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Explosive-Residue Compounds Resulting From Snow Avalanche Control in the Wasatch Mountains of Utah

U.S. Geological Survey Water-Resources Investigations Report 03-4007

Explosives are Used Throughout the Western United States to Controll the Release of Snow Avalanches

A snow avalanche is a powerful force of nature that can play a significant role in developing mountain landscapes (Perla and Martinelli, 1975). More importantly, loss of life can occur when people are caught in the path of snow avalanches (*Grossman, 1999*). Increasing winter recreation, including skiing, snowboarding, snowmobiling, snowshoeing, and climbing in mountainous areas, has increased the likelihood of people encountering snow avalanches (fig. 1).

Figure 1. Video clips of skier-triggered avalanches. Video courtesy of U.S. Forest Service, Utah Avalanche Forecast Center, Salt Lake City, Utah.

Explosives are used by most ski areas and State highway departments throughout the Western United States to control the release of snow avalanches, thus minimizing the loss of human life during winter recreation and highway travel (fig. 2).

Figure 2. Video clips of explosive use to control the release of a snow avalanche. Video courtesy of Friends of the Utah Avalanche Forecast Center.

Common explosives used for snow avalanche control include trinitrotoluene (TNT), pentaerythritoltetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), tetrytol, ammonium nitrate, and nitroglycerin (Perla and Martinelli, 1975). During and after snowfall or wind loading of potential avalanche slopes, ski patrollers and Utah Department of Transportation personnel deliver explosive charges onto predetermined targets to artificially release snow avalanches, thereby rendering the slope safer for winter activities. Explosives can be thrown by hand onto target zones or shot from cannons for more remote delivery of explosive charges. Hand-delivered charges typically contain about 2 pounds of TNT or its equivalent (Perla and Martinelli, 1975).

Depending on the size of the ski area, acreage of potential avalanche terrain, and weather conditions, the annual quantity of explosives used during a season of snow avalanche control can be substantial. For example, the three ski areas of Alta, Snowbird, and Brighton, plus the Utah Department of Transportation, may use as many as 11,200 hand charges per year (Wasatch Powderbird Guides, unpub. data,

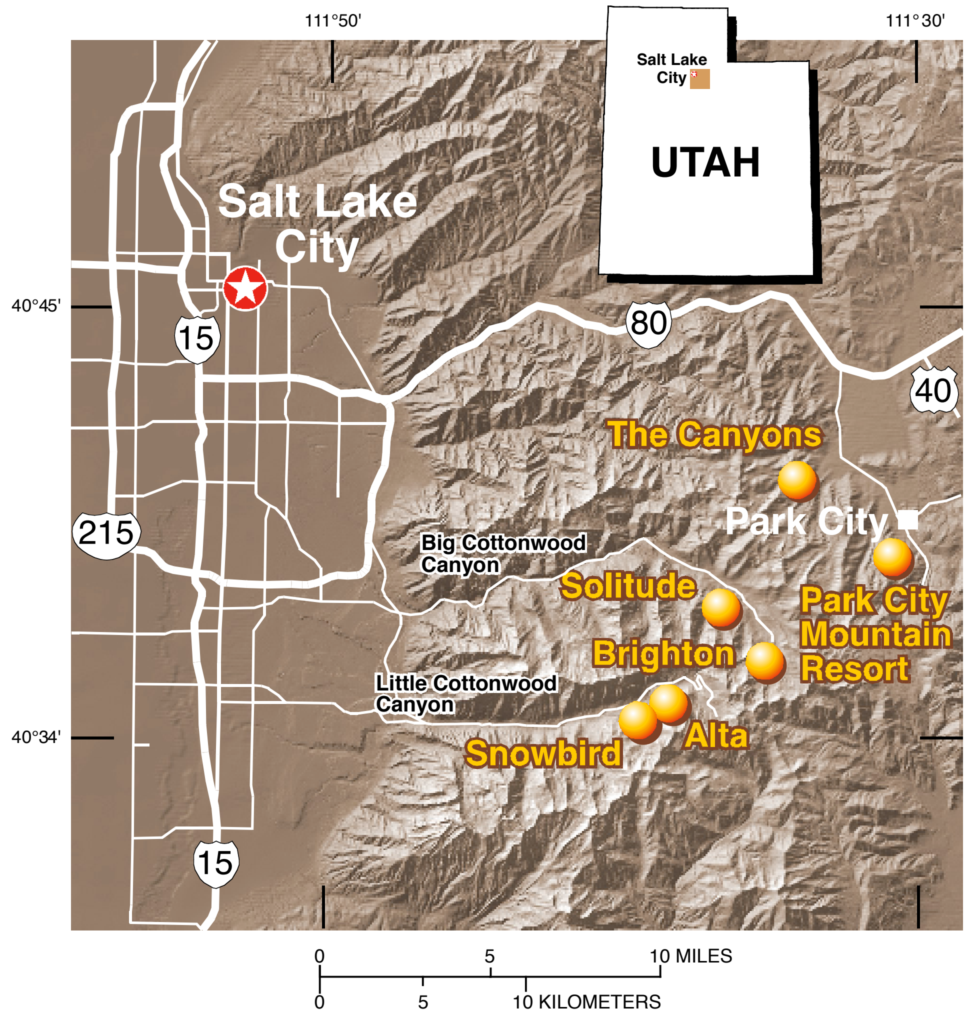

Figure 3. Selected ski areas where explosives are used for snow avalanche control, Wasatch Mountains, Utah.

> “The use of explosives for snow avalanche control may introduce potentially toxic chemical compounds into relatively pristine alpine and subalpine watersheds.”

1999) for snow avalanche control in Big and Little Cottonwood Canyons (fig. 3). If each charge is assumed to weigh 2 pounds, this equates to about 22,400 pounds of explosive hand charges per year. In addition, 2,240 to 3,160 Avalauncher rounds and 626 to 958 military artillery rounds (explosive mass not specified) are used each year by the three ski areas and the Utah Department of Transportation for snow avalanche control in Big and Little Cottonwood Canyons (Wasatch Powderbird Guides, unpub. data, 1999). The other ski area in Big Cottonwood Canyon, Brighton, uses about 2,000 pounds of explosives per year for snow avalanche control (Michele Weidner, Cirrus Ecological Solutions consultant, written commun., 2001).

Figure 4. Location of The Canyons ski area and Park City Mountain Resort.

The use of explosives for snow avalanche control may introduce potentially toxic chemical compounds into pristine alpine and subalpine watersheds. Previous studies have shown that use of explosives and ammunition has resulted in contamination of soils, stream-and lake-bottom sediment, and aquifers with nitroaromatic compounds (Gerlach and others, 1999; Weissmahr and others, 1999). Nitroaromatic compounds, such as TNT, have potential toxic and mutagenic effects on many organisms (Stahl and Aust, 1995). To date (2002), the introduction of chemical compounds, including nitroaromatics, from explosives used for snow avalanche control has not been assessed.

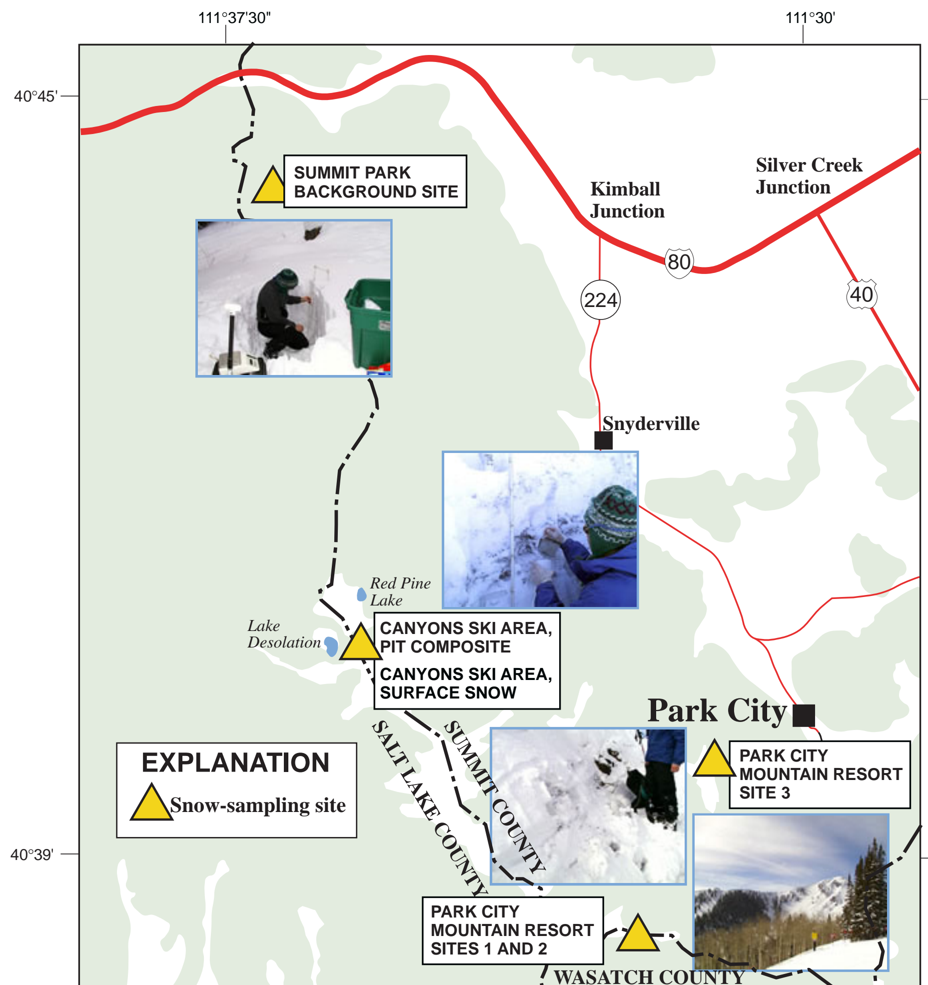

Figure 5. Location of snow-sampling sites at two ski areas and a background site, Wasatch Mountains, Utah.

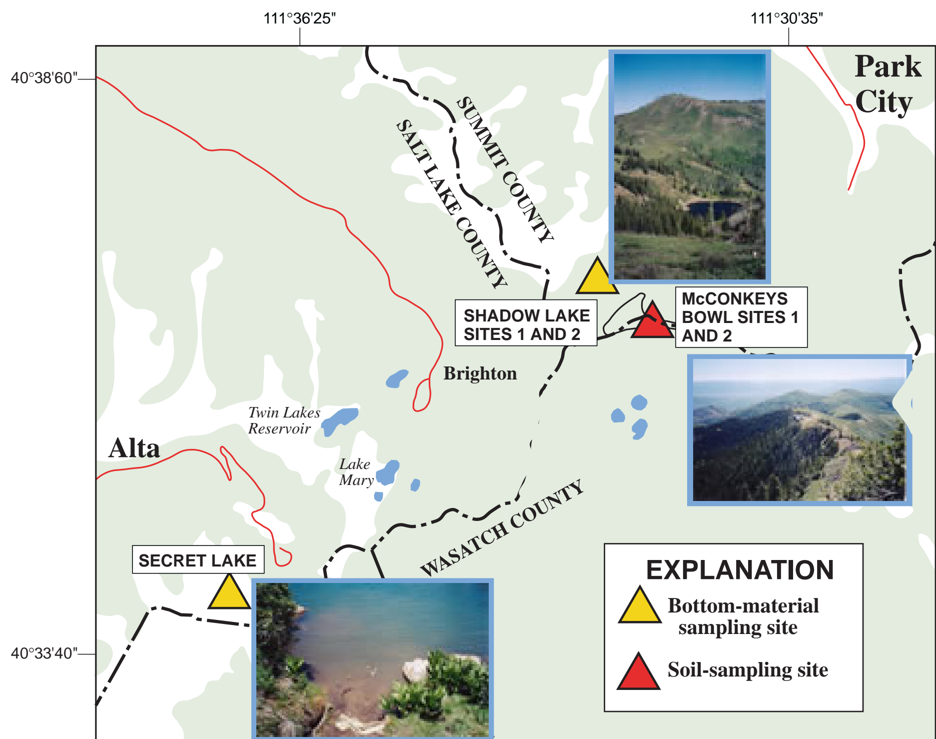

Figure 6. Location of soil and stream-bottom and lake-bottom sediment sampling sites at Park City Mountain Resort and Alta ski areas, Wasatch Mountains, Utah.

The objective of this report is to determine the concentration of selected organic compounds in snow, soils, and lake-bottom sediment in areas where explosives are used for snow avalanche control in the Wasatch Mountains of Utah (figs. 4, 5, and 6).

Explosive-Residue Compounds Detected in Snow Collected from Blast Craters

Jenkins and others (2000) *(pdf 344k)* were the first to measure the concentration of explosive-residue compounds in snow. The purpose of their study was to use snow to estimate the quantity of explosive residues remaining after munitions detonation. The use of snow as a sampling medium has a number of advantages over soil sampling *(Jenkins and others (2000)*: (1) newly fallen snow has not been contaminated from previous detonations; (2) black soot produced from the detonation allows for easy delineation of the blast zone in the snow; and (3) snow provides a convenient and relatively interference-free matrix for the chemical analysis of explosive residues. Explosive-residue compounds detected in snow samples analyzed by *Jenkins and others (2000)* included RDX; 2,4-Dinitrotoluene; 2,6-Dinitrotoluene; 2-Amino-4,6-Dinitrotoluene; and 4-Amino-2,6-Dinitrotoluene.

Table 1. Explosive-residue method analytes and minimum reporting limit. [µg/L, micrograms per liter; µg/kg, micrograms per kilogram; <, less than; nd, not determined]

Compound	Lower method reporting limit for water samples, in µg/L	Lower method reporting limit for soil and sediment samples, in µg/kg
Nitrobenzene	< 0.05	nd
2-Nitrotoluene	< .2	nd
3-Nitrotoluene	< .2	nd
4-Nitrotoluene	< .2	nd
1,3-Dinitrobenzene	< .05	< 2.0
2,6-Dinitrotoluene	< .01	< 2.0
2,4-Dinitrotoluene	< .01	< 2.0
2,3-Dinitrotoluene	< .01	< 2.0
*3,4-Dinitrotoluene (surrogate)	< .01	nd
1,3,5-Trinitrobenzene	< .1	< 5.0
2,4,6-Trinitrotoluene	< .01	< 2.0
RDX	< 1.0	nd
4-Amino 2,6-Dinitrotoluene	< .05	< 5.0
3,5-Dinitroanaline	< .2	< 5.0
2-Amino 4,6- Dinitrotoluene	< .05	< 5.0
Tertyl	< .1	< 5.0

Figure 7. Black areas in snow characteristic of blast zones created by explosives used for snow avalanche control, The Canyons ski area, Utah, February 15, 2001.

This study is the first to assess the potential effects of the use of explosives for snow avalanche control on the chemical quality of snow. Snow samples were collected from six sites (fig. 5) during February 2001. The control or background site at Summit Park is in a residential area where explosives have not been used for snow avalanche control. The remaining snow samples were collected from areas of recent and reoccurring explosive use for snow avalanche control.

Except for the background site, snow-sample sites were selected by identifying black "sooty" zones in the snow, characteristic of blast craters caused by the use of explosives (fig. 7).

Prior to sampling, about 4 inches of snow was removed to expose an undisturbed sampling surface. Snow samples were then composited with a metal scoop and placed in 1-liter, cleaned and baked (450 degrees Celsius), wide-mouthed glass jars (fig. 7). The samples were kept frozen and shipped to the U.S. Geological Survey (USGS)

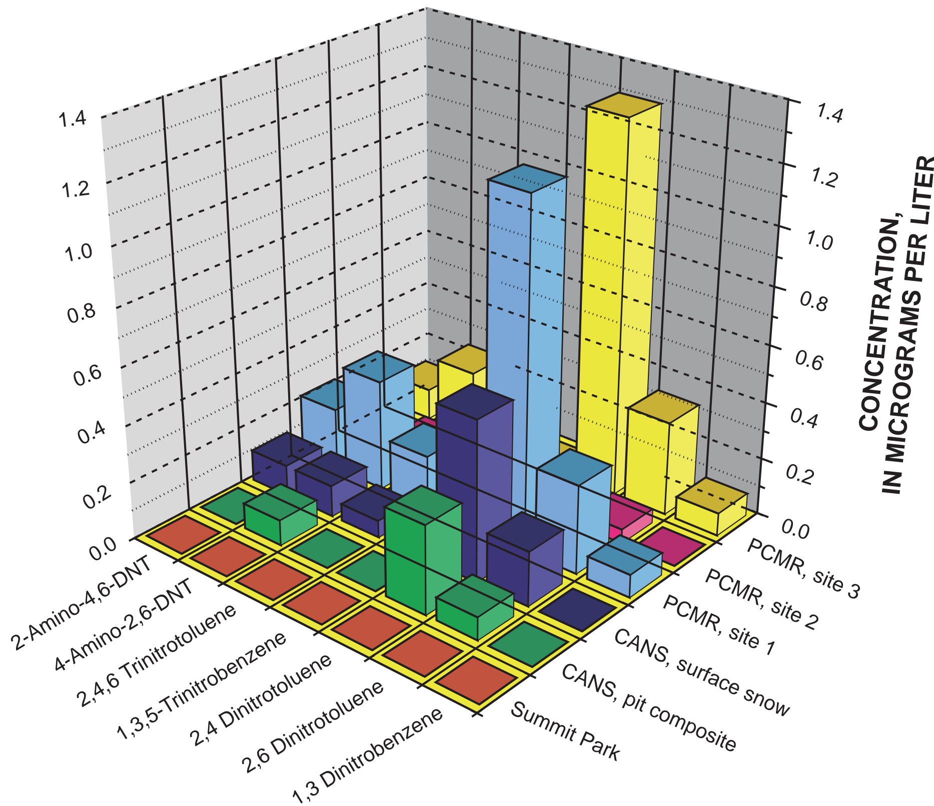

Figure 8. Concentration of explosive-residue compounds detected in snow samples collected from a background site (Summit Park) and multiple blast zones located at The Canyons (CANS) and Park City Mountain Resort (PCMR) ski areas, Utah.

National Water Quality Laboratory (NWQL) in Lakewood, Colorado, for processing and analysis.

Prior to chemical extraction, the snow samples were melted at room temperature. After complete melting, two 100-milliliter (ml) aliquots were extracted, one with toluene and one with isoamyl acetate, and analyzed for explosive residues by gas chromatography/electron capture detection (GC/ECD) with established analytical techniques (Schumacher and others, 1995). The specific extraction and analytical methodology used for the snow samples is described in *appendix A*. This extraction and analytical procedure is suitable for determination of the explosive-residue compounds listed in table 1. Most of these compounds can be detected at concentrations well below 1 microgram per liter (µg/L) in water samples.

Analysis of the snow samples resulted in detection of seven explosive-residue compounds (fig. 8). Explosive-residue compounds detected in the snow samples included 1,3-Dinitrobenzene; 2,6-Dinitrotoluene; 2,4-Dinitrotoluene; 1,3,5-Trinitrobenzene; 2,4,6-Trinitrotoluene; 4-Amino-2,6-Dinitrotoluene; and 2-Amino-4,6-Dinitrotoluene. Every snow sample collected from blast craters had at least three explosive residue compounds at detectable concentrations. Out of the seven compounds detected, 2,4-Dinitrotoluene was consistently the most abundant, with the highest concentration measured at site 3 (Park City Mountain Resort) (fig. 8). Explosive-residue compounds were not detected in the snow sample collected from the background site where explosives were not used (fig. 8).

Table 2. Concentration of explosive-residue compounds in snow samples collected from a background site at Summit Park and multiple blast zones located at The Canyons and Park City Mountain Resort ski areas, Wasatch Mountains, Utah

[Concentration reported in micrograms per liter or parts per billion; <, less than; E, estimated value: compound detected but cannot be quantified with high confidence; values in red are above the lower reporting limit]

Site ID	Date	Nitrobenzene	2-Nitrotoluene	3-Nitorotoluene	4-Nitorotoluene	1,3-Dinitrobenzene	2,6-Dinitrotoluene	2,4-Dinitrotoluene	2,3-Dinitrotoluene	1,3,5-Trinitrobenzene	2,4,6-Trinitrotoluene	RDX	4-Amino-2,6-Dinitrotoluene	3,5-Dinitroanaline	2-Amino-4,6-Dinitrotoluene	Tertyl
[1]Summit Park	2/15/01	< 0.05	< 0.2	< 0.2	< 0.2	< 0.05	< 0.01	< 0.01	< 0.01	< 0.1	< 0.01	< 1	< 0.05	< 0.2	< 0.05	< 0.1
The Canyons ski area, pit composite	2/15/01	< .05	< .2	< .2	< .2	< .05	.08	.31	< .01	< .1	< .01	< 1	.09	< .2	< .05	< .1
The Canyons ski area, surface snow	2/15/01	< .05	< .2	< .2	< .2	< .05	.19	.56	< .01	E .08	E .06	< 1	.11	< .2	.11	< .1
Park City Mountain Resort, site 1	2/16/01	< .05	< .2	< .2	< .2	.08	.31	1.20	< .01	< .1	E .19	< 1	.39	< .2	.22	< .1
Park City Mountain Resort, site 2	2/16/01	< .05	< .2	< .2	< .2	< .05	.05	.10	< .01	< .1	< .01	< 1	.05	< .2	< .0	< .1
Park City Mountain Resort, site 3	2/16/01	< .05	< .2	< .2	< .2	.08	.33	1.30	< .01	< .1	< .01	< 1	.24	< .2	.11	< .1

[1]Background site.

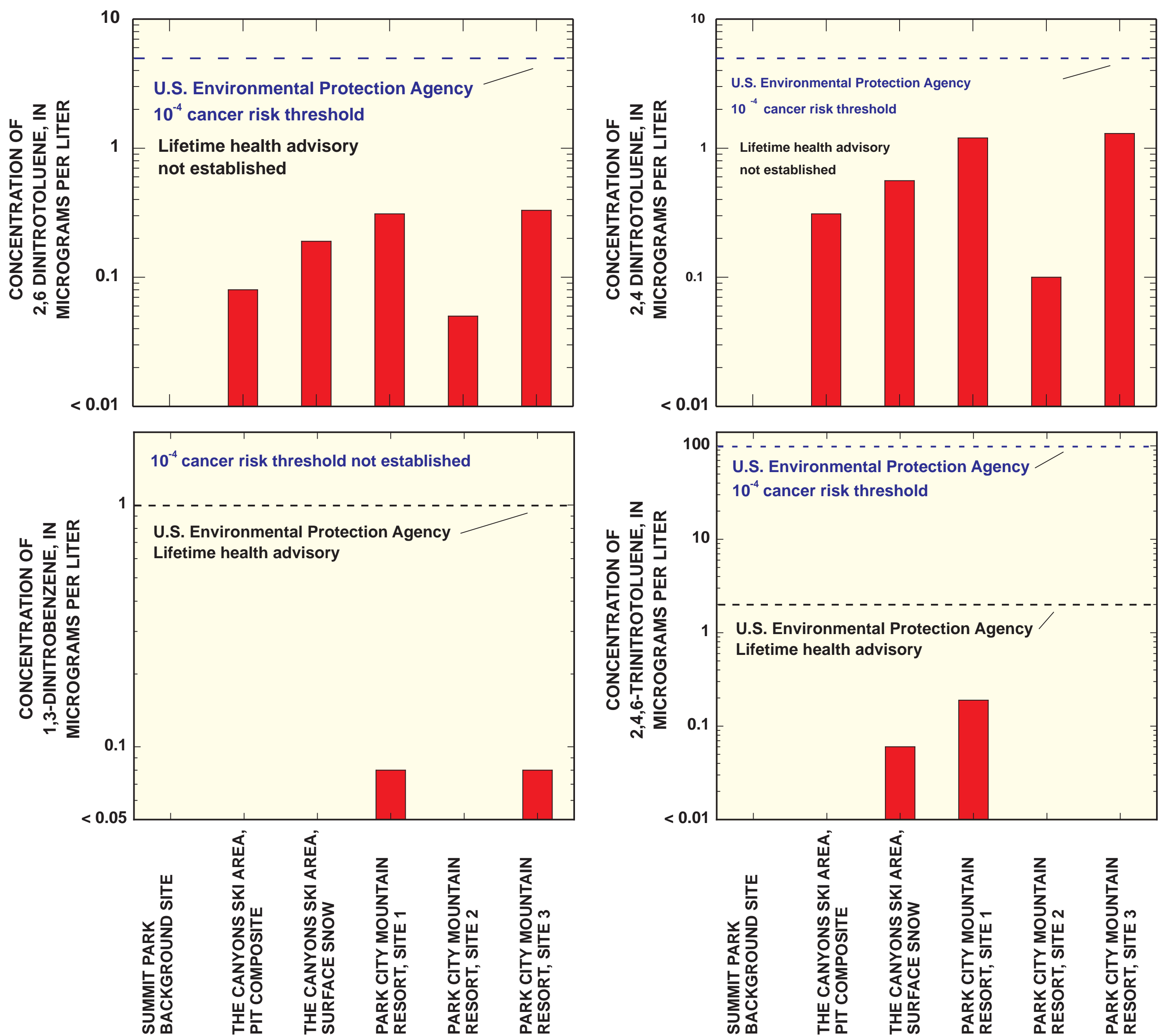

Figure 9. Relation of concentration of selected explosive-residue compounds in snow samples collected from background and blast crater sites to the U.S. Environmental Protection Agency (USEPA) 10^{-4} cancer risk threshold and lifetime health advisory (USEPA, 2000). The 10^{-4} cancer risk threshold is defined as the concentration of a chemical in drinking water corresponding to an estimated lifetime cancer risk of 1 in 10,000. The lifetime health advisory is the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure.

The maximum concentration of the seven detected explosive-residue compounds was less than 1.5 µg/L (table 2). Ranges in concentrations of the detected explosive-residue compounds at the five non-background-sites are shown in table 2: 1,3-Dinitrobenzene (< 0.05 to 0.08 µg/L); 2,6-Dinitrotoluene (0.05 to 0.33 µg/L); 2,4-Dinitrotoluene (0.10 to 1.30 µg/L); 1,3,5-Trinitrobenzene (detected in one sample, but not quantifiable); 2,4,6-Trinitrotoluene (<0.01 to 0.19 µg/L); 4-Amino-2,6-Dinitrotoluene (0.05 to 0.39 µg/L); 2-Amino-4,6-Dinitrotoluene (< 0.05 to 0.22 µg/L).

Four Explosive-Residue Compounds Detected in Snow Samples May Pose a Health Risk

The U.S. Environmental Protection Agency (USEPA) has set health advisories for four of the explosive-residue compounds detected in the snow samples from Wasatch Mountain ski areas, including 2,6 Dintrotoluene; 2,4-Dinitrotoluene; 1,3-Dinitrobenzene; and 2,4,6-Trinitrotoluene *(U.S. Environmental Protection Agency, 2000)*. A USEPA health advisory (HA) is not a legally enforceable Federal standard, but serves as technical guidance to assist Federal, State, and local officials. Two different HA limits were used for comparison with the explosive-residue data from the snow samples: (1) 10^{-4} cancer risk, which is the concentration of a chemical in drinking water corresponding to an estimated cancer risk of 1 in 10,000; and (2) lifetime HA, which is the concentration of a chemical in drinking water that is not expected to cause any adverse

Table 3. Concentration of explosive-residue compounds in bottom sediment and soil samples collected in the Wasatch Mountains, Utah

[Concentration reported in micrograms per kilogram or parts per billion; <, less than; E, estimated value: compound detected but cannot be quantified with high confidence; values in red are above the lower reporting limit]

Site ID	Sample medium	Date	1,3-Dinitro-benzene	2,6-Dinitro-toluene	2,4-Dinitoro-toluene	2,3-Dinitoro-toluene	Trinitro-benzene	Trinitro-toluene	4-Amino-2,6-Dinitro-toluene	3,5-Dinitro-analine	2-Amino-4,6-Dintro-toluene	Tetryl
Shadow Lake Site 1	Bottom sediment	6/28/01	< 2.0	< 2.0	< 2.0	< 2.0	< 5.0	< 2.0	< 5.0	< 5.0	< 5.0	< 5.0
Shadow Lake Site 2	Bottom sediment	6/28/01	< 2.0	< 2.0	< 2.0	< 2.0	< 5.0	< 2.0	< 5.0	< 5.0	< 5.0	< 5.0
McConkeys Bowl Site 1	Soil	6/28/01	< 2.0	< 2.0	< 2.0	< 2.0	< 5.0	< 2.0	**E 2.9**	< 5.0	< 5.0	< 5.0
McConkeys Bowl Site 2	Soil	6/28/01	< 2.0	< 2.0	**3.4**	< 2.0	< 5.0	**E 5.2**	**E 4.3**	< 5.0	< 5.0	< 5.0
Secret Lake	Bottom sediment	6/28/01	< 2.0	< 2.0	< 2.0	< 2.0	< 5.0	< 2.0	< 5.0	< 5.0	< 5.0	< 5.0

noncarcinogenic effects for a lifetime of exposure *(U.S. Environmental Protection Agency, 2000)*. Although some of the snow will eventually be used for drinking water, dilution of the explosive-residue compounds by mixing with non-contaminated water will likely decrease the concentrations well below analytical detection limits.

Concentrations of the explosive-residue compounds in snow samples did not exceed the 10^{-4} cancer risk threshold or the lifetime HA (fig. 9). Both 2,4- and 2,6-Dinitrotoluene are classified by the USEPA as probable human carcinogens and their 10^{-4} cancer risk threshold in drinking water is 5 µg/L *(U.S. Environmental Protection Agency, 2000)*. The highest concentration of 2,4-Dinitrotoluene was 3.7 µg/L less than the 10^{-4} cancer risk threshold and the highest concentration of 2,6-Dinitrotoluene was 4.7 µg/L less than the 10^{-4} cancer risk threshold (fig. 9). Lifetime HA limits have not been established for 2,4- and 2,6-Dinitrotoluene concentrations in drinking water.

Only two of the six snow samples had measurable concentrations of 1,3-Dinitrobenzene or 2,4,6-Trinitrotoluene (fig. 9). The measurable concentrations of 1,3-Dinitrobenzene were about one order of magnitude less than the lifetime HA of 1 µg/L (fig. 9). The measurable concentrations of 2,4,6-Trinitrotoluene were about one order of magnitude less than the lifetime HA of 2 µg/L and about three orders of magnitude less than the 10^{-4} cancer risk threshold (fig. 9). A 10^{-4} cancer risk threshold has not been established for 1,3-Dinitrobenzene.

Overall, substantially lower concentrations of the explosive-residue compounds may be expected in snowmelt, resulting from the mixing with meltwater derived from snow that is not associated with avalanche control operations. One exception to this could be the process of preferential elution of selected ions during initial melting of a snowpack. During the initial period of snowmelt, meltwater can contain initial inorganic solute concentrations that are 12 times higher than the average concentration in the snow (Williams and Melack, 1991). Preferential solute removal from a snowpack has not been documented for explosive-residue compounds; however, if active, preferential elution could substantially increase the concentration of explosive-residue compounds in early season meltwater.

Explosive-Residue Compounds May Persist and Accumulate in Soils and Lake-Bottom Sediment After Snowmelt

Annual snow-avalanche control operations at these locations creates the potential for an accumulation of explosive-residue compounds on surface soils. In addition, bottom sediment in streams and lakes that receive meltwater from areas where explosives are used also could act as a sink for explosive-residue compounds. Haderlein and others (1996) have shown that selected explosive-residue compounds, such as TNT, can strongly adsorb to clay minerals. This process could potentially accumulate selected explosive-residue compounds in soils and bottom sediment in areas where snow-avalanche control operations occur many times on an annual basis.

Soil and bottom-sediment samples were collected from five sites (fig. 6) during June 2001. Samples were collected after the snow had melted from the sites and about 2.5 months after any snow avalanche control had occurred with explosives. Bottom-sediment samples were collected from Shadow and Secret Lakes. Both Shadow and Secret Lakes receive runoff from adjacent slopes where explosives are used for snow avalanche control. Surface-soil samples were collected from McConkeys Bowl in areas where explosives are used for snow avalanche control.

Soil and bottom-material samples were composited with a metal scoop and placed in 1-liter, cleaned and baked (450 degrees Celsius), wide-mouthed glass jars. The samples were kept chilled and shipped to the USGS NWQL in Lakewood, Colorado, for processing and analysis. Details on the processing and analysis of the soil and bottom-material samples are reported in *appendix B*.

The chemical analysis of the soil and bottom material resulted in the detection of three explosive-residue compounds (table 3). No explosive-residue compounds were detected in the bottom-sediment samples; however,

both soil samples contained detectable amounts of explosive-residue compounds

that included 2,4-Dinitrotoluene; Trinitrotoluene; and 4-Amino-2,6-Dinitrotoluene (table 3).

Unanswered Questions Remain About the Effects of Explosive-Residue Compounds

Results from this initial study have raised a number of questions about the effects of explosive-residue compounds:

1. What percentage of the explosive charge remains in the snow as residue after detonation, and is this mass related to the type of explosive used?

2. Once the explosive residue is deposited in the snow, do certain environmental conditions (for example, ultraviolet radiation) promote natural degradation of the compounds?

3. During snowmelt is there a "pulse" of more-elevated concentrations of explosive-residue compounds that are preferentially eluted during the initial phase of melting?

4. Is there any bioaccumulation of explosive-residue compounds in alpine and subalpine ecosystems that receive snowmelt from areas where explosives are used for snow avalanche control?

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Acknowledgments

Cooperation from personnel at The Canyons ski area and Park City Mountain Resort during sample collection is appreciated.

Sources of Additional Information

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Sampling pit at Summit Park background site, February 2001.

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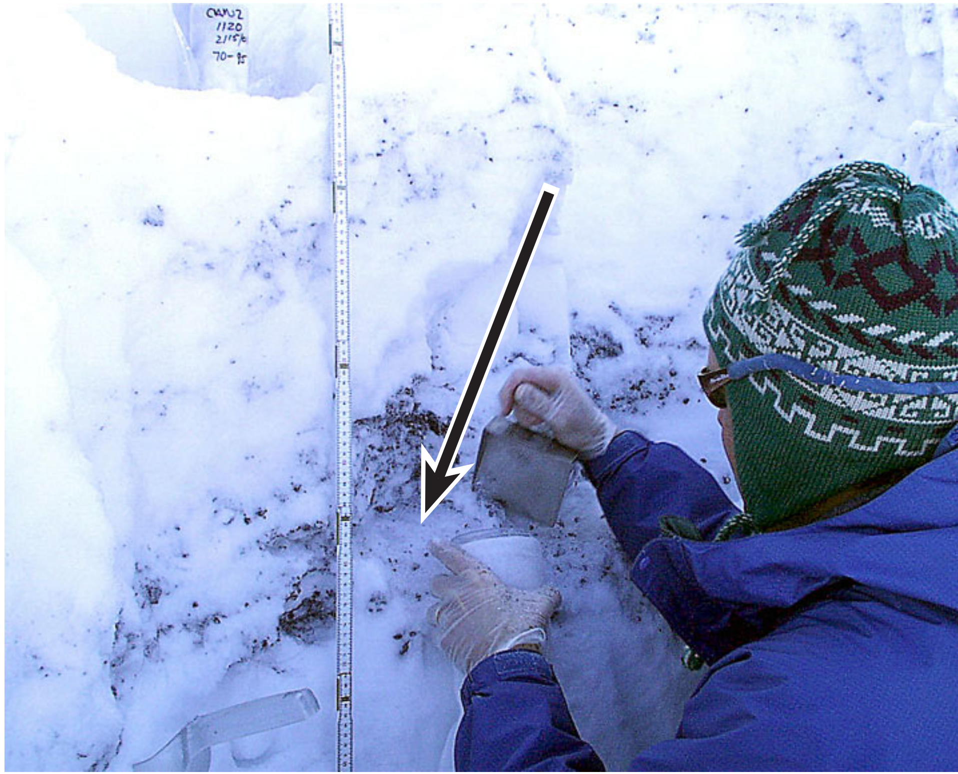

Canyons Ski area pit composite sample, February 2001. Black material is residue from explosives used for avalanche control.

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Blasting zone sampling sites at Park City Mountain Resort, site 3, February 2001.

Blasting zone sampling sites at Park City Mountain Resort, sites 1 and 2, February 2001.

Shadow Lake, site 1 and 2, June 2001. Explosives are used for snow avalanche control in the terrain surrounding Shadow Lake.

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McConkeys Bowl, sites 1 and 2, June 2001. Explosives are used for snow-avalanche control along the ridge line.

Secret Lake bottom material sample site, June 2001. Explosives are used for snow-avalanche control in the watershed above Secret Lake.

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Appendix A

1. Summary of Procedure

This procedure is suitable for the determination of nitroaromatic and nitramine compounds (explosives) present in water samples at individual compound concentrations of at least 0.01 *u*g/L. This method is applicable to those analytes that are (1) efficiently extracted from water by either toluene or isoamyl acetate as used in the extraction of two separate aliquots of samples, and (2) sufficiently volatile and thermally stable for determination by gas chromatography with electron-capture detection.

2. Scope and Application

2.1 Analytes:

This method is applicable to the following nitroaromatic and nitramine compounds:

Compounds	**Method Reporting Limit (*u*g/l)**
Nitrobenzene (NB)	<0.05
2-Nitrotoluene (2-NT)	<0.2
3-Nitrotoluene(3-NT)	<0.2
4-Nitrotoluene(4-NT)	<0.2
1,3-Dinitrobenzene(1,3-DNB)	<0.05
2,6-Dinitrotoluene(2,6-DNT)	<0.01
2,4-Dinitrotoluene(2,4-DNT)	<0.01
2,3-Dinitrotoluene(2,3-DNT)	<0.01
*3,4-Dinitrotoluene(3,4-DNT)	<0.01
1,3,5-Trinitrobenzene(TNB)	<0.1
2,4,6-Trinitrotoluene(TNT)	<0.01
RDX	<1.0
4-Amino 2,6-DNT(4-Amino)	<0.05
3,5-Dinitroanaline(3,5-DNA)	<0.2
2-Amino 4,6-DNT(2-Amino)	<0.05
Tetryl	<0.1

* 3,4-Dinitrotoluene is used as the method surrogate

2.2 Applicable matrices: Whole and dissolved water matrices.

2.3 Dynamic Range: 1-150 *u*g/L without dilution.

3. Safety Issues

Always use proper safety procedures when handling nitroaromatic and nitramine compounds as well as the extraction solvents-toluene and isoamyl acetate. It is essential to read Material Safety Data Sheets (MSDSs) on each compound and solvent prior to performing this method. MSDS's can be found in the safety office for these compounds and solvents.

4. Sample Preservation and Holding Times

Each water sample received for extraction and analysis must be extraction within seven days of collection or four days from receipt at the laboratory. As soon as a sample is received, place it in a dark, explosion-proof refrigerator until it is ready to be extracted.

5. Reagents and Standards

5.1 Reagents: Pestricide grade toluene and methanol

5.2 Standard Types (See SOP for Standard Making for preparation instructions):

Calibration standards-Working standards of the entire group of the individual analytes listed in section 2.1 are prepared at 1,5, 7, 10, 20, 50, 100, 200 pg/*u*l in toluene.

Spiking solutions- The spike solution includes all individual analytes minus 3,4-Dinitrotoluene at around 5000 pg/*u*l in methanol.

Surrogate solution-The surrogate solution contains 3,4-Dinitrotoluene at around 5000 pg/*u*l in methanol.

Third Party Check- The third party check solution is commercially available through Supelco or other vendors and contains Nitrobenzene, 1,3- Dinitrobenzene, 2,4-Dinitrotoluene, and 2,6-Dinitrotoluene at concentrations of 20 pg/*u*l each in toluene. This standard is used to verify the calibration curve for each gc run.

Continuing Calibration Check Solution- The continuing calibration verification solution (CCV) concentration is made at the mid-point calibration range, typically the 20 pg/*u*l standard. A CCV is run every ten samples. It verifies that the initial calibration is still linear.

5.3 Shelf life/Storage requirements: All standards are good for three months from date of preparation. Standards are stored in amber glass vials and kept in an explosion-proof freezer at approximately -10°C to -12°C.

6. QA/QC Requirements

Definitions of Analytical Run Sequence Samples, Acceptance Criteria, and Corrective Action Required

6.1 Wash: An initial injection of clean toluene to determine baseline is stable and instrument is clean.

6.2 Calibration Standards for Nitroaromatic/Nitroamine Individual Analytes: These standards contain NB, 2-NT, 3-NT, 4-NT, 1,3-DNB, 2,6-DNT, 2,4-DNT, 2,3-DNT, 3,4-DNT, TNB, TNT, RDX, 4-Amino, 3,5-DNA, 2-Amino and Tetryl at 1, 5, 7, 10, 20, 50,100 and 200 pg/uL concentrations. The analyst must include the 1, 5, 7, 10, 20, 50 and 100 pg/*u*L standards in every run. It is best to calibrate with a low curve that contains the 1, 5, 7, 10, and 20 pg/*u*L standards, and a high curve that contains the 7, 10, 20, 50 and 100 pg/*u*L standards. To be considered acceptable, the standards must come within 20% of their expected value and the R^2 value for the linear calibration line must be 0.995 or greater. If a standard seems to be nonlinear, see section 7.4.5 for instructions. The minimum number of standards considered acceptable for a curve is four.

6.3 Third Party Check Standard: The third party check standard is purchased premade from a vendor such as Supelco. The solution should contain at least 4 of the Nitroaromatic/Nitroamine analytes at individual concentrations of about 20 pg/*u*L. This solution must fall within +/- 30% of this value. If not, it is up to the analyst to determine the cause and rectify the problem.

6.4 Reagent Blank: A Reagent Blank of distilled water is prepared with each set to monitor potential contamination of the samples during the prep procedure. There must be one Reagent Blank prepared for every set of samples extracted. Reportable analytes should not be detected at or above the reporting level; if there are, a supervisor must be contacted to determine the course of action. Ten microliters of the method surrogate solution is added to each blank. Surrogate recovery in the blank must fall within current control limits, an example of which is given in Appendix A, or a supervisor must be contacted.

6.5 Reagent Spike: A Reagent Spike containing all of the individual nitroaromatic and nitramine analytes is prepared with each set to monitor method

performance. Ten microliters of the method surrogate solution and ten microliters of the method spiking solution is added to the Reagent Spike. There must be at least one Reagent Spike prepared for every set extracted. Surrogate and analyte recovery in the spike must fall within current control limits, an example of which is given in Appendix A, or a supervisor must be contacted to determine the course of action. It is the responsibility of each individual analyst to produce control charts on a monthly basis for surrogate and spike recoveries.

6.6 Samples: Ten microliters of the method surrogate solution is added to each sample prior to extraction. Surrogate recovery is monitored by the analyst and reported to the client as a way of measuring gross method performance. Surrogate recovery must fall within current control limits, an example of which is given in Appendix A, or a supervisor must be contacted to determine the course of action. Sample surrogate recovery should not be the sole criterion for rejecting sample data since individual matrices will occasionally interfere with surrogate recoveries. It is the responsibility of each individual analyst to produce real-time control charts of sample surrogate recoveries monthly.

6.7 CCV: Continuing Calibration Check. This is a mid-range standard (20 pg/*u*l) that is run every 10 samples to monitor analytical performance and reproducibility. Expected values should fall within +/-30% for all analytes. If the CCV exceeds the acceptable range for an analyte on one column but not on the other, it is acceptable to make calls on the column that is acceptable and confirm calls on the one that is not. If, during analysis, a calibration check standard shows any analyte is outside +/-30% of the expected value on both columns, the samples following the last acceptable CCV are suspect. If suspect samples contain detectable amounts of any of the out-of-control analytes, they will need to be rerun for those analytes. If the suspect samples

appear to be blank, and the report threshold can be met, then the samples will not require reruns. Document the action taken on the QC Check sheet (see Appendix A).

7. Procedure:

7.1 Comments:

7.1.1 Interferences: This procedure involves two seperate extrations using two different solvents on seperate-100 ml aliquots of the same sample. The second extraction is performed using isoamyl acetate. Isoamyl acetate must be double distilled prior to extraction to prevent interferences.

7.1.2 Once samples are received by the laboratory, they are logged in and prepared by the method given in secion 7.3.

7.2 Labware

7.2.1 Double Distillation of Isoamyl Acetate-Assemble a distillation apparatus like the one below: (figure 7.2.1)

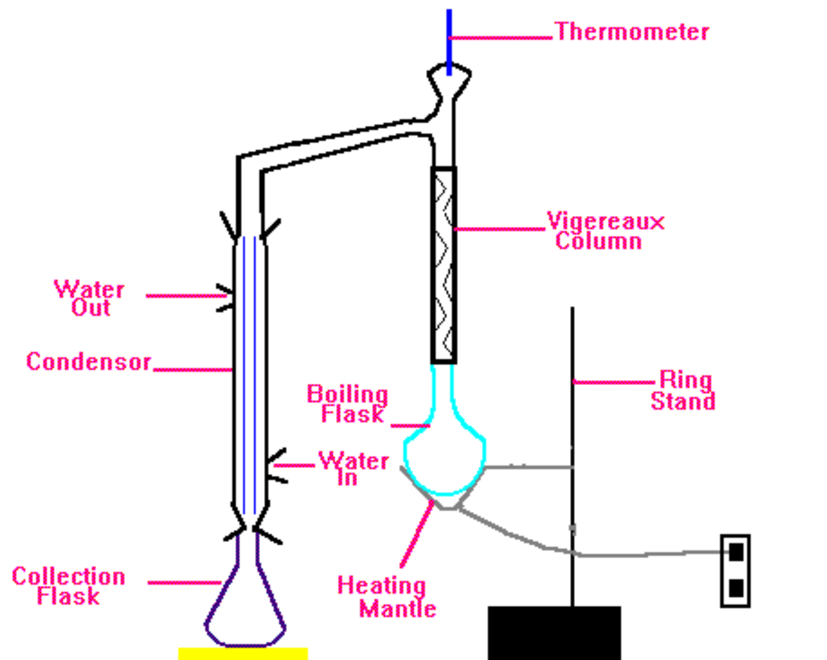

Figure 7.2.1 Distillation Apparatus

Place the undistilled isoamyl acetate in the boiling flask with a couple of boiling chips. Cover the boiling flask and vigereaux column with aluminum foil. Plug-in the heating mantle. Dispose of any solvent collected up to about 95°C. Collect any solvent after the solvent is heated greater than 95°C. When the solvent left in the boiling flask is about 2 mls with a tint of yellow, stop the distillation and discard the remaining solvent. Take the solvent collected and perform the same procedure again. After the second distillation, the solvent is ready to use for extraction.

7.3 Sample Preparation

7.3.1 Toluene Extraction:

Equipment and Consumables

(1) pesticide grade toluene

(2) method surrogate and spike

(3) 10 ul microdispenser

(4) rinse methanol for microdispenser

(5) 100 ml volumetric flasks and caps

(6) 1-inch teflon coated magnetic stir bars (cleaned with alconox detergent, rinsed in acetone, and heated at 260°C for 2 hours.)

(7) magnetic stir plates

(8) deionized water

(9) disposable borosilicate pipets (burned at 480°C for 3 hours)

(10) amber borosilicate vials (burned at 480°C for 3 hours)

Extraction Procedure

(1) Rinse all glassware with toluene and allow to dry completely.

(2) Remove samples from refrigerator and allow them to equillibrate to room temperature.

(3) Mix each sample well and measure 100ml of the sample into a 100ml volumetric flask.

(4) Make a blank by measuring 100ml of deionized water into a 100ml volumetric flask. Prepare a spike the same way.

(5) Carefully add a magnetic stir bar to each volumetric flask. Try to avoid spilling any. Replace with more sample in that case.

NOTE: Stir bars must be burned prior to extraction. They should be burned at 260°C for at least an hour.

(6) Add 10 *u*l of surrogate solution to each sample, blank, and reagent spike.

(7) Add 10 *u*l of spiking solution to reagent spike.

(8) Mix each sample well.

(9) Add, using a volumetric pipet, 1ml exactly of toluene to each sample, blank, and spike.

(10) Place each sample on a magnetic stir plate and extract for 30 minutes. The toluene should be pulled down by the stirring motion in tiny droplets. It should look like the motion of a tornado.

NOTE: Make sure stir bar is stirring in middle of volumetric flask and stirring continuously. Stir bars that spin out of control can break the volumetric flask, losing the sample.

(11) After the 30 minutes, turn off the stir plates and allow the toluene to move back up to the top of the sample. This should take about 15 minutes.

(12) After the toluene has settled, using a disposable pipet, pipet as much as the extract as possible into an amber GC vial without getting any of the water.

NOTE: Sometimes emulsions occur and must be broken. If they cannot be easily broken, pipet the emulsion into a centrifuge tube and centrifuge for 5 minutes. This should break the emulsion.

(13) Sample is ready for GC analysis.

NOTE: Toluene extracts all of the analytes with the exception of RDX. In addition, it extracts all of the analytes with high recoveries in the spike, except 4-amino, 2-amino, and 3,5-DNA. Iso-amyl acetate extracts RDX and provides higher extraciton recoveries of the above mentioned compounds.

7.3.1 Isoamyl Acetate Extraction:

Equipment and Consumables: The equipment and consumables are the same as the toluene extraction with the exception of using the double-distilled isoamyl acetate as the extraction solvent. Also, a new-unextracted aliquot of water is used.

Extraction Procedure-Perform procedure exactly like the toluene extraction, except extract, using isoamyl acetate, a new aliquot of sample.

7.4 Analyzing of Samples:

7.4.1 After the sample preparation is finished for the sample set, choose the next set to be analyzed by either picking the oldest set or by picking the set with the highest priority.

NOTE: The toluene extracts are run on a different instrument than the isoamyl extracts. The toluene extracts are run on a GC equipped with two 30-m columns, while the isoamyl extracts are run on one equipped with two 15-m columns. This is due to the fact that RDX does not chromatograph well on longer columns and will only be seen on the shorter ones. However, if the analysts knows that there will be no RDX in the sample, both fractions can be run on the same instrument with the longer columns.

7.4.2 Next, write the analytical sequence in Turbochrom (See SOP on Turbochrom Operation) in the order given using sample weights, dilution factors and final volumes indicated on the paperwork. Two sequences need to be created: one for the toluene extracts and one for the isoamyl extracts.

Sample Analytical Run Sequence:

1 Wash

2 Third-Party Check

3 Calibration Standard #1 (1 pg/*u*l)

4 Calibration Standard #2 (5 pg/*u*l)

5 Calibration Standard #3 (7 pg/*u*l)

6 Calibration Standard #4 (10 pg/*u*l)

7 Calibration Standard #5 (20 pg/*u*l)

8 Calibration Standard #6 (50 pg/*u*l)

9 Calibration Standard #7 (100 pg/*u*l)

10 Calibration Standard #8 (200 pg/*u*l)

11 Reagent Blank

12 Reagent Spike

13 Sample #1

14 Sample #2

15 Sample #3

16 Sample #4

17 Sample #5

18 Sample #6

19 Sample #7

20 Sample #8

21 CCV

22 Wash

7.4.3 Once the sequence(s) is created in Turbochrom, load a GC autosample tray with the corresponding sample and standard vials as given in the sequence. Check the volumes of the sample extracts. If evaporation has ocurred, use the appropriate solvent to bring the volume up to the line marked on the vial.

7.4.4 Replace the septum and liner in the GC and check all gas flows as specified in the SOP on GC Maintenance and Operation. Start the GC running the analytical sequence as described in the SOP on Turbochrom Operation.

7.4.5 Once the Standards for the Nitroaromatic and Nitroamine analytes have been run, update the retention times in the sample table if needed (See Turbochrom Operation SOP). Check to see if the standard curve is acceptable as previously defined (Section 6.2). If the standard curve is not acceptable, look at the curve to see if one standard or a single injection has affected the curve. As a general rule, a bad calibration

point is not automatically removed from the curve to achieve an acceptable R^2. The analyst must first determine what caused the errant calibration point, such as a bad injection or a poorly sealed vial. If every indication shows that the GC-ECD is operating properly, the bad calibration point was caused by a one-time problem such as poor vial sealing and there are at least four remaining points, then the point may be dropped from the calibration curve. Document on the QC check sheet the removal of any standards from the curve. If multiple points are bad, it is not acceptable to drop more than one point. The emergence of more than one bad point most likely indicates a systemic error that necessitates more investigation. The samples will need to be rerun after the problem is found and remedied.

7.4.6 Examine the Reagent Blank chromatograms. If there is an indication of blank contamination, contact the supervisor (see Section 6.4). Record the surrogate recovery.

7.4.7 Examine the Reagent Spike chromatograms. Record the individual analyte and the surrogate recoveries.

7.4.8 Run the rest of the analytical sequence. Look at the CCVs. If they meet the acceptable limits given in Section 6.6, analyze the samples. If not, take the action described and process all sample data that do not require reinjection.

7.4.9 To process the sample data, first get the prep sheet for the selected sample and confirm that the sample weight and sample number matches the ASR form. Next, process the sample data taking the precautions outlined in Section 7.7, or justify each peak that is not a call using the acronym suggested in that section. Record the surrogate values from the sample on the Final Report Sheet (See Appendix B) for the sample along with all properly confirmed calls.

7.4.10 Fill out the QC Check Sheet for the set (See Appendix A). Record as much information as possible on the QC check sheet for present and future reference.

7.4.11 File the hard copies of the Method, Sequence, CCVs, Samples, Reagent Blanks, Reagent Spikes and the QC Check Sheet in an expanding folder as described in Section 8.6. Put a copy of the sequence along with any notes on machine maintenance in the Instrument Logbook.

7.4.12 Have the packet checked by a peer analyst and have this analyst initial the appropriate boxes in the QC Check Sheet after review.

7.4.13 Fill out a spreadsheet (Appendix C) with all results from the samples in the set. Then create a custom letter to accompany the spreadsheet (Appendix D). Give both to the Organics secretary to be mailed to the district.

7.4.14 Fill out a D-M form for the samples (Appendix E) and submit to ADP, so that the samples are removed from the backlog.

7.4.15 Copy the electronic files from the PC hard-drive to the file server ("O" or "Organics Drive" to be saved to tape). Once confirmation is received that the files have been saved to mag. tape on two occasions, delete the file from the "O" Drive.

7.5 Instrumentation

7.5.1 Initial Start-up:

Not Applicable

7.5.2 Calibration and Performance Documentation:

See Section 6

7.5.3 Example Output:

See Appendix F for example Chromatogram Report Sheets and example Chromatograms for both channels.

7.5.4 Shut-down:

Not Applicable

7.5.5 Maintenance, maintenance records, and responsibilities:

All maintenance performed on the instrument will be logged in detail in the Instrument Logbook.

For explanation of maintenance to be performed, see the SOP of GC Maintenance

7.5.6 Apparatus:

Hewlett Packard 5890 or Perkin Elmer Autosystem dual capillary column gas chromatograph with dual electron capture detectors (or equivalent). The two columns are connected via a "Y" splitter and a 5 meter, 0.53 mm uncoated guard column with a 0.32 mm ID.

Toluene Extract Instrument

Column A: 30-m/0.25 mm ID, 95% dimethyl-5% diphenyl polysiloxane (Rtx-5) Restek, or equvalent.

Column B: 30-m/0.25 mm ID, 14% cyanopropyl-86% methyl polysiloxane (Rtx-1701) Restek, or equivalent.

Iso-Amyl Extract Instrument

Column A: 15-m/.25 mm ID, 100% dimethylpolysiloxane (Rtx-1) Restek, or equvalent.

Column B: 15-m/.25 mm ID, 95% dimethyl-5% diphenyl polysiloxane (Rtx-5) Restek, or equivalent.

Liners: A Perkin Elmer Cyclo-liner or HP Deactivated 4 mm liners, or equivalent.

7.5.7 Oven Temperature Program (See SOP on Turbochrom Operation to describe how to set the software to run the oven temperature program):

NOTE: All Rates are in Degrees Celsius per Minute, All Temperatures are in Degrees Celsius, All Times are in Minutes

Toluene Fraction Instrument

Initial Temperature: 60

Initial Hold Time: 0

Rate Temp Hold

Ramp 1	20.0	140	0.0
Ramp 2	5.0	230	13.0
Ramp 3	10.0	250	0.0

Run time: 37 minutes

Iso-Amyl Fraction Instrument

Initial Temperature: 60

Initial Hold Time: 0

	Rate	Temp	Hold
Ramp 1	5.0	140	5.0
Ramp 2	5.0	230	10.0

Run time: 49 minutes

7.6 Calculations:

7.6.1 Calculation of Sample Concentrations (See U.S.G.S. OFR Report,82-1004):

Response Factor:

RF = A/C x V

RF = Response Factor

A = Integrated peak area of identified component in the Calibration Standard, in area

C = Concentration of the Standard, in pg/ul

V = Volume of Standard injected, in ul

Sample Concentration (ug/l)

SC = A x FV x D/ I x W x RF

SC = Sample Concentration

A = Integrated Peak Area of identified Sample Component

FV = Final volume of Sample Extract, in ml

I = Volume of Sample Extract Injected, in ul

W = Volume of sample in ml

D = Dilution Factor

7.7 Data Analysis (Evaluation):

7.7.1 Look at each fraction separately for every compound. By the end of processing, every compound must be identified on the chromatogram report sheet as a call by circling it, or have an acronym written next to it that explains why it is not a call.

Acronym :

NT - Not a Target Compound

NC - Not Confirmed on Other Channel

BRL - Below Reporting Limit

WRT - Wrong Retention Time

WF - Wrong Fraction

RRL - Raise Reporting Limit (Specify new Reporting Limit)

Transfer all values from the chromatogram report sheets to the Final Report Form. If the amount is at or above the reporting limit and below the dilution threshold, report a call.

Also, correct baseline integrations as necessary using the technique given in the Turbochrom Operation SOP.

7.7.2 If the analyst makes a positive identification of a compound that is confirmed on both channels, but the compound is below the detection limit, they have the option of reporting a "Trace" on the spreadsheet that goes to this district. The Trace call is more of a side note for the benefit of the District who receives the hardcopy.

7.7.3 Dilutions: If a compound has a raw amount (concentration before the dilution factor is taken into account) of greater than the high standard it must be diluted and reshot. Estimate a dilution factor that will bring the sample's raw amount into the mid-range of the standard curve.

7.7.4 Coelutions: Some compounds will show irreproducible calibrations due to coelutions on one column, but not the other. In this case, make the call on the quantifiable channel and confirm on the coeluting one.

7.8 Data Packet Organization:

All data is to be organized in an accordion file wallet that should be labeled with the date the GC first began acquiring data written in the left hand corner, "NA Waters" written in the center, and the "packet number" written in the right hand corner. The packet number includes the instrument identification letter followed by the current year and the sequential packet number and should correlate with the Turbochrom file number (See Turbochrom Operation SOP, part 6.7.1). An example of a packet number is S95001; where S is the instrument S, 95 is the year the file was acquired, and 001 is the first packet. In addition, a copy of the run sequence should be glued or taped to the front of this folder. This wallet should then be subdivided with five manila file folders labeled as given and containing the following:

Sequence and Method: This folder should contain a copy of the sequence, copies of all of the instrument methods as well as calibration reports for both channels (SeeTurbochrom Operation SOP for how to produce these reports in Turbochrom).

Retention Times: This folder should contain the Retention Time Summaries for both channels (See Turbochrom Operation SOP for how to produce these reports in Turbochrom).

Standards: This folder should contain the QC Check Sheet , the GC report sheets and GC chromatograms for each of the standards.

Blanks and Spikes: This folder should contain the final report sheets (Appendix B), GC reports sheets, GC chromatograms as well as the ASR sheets for the Blanks and Spikes.

Samples: This folder should contain the final report sheets, GC report sheets, GC chromatograms as well as the ASR sheets for the Samples.

7.9 Data Review:

All data must be thoroughly reviewed by an experienced analyst before it is submitted to the District. The reviewing analyst must review the analyses of the samples to ensure no analyst oversights. The reviewer must check the samples for transcription errors that may exist on the final report sheet. Also, after thoroughly reviewing the samples, the reviewer must initial the sample's final report sheet. Finally, the reviewer must review and initial each point on the QC Check sheet after checking to ensure high quality data.

7.10 Reporting:

7.10.1 Reporting units

Micrograms per Liter (ug/L)-Used for Analyte Values

Percent recovery used for spike and surrogate recoveries

7.10.2 Reporting level - see MDL (Appendix G)

7.10.3 Significant figures - Follow U.S.G.S. NWQL protocol for reporting significant figures.

7.10.4 Deletion Reporting Codes

D-U Deleted - Due to Interference

D-R Deleted - Sample Ruined

7.10.5 The final report sheet for the Samples, Reagent Blanks, and Reagent Spikes is filled out by the analyst, reviewed and signed by a qualified reviewer, and sent (hard copy) to the district.

8. Archiving:

Sample extracts are held for a minimum of 90 days after results are sent to district. Data packets with final report sheets are held indefinitely at this point in the warehouse. Electronic copies of the raw data is archived onto DAT tapes and kept on file with the Computer Services Unit.

9. References

9.1 U.S.G.S. SOPs Referenced:

SOP for NWQL Standard Operating Procedures, SOP Team, 1994, SOP #QX0001.0

SOP for the Analysis of Organochlorine Compounds in Sediment (Schedule 1325), Dawn Hrinko, 1994, no SOP number.

SOP on Naming, Documenting and Verifying Standards, author unknown, no SOP number.

SOP on the Preservation of Water and Sediment Samples submitted for Organic Analysis, Jeff Stewart, 1994, SOP #OM0017.0.

SOP of Data Reporting and Worksheets, author unknown, no SOP number.

SOP of Organic Standards Preparation, Dennis Markovchick, 1994, no SOP number.

SOP of Turbochrom Operation, Leslie Merten , 1994, no SOP number.

SOP for GC Maintenance and Operation, Max Stroppel, 1994, no SOP number.

9.2 Additional References:

Standard Operating Procedure-Analysis of Nitroaromatics in Ground and Drinking Water, 1989, DOE and AEHA.

The Determination of Nitroaromatics and Nitramines in Ground and Drinking Water by Wide-Bore Capillary Gas Chromatography, U.S. Army Environmental Hygiene Agency, Organic Environmental Chemistry Division, Aberdeen Proving Ground, Maryland.

St. Louis Laboratory Standard Operating Procedure-Extraction and Analysis of Nitroaromatic and Nitramine Explosives by GC/ECD, 1994.

10. Key Words:

Gas Chromatograph, GC Vials, Turbochrom

SAMPLE PREPARATION OF NITROAMINES AND NITROAROMATICS IN SEDIMENT

Log-In

- Match the sample(s) to its Analytical Services Request form(s) and fill out a data sheet.
- Decant the excess water from each sample and dispose of it in the non-chlorinated waste stream.
- Place the samples in the sample storage refrigerator (4ºC ± 2º).

Pre-extraction Preparation

- Retrieve the samples from the refrigerator and allow them to equilibrate to room temperature.
- Assemble the paperwork for all the samples and create a database record for the set adding a set blank and spike.
- Rinse a spatula and two centrifuge bottles/cap assemblies for each sample with acetone and allow to dry. In addition, rinse two extra centrifuge bottles/cap assemblies for the blank and spike with acetone and allow to dry.
- Mix and homogenize each sample with a different rinsed spatula.
- Zero a balance. Place a bottle and cap assembly on the scale and transfer the sample from shipping container to the centrifuge bottle until a gross weight of 80-grams(g) is reached.
- Centrifuge 4 bottles together for 20 minutes @ 35%.
- Decant the excess water from each sample and dispose of it in the non-chlorinated waste stream.
- Again mix and homogenize each sample with its corresponding spatula.
- Remove a 1.8 to 2.2-g sample for determining the percent dry weight. This is calculated automatically by the drying balance. Record this number on the sample data sheet.
- Determine the wet weight needed for this sample by dividing 20-g by the percent dry weight. Record this number on the sample data sheet.

Extraction

- Tare the other rinsed centrifuge bottle.
- Weight out the appropriate sample wet weight. Record the weight on the sample data sheet.
- Tare scale and add 20-g of burned reagent grade sodium sulfate. Mix thoroughly. Add more sodium sulfate, if needed, until mixture is dry and loose. Record the total weight of the sodium sulfate added on the sample data sheet.
- Create a set blank and spike by adding 40-g of burned reagent grade sodium sulfate to two labeled rinsed centrifuge bottles.
- Dispense 10-μL (5000 pg/μL) of surrogate to all samples, blank, and spike using a 10-μL micro dispenser and baked glass bore. Note: Allow surrogate to come to room temperature before dispensing into samples. Vortex mixture thoroughly before using.
- Dispense 10-μL (5000 pg/μL) spike mixture to set spike only using a 10-μL micro dispenser and baked glass bore. Note: Allow spike mixture to come to room temperature before dispensing into samples. Vortex mixture thoroughly before using.
- Record the identification number and amount of spike and/or surrogate added on the sample data sheet.
- Soak each sample, blank, and spike with two or three milliliters of methanol and recap. Allow 20 minutes for the methanol to percolate through the sample.
- Add 50-mL of a 70% water / 30% acetone mixture.
- Recap and shake for 2 minutes each, venting often.
- Centrifuge sample @ 35% for 20 minutes. Let stand 30 minutes to equilibrate.
- Decant the extract into a rinsed graduated cylinder and record the volume on the sample data sheet.

Filter

- Rinse a 5-mL gas-tight glass syringe with acetone.
- Attach a 1-uM polytetrafluoroethylene (PTFE) membrane filter to the gas-tight syringe. Then attach a 0.2-uM PTFE membrane filter to the 1-uM PTFE membrane filter (i.e. piggybacked filters).
- Place this apparatus on a stand suitable to hold the syringe/filter setup.

- Transfer the centrifuged extract into the syringe barrel with a Pasteur pipette, being careful not to dislodge any centrifuged solids or to spill any liquid sample.
- Place the filter tip over a rinsed and labeled 100-mL volumetric flask and carefully insert the syringe plunger.
- Pass the extract through the filter.
- Using a Pasteur pipette, rinse down the sides of the graduated cylinder with 3-mL of the 70% water / 30% acetone mixture.
- Transfer the rinse to the syringe.
- Filter the rinse into the flask and repeat a second time.
- Bring to volume with reagent grade water.
- Carefully add a magnetic stir bar to each volumetric flask. NOTE: Use only disposable stir bars due to 2,4,6-trinitrotoluene absorption onto PTFE surface.
- Using a volumetric pipette, add exactly 1-mL of reagent grade toluene to each sample, blank, and spike.
- Place each sample on a magnetic stir plate and extract for 30 minutes. NOTE: The toluene should be pulled down by the stirring motion in tiny droplets. It should look like the motion of a tornado. Make sure stir bar is continuously stirring in the middle of volumetric flask.
- After the 30 minutes, turn off the stir plates and allow the toluene to move back up to the top of the sample. This should take about 15 minutes.

Vialing

- After the toluene has settled, use a disposable Pasteur pipette to transfer as much of the toluene fraction (top layer) into a correspondingly labeled vial (with insert) as possible. Record on the data sheet if an emulsion was present. NOTE: Avoid getting any of the water fraction (bottom layer) into the vial insert. Sometimes emulsions occur and must be broken. If they cannot be easily broken, pipette the emulsion into a centrifuge tube and centrifuge for 5 minutes. This should break the emulsion.
- Tightly cap the vial. NOTE: Always hold the vial so the insert does not fall out if the insert breaks the bottom of the vial.
- After all the samples are vialed, label the tray with the set number and schedule. Place this rack in the sample extract refrigerator (4ºC ± 2º).
- Ensure that all laboratory paperwork concerning this set is filled out. Complete any database entries and place the paperwork in the appropriate analysts' bin.

Further Enhancements

- A iso-amyl acetate extraction that will recover cyclotrimethylenetrinitramine (RDX) and provide higher extraction recoveries of 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, and 3,5-dinitroanaline.
- A sample clean-up step that will remove chromatographic interferences.

Analyzing

- Performed exactly as the water method using 30 meter RTX-1 and RTX-5 columns with electron capture detectors. See SOP OMOO71.O Section 7.4.

NITROAMINES AND NITROAROMATICS IN SEDIMENT

Sample Preparation

Centrifuge the sample matrix and decant as much standing water as possible. Remove any large rocks or debris from the sample matrix and homogenize. After a moisture determination of the sample matrix, place 20 g., dry weight, of the sample matrix into another centrifuge bottle. Add 20-g. of burned reagent grade sodium sulfate to the centrifuge bottle. Thoroughly blend together the sample matrix and sodium sulfate. Repeat the process until the sample mixture is dry and loose. Surrogate the sample mixture with 10-μL's of a 5000-ρg/μL solution containing 3,4-dinitrotoluene. Dispense two or three milliliters of methanol onto the sample mixture and allow it time to percolate. Dispense 50-mL of a 70% water/30% acetone solution into the centrifuge bottle and shake it for 2 minutes, venting frequently. Centrifuge the sample mixture for 20 minutes and let it equilibrate undisturbed for 30 minutes. Decant the sample extract into a graduated cylinder. Filter the sample extract through a 0.2-μm polytetrafluoroethylene (PTFE) membrane filter into a 100-mL volumetric flask. Bring the flask to volume with reagent grade water. Add precisly one milliliter of toluene and a magnetic stir bar to the flask. Vortex the flask on a magnetic stir plate for 30 minutes and let it equilibrate undisturbed for 15 minutes. Remove the toluene or top layer in the flask containing the analytes of interest with a pipette and put it into a GC vial. The processed sample matrix is now ready for analysis. Future enhancements to this extraction method may include an iso-amyl acetate fraction to recover cyclotrimethylenetrinitramine (RDX) and to provide higher extraction recoveries of 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, and 3,5-dinitroanaline. Additionally, a sample clean-up procedure may be implemented to remove some chromatographic interferences.

Sample Analysis

Performed exactly as the water method, 8371, using 30 meter RTX-1 and RTX-5 columns with electron-capture detectors. See SOP OMOO71.O Section 7.4.