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Cold Regions Research
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Measuring Energetics Residues on Snow

Michael R. Walsh, Marianne E. Walsh, and Charles A. Ramsey

October 2007

Cover: Recording a firing point decision unit, Donnelly Training Area (Ft. Greely), Alaska, January 26, 2005. (Image by Marianne Walsh.)

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Abstract: Quantifying energetics residues resulting from firing and detonating military munitions are necessary components in developing range sustainability models and plans. Determination of the residue plume area, discrimination from previous activities, separation of the residues from the collection matrix, and processing of the samples are all difficult tasks when dealing with residues on soils. To circumvent these problems, the U.S. Army Cold Regions Research and Engineering Laboratory has been sampling for energetics residues on snow. At firing points, a clean snow surface allows the collection of residues from a known quantity and type of munition and testing can be performed in conjunction with a scheduled training exercise. Detonation residues from live-fire training can be sampled on a snow-covered surface in an active impact area when the area fired into has not been utilized since the last snowfall. Tests with blown-in-place munitions may be conducted on clean snow-covered surfaces on active impact areas as well. This report outlines the methods developed by CRREL over the last seven years for sampling residues on snow and deriving estimates for energetics residues on a per-round basis. Sampling, quality control, and sample processing methods are covered.

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Preface

This report was prepared by Michael R. Walsh, Engineering Resources Branch (ERB), Cold Regions Research and Engineering Laboratory (CRREL), U.S. Army Engineer Research and Development Center (ERDC), Hanover, NH; Marianne E. Walsh, Environmental Sciences Branch, CRREL, ERDC; and Charles A. Ramsey, Envirostat, Fort Collins, CO.

The methods described in this report were developed over many years, leveraging funding from many sources. Primary among these were the U.S. Army Garrison Alaska (USAGAK) Soil and Water Quality Program (Charles M. Collins, CRREL); the U.S. Department of Defense Strategic Environmental Research and Development Program (ER-155: Dr. Judith Pennington, Environmental Laboratory, ERDC, and ER-1481: Dr. Thomas Jenkins, CRREL); the USAGAK Eagle River Flats remediation project (William Gossweiler, USAGAK); and the U.S Army Environmental Center (Dr. Bonnie Packer, AEC).

The report was prepared under the general supervision of Thomas Tantillo, Chief, ERB; Dr. Lance Hansen, Deputy Director; and Dr. Robert E. Davis, Director, CRREL.

The Commander and Executive Director of ERDC is COL Richard B. Jenkins. The Director is Dr. James R. Houston.

1 Introduction

Utilization and sustainment of training ranges are important issues for both range managers and those responsible for the training of our military. Without access to training areas, soldier skill and competency levels will fall, resulting in degraded battlefield performance and increased casualties. Stewardship of these public lands and protection of the natural resources on them will be degraded and access for military training may ultimately be limited or curtailed.

The U.S. Army has been taking a proactive role in characterizing ranges and the effects of training on them. The Corps of Engineers' Cold Regions Research and Engineering Laboratory (CRREL) has been on the forefront of these investigations, examining impact areas, open burning/open detonation areas, propellant burn points, and firing points at military bases throughout the United States and Canada as well as consulting with several NATO countries on range design. The establishment of areas of concern, not only in impact areas but also at firing and burn points, has indicated the need for more detailed data on the quantities of residue deposited, the fate of these residues, and whether or not these residues are transported from their area of deposition into the wider environment.

This report describes methodologies developed by CRREL in addressing the first factor: quantifying energetics residues. Using snow as a sampling matrix, we are able to determine residue quantities on a per-round basis and easily process the samples for analysis. Collection methods and tools, sampling design, quality control methods, and sample processing techniques are all described. References for further information are cited at the end of this report.

2 Test Area Descriptions

To obtain reliable estimates of energetics on snow, a good test site is required. The best test sites are those that most closely resemble actual training areas. For our tests, we utilize firing points, burn points, and impact areas at active military bases and facilities. A general description of these areas and the ideal test conditions for each are described below.

Impact Areas

Impact areas are generally defined as multi-zone areas containing targets into which ordnance is fired. Although these areas are generally large, a significant portion may be excluded because of the safety and buffer zones associated with the types of fire, weapon systems, and ordnance. The result is that fire is focused on limited segments within the impact area, resulting in a concentration of explosive residues. Determining residue quantities on a per-round basis is impossible on a well-used range because of deposition in and on the soils from previous activities.

To circumvent this problem, CRREL has tested on impact ranges in Alaska in winter. The ideal winter impact test area will be underlain with ice above frozen ground to separate past range activities from the current testing. The ice will be thick enough to prevent penetration of the blast crater to the ground, from 15 to 60 cm depending on the munition and the condition of the substrate beneath the ice. There will be enough snow on the surface of the ice to allow sampling but not so much as to make access difficult (10–30 cm). There will be little or no vegetation above the surface of the snow. The range will be easily accessible by road and a short to moderate distance (<10 km) from a facility where logistical activities can be coordinated and samples can be stored and processed. If possible, it will be possible to drive onto the range with a vehicle or snowmobile to access the impact points and retrieve the samples. The temperature at the time of testing will be in the –2° to –10°C range with overcast skies and calm (<2 m/s) winds. No precipitation will occur during the test. There should have been no prior activity in the test area following the last snowfall. These criteria are possible and have been met for most of our tests in Alaska over the course of six years and ten tests. The two ranges where we have conducted tests are the Eagle River Flats impact area located on Fort Richardson and the Donnelly Training Area (Washington

Range) on the former Fort Greely (Fig. 1, 2). Both areas are well configured for winter testing. We have never had a weather-related delay, although they are quite possible and there have been some very close calls.

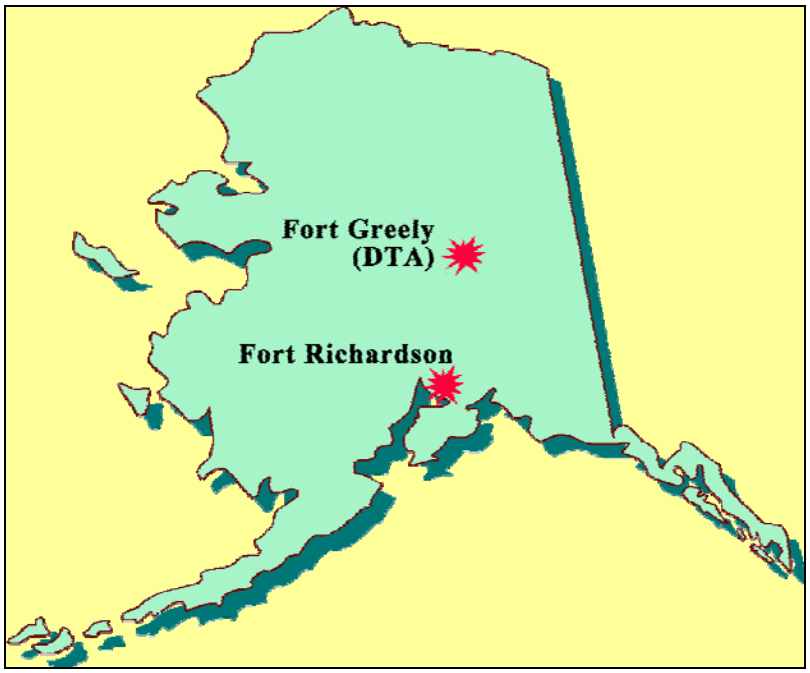


Figure 1. Test locations in Alaska.

a. Eagle River Flats impact range, Fort Richardson, Alaska.

Figure 2. Impact ranges in Alaska where winter testing has occurred.

b. Washington Range, Donnelly Training Area, Fort Greely, Alaska.

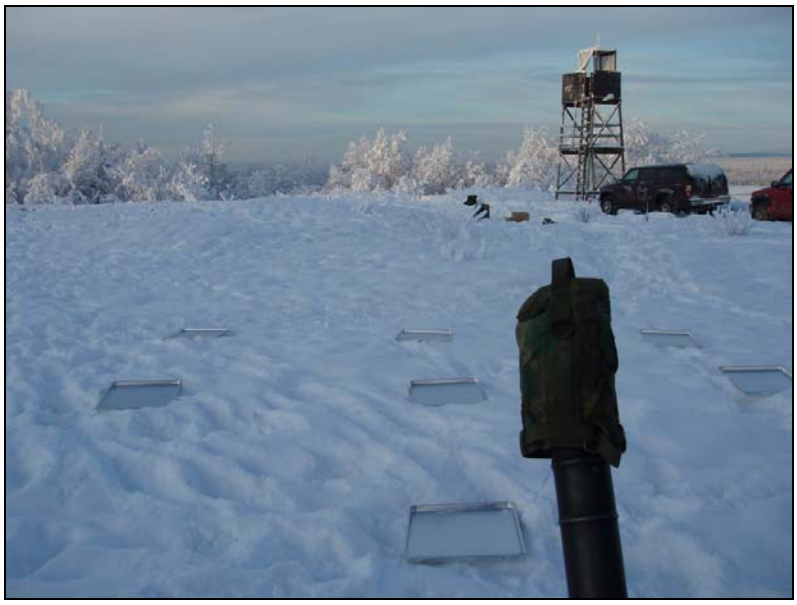
Figure 2 (cont.). Impact ranges in Alaska where winter testing has occurred.

Firing Points

Firing points are located peripheral to the impact area. They can be directly adjacent to the impact area (small-caliber mortars and direct fire) or many kilometers away (indirect fire). Access is normally by well-established and maintained roads. They tend to be smaller, more intensely used areas with quasi-established firing positions (Fig. 3). During training exercises, there is a lot of activity associated with firing points in support of the gunners.

The criteria for the ideal firing point are essentially the same as for impact areas. The firing point does not need to be underlain with ice, however. Additional criteria for firing points include sufficient down-range area free of dense vegetation to allow wide-area sampling (≈100 m), enough room for separation between firing points to prevent cross-influence, and the ability to restrict activity near and down-range of the positions tested. These additional criteria are difficult to meet when testing during a training mission, but we have succeeded by carefully outlining our reasons for testing and our test goals to the officer-in-charge (OIC) prior to the mission.

a. Firing Point Bondsteel, Donnelly Training Area.



b. Firing Point Upper Cole Point, Fort Richardson.

Figure 3. Indirect and direct-fire firing points.

Burn Points

Burn points are located near or at firing points. There are two types of burn points, which could be described as propellant disposal areas and open burn points. Propellant disposal areas have a burn pan in which excess propellants are disposed. There seems to be no standard design for these devices, and they may not be in the best of repair. Open burn points tend to be areas where excess propellants are simply collected and ignited directly on the surface of the ground or snow. We have sampled both types

of burn points, but the second, the open burn point, allowed us to sample residues from a known type and quantity of propellant.

As with firing points, the open burn point must be separated from other activities in adjacent areas associated with energetic materials. Sufficient snow must be present to prevent residue penetration to ground. We have managed this by burning a fixed quantity of propellant at each location. This has also allowed us to completely sample the burn location and replicate the burn.

a. Setting up propellant burn at burn pan, OP7, DTA.

b. Burning propellants on the ground, FP Upper Cole, Fort Richardson.

Figure 4. Burn points and different burn configurations.

OB/OD Areas

OB/OD areas differ from burn points in that they are designated for the disposal of munitions rather than propellants, although propellants may also be disposed of there. OB/OD areas have evolved over the years as a result of environmental regulations. The ones we have experience with consist of an open area with gravelly soils that contains several disposal pits ranging in diameter from a couple of meters to over 10 m and up to 2 m in depth. OB/OD activities are difficult to model for physical tests as they tend to involve several types of munitions and disposal mechanisms, making delineation of contributing munitions difficult.

To test for residues resulting in the type of activities that occur in OB/OD areas, we have detonated single munitions in groups of up to seven in impact areas. This is similar to the blow-in-place (BIP) operations that also occur during clean-up of active ranges. The results of these tests have been reported as BIP studies. The test location criteria are the same as for impact areas. Vehicular access to the interior of the impact range is critical in this case to allow the efficient setup of the tests. Most BIP tests occur with the projectile horizontally oriented, which results in more of the blast and fragmentation directed into the ice as the munitions are generally designed to distribute the most energy radially. For larger munitions, thicker ice is needed, up to a meter in thickness. Where this is not possible, we have cut ice blocks from a nearby lake and set the projectiles on these prior to testing. There is more control on the distribution of the munitions during testing, and we have generally separated the rounds by 50 m, oriented in a single line perpendicular to the prevailing wind direction and the access road over the ice.

3 Preparations Prior to Testing

Test preparations help ensure efficient operations and reliable measurements. There are many factors and contributors to a successful test, not all of which are controllable. Every test situation will be different, so only a few general recommendations are given here.

Coordination is essential to testing on any part of an active range. It's also very helpful to partner with an active military officer who can act as a liaison to communicate with the military contingent conducting the firing exercise. A civilian point of contact on base to help with logistics and receive equipment and supply shipments, as well as having a good plan and a good team, will help ensure the success of a test.

Range Control is a good source of information when planning tests. They will have scheduled all range activities, including those that will fulfill the test requirements. If access to those ranges is obtained, the military liaison should try to get permission to participate in a scheduled exercise from the unit commander and the officer in charge (OIC). An information packet is a handy tool at this point for informing both the liaison and his contacts in the unit. Once an agreement is reached, it is important to keep in contact with Range Control and the OIC in case there is a change of schedule. We have not had good luck in being included in the loop when schedule changes have occurred. It is wise to be in place at least two days ahead of schedule to cover any last-minute changes. This has happened to us twice, and advanced preparation saved the project. Any excess time between arrival and the exercise can be used to prepare for sampling and sample processing.

Time is money on any field trip. There is a tendency to try to schedule too much in the allotted time. This is risky because so many factors are not controllable. Even when an exercise is being set up specifically for your tests, it is always wise to include make-up days in the schedule. Do not pack in too many activities in one day. In winter, days are short, and in Alaska, days are really short. With the cold, progress is slow. Try to schedule only one major test per day. This should allow time to fire or detonate the munitions and sample on the same day. Twice we have not been able to do this due to extraneous circumstances, but the weather

cooperated with us and we were able to complete the sampling the next morning. It could easily have gone the other way. If the test is tied to a training exercise, things will not go smoothly as the troops are being trained under duress. Although you will be working with a plan and a schedule, try to anticipate delays and be flexible. Always set priorities. This will help keep things in perspective.

Access to lab space is important when sampling on snow. The raw samples can be very bulky, and there is a good chance they will melt if shipped. It is best to process the samples first. Necessary supplies and equipment needed for sample processing are listed in a later section. If equipment and supplies are being shipped to the test destination, have them arrive prior to your departure for the test site. If anything is missing, replacement items can be shipped. Ship samples to the analytical lab by Wednesday if using overnight delivery and by Tuesday if using two-day delivery to ensure they get there before the weekend and are stored appropriately. Overnight and second-day delivery are no longer as reliable as they once were.

Summarizing test preparations, we do the following:

1. Define and prioritize the test objectives.

2. Determine what is needed to fulfill the requirements of the tests.

3. Contact Range Control for the training schedule and range access opportunities related to testing.

4. Contact the unit involved with the training that includes the munitions of interest in the test objectives through a military liaison.

5. Develop a test plan, allowing ample time for testing and at least one make-up day per activity. Plan on arriving a few days early for set-up and unforeseen contingencies.

6. Line up a team and facilities.

7. Keep in touch with all the players.

4 Sampling Strategies

Good samples start with good sampling. This may seem obvious, but most quality assurance work is done in the lab, not in the field. With a poorly collected sample, even the best lab procedures will yield poor results. In this discussion, we will refer to detonation point sampling, but the techniques can be applied to other sampling.

Much work has been done to develop a rational and effective sampling plan for non-homogeneous, particulate-derived residue plumes. Even under the ideal conditions described above, the distribution of energetics residues will not be uniform. In the past, sampling consisted of taking a few large (1-m^2) surface samples in the decision unit area, a decision unit (DU) being an area of interest. On soils, it is virtually impossible to tell if the DU encompasses a significant portion of the area that may contain residues of interest. On snow, the area containing the majority of the residues is more easily demarcated (Fig. 5), but where does one sample within the plume? If the samplers are to collect five or even 10 samples in a 1000-m^2 plume, the tendency is to bias the samples in two ways: Sampling near the detonation point (proximity bias) and sampling the darker areas containing the most or darkest soots (density bias). Both biases will result in inflated residues concentrations. Through a concerted effort, these biases can be minimized but not eliminated.

Figure 5. Impact plumes from 105-mm HE rounds.

Taking 1-m² discrete samples is the original method of sampling residues following an event. Collection is time-consuming, and great care must be taken to obtain a good sample without spillage or missing residues. Two people are required, one to hold the collection bag and one to sample. There are also several unknowns. Are the samples representative of the plume? Is the plume demarcated correctly? Are the samples deep enough? How many samples are required to characterize the DU? Once the samples have been collected, the problem becomes one of handling and processing. Each sample (1 × 1 × 0.02 m) must be treated separately until after analysis.

Using a multi-increment sampling method, we have been able to work through these unknowns and biases. The first objective was to overcome the proximity and density biases to obtain a representative sample. Taking a sample composed of many small increments in a manner based on a loose grid or concentric circles forces the sampler into areas of the DU that would not normally be sampled using the previous sampling method (Fig. 6). A systematic-random approach, which entails a randomly derived starting point that is carried throughout the sampling grid, normally results in the most repeatable results. However, it is difficult to implement in non-rectangular decision units. We examined results from obtaining 40 increments with a 20- × 20-cm scoop and 100 increments using a 10- × 10-cm scoop. Initial results based on duplicate and triplicate sampling were promising, indicating replication well under an order of magnitude (usually within a factor of four) for the 10-cm scoop and within ±50% for both duplicate and triplicate samples for the 20-cm scoop. There was close agreement between the two protocols when conducted on the same plume.

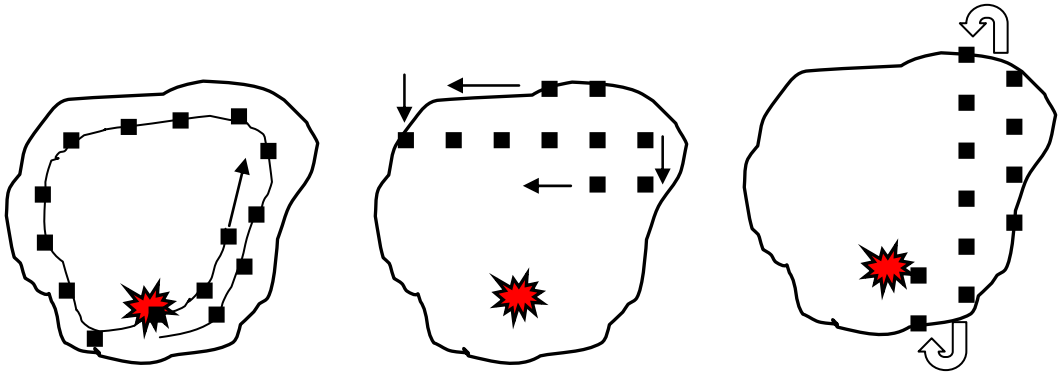


Figure 6. Various sampling strategies used to sample within a demarcated detonation plume.

Further refinement of the process has lowered triplicate replication for the 10-cm scoop to ±43% of the mean when sampled by three individuals and ±8% to ±35% when the triplicates for a plume were obtained by one sampler (lap method). The larger scoop has a range of less than ±20% for replicate sampling. This indicates that the plumes are being representatively sampled. The advantage of the multi-increment sample is that with three samples, the plume has been quickly sampled and intensively covered, and the samples are less likely to be biased. The samples can also be obtained by one person, freeing the other person to do quality control work (Fig. 7).

Demarcating the residue plume is the most subjective task associated with sampling residues. To determine if the DU demarcation is adequate, we obtain multi-increment samples outside the plume (OTP) using the method developed for inside the plume. A multi-increment sample is taken in a 0- to 3-m annulus outside the plume, and, if time permits, a second multi-increment sample is taken in a 3- to 6-m band outside the plume (Fig. 8). Where residues in the OTP area are significant (>5%), the area and mass are added to the plume calculations. This has happened only three times in 95 tests. Replicate sampling of OTP areas has also been conducted for quality control.

Figure 7. Detonation plume on snow-covered ice after multi-increment sampling.

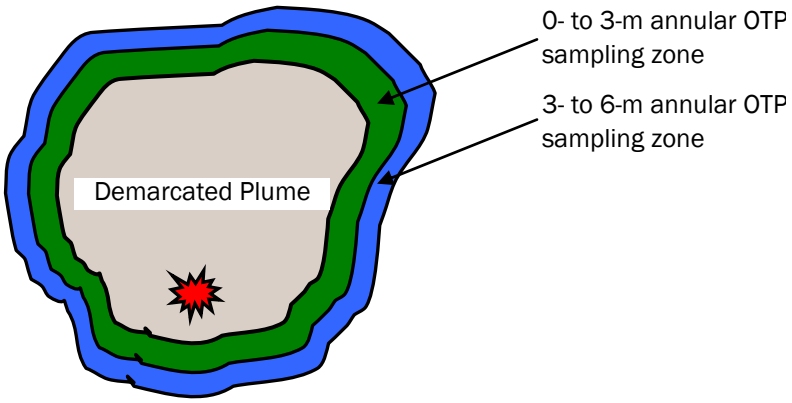


Figure 8. Sampling outside the (demarcated) plume: OTP sampling.

Addressing the question of depth of sample, we typically do subsurface sampling on at least one plume. Subsurface sampling entails first obtaining a sample increment with a larger scoop (20-cm) and then resampling the same point with a 10-cm scoop (Fig. 9). Care must be taken when obtaining the subsurface increment to ensure that only the interior of the sampled area is addressed. Significant (>5%) quantities of residues have been found in a subsurface sample only once. Depth of sampling has varied from <1 cm to over 5 cm based on snow depth and conditions. A light, fluffy snow surface will require deeper sample increments than a thin, firm layer of snow. In the former case, subsurface sampling is essential to ensure that residues are not missed.

Figure 9. Duplicate 20-cm sampling with follow-on 10-cm subsampling.

The final question is the number of increments required. We have found that results from using a 10-cm scoop (≈100 increments) and a 20-cm scoop (≈40 increments) are very close. Collecting the 40-increment sample is obviously quicker and easier, but the 100-increment sample is less prone to bias. We therefore recommend the 100-increment sample for inside-the-plume sampling. For subsurface samples, the original sample is best taken with a 20-cm scoop and the subsurface sample with the 10-cm scoop. Therefore, 40 increments is the goal for coverage. OTP samples can range from 40 to 100 increments, depending on the area of the annulus sampled.

Based on our experience and the results of the many tests we have performed, the following is the recommended protocol for sampling on snow:

1. Prior to the exercise, measure snow and ice thickness and take background samples in the test areas.

2. Clear all detonation areas (UXO technician or EOD specialist) prior to accessing plumes.

3. Plume demarcation – Walk around the plume 1 m from the edge where consistent deposition of residues can be discerned. Record this outline with a GPS system (<1 m accuracy). Also delineate the detonation point and crater outline for munitions detonations.

4. Inside-the-plume sampling – Triplicate plume samples should be taken for each DU using a 10- × 10-cm scoop to a minimum depth of 2 cm where possible. The number of increments should be around 100 (75–125). The depth must be adjusted based on snow conditions: deeper sampling for lighter snow. Increments should be placed in a clean 38- × 76-cm polyethylene (PE) bag. Upon completion of each sample, the exterior of the bag should be labeled with a description of the sample and a labeled tag attached to the top of the bag using a black tie-wrap. Double-bag the samples in the field prior to transport for processing.

5. Subsurface sampling – Subsurface samples should be obtained following sampling with a 20-cm scoop. Use a 10-cm scoop to obtain subsurface samples to avoid edge contamination. Duplicate subsurface samples should be obtained on at least two plumes if multi-plume (7+) tests are conducted. Always obtain at least one subsurface sample if possible.

6. OTP sampling – OTP sampling with a 10-cm scoop should be conducted outside each plume. A 0- to 3-m annulus should be sampled on each plume. When possible, obtain a sample from the 3- to 6-m band. Replicate sampling can also be done on OTP samples.

7. Transects – For firing points, downrange transects are recommended. These are 2- × 3-m to 3- × 10-m areas at fixed intervals downrange and in the direction of fire from the firing position, beyond the demarcated plume. We generally take samples from three transects located at 10- to 25-m intervals beyond the demarcated plume, depending on the weapon system. Duplicate or triplicate 30- to 40-increment samples are recommended for these DUs.

A total of four and seven samples, including quality control samples, are thus required to characterize a plume. For burn points, we have collected two to three samples per point. One to two samples are collected at the limited plume area, typically encompassing the whole area of the burn and adjacent residues and debris. An OTP sample is also collected. For firing points, we have sampled both circular and rectangular areas that encompass both the gun and the downrange plume. OTP and subsurface sampling is conducted on this DU. Transects downrange of the firing point are sampled to estimate the residue deposition extent beyond the plume area (Fig. 10).

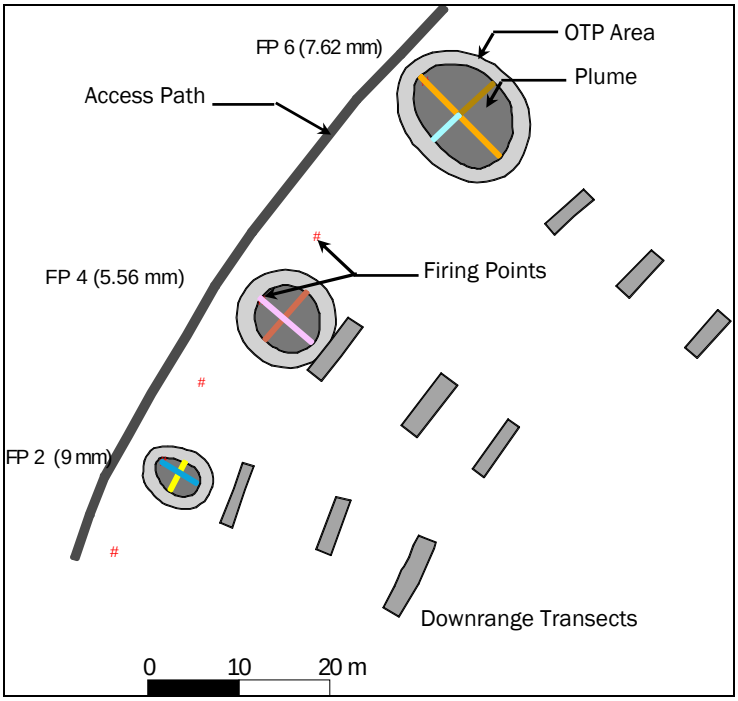


Figure 10. Small arms test sampling layout, Camp Ethan Allen, VT.

5 Sample Storage and Processing at Field Lab

Many residue tests span several days. Storage of samples prior to processing can be an issue that needs to be addressed to both protect the sample and expedite processing. Fortunately, we have only lost a few of the hundreds of samples we have obtained, but the lessons learned are valuable ones.

The bags must be handled carefully. Seams can break at low temperatures, and rough handling will increase the chances of fragmented ordnance (frag) penetration from the sample. At the processing lab, place the samples in a cold area away from the sun. Don't allow the samples to start melting. If there are broken seams or penetration from frag, the sample will leak and may be lost.

When enough samples have been collected to begin processing, bring the samples inside for rebagging, ordering, and melting. Rebagging the samples reduces the chances of cross-contamination from residues that may have come in contact with the sample bag either though field exposure or contact with other sample bags during transport or storage. This may seem superfluous, but we have cut the range between replicate samples in half since doing this. Place the rebagged samples in a polyethylene (PE) bin to contain the sample in case of leakage. At our site facility, we place samples to be processed under an overhead heater and those that can wait near a large overhead door where they remain cool (Fig. 11). Do not allow the melted samples to warm above 10°C. We try to keep samples collected from each decision unit together to process as a batch, with the samples likely to have the least residues (OTPs and subsamples) processed before those containing the most residues. If several different tests have been conducted during a deployment, run the samples from similar tests together with the ones containing the most residues last. Keep a log of all samples coming in and those going to the lab area to be processed.

When the sample is melted and logged in, you are ready for the next step—processing. The first task is to separate the aqueous portion from the particulate matter. To accomplish this, we use a filtration bank that relies

Figure 11. Sorting, rebagging, and preparing samples for melting.

Figure 12. Filtering of a burn point sample.

on vacuum separation (Fig. 12). Samples are poured into a container on the top of the system, and the aqueous fraction is drawn through a Whatman® 90-mm-diameter grade-GF/A glass microfiber filter. For samples containing heavy residues, several filters may be required to complete filtration. The last volume of the sample in the bag is shaken vigorously to suspend any remaining soot clinging to the sample bag prior to pouring it into the filtration system. Rinsing the bag with a small amount of distilled (DI) or filtered water from a spray bottle may also be

necessary. When the last of the sample has passed through the filter, the inside of the top of the apparatus is rinsed down with DI water and filtered. If any of the sample has leaked into the PE tubs during melting, the volume is measured. This volume is filtered only if the quantity is significant (>10% of the total sample) and the leakage has been kept from cross-contamination with other samples. Filters containing the residues (soot fraction) are placed in a labeled 4-oz (120-cc) amber jar with the number of filters used noted on the jar and recorded in a logbook. They are then set out to dry in a warm place away from the processing area. The total aqueous fraction is then measured, and two 500-mL aliquots are taken, one for further processing and the other as a backup. We use 500-mL amber glass bottles, noting the original aqueous volume on the label. The aqueous fraction aliquots are then recorded in a logbook and placed in a refrigerator. Glassware is washed in an Alconox solution and double-rinsed in DI water between samples. PE tubs that contained leakage are also washed and rinsed prior to reuse.

The next step is the concentration of the aqueous fraction. This is done using solid-phase extraction (SPE) and elution (Fig. 13). Up to 12 samples can be run at a time on the extraction device, so this step generally takes place when we are well into the separation process and have accumulated enough aliquots to run a full bank. A Waters Porpak RDX cartridge (Sep-Pak, 6-cm^3, 500-mg) is used for separation and is eluted with 5 mL of acetonitrile, resulting in a 100:1 concentration of the analytes of concern:

Figure 13. Solid-phase extraction of 12 aqueous sample fractions.

research and development explosive (RDX), high-melting-point explosive (HMX), trinitrotoluene (TNT), nitroglycerine (NG), and dinitrotoluene (DNT). The concentrated solution is then split into two aliquots—3.5 mL for analysis and 1.5 mL for archiving— and the vials are labeled, logged in, and placed in a refrigerator. When processing is complete, the 3.5-mL split and the filters are shipped to the analytical lab for final processing of the filters and analysis.

There are several quality control measures we perform during this phase of the process. Triplicate (plus one) filtrate aliquots are periodically taken to check on the repeatability of the split, concentration, and analysis processes. Runs of ultra-filtered (>80 MΩ) or DI water are also performed through washed and clean glassware to determine if any residual contamination may be occurring due to the inter-sample cleaning process. We also run spikes and blanks through the SPE cartridges to determine retention efficiency and check for contamination.

Summarizing the processes involved, we have the following:

1. Store the samples prior to processing in a cold area away from sunlight.

2. Sort the samples by plume or decision unit and rebag them in clean, labeled polyethylene bags. Double-bag if possible and place re-bagged sample in a clean PE tub.

3. Melt the samples, taking care not to allow the sample temperature to exceed 10°C. Do not allow them to refreeze.

4. Start the processing procedure by logging in the samples and ordering them based on their apparent residues content.

5. Using a vacuum filtration unit, separate the aqueous from the soot or particulate fraction. Track the number of filters used and filtrate generated.

6. Place the filters in a labeled jar and set them out to dry. Refrigerate the sealed jars after drying.

7. Mix the filtrate fraction by vigorous shaking. Take two or four 500-mL aliquots. Place the labeled bottles in a refrigerator after logging in the sample.

8. Wash all glassware and the PE tub.

9. Obtain a filtration blank by running 1000 mL of DI water periodically through a freshly cleaned filtration apparatus and collecting the filter and filtrate fractions.

10. Pre-concentrate one or three filtrate aliquots by passing them through a Porpak RDX cartridge. Spikes or blanks are run at this time.

11. Elute the cartridge with 5 mL of acetonitrile (AcN), giving a 100:1 concentration.

12. Split the elution into 3.5-mL and 1.5-mL fractions. Log and store the fractions in a refrigerator.

13. Ship the 3.5-mL pre-concentrated aqueous split and filters to the analytical lab.

6 Final Processing and Analysis

The filters containing the soot fractions are extracted using acetonitrile (AcN). The quantity of AcN for each set of filters is determined by the amount required to cover the filters prior to shaking. AcN is added in 10-mL increments and recorded in the sample logbook. Generally, 20–40 mL are required per jar. Each sample is shaken with the solvent for 18 hours. The AcN extracts from the solid-phase extraction of the aqueous aliquots and the AcN from the extraction of the solid residues on the filters are analyzed by either high-performance liquid chromatography (HPLC) or gas chromatography–electron capture detector (GC-ECD), depending on the analyte concentration.

Analyte concentrations greater than 100 µg/L are determined following the general procedures of SW 846 Method 8330 (Nitroaromatics and Nitramines by High-Performance Liquid Chromatography [HPLC]). Lower concentrations are determined using Method 8095 (Nitroaromatics and Nitramines by GC), which uses an electron capture detector and provides detection limits near 1 µg/L for RDX and 20 µg/L for NG in solvent extracts. The advantage of the HPLC method is that the analytical error is very small, about 2% relative standard deviation (RSD) for replicate injections. Although the GC-ECD method can detect much lower concentrations, the analytical error is much greater, approaching 20% RSD.

Prior to HPLC analysis, 1.0 mL of each acetonitrile extract is mixed with 3.0 mL of reagent-grade water. Determinations are made at our lab on a modular system from Thermo Electron Corporation composed of a Finnigan SpectraSYSTEM Model P4000 pump, a Finnigan SpectraSYSTEM UV2000 dual-wavelength UV/VS absorbance detector set at 210 and 254 nm (cell path 1 cm), and a Finnigan SpectraSYSTEM AS300 autosampler. Samples are introduced with a 100-µL sample loop. Separations are achieved on a 15-cm × 3.9-mm (4-µm) NovaPak C8 column (Waters Chromatography Division, Milford, Massachusetts) at 28°C and eluted with 1.4 mL/min of 15:85 isopropanol/water (v/v).

For GC analysis, the acetonitrile extracts are transferred to autosampler vials, which are then placed into an HP 7683 Series autosampler tray that

is continuously refrigerated by circulating a 0°C glycol/water mixture through the trays. A 1-µL aliquot of each extract is injected directly into the HP 6890 purged packed inlet port (250°C) containing a deactivated Restek Uniliner. Primary separation is conducted on a 6-m- × 0.53-mm-ID fused-silica column, with a 0.5-µm film thickness of 5% (phenyl) methylsiloxane (RTX-5 from Restek). The GC oven is temperature-programmed as follows: 100°C for 2 min, 10°C/min ramp to 250°C. The carrier gas is hydrogen at 0.85 psi inlet pressure. The µECD temperature is 280°C; the makeup gas is nitrogen at 60 mL/min. Extracts are also analyzed using an RTX-TNT2 confirmation column. The column dimensions are 6 m × 0.53-mm ID with a 1.5-µm film thickness. The GC oven is temperature-programmed as follows: 130°C for 1 min, 10°C/min ramp to 160°C, 30°C/min ramp to 270°C. The carrier gas is hydrogen at 1.6 psi inlet pressure. The µECD temperature is 310°C, and the makeup gas is nitrogen at 60 mL/min.

In summary. our final processing and analysis steps are:

1. Process the filters by adding AcN in 10-mL increments until the filters are covered and shaking the closed jar for 18 hours. Record the volume of AcN.

2. Mix 1.0 mL of AcN extract with 3.0 mL of reagent-grade water for HPLC analyses.

3. Analyze the filter extracts and aqueous concentrates on an HPLC using the mixture above or by direct injection of a 1-µL aliquot. Run the samples from areas more likely to have a light residue load first to avoid carry-over.

4. If the results of the HPLC analysis are at or below detection limits, follow the procedure above for GC–ECD analysis.

5. Perform lab quality control such as spikes and blanks at this time.

7 Summary

Measuring energetics residues on snow is an effective method of obtaining data on residue generation of individual munitions from various activities. Residue plumes are visually discernable, making the determination of geometry and areas of these decision units practical. Active ranges can be utilized when minimal conditions are met. Using the systematic-random multi-increment sampling technique, plumes can be representatively sampled with a single sample taken by one person. Quality control methods such as replicate sampling, sampling outside the demarcated plume, and sampling below previously sampled points can be conducted more easily because of the efficient manner of sample collection. Processing of the samples is greatly simplified because snow (frozen water) is the medium upon which the residues are deposited rather than soils. Using the methods outlined above, we have achieved triplicate repeatability of less than 10% for detonation plumes and can easily sample up to seven decision units in a few hours. Few if any samples taken outside the demarcated plumes and below previously sampled points contain detectable quantities of the residues of concern. Using these techniques, both range modelers and range managers can have meaningful data from which they can determine the effects of munitions on range usage and sustainability.

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The following list of references is arranged to enable quick access to material that will assist in understanding the procedures outlined above or that demonstrate the procedures in actual field tests. Arranging these references in this manner allows quicker, more useful access to this information outside the body of this report. In the citations, ERDC stands for the U.S. Army Corps of Engineers Engineer Research and Development Center. CRREL stands for Cold Regions Research and Engineering Laboratory. USEPA stands for United States Environmental Protection Agency.

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14. ABSTRACT

Quantifying energetics residues resulting from firing and detonating military munitions are necessary components in developing range sustainability models and plans. Determination of the residue plume area, discrimination from previous activities, separation of the residues from the collection matrix, and processing of the samples are all difficult tasks when dealing with residues on soils. To circumvent these problems, the U.S. Army Cold Regions Research and Engineering Laboratory has been sampling for energetics residues on snow. At firing points, a clean snow surface allows the collection of residues from a known quantity and type of munition and testing can be performed in conjunction with a scheduled training exercise. Detonation residues from live-fire training can be sampled on a snow-covered surface in an active impact area when the area fired into has not been utilized since the last snowfall. Tests with blown-in-place munitions may be conducted on clean snow-covered surfaces on active impact areas as well. This report outlines the methods developed by CRREL over the last seven years for sampling residues on snow and deriving estimates for energetics residues on a per-round basis. Sampling, quality control, and sample processing methods are covered.

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