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Analytical method for nitroaromatic explosives in radiologically contaminated soil for ISO/IEC 17025 accreditation

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Abstract

Unique hazards are presented in the analysis of radiologically contaminated samples. Strenuous safety and security precautions must be in place to protect the analyst, laboratory, and instrumentation used to perform analyses. A validated method has been optimized for the analysis of select nitroaromatic explosives and degradative products using gas chromatography / mass spectrometry via sonication extraction of radiologically contaminated soils, for samples requiring ISO/IEC 17025 laboratory conformance. Target analytes included 2-nitrotoluene, 4-nitrotoluene, 2,6-dinitrotoluene, and 2,4,6-trinitrotoluene, as well as the degradative product 4-amino-2,6-dinitrotoluene. Analytes were extracted from soil in methylene chloride by sonication. Administrative and engineering controls, as well as instrument automation and quality control measures, were utilized to minimize potential human exposure to radiation at all times and at all stages of analysis, from receiving through disposition. Though thermal instability increased uncertainties of these selected compounds, a mean lower quantitative limit of 2.37 µg/mL and mean accuracy of 2.3% relative error and 3.1% relative standard deviation were achieved. Quadratic regression was found to be optimal for calibration of all analytes, with compounds of lower hydrophobicity displaying greater parabolic curve. Blind proficiency testing (PT) of spiked soil samples demonstrated a mean relative error of 9.8%. Matrix spiked analyses of PT samples demonstrated that 99% recovery of target analytes was achieved. To the knowledge of the authors, this represents the first safe, accurate, and reproducible quantitative method for nitroaromatic explosives in soil for specific use on radiologically contaminated samples within the constraints of a nuclear analytical lab.

Highlights

- Analytical method for nitroaromatic explosives in radiological soil is proposed
- Developed and optimized for gas chromatography / mass spectrometry
- Method was validated for accreditation by interlaboratory proficiency testing

Keywords

Nitroaromatic explosives; radiological forensics; GC/MS; radiological safety; proficiency testing

Technological Readiness Level: 3

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1. Introduction

The analysis of post-detonation nitroaromatic explosives can present unique challenges, which can be compounded by the trace levels of residue left behind, the area over which the detonation occurred, and the hazardous nature of the detonation or sample matrix.[1, 2] Samples collected from a site post-event may contain byproducts of explosive, thermal, or environmental degradation, as well as other matrix interferences. Researchers have developed ultra-trace analytical methods to help overcome challenges in sensitivity and interferences, including specialized analyte pre-concentration devices [3], extraction media [4], and tandem mass analysis [5]. These common and standard methods aid examiners in exercising control over the potential hazards posed by post-detonation samples while maintaining evidentiary value.

Research and public interest have been dedicated to a speculative class of weapons called radiological dispersal devices (RDDs), sometimes called "dirty bombs."[6] An RDD is a theorized radiological weapon that combines radioactive material with a conventional high-explosive dispersal system. This type of weapon, by definition, does not contain a critical mass of nuclear material and does not detonate via nuclear reaction.[7] Instead, conventional high-explosives would be used to disperse a radioactive material to contaminate a large area with radioactive isotopes, with the intent of causing primarily psychological, not physical, harm.[8] While awareness of the RDD threat has increased in recent decades, no documented RDD detonation event is known to have ever occurred. In the case of such an event occurring, analytical and forensic methods for conventional explosives identification and quantification would be required to be performed within a radiological safety and security framework.[9] Few practical methods exist to decontaminate radioactive materials that would permit examination in a low- or non-radiation environment. The analysis of samples from an RDD event, which may include radioactively contaminated soil, water, or solid material, could be performed at analytical laboratories capable of handling high-activity radiological materials.

Sample extraction or isolation techniques, which include specialized pre-concentration or extraction devices, serve to isolate and concentrate target analytes from a sample matrix with very high efficiency. In radiologically contaminated samples, these devices have been efficiently used to concentrate radioactive material from a matrix. [10] In analytical work on radiologically contaminated samples, however, the extraction device could become highly contaminated,

eliminating possible reuse and significantly increasing high-activity laboratory waste generated. Chromatographic and mass analysis present further challenges of containment: ensuring that a contaminated sample remains within a sealed system or inside of a radiological hood throughout the analysis. Waste handling, including roughing and turbo pump exhausts, must be controlled and contained in a manner that conforms to existing environmental and safety regulations and policies.

Savannah River National Laboratory (SRNL), as part of the Department of Energy (DOE) complex, provides expertise in environmental management, waste cleanup, and nuclear materials management, while housing the only radiological crime investigation laboratory.[11, 12] This work describes the development and validation of an analytical method to quantify nitroaromatic high-explosive compounds in soil samples, while demonstrating the implementation of necessary controls to ensure compliance with required safety, environmental, and nonproliferation policies. This work is not intended as a review of all required safety and security practices; rather, it is intended to provide practical context for development, optimization, and implementation of an analytical method within the unique framework and constraints of a radioanalytical laboratory. SRNL routinely processes and examines high-activity nuclear waste; though, being development in design, this work was not performed on artificially radiologically contaminated soil samples, as this would expose analysts to additional and unnecessary radiation, a violation of the "as low as reasonably achievable" (ALARA) principle.

Methods for qualitative and quantitative analysis of nitroaromatic high-explosives have been vital to forensic investigations.[13] This work sought to demonstrate the viability of a validated method to produce quantitative results while conforming to the unique challenges presented by a potential RDD event, while adhering to ISO/IEC 17025 laboratory analysis guidelines. This research included the target compounds 2-nitrotoluene (2-NT), 4-nitrotoluene (4-NT), 2,6-dinitrotoluene (2,6-DNT), and 2,4,6-trinitrotoluene (2,4,6-TNT), as well as the degradative product 4-amino-2,6-dinitrotoluene (4-amino-2,6-DNT). While methods currently exist for the analysis of nitroaromatic explosive compounds by GC/MS, the validation of this method required extensive engineering and analytical development unique to the analysis of radiological samples: such as the radiological enclosure of a water-bath sonication system, reduction in radiologically contaminated liquid waste generated, gaining control over GC/MS

pump and vent out-gas, and various other safety and security method optimizations.The work presented here represents a portion of the packet submitted for ISO/IEC 17025 accreditation.[14]

2. Materials and Methods

2.1. Controls, Safety, and Security

SRNL and DOE have implemented operating guidelines to describe the means by which one may be granted access to secure, limited, and posted radiation areas. Administrative guidelines, protocols, briefings, and training packages have been applied prior to this research to control introduction of hazardous materials into radiological processing areas, use of radiological monitoring equipment, handling and disposition of high- and low-activity waste, nuclear criticality awareness and safety, and many other aspects of the handling, processing, analysis, storage, and release of nuclear materials within SRNL.

The work performed as part of this research was conducted inside of laboratories expected to contain radiological contamination, called contamination areas (CA). The CA used for sample preparation was operated under a radiological work permit (RWP) with dose rate limits of 0.05 mSv/hr (at 30 cm) and transferable contamination levels of 3.33 Bq/100 cm^2 α and 166 Bq/100 cm^2 $\beta\gamma$. Additional limits of 5 mSv/hr skin dose rate, 0.05 mSv/hr of whole body dose, and 20 mSv/hr extremities were implemented as working dose rate limits. No measurable airborne contamination was permitted by the RWP. The CA radiological hood was within a laboratory designated as a radiological buffer area (RBA), in which dose limits were established as 0.05 mSv/hr (at 30 cm) and transferable contamination levels of 0.02 Bq/100 cm^2 α and 0.20 Bq/100 cm^2 $\beta\gamma$. Additional RBA limits of 5 mSv/hr skin dose rate, 0.05 mSv/hr of whole body dose, and 20 mSv/hr extremities were implemented as working dose rate limits. The CA radiological hood used for sample preparation was surveyed for whole body and skin dose rates as well as transferable contamination levels and airflow rates. In the survey, the CA hood used for this work demonstrated acceptable whole body and skin dose rates, as well as airflow velocity and volume.

A Hazards and Safety Package was prepared to identify the hazards associated with this analysis and the controls implemented to reduce risk. Explosive materials were maintained at concentrations <25% of explosivity concentration, where the primary hazard remained

attributable to solvent flammability. Syringe spatter, which may include radioactive material, was avoided by use of a syringe with 2X the capacity of the total volume of liquid to be withdrawn. Chemical and radiological solutions were disposed of following SRNL and DOE procedure and policy.

2.2. Reagents

Two sets of stock solutions were prepared for comparison purposes. A custom mix of all target compounds was obtained at 1000 µg/mL in acetonitrile/methanol (NSI Lab Solutions, Raleigh, NC). A second mixture containing 4-amino-2,6-DNT (99% purity), 2,4,6-TNT (99%), 2,6-DNT (99%,) at 1000 µg/mL in acetonitrile; and 2-NT (99%) and 4-NT (97%) at 5000 µg/mL in acetonitrile was obtained (Restek, Bellefonte, PA). Naphthalene-d8 at 2000 µg/mL in methylene chloride (Restek) was purchased for use as SV internal standard. A quality control (QC) sample (NSI Lab Solutions) contained known concentrations of nitroaromatic compounds in soil, including all target HE compounds. Methylene chloride was used for liquid extractions (Fisher Scientific, Hampton, NH). All target analyte reagents were provided with ISO-accredited certificates of analysis indicating concentration and purity.

2.3. Sample preparation and Instrumentation

Calibration samples, initial calibration verifications (ICV), initial calibration blanks (ICB), continuing calibration verifications (CCV), and continuing calibration blanks (CCB), were prepared according to spike and matrix found in table 1. Quality control (QC) and proficiency test (PT) samples were obtained as ~10g of soil spiked with known (QC) or unknown (PT) amounts of the select HE compounds from NSI Lab Solutions (Raleigh, NC) and were certified following procedures meeting the guidelines for ISO 9001, ISO 17025, and ISO 34. The laboratory control spike (LCS) was prepared identically to the CCV samples, but underwent sonication extraction and evaporative concentration similar to the QC and PT samples. The matrix spike and matrix spike duplicate (MS/MSD) samples were prepared using PT soil (containing an unknown spike of target analytes) spiked with an additional known concentration of target analytes. The MS/MSD underwent identical sample preparation as the QC and PT.

Table 1: Sequence and sample preparation table for calibration, QC, and PT analysis

ID	Matrix	Spike
ICV	1mL CH2Cl2	Restek 50uL Mix A & 10uL Mix B
ICB	1mL CH2Cl2	N/A
Cal 5	1mL CH2Cl2	5uL of 1000 ug/mL NSI Cal Std
Cal 20	1mL CH2Cl2	20uL of 1000 ug/mL NSI Cal Std
Cal 50	1mL CH2Cl2	50uL of 1000 ug/mL NSI Cal Std
Cal 70	1mL CH2Cl2	70uL of 1000 ug/mL NSI Cal Std
Cal 100	1mL CH2Cl2	100uL of 1000 ug/mL NSI Cal Std
ICB	1mL CH2Cl2	N/A
LCS	1 mL Prepared LCS Extract	Restek 50uL Mix A & 10uL Mix B
ICB	1mL CH2Cl2	N/A
QC	1 mL Prepared QC Extract	N/A
CCB	1mL CH2Cl2	N/A
PT	1 mL Prepared PT Extract	N/A
CCB	1mL CH2Cl2	N/A
MS	1 mL Prepared PT Extract	50uL of 1000 ug/mL NSI Cal Std
MSD	1 mL Prepared PT Extract	50uL of 1000 ug/mL NSI Cal Std
CCV	5mL DID-H_2O	Restek 50uL Mix A & 10uL Mix B
CCB	5mL DID-H_2O	N/A

Sonication was performed on QC, PT, LCS, and MS/MSD samples with 10 mL of methylene chloride in a Branson (Danbury, CT) M1800 bath ultra-sonicator for 20 minutes at 40 kHz inside of a radiological hood. The LCS and MS/MSD samples were spiked with 50 µg/mL of target analytes prior to sonication. Following sonication, the organic layer was removed and transferred to a glass vial. The extract was concentrated by evaporation to 5 mL using low-pressure argon. The MS/MSD, LCS, QC, and PT extracts were transferred by 1 mL aliquot replicates to separate GC vials for analysis with 20 µL of internal standard. Without undergoing sonication, the prepared ICB, ICV, CCB, and CCV samples were transferred in 1 mL aliquot replicates to GC vials for analysis with 20 µL of internal standard. When transferring samples into or out of the radiological hood, they were probed for external contamination. In an instance in which initial analysis indicates that a selected analyte is present above the highest point of the calibration curve, or if the QC or PT paperwork indicates, then the analyst prepared one additional vial containing the transferred 1 mL aliquot from the PT or QC, 20 µL of internal standard, and 1 mL (or more) of methylene chloride to decrease the effective concentration. This dilution was accounted for mathematically by the data analysis software.

An Agilent Technologies, Inc. (Santa Clara, CA) 7890B gas chromatograph and 5977A quadrupole mass spectrometer (GC/MS), configured with a 150-sample robotic autosampler, was housed inside of a radioactive material area (RMA) hood for the closed-system analysis of

radiological samples. From sample introduction to pump exhaust and sample disposition, the entire flow-path of potentially radioactive material remained within the RMA. The GC/MS was marked to have internal radioactive contamination, but external contamination that did not exceed RMA limits. From all sample types, 5 µL of each GC vial were injected in sequence. The GC inlet was set to 220 °C in splitless mode at 13.1 PSI with 63.8 mL/minute total helium flow using an Agilent DB-5MS capillary column (25m X 0.20mm X 0.33 µm). The GC oven was set to 40 °C for 1 minute, then ramped to 330 °C at 30 °C/minute and held for 2 minutes, with a flow rate of 0.8 mL/minute. Single quadrupole mass spectrometry was performed in scan mode from 33 *m/z* to 450 *m/z* at source and quadrupole temperatures of 230 °C and 150 °C, respectively, with a scan speed of 1562 amu/s. Instrument operation was performed with Agilent MSD Chemstation D.02.00.275. Data analysis, calibration, and quantification were performed on Agilent MSD Chemstation F.01.01.2317 using the quantitative and secondary ions found in table 2. Target analytes were identified using relative retention time (RRT) and mass spectra.

Table 2: Quantitative and confirmatory ions for the target analytes and internal standard

Target Analyte	Quantitative ion (*m/z*)	Secondary ion (*m/z*)
2-NT	120	92, 91, 65
4-NT	137	91, 65
2,6-DNT	165	89, 63
2,4,6-TNT	210	89, 63
4-amino-2,6-DNT	180	104
Naphthalene-d8*	136	68

* Internal Standard

The analytical method protocol, system settings, sample preparation, data acquisition, report generation, and quality assurance were controlled internally to SRNL to attain compliance with ISO/IEC 17025. The analysts completed all SRNL and DOE required training packages for performance of advanced radiological work in accordance with Nuclear Forensic Analysis Center / International Organization for Standardization (NFAC/ISO) protocols and regulations.

2.4. Quality Control

All quality control checks and calibration standards were traceable to ISO Guide 34 requirements and were within expiration dates.[15] All pipettes, balances, and weights were within certification and calibration. Ampules of standard reagents were stored between 2 – 8 °C

and a new ampule was used for each analytical batch and discarded following each batch preparation. Calibration levels were prepared according to table 3, using one of two standard suppliers. Batch ICV/CCV samples were prepared using the standard supplier that was not used for calibration.

Table 3: Standard sample preparation protocol for calibration sample batch

				Standard 1	Standard 2	
Vial	CH2Cl2 (µL)	Final Conc. (mg/L)	Internal Standard (µL)	NSI (µL)	Mix A (µL)	Mix B (µL)
1	800	0	20	0.0	0.0	0
2	800	1	20	1.0	1.0	0.2
3	800	5	20	5.0	5.0	1.0
4	80.0	10	2.0	1.0	1.0	0.2
5	80.0	20	2.0	2.0	2.0	0.4
6	80.0	50	2.0	5.0	5.0	1.0
7	80.0	100	2.0	10	10	2.0
8	80.0	150	2.0	15	15	3.0
9	80.0	200	2.0	20	20	4.0

Control charts were generated with each calibration or experimental sample batch. Control charts were prepared using ICV/CCV values attained from each batch analysis. Experimentally observed CCV and ICV concentrations were plotted over time and used to compute concentration mean, warning limits (set to 2 standard deviations from mean [2σ]), and action limits (set to 3 standard deviations from mean [3σ]). Several factors triggered an action: an observable positive or negative trend over multiple points, a point falling outside of ±30% of control chart concentration mean, or a replicate falling outside of ±3σ of control chart mean. Multiple replicates between 2σ and 3σ will also trigger an action and performance evaluation.

Proficiency testing was conducted through NSI Lab Solutions. Blind soil samples, pre-spiked with the target HE compounds, were obtained from NSI and analyzed using the method described herein. Final data was sent back to NSI and final analytical results were reported back to the participating laboratories within one month. ISO/IEC 17025 accreditation was attained through American Association for Laboratory Accreditation. Some results presented herein were submitted for blind proficiency testing as part of a study designed and coordinated by NSI Lab Solutions as part of Study SM-111 conducted between October 2016 and December 2016.

3. Theory and Calculations

Analyte and peak identification, integration, calibration, and quantification were performed in Agilent Masshunter. Method detection limit (MDL) and method reporting limit (MRL) calculations were performed using the following equations:

$$\textit{Equation 1: } MDL = \sigma_n \times t_{99,n-1}$$

$$\textit{Equation 2: } MRL = MDL \times 3.33$$

σ_n = standard deviation

Precision was compared using 2σ, 3σ, or percent relative standard deviation (%RSD). The statistical hypothesis testing threshold for comparison of experimental (or observed) results and "true" or absolute values was $p = 0.05$. For comparison of accuracy, this work used error, relative error, or %error as a measure of the error present in a given experimentally observed value, compared to its known or calculated value. All confidence intervals (denoted by use of "±") are given as 95% confidence using a two-tailed cumulative probability. Three types of calibration were used in this work: relative response factor (RRF), linear, and second order polynomial (quadratic). A coefficient of determination (R^2) calculation was used to compare the performance among and between each calibration type. The RRF calculation is demonstrated in equation 3, where A_s is the peak area of the target compound, A_{is} is the peak area of internal standard, C_s is the concentration of the target analyte, and C_{is} is concentration of internal standard..

$$\textit{Equation 3: } RRF = A_s \times A_{is} \times C_s$$

4. Results and Discussion

4.1. Calibration of Target Analytes

A five-point calibration curve was generated for each target analyte at concentration levels of 5, 20, 50, 70, and 100 µg/mL. Mean experimentally calculated concentration at the lowest calibration point, pooled across all analytes, was 4.99 ±0.39 µg/mL. Mean error across all analytes at all calibration points was 6.4% with 14% RSD. The calibration curves for all five

target analytes, with best fit equations and coefficients of determination (R^2) can be found in figure 1.

Three calibration regressions were compared using R^2. Across all analytes, RRF produced a mean R^2 of 0.945 with 23% mean RSD, linear regression produced a mean R^2 of 0.988, and quadratic regression produced a mean R^2 of 0.998. Only quadratic regression produced calibration exceeding the SRNL required R^2>0.99 threshold, and produced a significantly higher mean R^2 compared with linear regression (p=0.0257) and RRF (p=0.0279) and was used for all calibration curve fitting. Best-fit analysis of the linear regression model was not distinguishable from RRF (p=0.0654). Comparisons between and among the best-fit schemes can be found in table 5.

Table 5: Comparison of coefficients of determination of three curve fit schemes used in this work

	2-NT	**4-NT**	**2,6-DNT**	**2,5,6-TNT**	**4-amino-2,6-DNT**
RRF					
%RSD	14.3	13.2	15.4	33.2	40.9
R^2	0.924	0.988	0.986	0.944	0.884
Linear					
R^2	0.978	0.985	0.981	0.997	0.999
Quadratic					
R^2	0.996	0.998	0.997	0.999	0.999

Experiments were conducted to investigate the non-linear instrument response of target analytes with increasing concentration. Mass spectrometry source saturation at the high calibration levels was investigated by generating five-point calibration curves with ranges of 5 – 50 µg/mL, 5 – 100 µg/mL, and 5 – 250 µg/mL curves. No significant change in quadratic fit or curvature was observed. Analyte degradation over time was investigated by randomizing the order in which sample vials were analyzed, relative to the order in which the vials were prepared. No significant change in quadratic fit or curvature was observed.

Correlations between parabolic regression curvature and chemical properties of each target analyte were explored. Arc length of each quadratic regression fit was calculated for each analyte between the low and high calibration points. The upper and lower calibration points were identical across all analytes; therefore, best-fit line with the longest arc length between the identical points must have the greatest curvature. No significant correlations were discovered

between arc length and hydrophobicity (measured as $K_{o/w}$), boiling point, molecular weight, number of nitro-substitutions, or flash point. A Pearson correlation showed moderate negative relationship between arc length and boiling point (r= -0.546), indicating a tendency for compounds to respond increasingly linearly over concentration with increasing boiling point. Further exploration of the quadratic regressive nature of these select HE compounds is required for sufficient explanation of the observed phenomenon.

4.2. Method Performance and Validation

Results for MDL and MRL analyses can be found in table 4. The mean MRL found using replicate (n = 10) analyses at the lowest calibration level of aqueous samples spiked with 5 µg/mL HE standards was reported as 2.37 µg/mL, exceeding the 2.55 µg/mL MRL required for ISO 17025 auditing. Therefore, the MRL was set as the lowest calibration level: 5 µg/mL. Precision was evaluated at the lowest calibration point in 10 aqueous replicates. Table 4 shows that, at the MRL, mean accuracy presented -16.8% bias and mean precision was 5.33% RSD, relative to mean concentration.

Table 4: Quantitative results, in µg/g, for replicate HE analyses at the lowest value of the calibration curve

	2-NT Results		4-NT Results		2,6-DNT Results		2,4,6-TNT Results		4-amino,2,6-DNT Results	
	Final Conc.	**%Accuracy**	**Final Conc.**	**%Accuracy**	**Final Conc.**	**%Accuracy**	**Final Conc.**	**%Accuracy**	**Final Conc.**	**%Accuracy**
5 mg/L - 1	3.76	75.1	3.67	73.4	3.83	76.7	4.67	93.5	3.52	70.3
5 mg/L - 2	3.97	79.4	4.16	83.2	4.04	80.9	4.88	97.7	3.43	68.6
5 mg/L - 3	3.94	78.7	4.17	83.3	4.11	82.2	5.02	100.3	3.77	75.3
5 mg/L - 4	3.93	78.6	4.14	82.7	4.2	84	4.92	98.4	3.41	68.3
5 mg/L - 5	3.98	79.7	4.4	88	4.44	88.8	5.36	107.1	3.86	77.3
5 mg/L - 6	3.84	76.8	4.06	81.1	4.08	81.5	4.8	96.1	3.39	67.8
5 mg/L - 7	4.06	81.1	4.21	84.2	4.11	82.3	4.65	92.9	3.47	69.4
5 mg/L - 8	3.96	79.2	4.76	95.3	4.27	85.4	4.67	93.3	3.23	64.5
5 mg/L - 9	3.92	78.4	4.83	96.7	4.21	84.2	5.05	100.9	4.2	84.1
5 mg/L - 10	3.83	76.7	4.07	81.5	4.03	80.7	4.86	97.2	3.65	73
Mean	3.92		4.25		4.13		4.89		3.59	
%Error	21.6		15.1		17.3		2.27		28.1	
%RSD	2.23		8.1		3.91		4.44		7.97	
MDL	0.284		1.12		0.525		0.705		0.93	
MRL	0.945		3.72		1.75		2.35		3.1	

Two independently prepared sets of CCV samples, from different manufacturers, were quantified at 50 µg/mL for all five HE compounds (n=8). At 50 µg/mL, mean accuracy was determined across both standard mixes and all analytes with 2.3% positive bias, and a mean

precision of 3.1% RSD. No significant difference in mean accuracy was discovered between the two sample sets (2.4% positive bias and 1.8% positive bias, p=0.488). CCV supplier 1 produced significantly better mean precision compared with CCV supplier 2 (p=0.0272), 2.09% and 4.10% RSD, respectively. All analytes within both CCV sets were quantified within the ±30%. QC acceptance criteria window established by SRNL to meet ISO 17025 testing criteria.

4.3. Quality Control

Control charts were generated and maintained for each analyte. The control chart used for 2-nitrotoluene in this work can be found in figure 3, showing CCV and ICV samples, warning and action limits, and one point that fall outside of the warning limit. The subsequent CCV/ICV analysis to the circled point fell within the warning limit and no trend was observable, therefore no action was initiated by the circled point in figure 3. No target control charts initiated QA/QC corrective actions during this development and validation work.

4.4. Soil Extraction Optimization

The PT samples were received as a mixture of HE compounds in ~10 g of soil. Sonication extraction was optimized by testing at two time intervals, 10 minutes and 20 minutes. These sonication results can be found in figure 4. For 4-NT and 2,4,6-TNT, a 2:1 dilution was performed with methylene chloride prior to GC/MS analysis to decrease the concentrations to be within the calibration window. As this dilution was performed after sonication but prior to GC/MS injection, extraction recovery was not affected once the dilution was mathematically accounted for. This dilution factor was calculated automatically by the Chemstation data analysis software.

The 20 minute sonication extraction produced concentrations indistinguishable from the certified values (p=0.995), distributed between positive and negative bias. The 10 minute extraction produced recoveries with negative bias distinguishable from the certified values (p=0.050). The concentrations produced by both extraction times were not statistically distinguishable (p=0.169) from one another. Given the agreement between the 20-minute sonication recovery and the certified value of the QC, additional sonication time was deemed

unnecessary. Mean total method runtime, including sample preparation, extraction, and batch QA/QC analyses, was 6.25 hours.

4.5. Performance Testing for HE

Single-replicate PT samples yielded a mean accuracy across all five HE compounds in soil with 9.8% error relative to the study assigned value. All target analytes met the PT acceptance criteria of the proficiency-testing program. Laboratory control spikes demonstrated a mean recovery of 94 ±4.8% and matrix spikes showed a mean recovery of 99.7 ±2.1%. For 2-NT, 4-NT, 2,6-DNT, 2,4,6-TNT, and 4-amino-2,6-DNT, z-scores of 1.03, 1.78, 1.16, 0.0639, and 1.69, respectively, were achieved. Acceptable PT evaluation is established for analytes with Z-scores < 3. All batch blank analyses (ICB and CCBs) contained no detectable quantities of the target analytes. Mean accuracy of ICV/CCV samples demonstrated -6% error compared with calculated concentrations. These PT results were submitted as part of a package to attain ISO 17025 accreditation.

5. Conclusions

A method has been optimized and validated for the quantification of select organic high-explosives to be used in radiologically contaminated soils by gas chromatography / mass spectrometry via sonication extraction, for analyses requiring ISO 17025 accreditation. Development and optimization was performed to produce an externally validated method that exceeds ISO 17025 analytical reporting requirements, while adhering to the extensive safety and security practices required by the U.S. Department of Energy. This research detailed the administrative, engineering, and quality assurance controls in place to attain safe, secure, and accurate handling and analysis of radiologically contaminated samples.

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7. Figure Captions

Figure 1: Five-point calibration of target analytes with best-fit regression curves showing best fit equation and coefficient of determination

Figure 2: Concentration values obtained from analysis of two calibration verification samples from different suppliers, showing 95% confidence intervals for each point. Grey area represents the ±30% calibration verification acceptance criteria
*Confidence intervals may be hidden by data point marker

Figure 3: Example control chart generated using CCV and ICV concentration values with each batch of samples. Calculated control chart mean, 2 standard deviations ("warning" limit) and 3 standard deviations ("action" limit) are shown. Circled point represents ICV/CCV response that generated a warning, but no action.

Figure 4: Optimization of sonication time for concurrence with certified value of analyte spike. Grey bars represent QC acceptance interval. Dashed line represents the top calibration level.