THE USE OF FIELD DEPLOYABLE INSTRUMENTATION FOR THE MONITORING OF EXPLOSIVES IN GROUND WATER

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ABSTRACT

The use of explosives at military installations has and does provide environmental concerns through soil and groundwater contamination, even after training or manufacturing activities have ceased. The concentration of munitions constituents in ground water is an ongoing concern that requires periodic monitoring. The traditional monitoring scenario requires that large amounts of sample (2 to 4 liters) be shipped overnight, under chain of custody control, to a fixed laboratory for analysis by regulatory-approved methods. Additionally, the samples must be packed on ice and be shielded from light to prevent any degradation of the samples during transport and storage. Once in the laboratory, the typical analysis and data reporting time is 30 to 45 days. This process results in data being unavailable to the customer, concentration data to be at least one month old, and expenses incurred for sample collection and shipping. The paper presents a field portable Gas Chromatograph-Mass Spectrometer (GC-MS) for analysis of the explosives on-site. This methodology provides near real time, within approximately 1 hour of sampling, data of the concentration of munitions constituents in a ground water sample. Furthermore, the use of the mass spectrometer as a detection technique provides absolute confirmation of the munitions constituents, and provides a means to identify unknown compounds present in the sample that might otherwise provide false positive detections. This paper also presents two new techniques that are under investigation to be used as field portable instrumentation. The first new technique uses a portable mass spectrometer without a chromatographic interface to monitor all contaminants present in the sample. The second technique utilizes surface plasmon resonance to monitor a single analyte through an antibody-antigen interaction.

1. INTRODUCTION

The long term monitoring requirement for facilities often involves periodic sampling of groundwater on at least a quarterly basis for several years, even after activities have ceased. Traditional sampling and analytical techniques require shipping multiple liters of water to fixed laboratories that perform regulatory-approved analytical methods. The typical analysis and data reporting time at many analytical laboratories can be up to 45 days, which delays vital information on contaminant concentrations being reported to the customer. During this delay, contaminants may be exceeding the approved regulatory limits. Additionally, most sample holding times have been tested for a small representative set of environmental matrices where the assumption has been made that analyte concentrations will not change significantly if analyzed within this window, typically 7 to 40 days (Jenkins, 1995a; Jenkins, 1995b; Jenkins, 1987). The use of a field portable Gas Chromatography-Mass Spectrometer (GC-MS) alleviates this to a certain extent.

This paper discusses application of extraction and analytical techniques adapted to provide for in-field quantitation of explosives in groundwater. Field portable instrumentation has been successfully used previously in the analysis of volatile compounds (MacMillan, 2005), it has not been extended to the analysis of semi-volatile analytes, such as explosives. Therefore, we present the use of the field portable GC-MS for analysis of munitions constituents in groundwater (Russell, 2007).

Two other techniques are presented. The use of a Mini-10 Mass spectrometer allows for the direct analysis of analyte mixtures in complex matrices through a membrane inlet sampling system (MIMS). The Mini-10 is equipped with a MIMS inlet which will allow for

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
DEC 2008	**N/A**	**-**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
The Use Of Field Deployable Instrumentation For The Monitoring Of Explosives In Ground Water	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **U.S. Army Engineer Research and Development Center, Environmental Laboratory, 3909 Halls Ferry Rd., Vicksburg, MS 39180**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**UU**	**6**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

volatile and semi-volatile compounds to permeate the membrane and be analyzed using a mass selective detector.

Finally for specific single analyte detection, a Discovery SensiQ unit is employed. The analogue of the analyte of interest is attached to a gold surface via a organic chain linker. Antibodies for the specific analyte are than added to the unknown solution and that solution analyzed. The free antibody proteins that attach themselves to the compounds of interest are not available to attach to the analogues on the surface. This attachment gives a response on the gold surface which is measured using surface plasmon resonance and is proportional to the amount of analyte in the sample. This antibody-antigen reaction is extremely analyte specific and matrix independent, and therefore provides opportunities for low-level analyte specific quantitation in complex matrices.

2. EXPERIMENTAL

2.1 Reagents

All chemicals used were of reagent grade or higher purity and used without further purification; the deionized water used had a resistivity of 18.2 MΩ · cm. Sodium chloride and sodium tartrate were purchased from Sigma Aldrich (St. Louis, MO). Gold surfaces were purchased from ICx Nomadics(Arlington, VA).. The antibody and hapten compounds were purchased from Strategic Biosolutions (Newark, DE) Solid phase extraction cartridges (SPE) and solid phase microfiber extraction (SPME) were purchased from Supelco (Bellefonte, PA)

2.2 Sample Collection and Preparation

Samples were collected from traditionally installed wells by a low flow technique from a military installation in Louisiana (Russell et.al., 2007) Water samples were stored in amber glass bottles, in the dark, and on ice to prevent degradation of the analytes. For the SPE cartridge extractions, 500 mL of sample water is passed through the cartridge by vacuum. The cartridge is then dried by pulling air through it for 10 minutes after which 5 mL of acetonitrile is used to extract the bound explosives, thereby yielding a 100-fold concentration factor. The samples were then dried with sodium sulfate to remove any water, which helps extend the life of the GC-MS column.

For the SPME fibers, 9 grams of sodium chloride was added to 30 milliliters of a collected water sample resulting in a 30% W/V solution of sodium chloride. A SPME fiber was then exposed in 30 mL of vortexing 30% sodium chloride sample for 5 minutes to allow for sorption of the explosives to the fiber. All SPE cartridges and SPME fibers were kept on ice until they were ready to be analyzed.

The samples for the MINI-10 were prepared by making a solution of 30% W/V of salt, either sodium chloride or sodium tartrate. The samples were then recirculated through the MIMS inlet. The sample was analyzed for 10-30 minutes then the system was flushed with water. This analysis procedure was repeated three times to obtain an average. The average peak height was used to generate a calibration curve. A calibration curve has also been generated by integrating the area under the peak at 10% peakheight.

The Discovery SensiQ samples are prepared by using <10 mL of filtered (0.45 μm) sample, and adding the antibody to a 1 mL aliquot. The solution is then analzed on the instrument. Any free antibody binds to the hapten analogue on the gold surface and the difference in the surface plasmon resonance signal between the sample and the control is collected and used for quantification.

2.3 Instrumentation

A Griffin 400 Minotaur Gas Chromatograph-Mass Spectrometer was used to analyze all samples by GC-MS both in the field and laboratory. SPE cartridges were used to extract the explosive compounds to allow for a 100 fold concentration factor. The compounds were extracted from the cartridge by using acetonitrile. Each sample was dried using sodium sulfate to help extend the life of the GC-MS column. Samples prepared in the field were analyzed in the field and a second set was analyzed both by HPLC (following EPA Method 8330B) and the Minotaur in the laboratory.

A Mini-10 mass spectrometer was purchased from Purdue University. The instrument is equipped with a MIMS inlet system. The PDMS membrane allows many volatile and semi-volatile compounds to pass through, while excluding the water matrix they are dissolved in.

The Discovery SensiQ surface plasmon resonance spectrometer was purchased from ICx Nomadics. The instrument is equipped with a dual flow cell, which allows for background subtraction or dual analyte detection. The gold SPR sensor surface may or may not be coated with a functionalized polymer allowing for haptan attachment.

2.4 Calibration

For each of the field instruments at least 4 standards were used for calibration. The calibration curves and data analysis was accomplished using Microsoft Excel to plot the data and establish the response function for the calibration standards. For the Minotaur 400 GC-MS, the curve was determined to be quadratic and was forced through zero. All correlation coefficient (R^2) values were greater than 0.99. The Discovery SensiQ and Mini-10 used a linear response functions.

3. RESULTS AND DISCUSSION

3.1 Griffin 400 GC-MS Analysis of SPME Fibers

Analyte degradation or loss during sample storage and shipment to fixed laboratories may occur due to biotic and abiotic degradation reactions. Shown in figure 1 are concentrations of several explosives in three well samples that were sampled using SPME fibers. Three SPME fibers were collected and analyzed in the field, immediately after sampling, and three SPME fibers were collected and then analyzed 7 days later in the laboratory. Several of the explosive compounds show degradation, with lower analyte recoveries observed in the SPME samples analyzed 7 days after collection. Not shown are the corresponding byproducts that are easily identifiable, for example 2,4,6-trinitrotoluene (TNT) degrading to 6-amino-2,4-dinitro-toluene (6A-DNT).

This degradation can occur via several pathways, including photodegradation, hydrolysis (particularly under alkaline pH conditions), microbial interactions, reduction-oxidation reactions with inorganic material in the sample, and sorption to suspended colloids. All of these pathways require time and the longer the samples are stored the greater the opportunity for degradation.

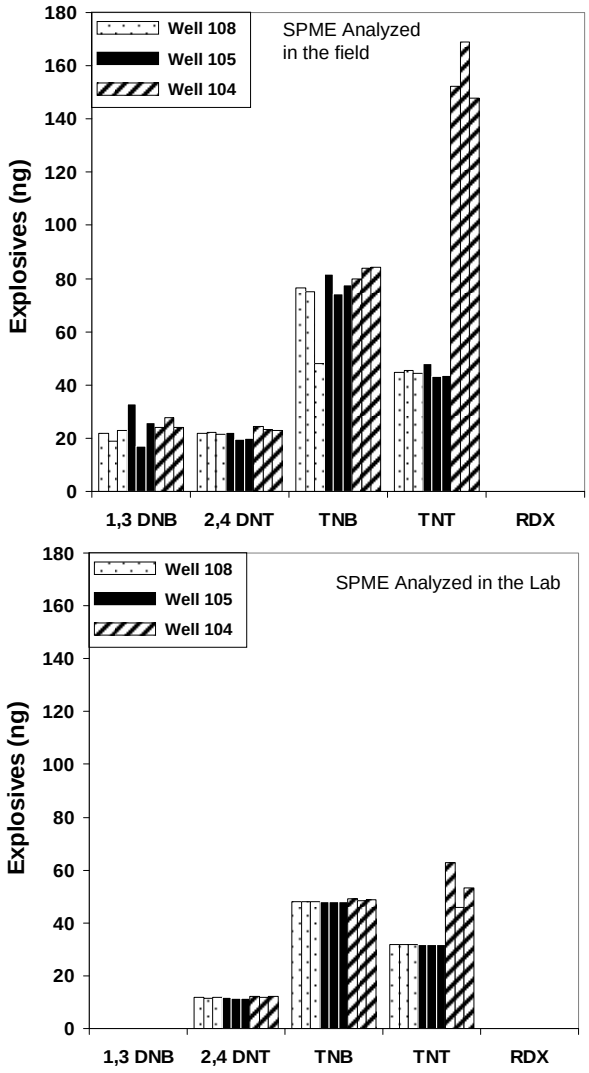

Figure 1. Top: SPME results from field analyzed samples; Bottom: SPME results from samples analyzed seven days later in the laboratory. Three well samples were analyzed in triplicate to produce the data shown.

3.2 Griffin 400 GC-MS Analysis of SPE Extracts

Traditional extraction techniques for water samples using solid phase extraction cartridges were also tested for use with the Griffin 400 GC-MS. As described previously, 500 mL of sample were eluted through a SPE cartridge and the analytes of interest were extracted from the cartridge using 5 mL of acetonitrile.

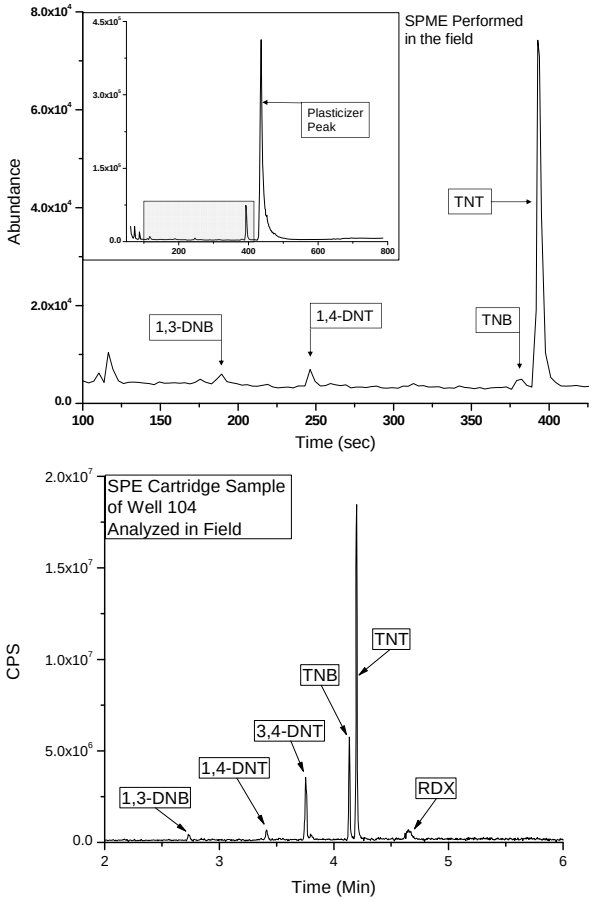

Figure 2. Top: GC-MS chromatogram of SPME analyzed in the field; Bottom: GC-MS chromatogram of SPE cartridge extract analyzed in the field

The data for the in-field analysis of the SPME fiber and the SPE cartridge, Figure 2, were collected using the Griffin 400 GC-MS. In addition to detecting the explosives, the GC-MS detected a plasticizer compound in the SPME fiber field sample and identified it as N-(n-butyl) benzene sulfonamide; the identification of unknown compounds present in samples shows the versatility of the instrumentation. It is clear that the information quality obtained in the field exceeds that of the fixed laboratory, mainly due to degradation of the sample analytes, and the ability to detect and identify unknowns that could cause false positives on non-selective detectors.

3.3 Mini-10 Mass Spectrometer

The Mini-10 mass spectrometer is equipped with a membrane inlet sampling system that allows for direct analysis of water samples without prior sample preparation beyond simple filtration (if needed). The membrane inlet sample introduction system is a semipermeable membrane that allows organic analytes of interest to diffuse into the mass spectrometer ionization source while excluding aqueous matrix components.

A comparison between a water blank (solid line) and a groundwater sample (Well 104 with 20 % W/V sodium chloride, dashed line) is shown in figure 3. A clearly defined peak is observed at m/z 211, which is identified as TNT, and represents about 6 mg/L dissolved in the sample.

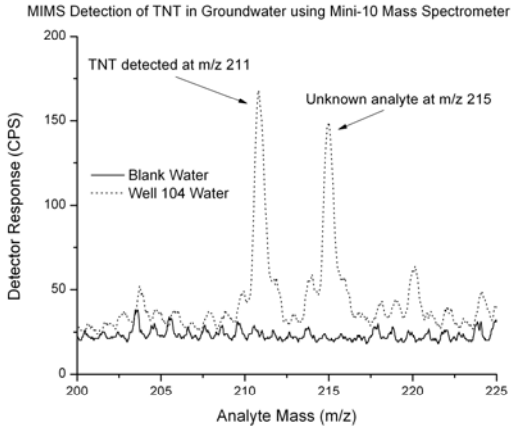

Figure 3 Direct detection of TNT in a groundwater sample using the Mini-10 mass spectrometer with membrane inlet sampling system.

The elimination or reduction of sample preparation for direct analysis of water is advantageous in that analyte loss or degradation is a potential problem whenever extensive sample preparation or manipulation is required. Ongoing research on this detection technology includes the use of different salts, such as sodium tartrate, sodium sulfate and tetra sodium EDTA to increase analyte diffusion through the membrane sampling system and thereby increase sensitivity.

3.4 Discovery SensiQ Spectrometer

Figure 4 is a diagram of the detection technique employed by of the Discovery SensiQ unit. Surface plasmon resonance is a very sensitive technique measuring the change in the surface reflection when an analyte moiety binds to the reflective surface. The data is Figure 5 demonstrates the detection of TNT using a TNT analog bound to the surface and the free antibody binding with the aqueous analyte. The difference between the valley and peak is taken as the signal and used to calculate a response function. As the amount of TNT decreases in the sample the original signal will

increase. From this experiment, TNT was quantified at 500 ng/L.

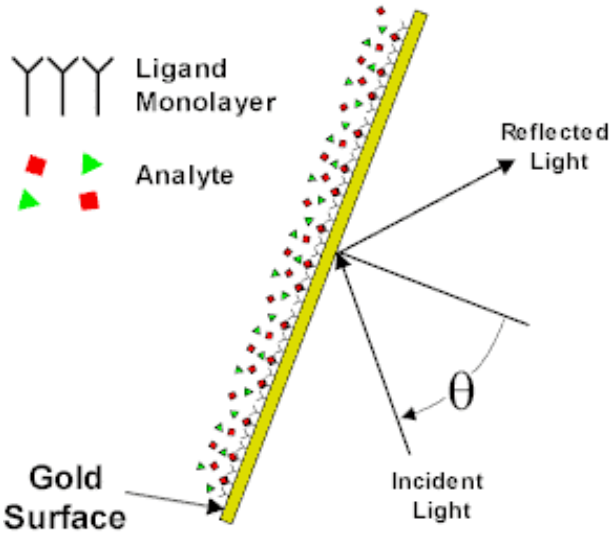

Figure 4. Diagram of the surface plasmon resonance detection technique using the Discovery SensiQ spectrometer.

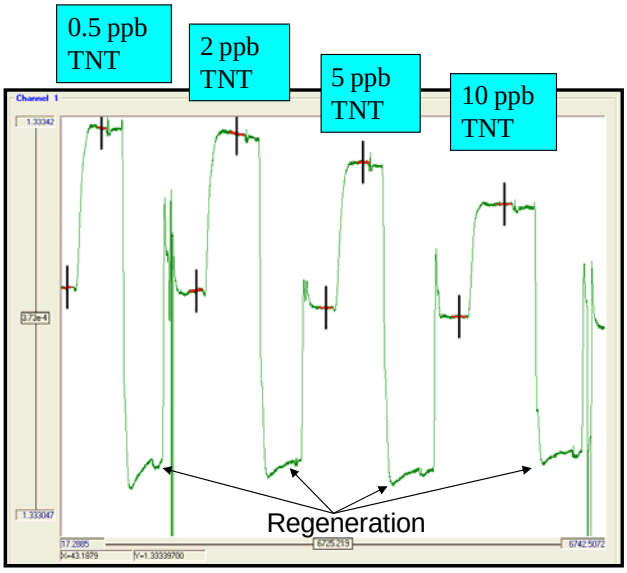

Figure 5. TNT detection using the Discovery SensiQ system

The main challenge for applying this technique is designing analyte analogs that are able to bind to the gold surface. Ongoing research in this area is focused on the detection of RDX, which includes the synthesis of an appropriate analogue that will bind to the gold sensor surface. Due to the RDX drinking water limit of 2 μg/L the detection system shows promise to surpass this requirement if it proves as sensitive as the TNT system.

4. CONCLUSIONS

The use of in-field instrumentation to detect and quantitate explosives in groundwater is described which provided for faster data reporting time and reduced likelihood of erroneous analyte concentrations due to degradation reactions. Specifically, the use of mass spectrometric detectors, such as the Griffin 400 GC-MS and the Mini-10 mass spectrometer, has shown that samples can be collected, prepared, and analyzed directly in the field. Additionally, unknown compounds in the sample matrix can be identified using the mass spectrometer, which otherwise might have lead to false positive detections. The Discovery SensiQ surface plasmon resonance spectrometer has shown promise as a sensitive and selective technique for the quantification of explosives in groundwater. However, to date, its robustness to field deployment has not been investigated, which remains an avenue of future research.

ACKNOWLEDGEMENTS

The use of trade, product, or firm names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Government. The tests described and the resulting data presented herein, unless otherwise noted, were obtained from research conducted under the Environmental Quality Technology Program of the United States Army Corps of Engineers by the USAERDC. Permission was granted by the Chief of Engineers to publish this information; Distribution is unlimited. The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents. The authors also thank Jeffrey Davis and Deborah Felt of the USACE for their editorial comments.

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