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ION-PAIRING RP-HPLC METHOD FOR DETERMINING TETRAZENE IN WATER AND SOIL

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ABSTRACT

Ion-pairing reversed phase-high performance liquid chromatography methods were developed to determine tetrazene in water and soil. Determinations were achieved using an LC-18 column, a mobile phase of 2/3 v/v methanol-water containing 0.01 M 1-decanesulfonic acid sodium salt, and a UV detector set at 280 nm. The pH of the mobile phase was adjusted to 3 with glacial acetic acid, which was optimal for separation of tetrazene from potential interferences by other explosives. The retention time for tetrazene was 2.8 minutes.

A linear model with zero intercept was found to adequately describe the calibration data for concentration ranges of 6.1 to 122 μg/L for water samples and 0.204 to 40.8 μg/g for soil samples. Method accuracy was 100% for most water samples and varied from 68-88% for soil samples. Reporting limits of 3.04 μg/L and 1.10 μg/g were estimated for water and soil, respectively.

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Water samples are analyzed directly without pretreatment or preconcentration. Soils are extracted on a platform, orbital shaker with 55/45 v/v methanol-water containing 0.01 M 1-decanesulfonic acid sodium salt.

Tetrazene was found to be unstable in an aqueous medium at room temperature. Concentrations decreased by 96-100% over 24 hours. The rate of degradation was reduced significantly when solutions were maintained near 0°C.

INTRODUCTION

Tetrazene is an initiating explosive used as a component of primer mixes and caps. Although contamination of water and soil with this compound is of environmental concern at a number of Army installations, no analytical protocol has been developed to determine tetrazene in water at levels of less than 500 μg/L, and no methods exist for tetrazene in soil. The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) asked the Cold Regions Research and Engineering Laboratory to develop methods for the determination of tetrazene in water and soil with reporting limits at or below 10 μg/L for water and 19 μg/g for soil.

Most of the published analytical methods for tetrazene were developed for product quality control of primer mixes or caps since these mixtures must contain 2-8% tetrazene by weight to be activated by friction or impact. Published quantitative methods

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for the determination of tetrazene in primer mixes include polarographic[1,2,3,4,5,6], spectrophotometric[7,8], and thermoanalytical[9] protocols. Only one technique has been developed for the determination of tetrazene in an aqueous medium such as ground water.[10] This method uses colorimetry to determine tetrazene at concentrations above 500 μg/L. No chromatographic methods for the determination of tetrazene were found in the literature. Analysis by gas chromatography is prohibited by the thermal instability of tetrazene, and analysis by liquid chromatography is complicated by the limited solubility of tetrazene in water or common organic solvents.

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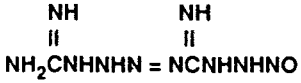
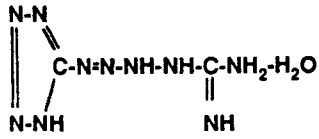
Chemistry of Tetrazene

In 1910 Hofmann and coworkers[11] treated aminoguanidium nitrate with sodium nitrite in neutral solution and isolated a white crystalline solid later named tetrazene (CAS REG No 31330-63-9, tetrazene-1-carboxamidine-4-(1H-tetrazol-5-yl) monohydrate). The physical constants of tetrazene are presented in Table 1. The structure of the compound was considered to be



until 1954, when Patinkin et al.[11] proposed the following structure based on the results of degradative studies:



Tetrazene dissolves readily in formic acid[4,8], concentrated hydrochloric acid[1,3], 4N sulphuric acid[2], and cold 16% nitric acid[5]. Preliminary tests conducted during this study indicated that tetrazene is practically insoluble in acetonitrile and tetrahydrofuran and is insoluble in acetone. Solubility in methanol was estimated by this laboratory to be 240 mg/L.

TABLE 1.
Physical Constants of Tetrazene.

Empirical formula	$C_2H_8N_{10}O$*
Molecular weight	188.2*
Crystal density (g/cm^3)	1.7*
Energy of formation	+1130 kJ/kg*
Enthalpy of formation	+1005 kJ/kg*
Melting point	140-160°C (explodes)*
Solubility (mg/L)	
Water	4.5†
Methanol	240†
Tetrahydrofuran	2†
Acetone	<d†

* Reference 13
† Estimated by CRREL.

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Tetrazene is thermally unstable. This poor thermal stability leads to loss of activity with time as a sensitizer in primer caps[1,12,14]. Tetrazene in aqueous solution decomposes completely upon boiling; for each mole of tetrazene hydrolyzed by boiling in water, 1.5 to 2.0 moles of nitrogen are produced along with ammonia, guanidine 1-H-tetrazole, and 5-aminotetrazole[15]. Solutions used as analytical standards are also known to decompose at room temperature[2].

EXPERIMENTAL

Instrumention

RP-HPLC determinations were conducted on a Perkin-Elmer series 3/LC65T High-Performance Liquid Chromatograph equipped with a variable-wavelength UV detector set at 280 nm and a Rheodyne 7125 sample loop injector. A 100-μL sample loop was overfilled by passing 500 μL of sample through it; the sample was then injected onto an analytical column. For the instrument calibration and the spike recovery study, an LC-18 (Supelco, Inc.) column was eluted with 1.5 mL/min of a solvent consisting of 2/3 v/v methanol-water containing 0.01 molar 1-decanesulfonic acid sodium salt. The pH of this mobile phase was adjusted to about 3 by adding 4 mL glacial acetic acid to each liter of eluent for the analysis of water samples and 8 mL to each liter for analysis of soil extracts. The mobile phase was chosen to minimize interferences from peaks observed in natural waters and to elute potential co-contaminants in a reasonable period of time.

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Chemicals

Analytical standards for tetrazene were prepared from Standard Analytical Reference Materials (SARM) obtained from USATHAMA, Aberdeen Proving Ground, Maryland. Standards were dried in the dark to constant weight over dry calcium chloride in a vacuum desiccator. The methanol used to prepare tetrazene standards and the mobile phase for HPLC analysis was either Mallinckrodt ChromAR HPLC or Baker HPLC grade. The ion pairing reagent for HPLC was 1-decanesulfonic acid, sodium salt (98%) obtained from Aldrich. Glacial acetic acid was Mallinckrodt (99.5%). Water used for spike recovery, dilution of standards, and preparation of the mobile phase was purified by a MilliQ Type I Reagent-Grade Water System (Millipore). The mobile phase was vacuum filtered through a Whatman CF-F microfiber filter to remove particulates and degas the eluent. Two soils were obtained from USATHAMA: a standard blank soil and a tetrazene-spiked Minneapolis soil. Other blank

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TABLE 2.
Soil Properties.

Soil	Clay (%)	Total organic carbon (%)	pH
USATHAMA standard soil	53.6	1.45	6.4
Fort Edwards clay 1	100	0.52	8.4
Lebanon landfill	11.3	0.3	6.2
Manchester sand	0	0.3	5.5

soils used included Fort Edwards clay, Lebanon (New Hampshire) landfill, and Manchester (New Hampshire) sand (Table 2).

Optimum Detector Wavelength

The optimum wavelength setting on the variable UV detector was determined by repeated analysis of the same tetrazene solution at settings ranging from 240 to 305 nm in increments of 5 nm. Maximum response was in the region of 280-285 nm. Since 280-nm fixed-wavelength detectors are commercially available, 280 nm was selected for this analysis.

Calibration Standards

Analytical stock standards of tetrazene were prepared by dissolving approximately 20 mg of dried SARM in 200 mL of methanol by stirring for 60 minutes at 0°C. To test the linearity of instrument response with respect to analyte concentration, a series of intermediate standards were prepared by diluting the stock to the concentration range of interest in methanol. Prior to analysis each standard was further diluted in chilled water.

Spiking of Soil Samples

Two methods for spiking soils were used. First, the Minneapolis soil was spiked by mixing 1.8 g of dry tetrazene with 639 g of undried soil and aging it for six months. The soil thus contained 2.8 μg/g tetrazene, assuming thorough homogenization.

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However, complete homogenization of a soil-analyte mixture is nearly impossible. Since we wished to spike soil at the low μg/g level, another spiking method was also used. A spike stock solution was made by dissolving dry tetrazene in methanol. This stock was then diluted such that 1 mL aliquots added to 2-g of soil yielded concentrations in the range of 1.0 to 50 μg/g. Several soils were spiked with tetrazene-methanol solutions, and each sample was aged uncapped for 1 hr prior to extraction to allow the methanol to evaporate.

Extraction Kinetics for Soil Samples

Experiments were conducted to determine the time required to attain maximum analyte recovery from spiked soil samples. Two spiked soils were studied. Two-gram subsamples of the spiked Minneapolis soil obtained from USATHAMA were weighed into individual 125-mL Erlenmeyer flasks equipped with ground glass stoppers. Two-gram subsamples of USATHAMA Standard blank soil were weighed out in a like manner, then 1 mL of a tetrazene-methanol spike solution was added to each sample to yield a target concentration of 25.6 μg/g. The samples were allowed to stand 1 hr uncapped to allow evaporation of the methanol, then 50 mL of extracting solvent were added. The samples were vortexed for 15 s and shaken at 200 rpm on a platform orbital shaker. Aliquots of the extract were removed for analysis at time intervals ranging from 0 to 75.5 hr. Extractions were performed at 0 and 22°C.

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Initial kinetic studies used methanol as the extracting solvent but this was later changed to 55/45 v/v methanol-water with 1-decanesulfonic acid, sodium salt at a 0.01 M concentration. The mixed solvent, in general, resulted in higher recoveries from a variety of spiked soil samples.[16]

Precision and Accuracy

To assess the effect of matrix variability on method precision and accuracy, six replicates of different natural water and soil samples (Table 2) were spiked with tetrazene-methanol solutions. The target concentrations for the water and soil samples were 99.4 μg/L and 25.6 μg/g, respectively. The analytical precision was estimated by the standard deviation for each set of samples. The method accuracy was calculated by dividing the found concentrations for each set of samples by the target concentration and multiplying by 100.

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Spike Recovery Studies

Reporting limits were obtained using the procedure developed by Hubaux and Vos.[17] Spiked samples were prepared by adding a known amount of analyte, using a series of spiking solutions, to a known quantity of either water or soil. Duplicate samples were spiked on each of four consecutive days over the concentration range of 0 to 10 times the estimated reporting limit. The spike levels were 0 to 145 μg/L and 0 to 25.6 μg/g for water and soil,

respectively. After 1 hr equilibration time, water samples were filtered through 0.45 μm Millex HV filter units and analyzed. Soil samples were extracted by adding a 50-mL aliquot of a solution containing 55/45 v/v methanol-water with 1-decanesulfonic acid, sodium salt at a 0.01 M concentration level, vortexing for 15 s and shaking for 1.5 hr. Soil extracts were filtered through 0.5 μm Millex SR filter units, chilled, and analyzed.

RESULTS AND DISCUSSION

Eluent Selection

Several eluents were tested on an LC-18 column. When the mobile phase consisted of a combination of water and an organic solvent such as methanol, tetrazene eluted too rapidly for accurate peak area measurements. Elution with 100% water produced a tetrazene retention time of 6.3 min. However, HMX and RDX had retention times of 31.5 and 47 min, respectively. The very long run times for samples where these components were present would be unacceptable. Ideally, the column-eluent combination should elute tetrazene without interference and elute other potential contaminants within a reasonable run time. While gradient elution could minimize this problem, equilibration time between runs would significantly decrease daily sample throughput, and not all HPLC systems are equipped to do gradient elution.

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Thus, an ion-pairing technique was tested to determine if the retention time of tetrazene could be increased with a methanol-water eluent that would shorten overall run times. The ion-pairing reagent selected was 1-decanesulfonic acid, sodium salt at an eluent concentration of 0.01 M. The pH of the mobile phase was adjusted with glacial acetic acid to ensure complete ionization of tetrazene. The required amounts of glacial acetic acid were 4 mL/L of eluent for water analysis and 8 mL/L for soil analysis. Retention time for tetrazene was 2.8 minutes using an eluent composed of 2/3 v/v methanol-water containing 0.01 molar ion-pairing reagent at pH 3. Retention times for HMX, RDX, and TNT were 3.6, 6.0, and 12.9 min, respectively. Figure 1 shows a typical chromatogram for these analytical conditions.

The tetrazene retention time can be adjusted to suit the needs of a particular analytical situation by changing the ratio of methanol to water and by adjusting the amount of acid.

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Stability Study

In the initial phase of this study, we observed that solutions of tetrazene in water or methanol were unstable over time. Before quantitative analyses could be performed, calibration standards and aqueous samples had to be stabilized. Two saturated test solutions of tetrazene were prepared, one in water and the other in methanol. The solutions were diluted, vacuum-filtered through a 0.45 μm Nylon-66 Supelco filter membrane, and maintained

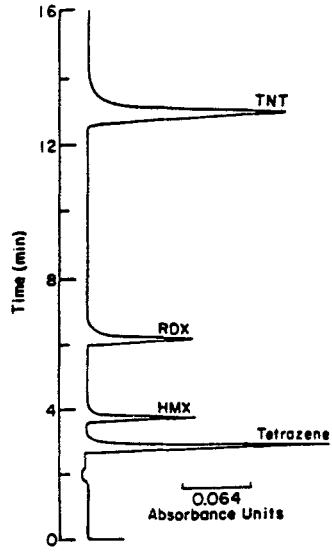

FIGURE 1
Typical chromatogram showing separation of tetrazene from other explosives.

at 4°C. Aliquots of each of these solutions were analyzed over 4 days. On two of the days, subsamples of each solution were allowed to warm to room temperature. These subsamples were analyzed along with the the chilled solutions over a 24-hr period.

Degradation was slowed by keeping the solutions at 4°C. The detector response during 24 hr decreased by only 3% for the chilled aqueous samples as opposed to 96-100% for the room- temperature samples (Figure 2a). Degradation of tetrazene was slower in methanol than in the aqueous solutions. Response declined by 1% and 55% for the chilled and room-temperature methanol samples, respectively, in a 24-hr period (Figure 2b).

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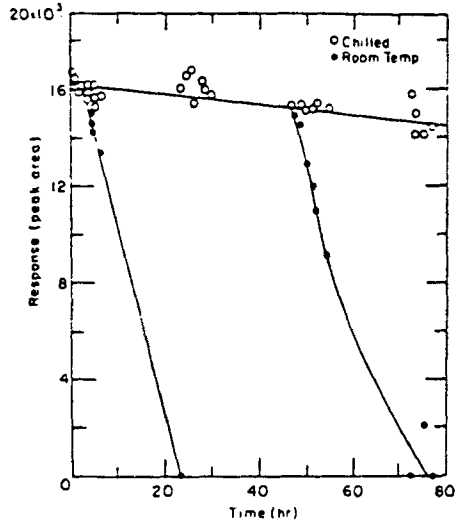
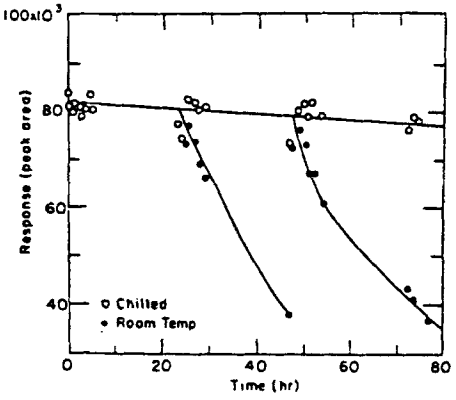


a. Tetrazene in water.



b. Tetrazene in methanol.

FIGURE 2
Effect of temperature on the stability of tetrazene solutions.

Instrument Calibration

To determine if the detector response was a linear function of analyte concentration, calibration data were subjected to regression analysis for a nonzero intercept linear model ($y = a + bx$) and a zero intercept model ($y = bx$). Regression coefficients a and b were estimated using the method of least squares.

The fitted equations for both models were subjected to the Lack of Fit (LOF) test.[18] A linear model was found to be acceptable at the 0.05 significance level. The intercept was then tested to determine if it was significantly different from zero. The F-ratio was calculated by dividing the difference between the residual sum of squares for the nonzero and zero intercept models by the residual mean square for the model with nonzero intercept. Since the calculated F-ratio was less than the critical value at the 0.05 significance level, the zero intercept linear model was accepted. Thus, daily calibration can be obtained using a zero intercept model.

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Kinetic Studies

Initially, kinetic studies were conducted to determine the length of contact time required for maximum recovery of analyte. Methanol was used as the extracting solvent. Since previous experience[16] has indicated that tetrazene is unstable in solution at room temperature, all samples were kept cold throughout the extraction procedure. Two-gram subsamples of the spiked Minneapo-

lis soil obtained from USATHAMA (target concentration = 2.8 mg/g) were extracted with methanol by shaking at 0°C for 75.5 hr. Samples of the extract were removed and analyzed at 5 min, 1, 4, 6, 24, 30, 48, and 75.5 hr. Results are presented in Figure 3. Maximum concentration was achieved rapidly, between 0 and 4 hr, followed by a decrease in concentration. The maximum found concentration was above that of the target concentration, probably due to incomplete homogenization of the soil-tetrazene mixture.

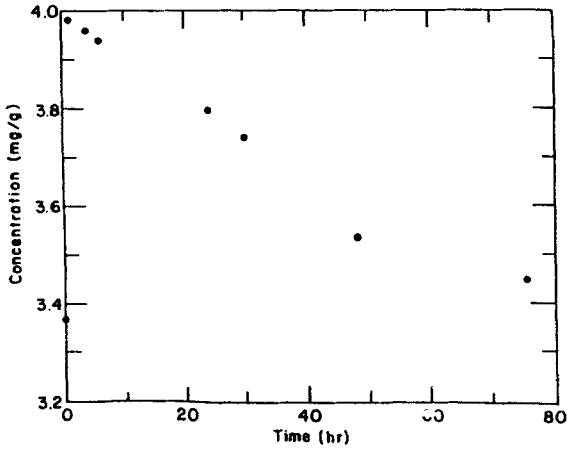

FIGURE 3
Kinetic study using Minneapolis soil and methanol.

A second kinetic study, again using the Minneapolis soil and methanol, was performed over a 2-hr time period with aliquots removed at 5, 15, 30, 60 and 120 min. In addition to the samples shaken at 0°C, a duplicate set was shaken at room temperature. Results are presented in Figure 4. Equilibrium was reached faster

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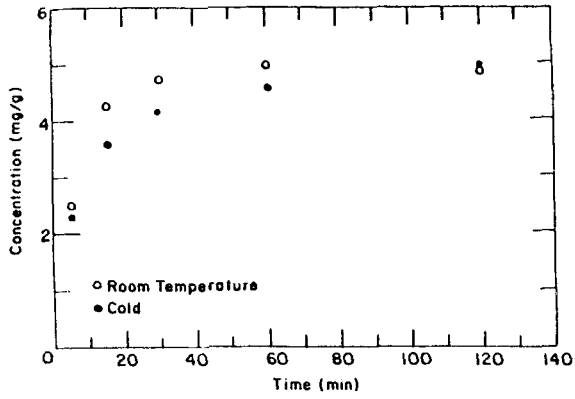

FIGURE 4
Kinetic study using Minneapolis soil and methanol with extraction at room temperature and 0°C.

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TABLE 3.
Recovery from Various Soils Using Two Different Extracting Solvents.

	Solvent			
	Methanol		Mixed*	
Soil	Found Conc. (μg/g)	Recovery (%)	Found Conc. (μg/g)	Recovery (%)
Lebanon Landfill	41#	82	23†	88
Fort Edwards Clay	12#	24	37#	73
USATHAMA Std. Soil	28#	55	38#	74
Manchester Sand	--	--	45#	88

* 2/3 v/v methanol-water, 0.01 M 1-decanesulfonic acid sodium salt.
\# Target concentration = 51 μg/g
† Target concentration = 26 μg/g
-- Not tested.

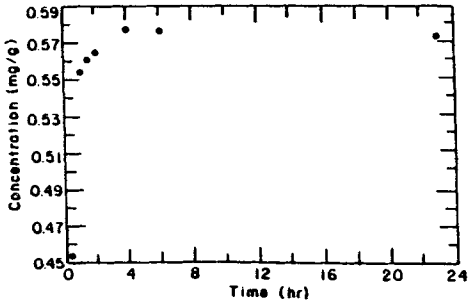

FIGURE 5
Kinetic study using Minneapolis soil and mixed extracting solvent.

at room temperature and degradation was not observed within the 2-hr time period as compared to extracts from the 0°C subsamples.

Next, a mixed extracting solvent containing methanol, water, and 1-decanesulfonic acid, sodium salt was tested at room temperature. Interim experiments showed that this mixed solvent resulted in higher recoveries for soils spiked at the low μg/g level (Table 3). Maximum recovery was achieved from the Minneapolis soil after 5 hr of shaking (Fig. 5), with no degradation apparent after 23 hr. Such a pattern suggests that the extracting solvent became saturated. If field samples contain tetrazene at levels exceeding 0.5 mg/g, either sequential extractions must be performed or more solvent used.

For the USATHAMA Standard soil spiked with a tetrazene-methanol solution (target concentration = 25.6 μg/g) and aged 1 hr, extraction kinetics were quite different (Figure 6). Using the mixed extracting solvent, maximum recovery of 70% was achieved

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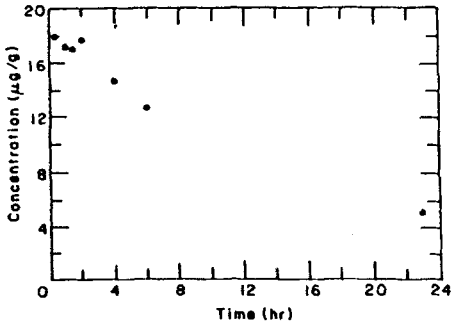

FIGURE 6
Kinetic study using spiked USATHAMA Standard soil and the mixed extracting solvent.

after only 15 min of shaking. Shaking beyond 2 hr resulted in tetrazene degradation. After 23 hr, recovery was only 20%.

Based on this data, a set shaking time cannot be recommended. Additional work with low-level field-contaminated soils is indicated since soils contaminated at the low µg/g level are hard to simulate in the laboratory.

Precision and Accuracy

Method precision and accuracy were estimated by spiking replicate samples of various types of soil and water. Results are presented in Table 4.

For well water, spring water, pond water, Milli-Q water, and USATHAMA standard water, the method accuracy averaged 101%. Recovery was only 4% for the tap water samples. To test if tetrazene was degraded by the tap water, a fresh tap water subsample was spiked and analyzed twice within 10 min. Found con-

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TABLE 4a.

Recovery from Various Spiked Water Samples.

	Well water		Spring water		Pond water		Milli-Q		USATHAMA std. water		Tap water	
Rep	Found Conc. (µg/g)	Recovery (%)	Found Conc. (µg/g)	Recovery (%)	Found Conc. (µg/g)	Recovery (%)	Found Conc. (µg/g)	Recovery (%)	Found Conc. (µg/g)	Recovery (%)	Found Conc. (µg/g)	Recovery (%)
1	104	105	98.9	99.6	103	104	101	102	97.7	98.4	<d*	<3.06
2	99.9	101	95.8	96.5	106	106	102	102	102	102	<d	<3.06
3	110	111	101	101	105	105	98.5	99.2	101	102	<d	<3.06
4	96.0	96.7	100	101	100	101	101	102	101	101	10.8	10.9
5	96.8	97.5	105	106	104	105	104	105	99.6	100	5.38	5.42
6	93.4	94.1	94.0	94.7	104	105	97.9	98.6	102	102	<d	<3.06
Mean	100	100	99.1	99.8	104	104	101	101	100	101	4.72	4.76
Std. dev.	6.15	6.20	3.86	3.89	1.88	1.89	2.25	2.26	1.54	1.55	3.12	3.15
Variance	37.9	38.4	14.9	15.1	3.52	3.57	5.05	5.12	2.36	2.39	9.76	9.91
% RSD	6.15	6.15	3.89	3.89	1.81	1.81	2.23	2.23	1.53	1.53	66.2	66.1

*d = 3.04 µg/L

TABLE 4b.

Recovery from Various Spiked Using 2/3 v/v Methanol-Water, 0.01 M 1-Decanesulfonic Acid, Sodium Salt.

	USATHAMA std. soil		Lebanon landfill		Ft. Edwards clay		Manchester sand	
Rep	Found Conc. (µg/g)	Recovery (%)	Found Conc. (µg/g)	Recovery (%)	Found Conc. (µg/g)	Recovery (%)	Found Conc. (µg/g)	Recovery (%)
1	17.8	69.7	22.4	87.6	17.7	69.2	22.5	87.7
2	17.0	66.5	22.4	87.6	17.4	67.9	22.3	87.1
3	17.7	69.2	22.5	87.9	17.5	68.5	22.4	87.4
4	17.4	67.9	22.4	87.4	17.4	68.1	22.0	86.0
5	17.0	66.5	22.7	88.6	17.7	69.1	22.5	87.8
6	17.7	69.1	22.7	88.5	17.4	67.9	23.1	90.1
Mean	17.4	68.1	22.5	88.0	17.5	68.5	22.4	87.7
Std. dev.	0.360	1.41	0.147	0.584	0.148	0.572	0.347	1.36
Variance	0.129	1.98	0.0216	0.341	0.0218	0.327	0.120	1.84
% RSD	2.06	2.06	0.653	0.664	0.842	0.836	1.55	1.55

centration for the first analysis was 24.0 µg/L, and no tetrazene was detected in the second analysis. Clearly, the tetrazene was degraded by some component of the tap water. The method precision for all water types excluding tap water averaged 3.13 µg/L.

The method accuracy varied with soil type. The accuracy was higher for the two sandy soils, Lebanon landfill and Manchester sand. Other factors such as total organic carbon content, cation exchange capacity, pH, and mineralogy can affect recovery as well. The precision of the method was fairly constant among the four soils tested and averaged 0.250 µg/g or 1.28% relative standard deviation.

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Spike Recovery Studies

Spike recovery studies were conducted to allow estimation of the method reporting limit according to the procedure of Hubaux and Vos.[17] Data from each of the 4 days of analyses were pooled and tested for linearity (LOF) and homogeneity of variance (Bartlett's test). The data sets used to calculate the method reporting limit for water and soil included the found concentrations for the target concentrations 0 - 29 μg/L and 0 - 12.8 μg/g, respectively. Method reporting limits of 3.04 μg/L and 1.10 μg/g were calculated for water and soil, respectively.

SUMMARY AND CONCLUSIONS

Methods were developed for determining tetrazene in water and soil. The water method involves: 1) maintenance of samples at 4°C, 2) filtration of cold aqueous samples through a 0.45-μm membrane; and 3) analysis by an ion-pairing RP-HPLC technique. The soil method is similar, however the soil must be first extracted by addition of a solvent containing methanol, water, and 1-decanesulfonic acid, sodium salt and shaking on a platform shaker. An LC-18 column is eluted with a methanol-water 2/3 v/v eluent modified with 1-decanesulfonic acid, sodium salt and glacial acetic acid. Detection was accomplished with a variable-wavelength UV detector set at 280 nm. Tetrazene retention time using this method was 2.8 min while TNT, a late eluting contaminant, is obtained within a 15-min run time. When TNT is not

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present in samples, a lower percentage of methanol can be used to give a longer retention time for tetrazene.

The variances from each target level were compared using Bartlett's test, and the relationship of found concentration and target concentration was tested for linearity. Method reporting limits of 3.04 μg/L and 1.10 μg/g were calculated for water and soil, respectively.

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