examples are presented below to illustrate results that can be expected from application of the analysis methodology. It should be emphasized that difficult tissues from an analytical perspective were chosen to highlight the methodology. Fig. 2 presents chromatograms of a carrot RDX tissue spike (top) and the corresponding blank (bottom). Considerable carotene pigment was present in the RDX-containing Florisil fraction. These pigments eluted during the later portions of the chromatograms and did not interfere with the determination of RDX. Fig. 2 is representative of the metabolic profiles that were obtained for most tissues, except that the carrot samples contained a higher number and quantity of later-eluting components. As previously mentioned, carrot tissues harvested from the Cornhusker Army Ammunition Plant site contained an interfering compound that co-eluted with RDX; however, tissues obtained from other sources were devoid of the interfering compound (Fig. 2). The RDX peak shown in the top chromatogram of Fig. 2 corresponds to a fresh-mass RDX spike concentration of 525 ng/g. As can be seen in the bottom of Fig. 2, small fluctuations in the baseline around the elution window of RDX define the matrix-limited detection limit for this sample.

Among the most complex samples we encountered were extracts originating from alfalfa tissues. Fig. 3 presents an RDX spike (top) and corresponding tissue blank (bottom) chromatographic profiles from alfalfa. The complexity of the sample is evident by inspection of the tissue blank chromatogram shown in the bottom of Fig. 3. Despite the presence of numerous indigenous metabolites throughout the entire chromatographic elution range, the region

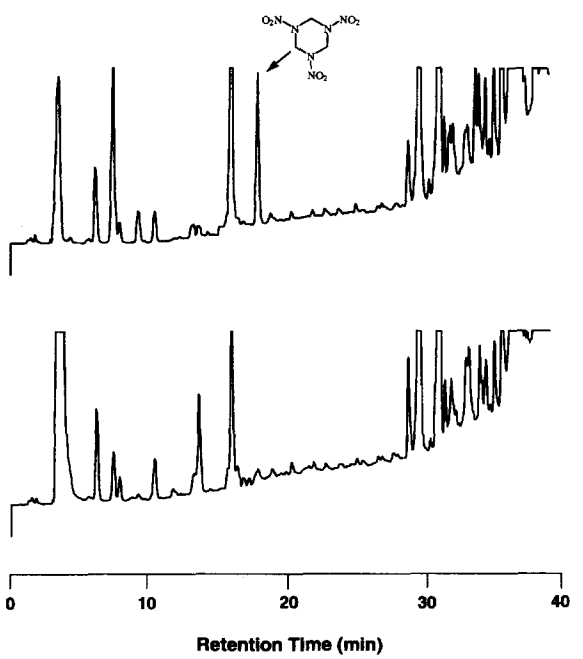

Fig. 2. Chromatographic profiles of a carrot blank tissue (bottom) and carrot tissue spiked with 525 ng/g RDX on a fresh-mass basis (top). Chromatograms resulted from 10-μl sample injections. See Section 2 for chromatographic conditions.

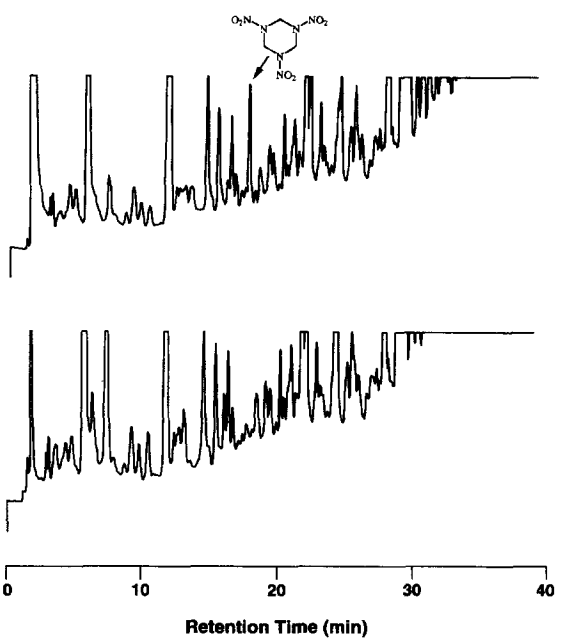

Fig. 3. Chromatographic profiles of an alfalfa blank tissue (bottom) and alfalfa tissue spiked with 462 ng/g RDX on a fresh-mass basis (top). Chromatograms resulted from 17-μl sample injections. See Section 2 for chromatographic conditions.

surrounding RDX is relatively free of interference. The chromatographic peak indicated by the arrow in Fig. 3 results from RDX fortification at a fresh-mass concentration of 462 ng/g.

3.3. Tissues that require special consideration

Complications were encountered during soybean analysis due to the large amount of oil contained in this tissue. Substantial oil residue remained after evaporating the combined diethyl ether extracts. Upon reconstitution of the residue with methylene chloride and subsequent solid-phase extraction clean-up, it was found that the majority of oil (~100 μl) eluted with the explosive-containing fraction. Addition of 1.0 ml of methanol or acetonitrile for TNT or RDX, respectively, to the oil residue resulted in an immiscible mixture. After mixing and centrifugation (16 000 *g* for 10 min), the top organic solvent layer was removed for HPLC analysis. Concerns were raised that the explosives might exhibit altered retention characteristics on Florisil adsorbent in the presence of large quantities of oil. Additional concerns were based on the possible partitioning of explosive between the immiscible solvent and oil layer in the final extract. Both phenomena would result in diminished recovery of explosive. These concerns were deemed unfounded when high recoveries of explosives were obtained (Table 1). Recovery of RDX was determined to be 70±2%, whereas a slightly lower 66±2% recovery was obtained for TNT-spiked soybeans. The high precision of both spike recoveries was also notable.

Caution should be exercised when analyzing carrot tissue for RDX. In the field-grown carrots obtained from the Cornhusker Army Ammunition Plant area, a peak was observed that co-eluted with RDX. This peak corresponded to 0.48±0.38 μg/g RDX equivalents. However, examination of the ultraviolet absorption spectrum collected by photodiode array detection indicated that this compound was not RDX. In fact, altering the analysis selectivity by substituting methanol for acetonitrile in the gradient delivery resulted in complete resolution of RDX from this indigenous component, with the metabolite now displaying a longer retention time relative to RDX. Interestingly, as illustrated in Fig. 2, analysis of carrot tissue from a different source with the acetonitrile–water gradient gave no indication of the previously observed interference.

4. Conclusions

This study demonstrated the remarkable ability of the plant analytical method to successfully address a diverse range of agricultural crops and other plant material. The original analysis protocol was determined to be applicable to natural vegetation such as tree leaves and cover grasses. The modified methodology appears viable regardless of whether plants are grown in the field or under laboratory conditions, whether the plant is a root crop or an aerial green tissue, or whether the tissue is a seed (as in the soybeans) or a fruit. It is notable that of all the different plant types analyzed, only two required extra analytical consideration. The large quantity of oil contained in soybeans required an additional centrifugation step to separate the oil from an immiscible organic solvent before analysis by HPLC. Also, caution should be exercised when analyzing carrot tissue, as a metabolite that co-elutes with RDX has occasionally been observed. It is advisable to verify RDX identity by confirming co-elution of the suspect peak with an RDX standard under methanol–water gradient elution conditions.

In addition to extending the analytical methodology to a variety of different plants, another objective of the present study was to decrease the obtainable detection limits. This was accomplished by analyzing 1.0-g quantities of lyophilized tissue rather than fresh tissue. In general, this minor modification allowed detection limits to be decreased into the low-ng/g range for both TNT and RDX. In most cases the detection limits observed in this study were constrained by matrix interferences eluting in the retention window of the explosives. In a few cases, chromatographic profiles were free of interferences in the elution range of the explosives and it is possible that analysis of larger quantities of tissue may allow further decreases in detection limits. It is likely, however, that practical sample handling limitations will prevent dramatic decreases in detection limits from those stated in Table 1 with ultraviolet (UV) absorption detection. Substitution of detection modes more sensitive and selective than UV absorp-

tion detection may allow lower detection limits to be achieved [9,10]. Past studies have described analysis methods for the explosive tetryl in plants and it is likely that the minor modifications described here would also be applicable to decreasing obtainable detection limits for this munition [6].

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