ERDC TR-20-13

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Environmental Analysis of Aqueous 3-Nitro-1,2,4-Triazol-5-One (NTO) by Ion Chromatography with Conductivity Detection

Samuel A. Beal, Susan Taylor, Rebecca A. Crouch, and
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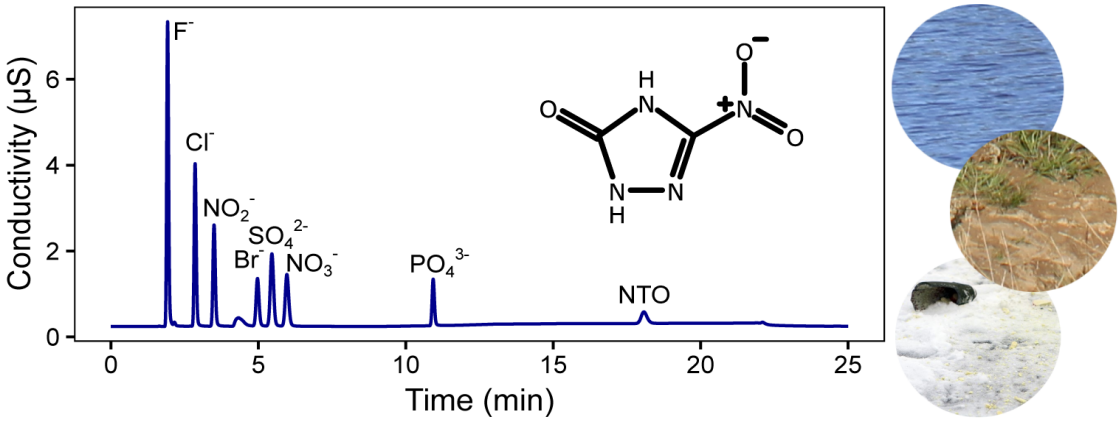
July 2020



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Samuel A. Beal and Susan Taylor

U.S. Army Engineer Research and Development Center (ERDC)
Cold Regions Research and Engineering Laboratory (CRREL)
72 Lyme Road
Hanover, NH 03755-1290

Rebecca A. Crouch and Anthony J. Bednar

U.S. Army Engineer Research and Development Center (ERDC)
Environmental Laboratory (EL)
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

Final Report

Prepared for Strategic Environmental Research and Development Program
Environmental Security Technology Certification Program
Environmental Restoration Program Area
4800 Mark Center Drive, Suite 16F16
Alexandria, VA 22350-3605

Under Projects ER-2727, ER-2722, ER-2219, ER19-1074, and ER19-5078,
Customer Order No. W74RDV83655930 and W74RDV90818426

Abstract

The newly fielded insensitive high-explosive compound 3-nitro-1,2,4-triazol-5-one (NTO) is mobile in the environment due to its high water solubility and low affinity for soils. The weak acidity of NTO (pK_a 3.67) presents a challenge to environmental analysis by high-performance liquid chromatography but enables direct separation by ion chromatography (IC). Here we developed an IC method for NTO in natural water, soil, and postdetonation residue. A gradient potassium hydroxide separation effectively resolved the inorganic anions (F^-, Cl^-, NO_2^-, Br^-, SO_4^{2-}, NO_3^-, and PO_4^{3-}) and NTO in 18 minutes. Suppressed conductivity of aqueous NTO was linear from 10 µg/L to 10 mg/L with a detection limit of 3 µg/L and quantitation limit of 9 µg/L. Recoveries of NTO-spiked natural water samples were 93%–118% at concentrations of 30, 100, and 500 µg/L. Recoveries of NTO-spiked soil samples were 91%–114% using deionized water (DI) extraction. NTO was completely recovered with DI-extraction in two postdetonation residue samples of IMX-101 but only partially recovered (58% and 69%) in two higher-concentration residues, potentially due to incomplete dissolution of the energetic particle matrix. These results support IC for confirmation analysis of environmental samples and for screening natural water samples while simultaneously analyzing inorganic ions.

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Preface

This work was partially supported by the Strategic Environmental Research and Development Program (SERDP) under projects ER-2727, ER-2722, ER-2219, and ER19-1074 and by the Environmental Security and Technology Certification Program (ESTCP) under project ER19-5078, Customer Order No. W74RDV83655930 and W74RDV90818426. Dr. Herb Nelson was Executive Director for SERDP-ESTCP, and Dr. Andrea Leeson was Deputy Director for SERDP-ESTCP and was the Project Monitor.

The work was performed by the Biogeochemical Sciences Branch (BSB) of the Research and Engineering Division, U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL). At the time of publication, Dr. Gina Ralph was Acting Chief, BSB; and Mr. J. D. Horne was Division Chief. The Deputy Director of ERDC-CRREL was Mr. David B. Ringelberg, and the Director was Dr. Joseph L. Corriveau.

The work was also performed by the Environmental Chemistry Branch (EPC) of the Environmental Processes and Engineering Division, ERDC Environmental Laboratory (EL). Ms. Amber Russell was Chief, EPC; and Mr. Warren Lorentz was Division Chief. The Acting Deputy Director of ERDC-EL was Dr. Justin Berman, and the Acting Director was Dr. Jack Davis.

We acknowledge Mr. M. F. Bigl, Dr. J. L. Clausen, Mr. B. P. Hubbard, Ms. M. E. Walsh, Mr. M. R. Walsh, Ms. H. H. Vermeulen, and Ms. A. M. Mossell.

COL Teresa A. Schlosser was Commander of the ERDC, and Dr. David W. Pittman was the ERDC Director.

Acronyms and Abbreviations

BSB	Biogeochemical Sciences Branch
CRREL	Cold Regions Research and Engineering Laboratory
DI	Deionized Water
DoD	Department of Defense
DNAN	2,4-dinitroanisole
EL	Environmental Laboratory
EPC	Environmental Chemistry Branch
ERDC	U.S. Army Engineer Research and Development Center
ESTCP	Environmental Security and Technology Certification Program
GW	Groundwater
HMX	1,3,5,7-Tetranitro-1,3,5,7-Tetrazoctane
HPLC	High-Performance Liquid Chromatography
IC	Ion Chromatography
IHE	Insensitive High Explosive
KOH	Potassium Hydroxide
NTO	3-Nitro-1,2,4-Triazol-5-One
pK_a	Acid Dissociation Constant
R^2	Coefficient of Determination
RDX	1,3,5-Trinitro-1,3,5-Triazinane
SERDP	Strategic Environmental Research and Development Program
SPE	Solid Phase Extraction
U.S. EPA	United States Environmental Protection Agency
v/v	Volume/Volume

1 Introduction

1.1 Background

The compound 3-nitro-1,2,4-triazol-5-one (NTO) is a component of some new insensitive high explosives (IHE) used in artillery and mortar munitions. NTO is less sensitive to unintended detonation than the conventional energetic compounds 1,3,5-trinitro-1,3,5-triazinane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane (HMX) (Lee et al. 1987). Additionally, studies have shown that NTO has lower oral toxicity (London and Smith 1985; Johnson et al. 2017) and ecotoxicity (Kennedy et al. 2017). However, postdetonation deposition rates of some IHE munitions have exceeded their conventional replacements by two to five orders of magnitude, with NTO as a predominant residual component (Walsh et al. 2014, 2018). NTO has relatively high water solubility (1.28 g/L* at 19°C; Spear et al. 1989) and a very low soil adsorption affinity (Mark et al. 2016, 2017), which make it susceptible to migration via ground and surface water. These factors, combined with the growing production and usage of IHE on training ranges, motivates the development of analytical methods to detect and quantify NTO in environmental matrices.

Relative to other energetic compounds, the polarity and weak acidity (pK_a† of 3.67; Lee and Coburn 1988) of NTO have presented an analytical challenge for conventional reverse-phased high-performance liquid chromatography (HPLC) with C8 and C18 columns (i.e., Method 8330B [U.S. EPA 2006]). Gas chromatography (i.e., Method 8095 [U.S. EPA 2007]) is not effective for NTO due to its thermal lability (Oxley et al. 1997). Previous methods for NTO determination in neat matrices have utilized HPLC with porous graphitic carbon columns (i.e., Hypercarb), acidified eluent (i.e., trifluoroacetic acid), and detection by ultraviolet absorbance near its peak at 315 nm (Le Campion et al. 1997; Walsh 2016). A reversed-phase gradient separation on polar endcapped C18 and biphenyl columns is currently being promulgated for simultaneous analysis of NTO and other insensitive and conventional energetic compounds in various environmental matrices

* For a full list of the spelled-out forms of the units of measure used in this document, please refer to *U.S. Government Publishing Office Style Manual*, 31st ed. (Washington, DC: U.S Government Publishing Office, 2016), 248–252, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

† Acid dissociation constant.

(Crouch et al. 2020; Russell et al. 2014). However, NTO elutes early with both stationary phases, so it would be beneficial to have alternative analytical methods with different separation mechanisms for applications in peak confirmation and sample screening, particularly in complex matrices.

Ion chromatography (IC) with conductivity detection has been successfully applied to the analysis of weak organic acids, in addition to its common usage for inorganic ions (e.g., Okada and Kuwamoto 1993). The deprotonation of NTO at typical environmental pH enables direct separation on anion chromatography columns using a basic mobile phase.

1.2 Objectives

We aimed to develop an IC method for the analysis of NTO and to examine its application in a variety of environmental matrices at concentrations relevant to environmental monitoring and assessment.

1.3 Approach

We first optimized an analytical method for the simultaneous analysis of NTO and inorganic anions using neat standards, and then we applied this method to a range of environmental samples spiked with NTO. We examined method robustness using natural waters and soils of wide-ranging composition and using samples of postdetonation residue.

2 Methods

We analyzed NTO and the anions F^-, Cl^-, Br^-, NO_2^-, SO_4^{2-}, NO_3^-, and PO_4^{3-}* on an IC (Thermo Integrion) equipped with an IonPac AG18-4 μm 4 × 30 mm guard column, IonPac AS18-4 μm 4 × 150 mm analytical column, Dionex ADRS600 4 mm suppressor, Dionex CR-ATC600 anion trap column, and Dionex EGC500 KOH (potassium hydroxide) eluent generator. Electrolytic-generated mobile phase was pumped at 1 mL/min following an optimized program of 23 mM KOH from minute 0 to 7, linear ramp to 60 mM KOH from minute 7 to 11, hold at 60 mM KOH from minute 11 to 20, and return to 23 mM KOH from minute 20.1 to 25. System temperatures were 20°C in the pump compartment, 35°C in the detector cell, and 30°C in the column compartment. A 100 μL sample loop was used with a fourfold flush between samples. NTO was quantitated using a 5- to 7-point external calibration curve. All aliquots and dilutions were determined gravimetrically by using an analytical balance (Mettler Toledo ME204TE).

We collected natural water samples in 50 mL polypropylene centrifuge tubes from groundwater (GW) and surface water in Lebanon and Grantham, New Hampshire. We spiked these untreated samples with an aqueous NTO stock made from neat NTO (BAE Systems). Soil samples collected from U.S. military installations were ground with a mortar and pestle and spiked with NTO, along with 25 other energetic compounds, in 90:10 (v/v†) methanol:acetonitrile to a concentration of 20 mg/kg dry soil. Triplicate 1 g subsamples of these soils were extracted in 50 mL polypropylene centrifuge tubes with 10 mL of 18.2 MΩ/cm deionized water (DI) by briefly vortexing and then placing them on a shaker table for 18 hours. Discrete subsamples of postdetonation residues from artillery munitions containing the insensitive munition formulation IMX-101 (Walsh et al. 2018) were extracted in triplicate identically to the soil samples but with 20 mL of DI and a 10× to 100× dilution with DI prior to analysis. All aqueous samples and extracts were syringe-filtered at 0.45 μm (Millex IC polytetrafluoroethylene) into 5 mL autosampler vials with plain caps (Thermo PolyVial).

* For a full list of the spelled-out forms of the chemical elements used in this document, please refer to *U.S. Government Publishing Office Style Manual*, 31st ed. (Washington, DC: U.S Government Publishing Office, 2016), 265, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

† Volume/volume.

DI-extracted IMX-101 residues were also analyzed by HPLC (Agilent 1260 Infinity) using a Hypercarb column (150 × 4.6 mm, 5 µm pore size) eluted with 3:1 (v/v) acetonitrile:water with 0.1% trifluoroacetic acid at 1.5 mL/min following Walsh (2016). The injection volume was 10 µL, the column temperature was 28°C, and NTO was detected with the diode array detector at 321 nm.

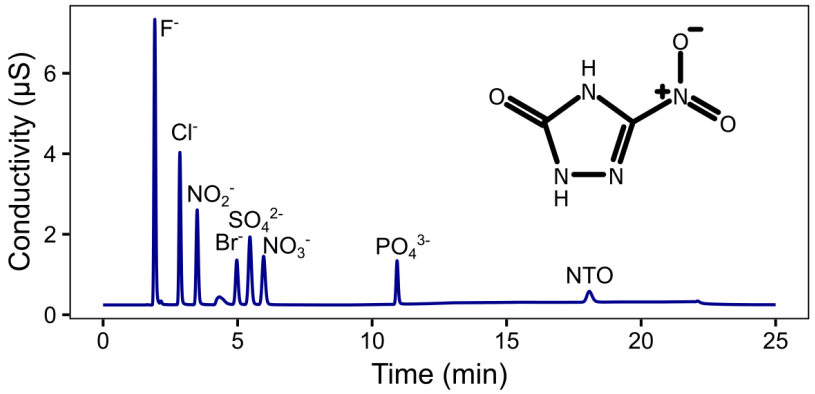
3 Results and Discussion

3.1 Chromatography

We found NTO to elute as a late Gaussian-shaped peak during standard inorganic anion analyses of aqueous samples containing NTO (Becher et al. 2019). Using 23 mM KOH mobile phase, NTO eluted at 60.4 min. To hasten analysis, an isocratic separation using 60 mM KOH produced a sharp NTO peak at 9.8 min but sacrificed resolution of the inorganic anions. The gradient method described herein preserves inorganic anion separation while also resolving NTO at a more acceptable retention time of 18 min (Figure 1). Although longer than typical NTO retention times by C18 HPLC (Felt et al. 2016; Russell et al. 2014; Crouch et al. 2020), the IC NTO retention time is similar to late-eluting energetic compounds by standard HPLC (i.e., EPA Method 8330B [U.S. EPA 2006]). Analysis time could be further reduced by increasing the mobile phase gradient ramp, using microbore or capillary columns, or reducing end-of-run equilibration time. NTO retention time was stable with a standard deviation of 0.04 min over 132 injections.

Conductivity response was linear (R^{2*} = 0.99999) over the standard concentration range from 0.01 to 10 mg/L. Respectively, the detection limit and quantitation limit were determined as 3 and 10 times the standard deviation (n = 7) of DI water containing 8.89 µg/L NTO. The detection limit was 3 µg/L, and the quantitation limit was 9 µg/L.

Figure 1. Example IC chromatogram of a standard containing 1 mg/L each of the inorganic anion and NTO in DI water.

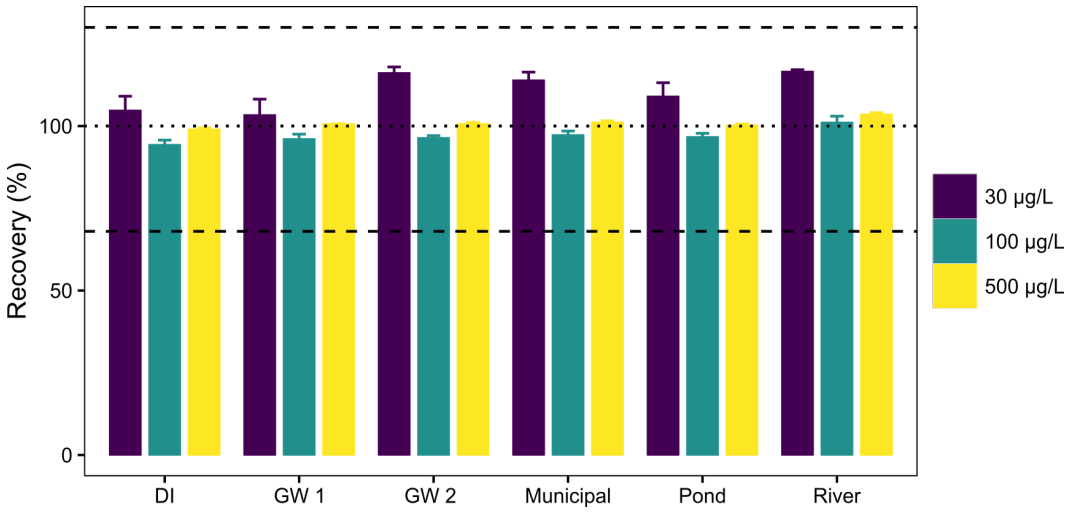


* Coefficient of determination.

3.2 Waters

Analysis by the IC method effectively recovered NTO from a range of different spiked laboratory and natural water samples at three concentration levels (Figure 2). Recoveries ranged from 93% to 118% and tended to be greater than 100% only for the low-level 30 µg/L spikes. While there are no current guidelines for NTO recoveries by HPLC, guidelines for the similarly mobile energetic compound RDX can serve as a reference. Laboratory control sample recovery limits for RDX by EPA Method 8330B are 68%–130% (DoD 2019), which is a wider range than the observed spiked water recoveries for all levels.

Figure 2. Mean NTO recoveries at three spike concentrations in water samples. Error bars are ± one standard deviation on triplicate measurements. For reference, the *dotted line* represents perfect recovery, and the *dashed lines* represent the upper and lower laboratory control sample limits for RDX in aqueous matrices by EPA Method 8330B (DoD 2019).



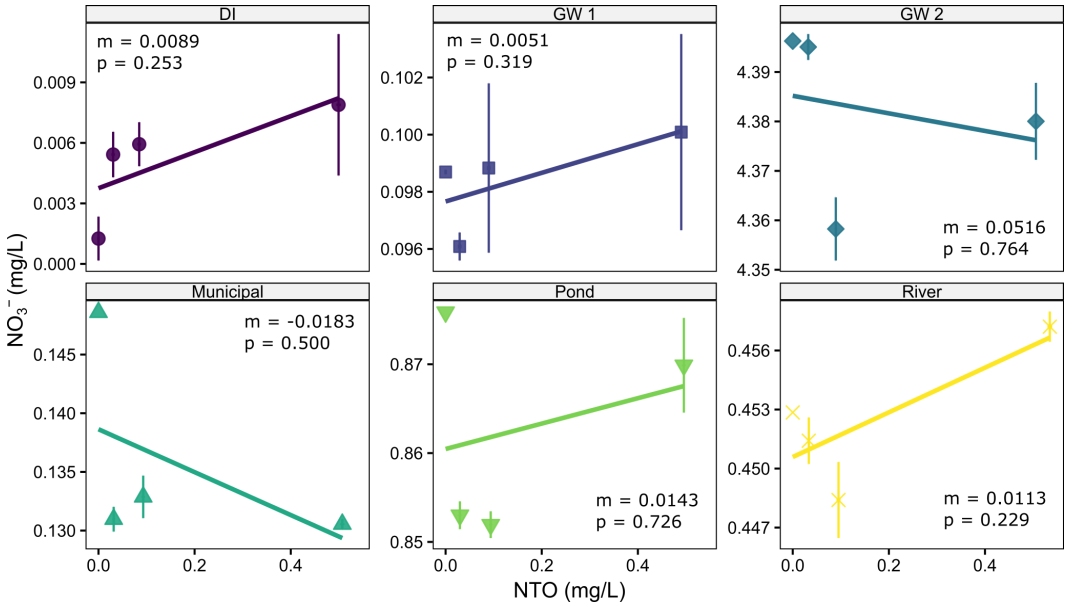
With the exception of DI, the water samples tested were circumneutral and contained detectable concentrations of the major anions (Table 1). Despite variations in major anion concentrations of up to two orders of magnitude, NTO recoveries did not vary systematically among the different water samples. To investigate possible effects of sample pH on NTO recovery, we adjusted the pH of municipal water samples with 1 M H_2SO_4 or 1 M NaOH in the range of pH 3–11 and measured recoveries of NTO spiked at 100 µg/L. Recoveries were 109%, 107%, 106%, 106%, and 107% for pH 2.97, 5.06, 7.34, 9.16, and 11.01, respectively. These results demonstrate that IC analysis within this pH range is robust and indicate that even at pH 3, NTO is not sensitive to protonation during analysis, likely due to the sufficiently basic mobile phase.

Table 1. Natural water sample pH and mean major anion composition (± one standard deviation) from $n = 7$ replicate measurements.

Sample	pH	Concentration (mg/L)					
		F^-	Cl^-	NO_2^-	SO_4^{2-}	NO_3^-	PO_4^{3-}
DI	5.08	<0.004	<0.004	<0.004	<0.004	0.005	<0.008
GW 1	7.82	1.278 ± 0.005	1.025 ± 0.006	<0.004	11.07 ± 0.03	0.098 ± 0.002	0.042 ± 0.001
GW 2	7.51	0.834 ± 0.004	5.30 ± 0.02	<0.004	15.39 ± 0.05	4.38 ± 0.02	<0.008
Municipal	7.28	0.532 ± 0.004	11.01 ± 0.06	<0.004	4.07 ± 0.01	0.137 ± 0.008	1.78 ± 0.02
Pond	7.16	0.025 ± 0.001	17.80 ± 0.07	<0.004	4.54 ± 0.02	0.86 ± 0.01	<0.008
River	7.03	0.044 ± 0.001	5.64 ± 0.02	<0.004	3.22 ± 0.01	0.452 ± 0.004	<0.008

Previous work has indicated that the presence of nitroglycerin and RDX can lead to an overestimate of nitrate and nitrite in water samples due to alkaline hydrolysis of these compounds during IC analysis (Bordeleau et al. 2012). Linear regressions of mean NTO and nitrate concentrations among the four spike levels for each natural water matrix did not yield slopes significantly different from zero (Figure 3), suggesting that the presence of NTO did not affect measured nitrate. Nitrite was not above the detection limit for any of the samples tested.

Figure 3. Linear regressions between mean NTO and NO_3^- concentrations in spiked natural waters. Nitrite concentrations were below the detection limit. Error bars are ± one standard deviation for NTO and NO_3^- concentrations on triplicate measurements.



3.3 Soils and postdetonation residue

DI extraction and analysis by the IC method effectively recovered NTO from five range soils and one clay standard (91%–114%; Table 2). These recoveries are within guidelines for RDX laboratory control sample recovery limits of 67% to 129% (DoD 2019). Soils for energetics analysis are commonly extracted with an organic solvent (i.e., acetonitrile) prior to analysis due to the hydrophobic character of conventional energetic compounds (US EPA 2006). However, NTO extraction recoveries from soils by using just acetonitrile are less than 60% (Temple et al. 2019). The hydrophilic nature of NTO, as well as another IHE compound, nitroguanidine, has prompted the development of alternative soil extractions involving an acidified aqueous (Felt et al. 2016) or partially aqueous stage (Crouch et al. 2020; Temple et al. 2019). The efficient recovery of NTO with a simple DI extraction from all of the spiked soils, which had wide-ranging organic content (<250 to 15,000 mg/kg total organic carbon) and particle size (12% to 100% fines), likely reflects both NTO's high water solubility and the spike delivery as a solution.

Table 2. Soil properties and NTO recoveries of DI-extracted soil samples spiked to 20 mg/kg. Mean values are shown ± one standard deviation on replicate (n = 3) subsamples.

Sample	Fines (%)	Total Organic Carbon (mg/kg)	pH	IC NTO (mg/kg)	Recovery (%)
Yuma Proving Ground	11.8	<250	6.98	20 ± 1	99 ± 5
Memphis, TN	99.5	610	7.56	19.4 ± 0.2	96.9 ± 0.8
Aberdeen Proving Ground	71.7	6700	7.12	19 ± 3	93 ± 12
Fort Riley	96.7	15000	5.96	22.7 ± 0.6	114 ± 3
Jefferson Proving Ground	80.3	1400	4.62	18.1 ± 0.8	91 ± 4
ASTM Fat Clay	99.3	3600	7.45	20 ± 2	101 ± 8

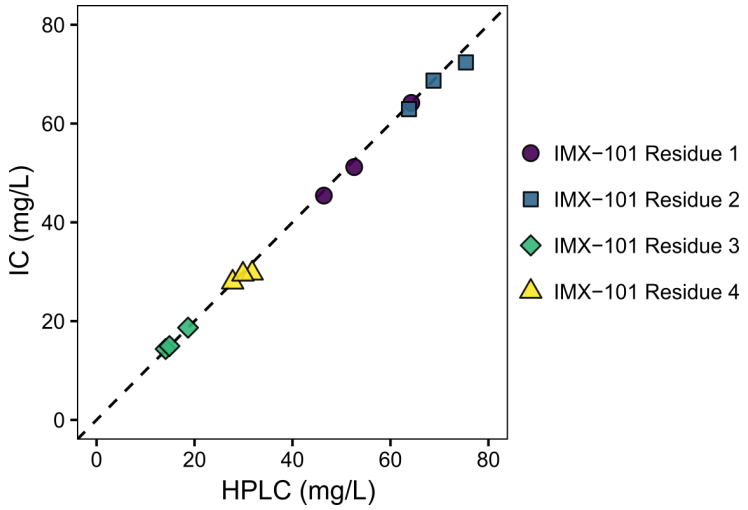
In munition formulations, NTO is present as crystals within a matrix of other compounds (e.g., 2,4-dinitroanisole [DNAN]; Taylor et al. 2015) that may inhibit its dissolution in solid detonation residues without adding organic solvent. Incomplete dissolution from energetic particles may explain the relatively low recoveries from two high-concentration postdetonation IMX-101 residues (Table 3). Residue extract concentrations (14–70 mg/L) were significantly lower than the water solubility of NTO (~1300 mg/L; Spear et al. 1989), indicating the residues were not solubility limited. Instead, access of water to NTO within the relatively water-insoluble matrix of IMX-101, composed of DNAN (water solubility of 276 mg/L [Boddu et

al. 2008]), was likely the primary limitation on total NTO recovery. Further extraction steps, such as sequential DI additions, heat, or ultrasonication, could improve NTO recovery from soil samples known to contain high-concentration particulates. Nevertheless, DI extractions of residues produced identical NTO concentrations by HPLC and by IC (Figure 4), which further supports the robustness of the analytical method.

Table 3. Recoveries of DI-extracted postdetonation IMX-101 residues. Mean values are shown ± one standard deviation on replicate (n = 3–7) subsamples. IMX-101 residues were previously measured by HPLC after total extraction with 1:1 acetonitrile:water (Walsh et al. 2018). Total IMX-101 residues were measured on multi-increment subsamples compared with discrete subsamples by IC.

Sample	Total NTO (mg/kg)	IC NTO (mg/kg)	Recovery (%)
IMX-101 Residue 1	1380 ± 40	950 ± 50	69 ± 4
IMX-101 Residue 2	2160 ± 60	1250 ± 30	58 ± 1
IMX-101 Residue 3	234 ± 7	291 ± 2	124 ± 1
IMX-101 Residue 4	490 ± 20	530 ± 30	109 ± 5

Figure 4. NTO concentrations in DI extracts of IMX-101 residues by IC and Hypercarb HPLC. Extracts were diluted twofold prior to HPLC analysis and a hundredfold prior to IC analysis. The *dashed line* represents a 1:1 slope.



3.4 Potential applications and limitations

The primary advantage of IC for analysis of NTO is its relatively low cost and direct analysis with minimal sample preparation (i.e., filtering). In areas that are already being monitored for inorganic anions, such as nitrate, and that may be affected by IHE compounds, IC methods could be modified to add NTO and potentially serve as an efficient screening tool. Another advantage of IC is its potential application in confirming HPLC-

identified NTO peaks that usually elute early and may coelute with other polar compounds. The detection limit by IC (3 µg/L) likely accommodates potential future screening levels in water (Kennedy et al. 2017), but this limit is still not as low as those achievable for most energetic compounds by solid phase extraction (SPE) and HPLC (US EPA 2006). Application of SPE for IC analysis depends on system-solvent compatibility and the SPE matrix. Similarly, reliance on water extraction may underestimate soil concentrations in areas where large solid explosive particles are present, which using an IC system with organic solvent compatibility may address. Finally, brackish water and saltwater may present a challenge due to high background conductivity. Overall, NTO analysis by IC may be best suited for groundwater, fresh surface waters, and soils that are not directly affected by high concentrations of explosive particles.

4 Conclusions

IC is a sensitive and robust analytical method for detecting and quantifying NTO in natural fresh waters; soils; and, to an extent, postdetonation residue. The method's relative simplicity makes it an attractive option for sample screening, and its codetermination of inorganic anions makes it amenable to incorporation into routine water quality monitoring. Finally, the method's unique separation mechanism makes it particularly applicable to peak confirmation following HPLC. As production of and training with NTO-containing explosives increases, this IC method can serve to assess environmental impacts and to mitigate environmental liabilities and range impacts.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
July 2020	Technical Report/Final	

4. TITLE AND SUBTITLE

Environmental Analysis of Aqueous 3-Nitro-1,2,4-Triazol-5-One (NTO) by Ion Chromatography with Conductivity Detection

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT

6. AUTHOR(S)

Samuel A. Beal, Susan Taylor, Rebecca A. Crouch, and Anthony J. Bednar

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Engineer Research and Development Center (ERDC)
Cold Regions Research and Engineering Laboratory (CRREL)
72 Lyme Road
Hanover, NH 03755-1290

U.S. Army Engineer Research and Development Center (ERDC)
Environmental Laboratory (EL)
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

8. PERFORMING ORGANIZATION REPORT NUMBER

ERDC TR-20-13

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Strategic Environmental Research and Development Program
Environmental Security Technology Certification Program
Environmental Restoration Program Area
4800 Mark Center Drive, Suite 16F16
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)

SERDP and ESTCP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

Funded under Projects ER-2727, ER-2722, ER-2219, ER19-1074, and ER19-5078, Customer Order No. W74RDV83655930 and W74RDV90818426

14. ABSTRACT

The newly fielded insensitive high-explosive compound 3-nitro-1,2,4-triazol-5-one (NTO) is mobile in the environment due to its high water solubility and low affinity for soils. The weak acidity of NTO (pK_a 3.67) presents a challenge to environmental analysis by high-performance liquid chromatography but enables direct separation by ion chromatography (IC). Here we developed an IC method for NTO in natural water, soil, and postdetonation residue. A gradient potassium hydroxide separation effectively resolved the inorganic anions (F^-, Cl^-, NO_2^-, Br^-, SO_4^{2-}, NO_3^-, and PO_4^{3-}) and NTO in 18 minutes. Suppressed conductivity of aqueous NTO was linear from 10 µg/L to 10 mg/L with a detection limit of 3 µg/L and quantitation limit of 9 µg/L. Recoveries of NTO-spiked natural water samples were 93%–118% at concentrations of 30, 100, and 500 µg/L. Recoveries of NTO-spiked soil samples were 91%–114% using deionized water (DI) extraction. NTO was completely recovered with DI-extraction in two postdetonation residue samples of IMX-101 but only partially recovered (58% and 69%) in two higher-concentration residues, potentially due to incomplete dissolution of the energetic particle matrix. These results support IC for confirmation analysis of environmental samples and for screening natural water samples while simultaneously analyzing inorganic ions.

15. SUBJECT TERMS

Chemical agents (Munitions), Energetic compound, Explosives--Environmental aspects, Explosives--Residues, IMX-101, IMX-104, Insensitive munition, Ion exchange chromatography, Propellants--Residues, Range sustainment

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)
Unclassified	Unclassified	Unclassified	SAR	23	