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Electrochemical techniques for detection of Tnt and other explosives using disposable screen-printed carbon electrodes

Rebecca Ann Pearson
University of Nevada, Las Vegas

ELECTROCHEMICAL TECHNIQUES FOR DETECTION OF TNT AND OTHER EXPLOSIVES USING DISPOSABLE SCREEN PRINTED CARBON ELECTRODES

by

Rebecca Pearson

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REBECCA A. PEARSON

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ABSTRACT

Electrochemical Techniques for Detection of TNT and Other Explosives Using Disposable Screen-Printed Carbon Electrodes

by

Rebecca Pearson

Dr. Shawn L. Gerstenberger, Examination Committee Chair
Assistant Professor of Environmental Studies
University of Nevada, Las Vegas

Nitroaromatic and nitramine explosives have been found in the soil and water from many government military bases due to improper storage, weapons testing and production. Run-off from contaminated soil and water can enter underground water and potentially contaminate drinking water for near-by communities. With the closing of military bases throughout the U.S. and Europe, contamination will need to be assessed and remediated before the land and water can be used again for other purposes. The use of a fast and inexpensive field screening technique can save time and money typically incurred during intensive laboratory analysis of clean samples.

Screen-printed thick film electrodes are examined as voltammetric sensors for measurement of 2,4,6-Trinitrotoluene (TNT), and Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). The square wave voltammetric (SWV) scan technique can be used to measure TNT and RDX in as little as 50 μL sample volumes applied to the electrode surface

within minutes. The detection limit of this electrochemical assay can also be significantly improved by coupling it with a solid phase extraction (SPE) protocol using Empore SDB-RPS membranes. The simple, rapid, cost-effective, and sensitive characteristics of this assay make it an excellent candidate for development as a field analytical method for onsite explosives detection. This research project successfully developed a new method to examine the capabilities, use and optimization of screen-printed carbon electrodes for detection of TNT, RDX and metabolites from various matrices.

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I would also like to thank my committee members, Dr. Spencer Steinberg and Dr. Brian Johnson. Both of them were wonderful teachers to me over the years and were a great support in my graduate work. I want to especially thank my chair, Dr. Shawn Gerstenberger, who gave me direction in my graduate program, challenged me in my research, nagged at me to write, and was a great friend over the years. I will always have fond memories of collecting dead frogs for him. All of my committee members were wonderful with helping me stay on track with my graduate work during the birth of my son. Another thanks go out to my old friend and mentor, Dawn Neuman. I will always remember the help you gave me that got me started.

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CHAPTER 1

INTRODUCTION

Properties

Explosives are generally a group of nitroaromatic compounds (NAC's) that are used in ammunition, however not all of them are aromatic. The major explosives produced are TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine, Royal Demolition Explosive). The focus of this research is mainly on TNT, but RDX was also examined since the two compounds are often used in mixtures and found together in contaminated areas. TNT breakdown products such as 2-amino-4,6-dinitrotoluene (2-aDNT), 4-amino-2,6-dinitrotoluene (4-aDNT), 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitrobenzene (1,3,5-TNB) and paradinitrobenzene (p-DNB), which results from biodegradation or photodegradation, are also examined. Their structures are shown in Figure 1. Figure 2 shows a suggested photodegradation and microbial degradation pathway for TNT (Godejohann, 1998). Products include: 2-amino-4,6-dinitrotoluene (2-A-4,6-DNT); 4-amino-2,6-dinitrotoluene (4-A-2,6-DNT); 2,4,6-trinitrotoluene (2,4,6-TNT); 2,4,6-trinitrobenzyl alcohol (2,4,6-TNBOH); 1,3,5-trinitrobenzene (1,3,5-TNB); 3,5-dinitroanaline (3,5-DNA); 2-amino-4,6-dinitrobenzoic acid (2-A-4,6-DNBA); 2-hydroxy-4,6-dinitrobenzoic acid (2-OH-4,6-DNB); 3,5-dinitrophenol (3,5-DNP); 2,4-dinitrobenzoic acid (2,4-DNBA).

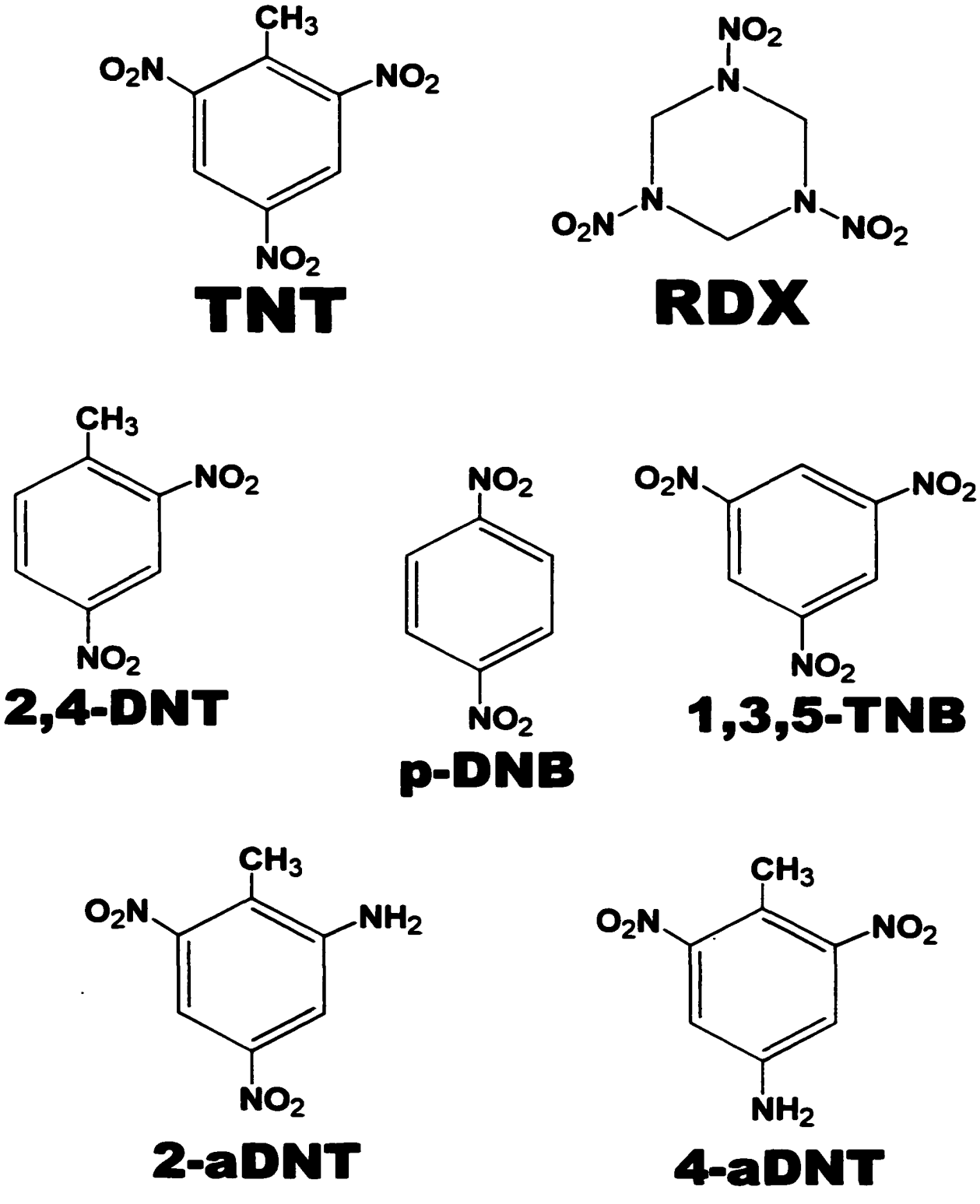


Figure 1 Structures of Explosives and TNT Breakdown Products

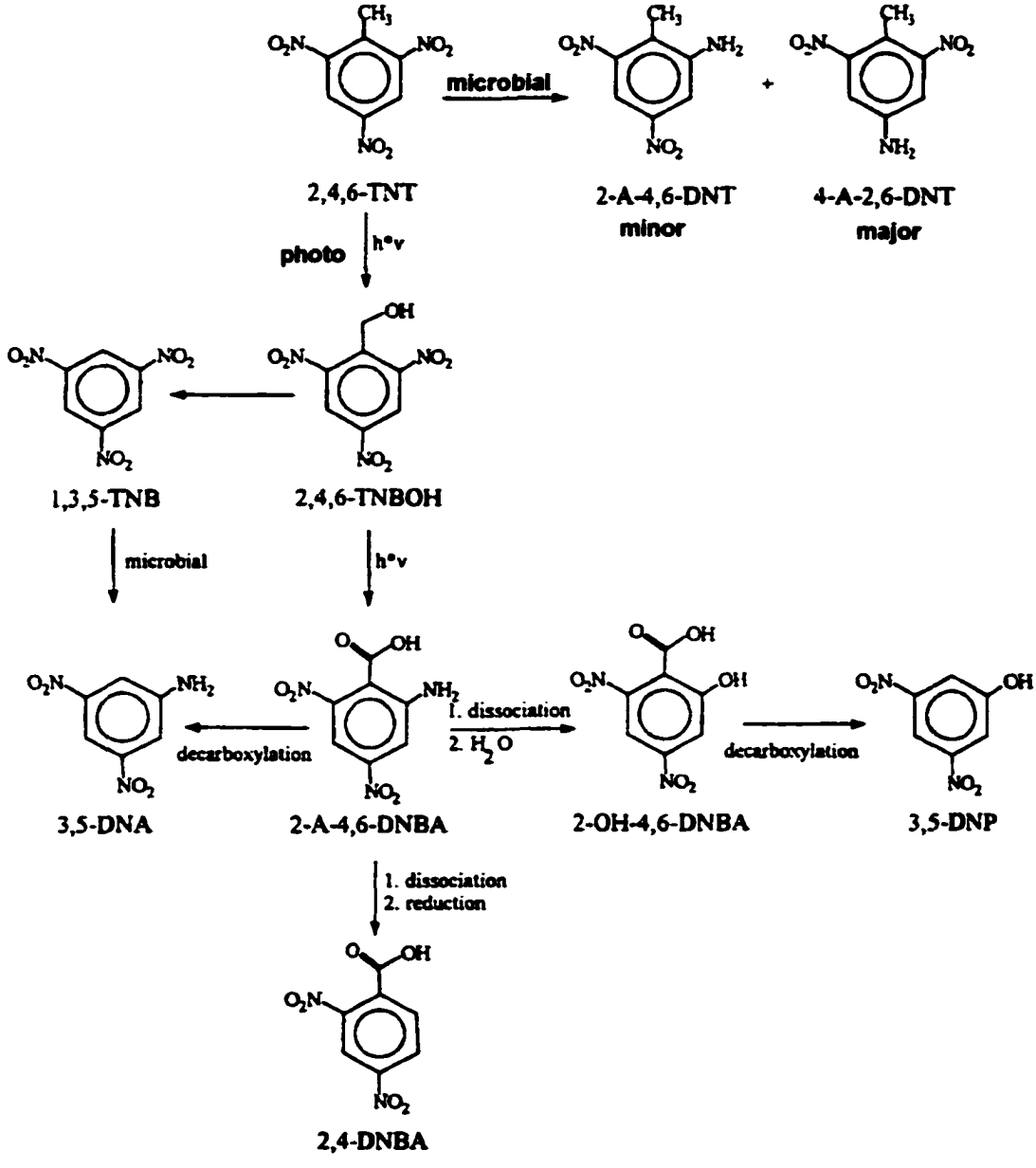


Figure 2 Suggested TNT Breakdown Pathways (Godejohann, 1998)

TNT is an aromatic, odorless, yellow compound that is soluble in acetone and alcohol (Merck, 1996). It does not occur naturally in the environment, but is made by nitration of toluene with nitric acid and sulfuric acid. It is slightly water soluble with a

K_{ow} of 1.6 (CRC, 1998). TNT has a very low vapor pressure ($1.99x10^{-4}$ mmHg at 20° C) and therefore will not evaporate out of water or soil into the atmosphere.

RDX is a synthetically made white powder that is 1.3 times more explosive than TNT based on energy released differences (Bose et al., 1998). It is produced by the Bachmann process, which reacts hexamine with nitric acid, ammonium nitrate, glacial acetic acid, and acetic anhydride. It is not aromatic, but rather a triazine ring. RDX is less hydrophobic than TNT with a K_{ow} of 0.87. RDX is also more water-soluble than TNT. RDX also has a very low vapor pressure ($1x10^{-9}$ mmHg at 20 C), so it will not evaporate into the atmosphere.

Sources

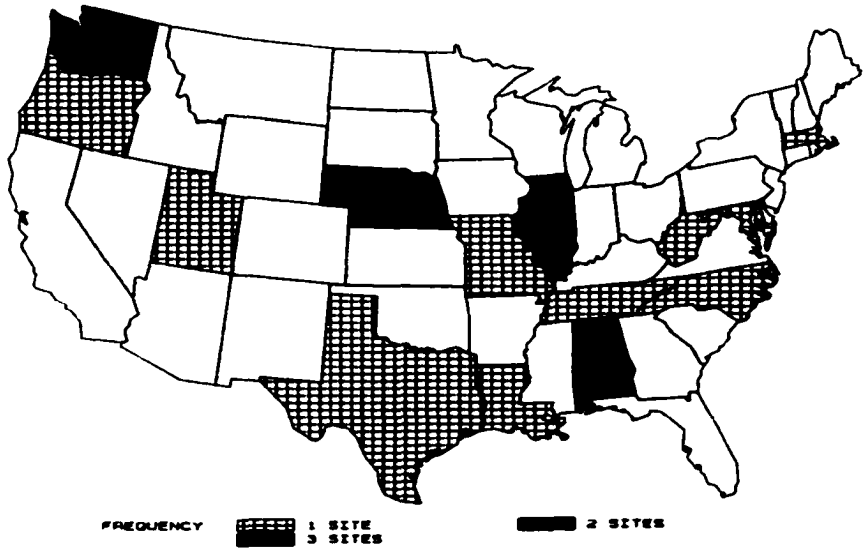
Contamination of water and soil by RDX, TNT and its metabolites has become an important topic in the U.S. Specific issues that are critical in this area include detection, clean up, and prevention of future contamination. TNT and RDX are not produced commercially in the United States and are manufactured only at military arsenals. Most of the clean-up efforts today are from the contamination of water and soil in government military facilities due to manufacturing, testing, waste disposal, and improper storage. Today's waste disposal laws are very strict, but in the past many of the leftover explosive wastes were simply dumped into lagoons or pools. Although in principle this procedure confines the waste to a controlled area, in time many of the compounds have become mobilized during heavy precipitation events causing pools to overflow. Photolysis of TNT in aqueous solutions is responsible for the development of "pink water". This has occurred in lagoons where TNT waste has been dumped and allowed to sit over time. As

the water evaporates in these lagoons, the TNT becomes more concentrated and approaches toxic levels. Both TNT and RDX do not readily evaporate, so once they are in the water system, they will stay there for long periods of time until biodegradation or photooxidation occurs. TNT has limited solubility in water, but unlike many other organic compounds it also has little affinity for soils and can rapidly migrate to the groundwater (Valsaraj et al., 1998). These sources of contamination to ground water can then travel in plumes to pollute near-by drinking water sources. This source of contamination is one of the U.S. Defense Department's most serious environmental problems. Plumes of contaminated groundwater have been identified at military sites with some extending beyond installation boundaries of the facility (Jenkins et al., 1994).

Explosives can enter the environment from improper disposal, storage leaks, particles that enter the air after detonation, or residue that can fall into the soil and water from ammunition testing. Contaminated soils are common to many inactive and abandoned industrial and commercial sites, federal munitions facilities and military reservations throughout the country (Qaisi et al., 1996). Depending on the type of soil, TNT may or may not be easily released. It has been shown that clay has a high affinity for the sorption of TNT (Weissmahr, 1999). Contaminated clay soils could pose a long-term chronic source of TNT. However, TNT has little affinity for organic soils and can rapidly migrate to produce groundwater pollution. TNT has been found in soils in volumes as high as 60% by-weight (Elovitz et al., 1999).

The Environmental Protection Agency has identified 1,397 hazardous waste sites on its National Priorities List. TNT has been found in at least 20 of these sites (ATSDR,

1998) and RDX has been found in at least 16 of these sites (ATSDR, 1998). The location and frequency of these sites throughout the United States can be seen in Figure 3.



U.S. Distribution and frequency map of TNT contaminated NPL sites.

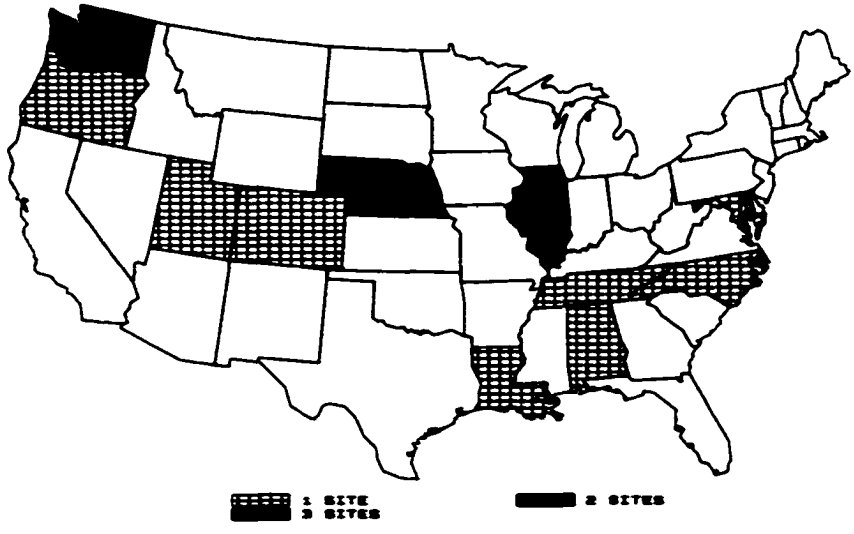


Figure 3 U.S. Distribution and frequency map of RDX contaminated NPL sites.

Health Effects

Due to their toxicity and instability, shipping, handling, and disposal of explosives are highly regulated and have strict government implemented guidelines. EPA has designated all explosive, flammable and toxic compounds as hazardous wastes and has determined allowable concentrations in our drinking water to minimize exposure to toxic compounds. The Department of Transportation regulates the transport of explosives due to their explosive hazard. The Occupational Safety and Health Administration regulates the levels of hazardous materials in the workplace that a worker can be exposed to. TNT, RDX and breakdown products have well documented health risks, which can include mutagenic and carcinogenic properties, reproductive abnormalities, liver and heart damage, seizures, dermatitis, blood disorders such as anemia in addition to minor effects (ASTDR, 1995). These compounds are still being studied for other health effects and for their long-term exposure effects on humans and wildlife species.

Exposure to toxic explosive compounds can come from inhalation, ingestion, or dermal contact. The main sources of exposure are dermal and ingestion, primarily associated with working with explosives and from contaminated water and foods grown in contaminated soils. When taken in by ingestion, TNT will readily enter the blood stream and travel throughout the body. Once it reaches the liver it is broken down and excreted in urine. The toxicity of TNT raises some concerns with remediation and the possibility of leaving behind more toxic breakdown products (ASTDR, 1998). The health effects and danger of TNT breakdown products are not fully understood.

Exposure to toxic compounds depends on several factors. These include the dose, the duration, the route by which you are exposed, and your own individual characteristics such as age, sex, nutritional status, and state of health (ATSDR, 1998). Most human populations exposed to TNT are workers at manufacturing or testing facilities and families that live close to contaminated sites where explosive residues have reached the ground and drinking water systems.

Remediation

The need to remediate explosive contamination from soil and water has stimulated much research. Current remediation methods involving incineration or secure landfilling are expensive and consume scarce landfill space (Williford et al., 1999). Other methods include microbial degradation, phytoremediation, and photo oxidation, of which the most promising technologies are bioremediation and phytoremediation (Drzyzga et al., 1999). In bioremediation, bacteria are used to naturally breakdown the aromatic rings and nitrogen substituent groups. This usually involves piling up large amounts of TNT and RDX contaminated soil and supplying a constant source of oxygen to allow aerobic biodegradation to take place.

Phytoremediation is a process in which the numerous nitroaromatic compounds are utilized as nitrogen sources for plants. Biodegradation can be slow and leave behind toxic breakdown products, similar to photo oxidation processes. To be successful, remediation processes need to be effective, simple, inexpensive, and should not be time consuming. Because of these problems the research into phytoremediation has demonstrated some promising techniques related to the clean-up efforts. Past research

has included the use of wetlands (Best et al., 1999), and aerobic biodegradation by the genus *Rhodococcus* (Coleman et al., 1998) for the clean up of RDX. Research on TNT has included the use of Poplar trees (Thompson et al., 1998), and aquatic plants (Hughes et al., 1997). Much of the research has dealt with hydroponic systems, that use water contaminated with TNT. It has been reported that almost 100% of the TNT was removed from the water by *Myriophyllum aquaticum* plants (Rivera et al., 1998).

Contaminated water needs to be treated quickly, since explosive residue in water is very mobile and can potentially lead to contamination of community drinking water sources. Once drinking water sources are contaminated, human health is at risk.

Detection Methods

To assess the occurrence and levels of TNT and RDX contamination, water and soil samples must be routinely tested. Testing for TNT requires accurate methods, which can detect low-level concentrations in ranges of parts per billion (ppb) or less. Current analytical detection methods include the use of High Performance Liquid Chromatography (HPLC), Gas Chromatography with Mass Spectroscopy (GC-MS) and Ultra-Violet (UV) detection (Bouvier & Oehrle, 1995). TNT and its metabolites can be detected in air, water, soil, plant tissue, urine, blood, kidneys, liver, and hand swabs taken from workers for dermal exposure. Because TNT is found in numerous media, there are many different methods for sample extraction and detection (Jenkins & Thorne, 1995).

HPLC and GC-MS are the most common analytical methods and separation and detection by these instruments are considered reliable and sensitive (Walsh & Ranney, 1998). They are however, expensive and time-consuming techniques that require skilled

laboratory scientists or technicians to perform. Their use involves complex equipment, supplies, and procedures. Bioassay is another detection method that shows specificity for TNT and RDX, but with a higher detection limit. All of the aforementioned methods have certain problems associated with them. They can be costly, insensitive, lack specificity, time consuming and intensive with respect to the length of the procedure and amount of supplies needed.

In regards to remediation, one important factor when looking at contamination is phase assessment sampling of water and soil from contaminated sites. This procedure uses random environmental samples from sites and tests for "hot-spots" of contamination and areas where the soil and water are clean. The samples collected have to then be sent to a laboratory for analysis, which can take days, or even weeks. Shipment and storage of samples is costly. Another problem with conventional explosive analysis and detection methods is the portability of the equipment. Equipment such as HPLC and GC-MS systems are not convenient to take on-site for sampling testing. Bioassays are portable but a new assay must be done for every different compound in question.

The goal of this research project was to investigate new detection methods for TNT, RDX, and metabolites using electrochemical detection techniques. The idea behind the electrochemical approach is to develop a procedure that is portable, fast, inexpensive, sensitive and able to differentiate between TNT and RDX. This method would allow for simple on-site sampling of water, soil, and other media and allow researchers to quickly identify heavily contaminated areas saving time and money.

CHAPTER 2

THEORY

Electrochemistry

Electrochemistry deals with the interrelationship of electricity and chemical reactions and with the potential interconversion of chemical and electrical energy. Using different chemical parameters, electrical quantities such as current, potential, and charge can be measured. Most inorganic and some organic chemical compounds become ionized when dissolved in water or other liquids. Their positively and negatively charged ions have the ability to conduct an electric current. If a pair of electrodes is placed in a solution of an electrolyte, or an ionizable compound, and a source of direct current is connected between them, the positive ions in the solution move toward the negative electrode and the negative ions toward the positive. On reaching the electrodes, the ions may gain or lose electrons and be transformed into neutral atoms or molecules; the nature of the reactions at the electrodes depends on the potential difference, or voltage, applied (Wang, 1994).

Electrochemical processes take place at the electrode-solution interface in an electrochemical cell. The cell consists of at least two electrodes and an electrolyte solution. The electrodes consist of a working electrode, which responds to the target analyte, and a reference electrode, which is at a constant potential that is independent of the properties of the solution. For a current to develop in a cell, it is necessary that the

electrodes be connected to an external metal conductor and that an electron transfer reaction can occur at each of the two electrodes. Since the electrode-solution interface is limited, a continuous mass transfer of reactive species from the solution to the electrode surface must be provided (Christian, 1994). The movement of reactive species is accomplished by convection, migration, or diffusion. Convection involves motion as a result of stirring of the solution. Migration is the movement of ions through the solution brought about by electrostatic attraction between the ions and the electrode's charge. Diffusion is the motion of species brought about by a concentration gradient (Kissenger & Heineman, 1996).

The quantity of material reacting at each electrode when current is passed through an electrolyte is proportional to the quantity of electricity passed through the electrolyte. Electrochemistry is based on Faraday's Law, which states that in a controlled-potential experiment, a change in current is related to the concentration of the target analyte. Analytical measurements involve monitoring the transfer of electrons during the redox process of the analyte while scanning through electrode potentials. The current resulting from the change in oxidation state of the electroactive species is termed the faradaic current, and is a direct measure of the rate of the redox reaction (Figure 4). This change in current (y-axis) is plotted against the applied potential (x-axis) of the electrode called a voltammogram (Wang, 1994).

$$O + ne^- \Leftrightarrow R$$

Figure 4 Redox Equation

Square-Wave

Electrochemistry can be classified into several specific techniques. Square Wave Voltammetry (SWV) is one example. SWV consists of a large-amplitude differential technique in which a waveform composed of a symmetrical square wave (same frequency), superimposed on a base staircase potential, is applied to the working electrode. The current is sampled at the end of forward (cathodic) pulse (dots) and at the end of the reverse (anodic) pulse (crosses) (Figure 5)(Sawyer et al., 1995). The difference between the two measurements is plotted vs. the base staircase potential. The result is a peak-shaped voltammogram, where the peak current is proportional to the concentration of the species (Figure 6)(Lund &Hummerich, 2001). Square wave voltammetry is very fast with high sensitivity. An entire square wave scan can take only 10 ms. Because of its sensitivity, it is useful for samples with low concentrations; as low as 1e-8M can be detected (Wang, 1994). Also because of its speed, it is useful for analysis of large batches of samples, by decreasing the time it would normally take to analyze them by other methods.

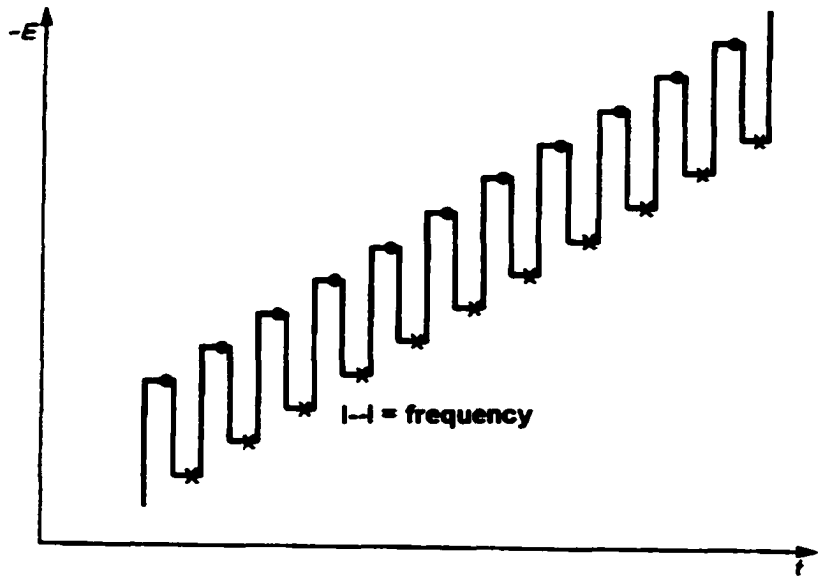


Figure 5 The Change in Potential of the Working Electrode with Time in SWV (Sawyer et at., 1995)

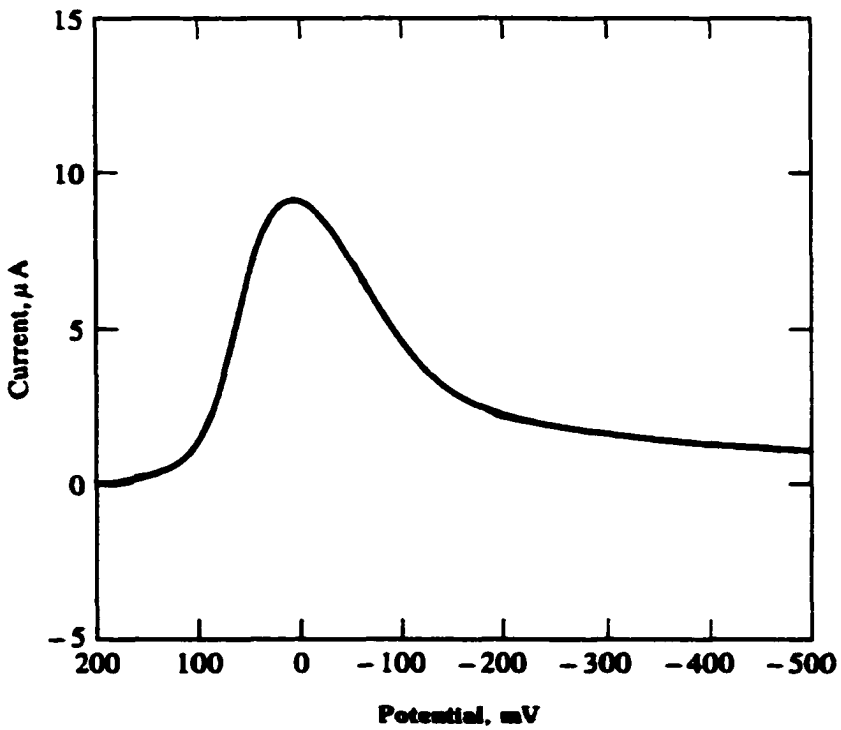


Figure 6 Square Wave Voltammogram (Adapted from Lund & Hummerich, 2001)

Cyclic Voltammetry

Cyclic voltammetry (CV) is useful for determining qualitative information about electrochemical reactions. It rapidly provides information on the location of redox potentials of the electroactive species. In general a cyclic scan can take from 1 ms to 100 seconds. CV consists of scanning linearly the potential of a stationary working electrode using a triangular potential waveform (Figure 7)(Skoog et al., 1998). During the potential sweep, the potentiostat measures the current resulting from the applied potential, resulting in a current vs. potential plot. The forward scan is the reduction of the species and generates a cathodic peak at a characteristic E° value for the redox process. The reverse scan oxidizes the species and an anodic peak results. Figure 8 is an example of a cyclic voltammogram for a ferri cyanide solution (Skoog et al., 1998).

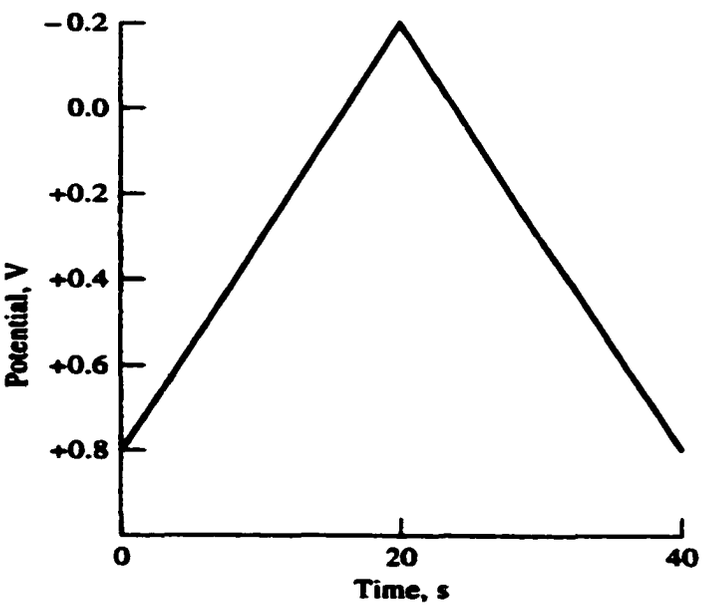


Figure 7 Example of a Triangle Wave Form Graph
(Adapted from Skoog et al., 1998)

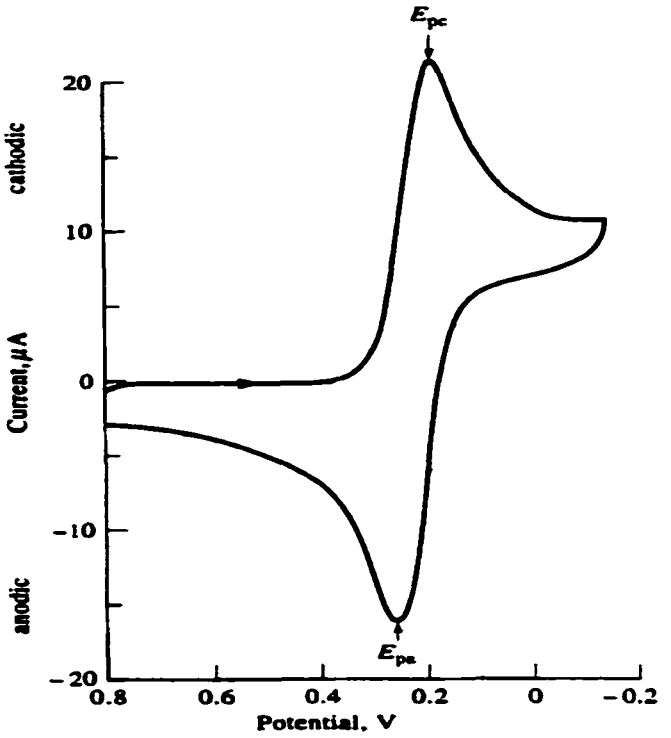


Figure 8 Cyclic Voltammogram of Ferri Cyanide Solution
(Adapted from Skoog et al., 1998)

Working Electrodes

Electrochemical detection of the analyte is done using a working electrode. Unlike optical detectors (fluorescence or UV/Vis), an electrochemical detector oxidizes or reduces the targeted molecule, converting it to another chemical entity. During the course of this reaction, electrons are gained or lost by the electrode. It is this flow of electrons that creates the signal that is generated by the electrochemical detector and used to quantify the amount of sample. Not all molecules are electrochemically reactive, and some chemicals will react only under certain circumstances. Manipulation of such factors such as the electrode material, solution pH, ionic strength and the applied potential of the

working electrode all contribute to the selectivity and efficiency of the electrochemical assay.

There are many types of working electrodes that can be used depending on the redox behavior of the electroactive species. Different electrode materials can be selected to maximize sensitivity and reproducibility. Other factors involved in selecting electrode types include electrical conductivity, surface reproducibility, cost, and toxicity. Common electrodes involve the use of mercury, carbon, and noble metals. This research project used carbon paste, glassy carbon, and screen-printed carbon electrodes.

Carbon paste electrodes involve the use of graphite powder mixed with organic liquids to form a paste. The paste is packed into an electrode with attached electrical leads. They are inexpensive and have low background-current contributions. The carbon paste composition and packing is very critical for good electron-transfer rates. For example, an increase in organic liquid content will decrease conduction.

Glassy-carbon electrodes use carbon that is treated and formed into a glassy, hard substance encased in a pre-molded polymeric resin body. They possess excellent mechanical and electrical properties, a wide potential window, chemical inertness, and reproducible performance.

Carbon based solid electrodes are commonly used because of their broad potential window, low background current, low cost, chemical inertness, and suitability for various sensing and detection applications. However, they also have some disadvantages. The surface of carbon electrodes is critical in performance and carbon electrodes have to be pre-treated, polished, and/or renewed between uses or the electron-transfer rate can be altered, attenuated or blocked.

Separation and Detection Methods

Electrochemical detection is often combined with a chromatographic technique, such as HPLC, allowing the analyte to be isolated and identified from the mixture of compounds. In this research, HPLC was used with a dual-glassy carbon detector. A small amount of solution containing various nitroaromatics is injected onto the HPLC column where the random molecules are individually separated and arranged. The chromatographic process separates these molecules from each other as they exit the column at different times and enter the electrochemical cell as organized packets. Those molecules that can react with the electrode, under the conditions created by the analyst, will gain or lose one or more electrons during the detection process (Figure 9). The detector monitors and amplifies the current (flow of electrons) during the passage of these molecules through the cell. It then converts the current to a voltage, which is recorded as a chromatographic peak. The elution time from the column can be used to determine the identity of the molecule, comparing the peak to previously established retention times from known samples. The size of the peak (height or area under the curve) can be used to determine the quantity of the specific compound present in that sample.

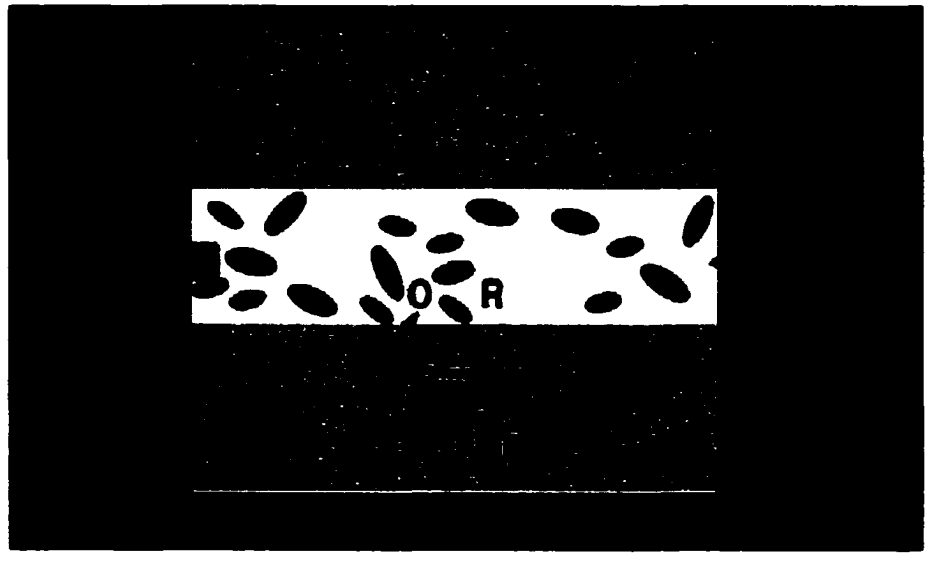


Figure 9 Analytes exiting column and entering electrochemical cell

Screen-Printed Carbon Electrodes

One of the important aspects of this research was the characterization of screen-printed carbon electrodes. The electrodes were manufactured by Dr. Joseph Wang's research group at New Mexico State University and have many advantages (Wang et al., 1998). The electrodes are small and light with dimensions of only 1cm x 3cm. The electrodes are made by first placing a sheet of specially made perforated ceramic in the screen-printing machine. Metal templates are then placed over the ceramic sheet and the carbon or silver ink is applied across them. The sheets are then placed in an oven to dry between each ink screening. The combination reference and counter electrodes are made from silver ink and the working electrode is made from carbon ink. Last, a dielectric coating is applied over both electrodes, to block any cross current and interference between the two electrode strips. The strips stick out of the dielectric coating about 0.3cm on each side. One side is used for the analysis of the solution (carbon and silver end) and the other side is used for the electrical connections (contact end) to the

electrochemical analyzer. (Figure 10) The carbon is used for the working electrode and the silver is used as the reference/counter electrode (Wang et al., 1998).

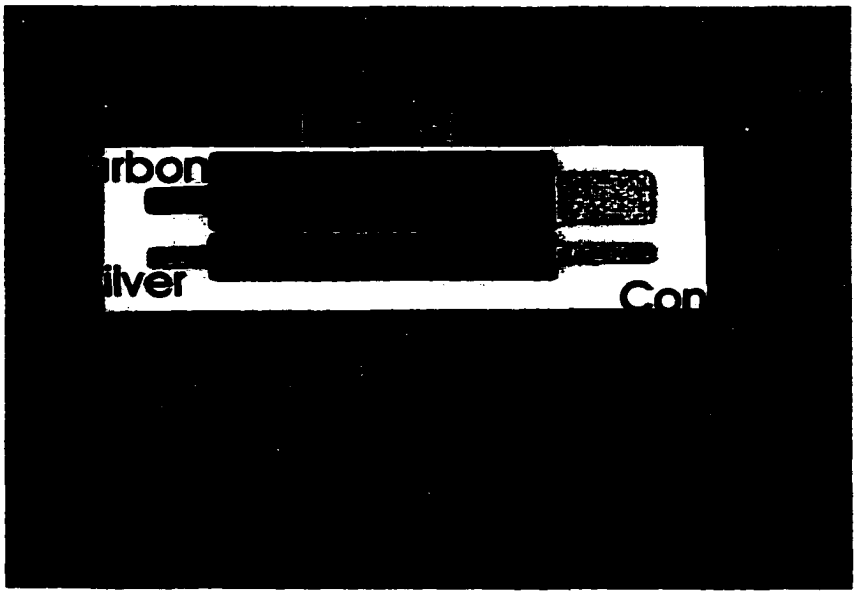


Figure 10 Components of Screen-Printed Carbon Electrode

Screen-printed carbon electrodes are inexpensive to produce and are disposable after each use, thus eliminating cross contamination. Also they require no preparation or polishing as is common with carbon paste and glassy carbon electrodes. A sample volume of 50 μL is needed for analysis on the electrode surface, so small amounts of solutions and samples are used and little waste is accumulated. The screen-printed carbon electrodes show high sensitivity, good reproducibility and good conductivity. Because of the low cost and preparation, and high quality characteristics of the electrode, they are ideal for traveling to field locations to analyze environmental samples. With a laptop computer and minimal supplies, the entire electrode and analyzer set-up can be made completely portable.

CHAPTER 3

EXPERIMENT MATERIALS AND METHODS

Initial TNT Standard Curves Using Screen-Printed Carbon Electrodes

Initial TNT standard curves were created to test the screen-printed carbon (SPC) electrodes to ensure contacts were good and working properly. A stock solution of 1000 μg/ml (1000 ppm) of TNT in acetonitrile was purchased from Chemservice. (TNT and all other stock solutions of explosives were kept in a metal canister away from any light source.) 5 μL increments of stock solution were added to 10 mL of 1M Hydrochloric acid in a standard addition method. Square wave voltammograms were scanned using a CHI 620 Electrochemical Analyzer. Using the provided software, parameters were set as: Initial E (V) = 0.1, Final E (V) = -0.6, Increment E = 0.004 V, Amplitude = 0.01 V, Frequency = 40 Hz, Quiet Time = 2 sec, Sensitivity = 1e-5 A/V. Using the same electrodes, points were taken for a range of 0 to 5 ppm, starting with the blank and increasing in 0.5ppm increments. For analysis, 50 μL of the prepared HCL-TNT solution was pipetted onto the electrode, making sure the solution completely covered both the working and reference electrodes. The scan was started immediately as described above. When finished, the solution was pipetted off and the next standard concentration was pipetted on. Since concentrations for the standard curve were increased with each scan, contamination from the previous sample was minimized.

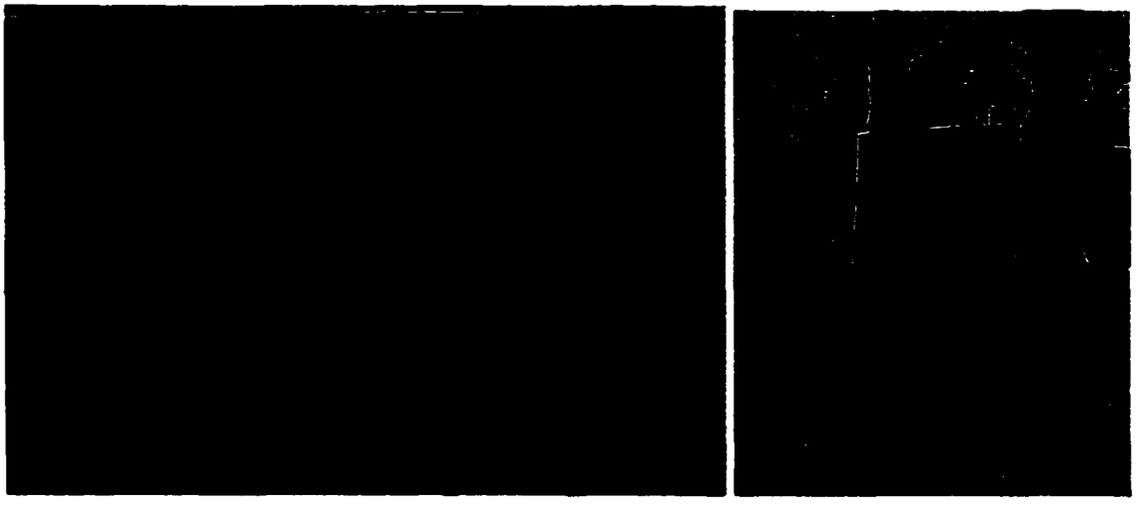


Figure 11 Picture of CHI Electrochemical Analyzer and Electrode Set-Up and Close Up Of Electrode Attached to Contacts

Optimization of TNT detection

Standard curves of TNT in the very acidic solution of 1M HCl had very clean baselines and reproducible peak definition, however the changes in current were very small between different concentrations of TNT. To optimize and try to increase the generated change in current, different percentages of acetonitrile solutions were tested to see what effect a higher pH buffer solution would have on the resulting SWV scans. The PBS is used as the electrolytic buffer, HCl is used to keep a clean and stable baseline, and acetonitrile is used because TNT is very soluble in it without being very acidic. TNT standard curves were created using solutions of 50, 25, 16.7, and 10% acetonitrile in phosphate buffer solution (PBS) with 1% 1M HCl to find the optimal solution to generate low noise, high peaks, and well-defined peaks. Various concentrations of TNT, from 0 to 4 ppm, were tested. This was the concentration range relevant for environmental samples. Parameters for the electroanalyzer were as previously described.

TNT Standard Curves Using HPLC

TNT standard curves were also created using a BioAnalytical System High Performance Liquid Chromatography (BAS-HPLC) with dual glassy-carbon electrochemical detection. Optimal conditions used for this confirmatory method were also used to design experiments for the screen-printed electrodes. The mobile phase consisted of 50% Acetonitrile in a Phosphate buffer solution (PBS, pH 6.5)(68 mL of 0.2M $Na_2H_2PO_4$, 32 mL 0.2M Na_2HPO_4, 300 mL of nanopure distilled water, and 400 mL of HPLC grade acetonitrile.) Using 1000 μg/mL TNT stock solution, dilutions were made at 0, 1, 2.5, 5, 10, 15, 20 and 25 ppm. Parameters for HPLC were as follows: C18 column, flow rate = 1.0 ml/min, filter = 0.10 Hz, -0.6V potential, 1.0 μA range, 20 μL sample loop. The mobile phase solution and solvents were degassed prior to use with nitrogen.

RDX Standard Curves Using Screen-Printed Carbon (SPC) Electrodes

RDX and TNT are often found as co-contaminants in environmental samples. To determine the possible interference from RDX, measurements using the SPC electrodes were done for standard curves for RDX, run under conditions determined as optimal for the TNT assay. An RDX stock solution (1000 μg/ml) was purchased from Chemservice. In a 10 % acetonitrile solution containing 9 mL of PBS(pH 6.5) and 1 mL acetonitrile, a standard addition technique was followed as the solution was spiked with 5 μL increments of RDX. Concentrations of 0, 0.5, 1, 3, 5, 7 and 10 ppm were analyzed on a SPC electrode in the same manner as TNT standard curves. These initial tests were used to determine the redox potential of the RDX molecule, the necessary potential range for

the scan, and the concentration range required for a linear current response. Once the redox potential and linear concentration ranges were established, the procedure was tested in triplicate using concentrations ranging from 0 to 3 ppm. Electroanalyzer parameters were the same as previously discussed for TNT samples.

In addition, RDX standard curves were tested using a 10% acetonitrile and 1% 1M HCl solution spiked with 1ppm TNT to see the effects of co-contamination. In an attempt to separate the RDX signal from the TNT signal, another experiment was completed which examined the effects of pH on the resulting signals. First a solution of 2 ppm concentration of TNT was analyzed in a 1% HCl and 10% acetonitrile in PBS. Then RDX was added to the TNT solution, for a final concentration of 2 ppm for both, and analyzed. The buffer solution was then acidified by adding 1M HCl to increase the concentration from 1% to 10%, and analyzed. All three scans were performed on the same electrode.

Analysis of Breakdown Products Using Electrodes

Another potential interference with TNT in environmental samples is the presence of TNT biotransformation products due to photo degradation and microbial degradation. These compounds were considered in order to gain a more complete understanding of these potential co-contaminants and how they might interfere with TNT detection. Five breakdown products that were considered included: 2-amino-dinitrotoluene, 4-amino-dinitrotoluene, 1,3,5-trinitrotoluene, 2,4-dinitrotoluene, and para-dinitrobenzene. Each compound was purchased from Chemservice, and dissolved in acetonitrile to make a 1000 μg/mL stock solution. Each compound was analyzed by the standard addition

method in a 10% HCl and 10% acetonitrile in PBS solution. Parameters of the analyzer were the same as previously described. Concentrations from 0 to 3 ppm were run. To test interference with TNT, 2 ppm of each compound was added to a TNT solution at the same concentration of 2 ppm.

TNT Extraction Method

An extraction method was performed to concentrate TNT from dilute water samples so they could be detected and quantified by the electrodes. A stock TNT solution of 1000 μg/mL was diluted in a 1:100 ratio with acetonitrile to make a new 10 μg/mL solution. From this solution a series of dilutions were made by pipetting 0, 10, 25, 50, 100, 150, 200, 250 μL TNT stock solution into 50 mL of distilled nanopure water. This made up eight solutions with concentrations of 0, 2, 5, 10, 20, 30, 40, and 50 ppb TNT. Each solution was then filtered by vacuum through a pretreated 3M Empore SDB-RPS extraction filter cartridge. The filter cartridge was pretreated by pipetting 1 mL of acetonitrile on the filter for two minutes to activate it, and then removed by vacuum filtration. This was followed by a one-minute wash with 1 mL of nanopure distilled water, then vacuum filtered, leaving a small amount of water to keep the filter moist. (Approximately a 2 mm layer of water.) 50 mL of the first prepared diluted sample was added to a 50 mL syringe attached to the filter cartridge. The dilution was then filtered under vacuum filtration until the solution was gone. The filter was vacuumed for one additional minute to assure all water was removed and the filter was completely dry. One ml of acetonitrile was added to the filter and allowed to incubate for two minutes. This treatment released the analyte from the filter. The sample was then vacuum filtered

into a labeled 1.5 mL vial for two minutes or until the solution was completely removed and the filter was dry. This entire filtration process was repeated for all prepared dilutions. (Figure 12)

Once all dilutions were filtered, they were placed under a low flow of nitrogen gas until the acetonitrile solvent was completely evaporated. Then 100 µL of acetonitrile was added back to each vial to re-suspend the analyte. Each vial was mixed thoroughly by vortexing for one minute. All vials were capped and stored at 40°C until analysis. Given 100% extraction and recovery, this process resulted in a theoretical 1:500 concentration of the initial TNT dilutions.

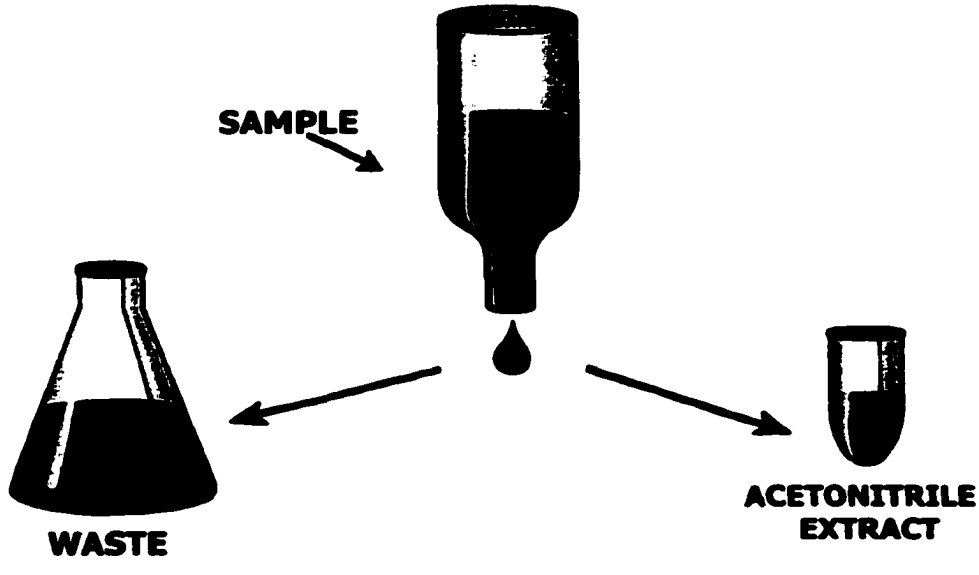


Figure 12 Schematic of TNT Extraction Method

TNT Extraction Analysis Using Electrodes

For electrode analysis, 50 µL of the concentrated filtered samples from each vial was placed in a beaker with 450 µL of PBS and 5 µL of HCl and mixed. This resulted in

a 1:10 dilution of each sample (Table 1). 50 µL of PBS was placed on the electrode to wet the surface and removed. A blank was run from a 10% acetonitrile solution containing no TNT. After the blank, 50 µL of each dilution was analyzed on the electrode following the same procedures and parameters as stated before. Using another electrode, a stock standard TNT curve was run to compare the extraction curve to and calculate percent recoveries. This extraction process was repeated in triplicate.

Table 1

Theoretical Concentrations for Extraction Process for Electrode Analysis

Original Concentration	Concentrated Conc (1:500)	Electrode Dilution Conc (1:10)
0 ppb	0 ppm	0 ppm
2	1.0	0.10
5	2.5	0.25
10	5.0	0.50
20	10.0	1.00
30	15.0	1.50
40	20.0	2.00
50	25.0	2.50

TNT Extraction Analysis Using HPLC

For HPLC analysis of extracted TNT samples, 25 µL of each extracted sample was added to 75 µL of acetonitrile, resulting in a 1:4 dilution (Table 2) of the concentrated sample, and mixed thoroughly. Using the same parameters used in the TNT standard curve analysis on HPLC above, each sample was injected into the HPLC. This procedure was done to compare results obtained from using the newly developed method on the electrodes to a standard technique using the HPLC. A standard curve using a TNT

stock solution diluted to 0, 1, 2, 3, 4, 5, 6 and 7 ppm was also run. From this standard curve a second percent recovery was calculated.

Table 2

Theoretical Concentrations for Extraction Process for HPLC Analysis

Original Concentration	Concentrated Conc (1:500)	HPLC Dilution Conc (1:4)
0 ppb	0 ppm	0 ppm
2	1.0	0.250
5	2.5	0.625
10	5.0	1.250
20	10.0	2.500
30	15.0	3.750
40	20.0	5.000
50	25.0	6.250

DNT Extractions

Extractions of 4-amino-dinitrotoluene (DNT) were tested to determine if separation from TNT is possible. It was thought that if the same procedure and filter cartridges did not have a significant affinity for the DNT molecule, it could be a possible means to remove the DNT from the TNT in the samples. This experiment was important because the redox potential for DNT measured using square wave voltammetry was similar to that shown by TNT and this compound is a major breakdown product of TNT from microbial degradation. DNT showed to be an interference with measuring TNT using SWV. A six-point extraction curve was performed using the same method used for TNT extractions. Original dilution concentrations were 0, 2, 5, 10, 20 and 30 ppb. Following the same procedure these would lead to maximum theoretical final

concentrations of 0, 1, 2.5, 5, 10 and 15 ppm samples. 50 μL of each filtered sample was added to 445 μL PBS and 5 μL HCl. From this mixture, 50 μL was pipetted and used for electrode analysis. Using a stock DNT solution of 1000 μg/mL, a standard DNT curve was also done by spiking a 10% acetonitrile in PBS with 1% HCl solution with DNT in a standard addition method. From this regression curve, percent recoveries of extracted DNT were calculated.

Plant Tissue Extractions

After initial testing of the electrodes, the methods developed were then applied to environmental samples. One application involved the extraction and analysis of TNT and DNT from plant tissue, including roots, stems, and leaves. Plant samples were obtained from Lee Wolfe at EPA in Athens, Georgia. Plant samples included *Yucca filamentosa* leaves, tuber and roots and also *Platanus occidentalis* leaves, stem and roots. These plants were part of a hydroponics study from plants grown in contaminated water dosed with TNT. Our laboratory completed a blind analysis on the plants to compare our new method to HPLC analysis run at the Athens lab (EPA Method 8330, EPA 1998).

For extraction of TNT and DNT from the plants, the tissue was first placed in an oven at 40°C and left until completely dry. Approximately 0.25 gram samples of plant tissue were weighed and placed in vials containing 10 mL of acetonitrile. Each vial was vortexed for one minute and then placed in a sonicator for one hour. After sonication they were allowed to settle overnight. The next day, each vial was centrifuged at 2500 rpm for ten minutes. Then 4 mL of the supernatant was collected and passed through a 0.45 μm Teflon filter into another vial, followed by the addition of 4 mL of distilled

water and vortexed for one minute. This solution was filtered one more time through a 0.45 μm filter into a 50 mL vial. To this 8 mL solution, 42 mL of water was added to make a 50 mL total volume dilution and vortexed for one minute. Each 50 mL solution was then run through the Empore SDB-RPS extraction filters under vacuum as in the above TNT extraction method. The TNT and DNT was re-extracted from the filter with 1 mL of acetonitrile into a 1.5 mL vial and allowed to evaporate completely. To this vial, 50 μL of acetonitrile was added to re-suspend the material. Then 445 μL of PBS and 5 μL 1M HCl were added and the vial was vortexed for 30 seconds. Two extractions were done for each plant sample, one for TNT analysis and the other for DNT analysis. The entire extraction and analysis procedure was done in triplicate for each sample.

For electrode analysis, 50 μL of the solution was pipetted on the electrode and run using square wave voltammetry. In a standard addition method, 5 μL of a 100 ppm TNT was added to the vial, vortexed, and 50 μL used on the electrode and run again. This added an increase in concentration of 1 ppm TNT to the solution. This process was done 3 times for a total of 4 scans on the electrode: a blank (extracted solution), +1ppm, +2ppm, and +3ppm TNT. These four points were plotted and a regression equation was created. From this equation, the unknown original concentration was calculated by extrapolating to zero.

For DNT measurements the same procedure was done using the second vial from the plant extractions. Here a stock solution of 100 ppm DNT was used for the standard addition to the original extraction. Four scans were run on each electrode and the original unknown was calculated from the regression curve equation.

Soil Extractions

TNT and DNT were extracted from soil samples obtained from the same source and experiment as the plant tissue samples. Soil was taken from a depth of 0 - 10cm from the top layer. For extractions, approximately 1 gram of soil was ground, weighed and placed in a vial with 10 mL of acetonitrile. Each vial was vortexed for one minute and placed in a sonicator for one hour. The vials were then placed on a shaker table overnight. The next day the samples were centrifuged for ten minutes at 2500 rpm. From each vial, 4 mL of the supernatant was collected and filtered through a 0.45 μm Teflon filter. To each filtered sample, 4 mL of calcium chloride ($CaCl_2$) was added and then vortexed for 1 minute. After mixing, the vials were allowed to sit and settle for 20 minutes, and were then filtered one more time through a Teflon filter into a 50 mL vial. To each vial, 42 mL of distilled water was added and vortexed for one minute. Each sample was run through the extraction filters and re-collected with 1 mL acetonitrile into a 1.5 mL vial and allowed to completely evaporate. Two extractions were done for each sample, one for TNT and the other for DNT analysis. Each extraction procedure was done in triplicate.

For electrode analysis, 50 μL of acetonitrile was added to each vial to re-suspend the sample and mixed. Then 445 μL PBS and 5 μL 1M HCl was added to the vial and vortexed for 30 seconds. Using the same standard addition method as with the plant tissue, increments of TNT and DNT were spiked into the samples and run on the electrodes. Four scans were done on each electrode, the points were plotted, and a regression curve equation was made from which the unknown original concentration was calculated.

Blank Extractions

Blank extraction samples on plant tissue and soil were tested to verify that the results from the soil and plant tissue extractions were valid and not just electroactive matrix interference. For plant tissue blanks, samples of *Yucca schidigera* were obtained from the University Nevada Las Vegas Greenhouse. These plants were grown from seed on site and grown in a clean mixture of soil, peat moss, and vermiculite. Because of the location and environment the Yucca was grown in, we assumed that there was no exposure to TNT and DNT. Soil samples were taken from the first 10 cm down from the top layer. Both the soil and plant tissue samples were extracted in the same method used on the contaminated samples above. Analysis of the blank samples on the electrode also followed the same method as above. Each sample was analyzed in triplicate. Concentration vs current was graphed and a regression curve was used to calculate the blank concentration.

Environmental Water Samples

Another application of our technique examined the analysis of contaminated water samples from various wells from designated coded sites. These samples were obtained through EPA, from other studies, and were analyzed previously by HPLC. Four samples of known concentrations were tested, with two spikes of 1 and 4 ppm TNT. To prepare each water sample, 8 mL were added to 1mL acetonitrile and 1mL PBS. This resulted in a 20% dilution of the original concentration. Samples analyzed consisted of:

Table 3

Codes and Known Concentrations for Water Samples

Sample Code	Original TNT Concentration
Milan 005-99228	0.156 ppm
Milan 006-99228	3.152 ppm
LAAP Well 12	0.694 ppm
LAAP Well 141	1.908 ppm

50 µL of each sample was pipetted on the electrode and run using square wave voltammetry. Electrochemical analyzer parameters were as previously described. The samples were tested in order of increasing concentrations, including the spikes and an initial blank.

A standard addition method was done on sample LAAP Well 168 with a known TNT concentration 1.516 ppm. 8mL of sample was added to 1mL acetonitrile and 1mL PBS. The original solution was treated as the blank and increments of 1ppm TNT was added to the sample and analyzed on the electrode. The resulting points were plotted and the regression curve equation was used to calculate the original concentration, as if it were an unknown sample.

CHAPTER 4

EXPERIMENTAL RESULTS

Initial TNT Standard Curves Using Screen-Printed Carbon Electrodes

Initial tests were performed on the screen-printed electrodes to test their capabilities and activity with TNT. The maximum current upon reduction of TNT using the screen-printed carbon electrodes appeared at approximately –0.25 Volts for the first reduction peak (Figure 13) and at –0.685 Volts for the second reduction peak (not shown). The second reduction peak was not evident over the background current below concentrations of 1.5ppm. The second peak was significantly smaller than the first reduction peak, electrodes showed a fairly high sensitivity for the TNT, detecting concentrations as low as 0.5 ppm. Overlapping scans for increasing concentrations of TNT are shown in Figure 13. A plot of the peak currents versus concentration resulted in a linear relationship (Appendix 1). For this plot, the current for the blank baseline was subtracted from the current for the sample. The dynamic concentration range for this assay was 0–5ppm ($R^2 = 0.9945$)

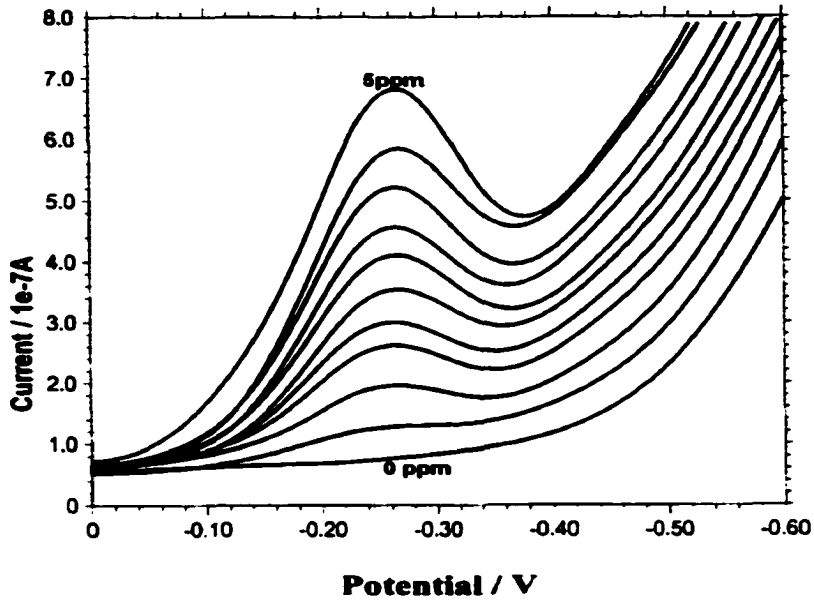


Figure 13 Overlapping Square Wave Voltammetry Scans of TNT Standard Curve in HCl

Optimization of TNT Detection

Optimization tests were performed by various changes to the buffer solution to try to increase current changes to smooth out baseline noise, increase analyte sensitivity, and to obtain a better linear range of TNT concentrations inside an optimal scale. Different concentrations of acetonitrile were tested in a 1% HCl solution in PBS. Acetonitrile concentrations of 50, 25, 23.1, 20, 16.7, 10 and 9.1% were tested using various ranges of TNT concentrations. Figure 14 shows examples of SWV scan from 10% acetonitrile, which was found to produce the best results. Triplicate analysis produced average R^2 value of 0.9987 (Appendix 1).

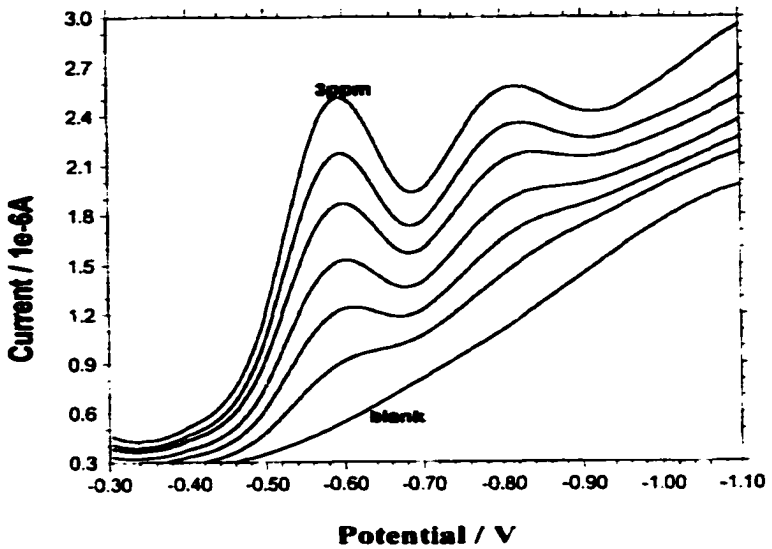


Figure 14 Square Wave Scans of TNT Standard Curve (10% Acetonitrile, 1% HCl)

TNT Standard Curves Using HPLC

TNT was analyzed on HPLC to verify the linear results obtained from the SPCE. TNT had an approximate retention time of 2.00 minutes. Peak area was plotted against concentration. Results showed a linear response with an R^2 value of 0.9872. Figure 15 shows the plot of peak area vs concentration.

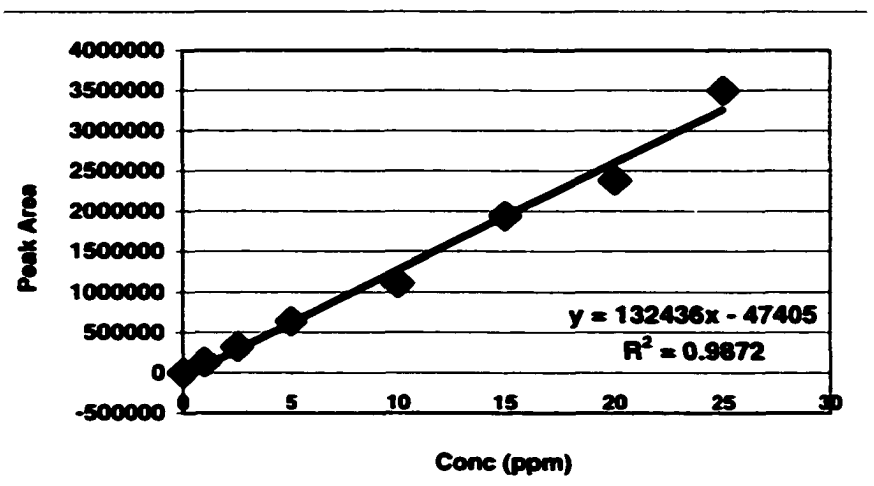


Figure 15 Regression Curve of TNT Standard Curve on HPLC

RDX Standard Curves Using SPC electrodes

As with TNT, RDX was tested on the SPCE to test sensitivity and activity. RDX had a first reduction peak value of approximately –0.8 Volts, although the reduction peaks were not well defined, especially as RDX concentrations increased. A second reduction peak was not seen. Figure 16 shows the overlapping SWV scans for RDX in increasing concentrations from 0 to 10 ppm. Once parameters were identified, the RDX was repeated in triplicate from 0-3ppm. This produced reproducible results with an average R^2 of 0.9309 (Appendix 1). Figure 17 shows the comparison of RDX and TNT reduction potentials, both at a concentration of 2 ppm. Although the peak potential for RDX occurs at a more negative potential than the first reduction peak for TNT, the peaks overlap causing potential interference.

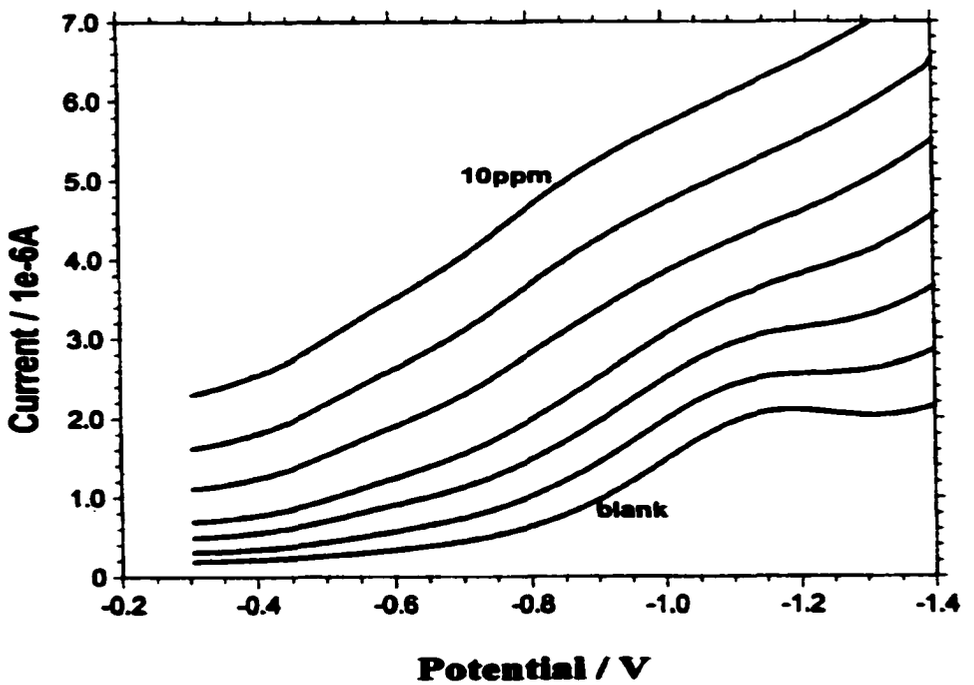


Figure 16 Square Wave Voltammetry scans of RDX Standard Curve in 10% Acetonitrile and 1% HCl

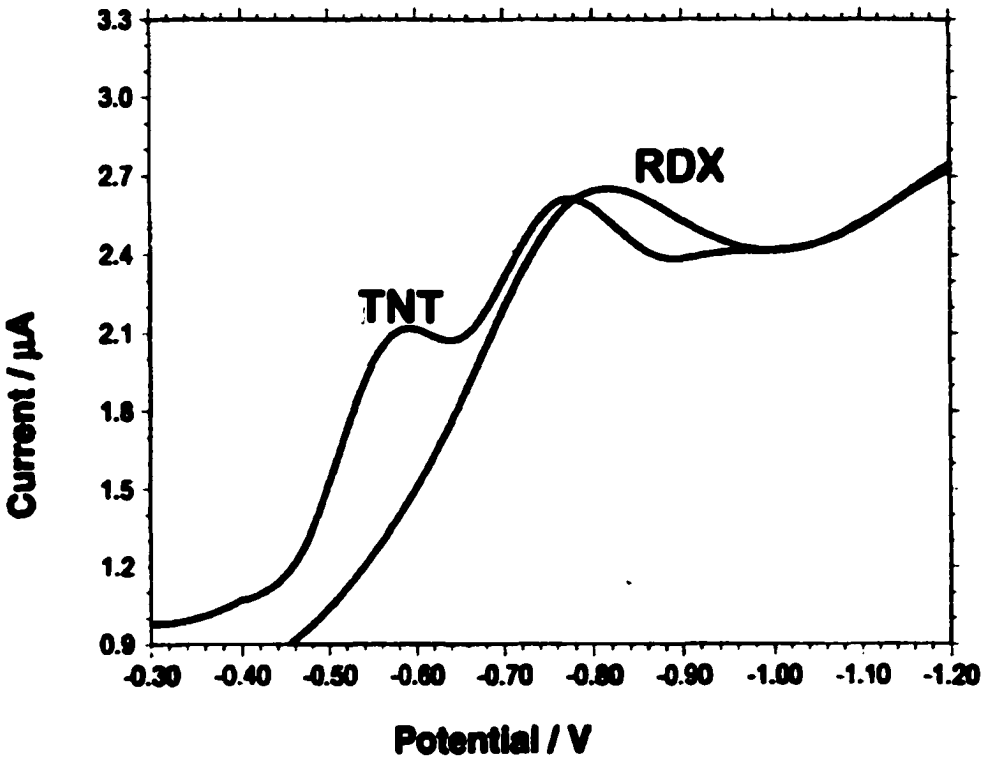


Figure 17 Comparison of TNT and RDX First Reduction Potentials in 10% Acetonitrile and 1% HCl

To test the interference of RDX with TNT, a standard curve of RDX was run in a fixed solution of 1ppm TNT. The first reduction peak of TNT was at –0.61 volts and the second reduction peak was at –0.80 Volts. Although the TNT potential is far enough away from the potential peak of RDX, the presence of RDX did increase and interfere with the TNT scans. Figure 18 shows the overlapping SWV scans of increasing concentration of RDX in the presence of 1 ppm TNT. This suggests that if RDX were present in a TNT sample, the result would be an overestimate of the correct TNT concentration.

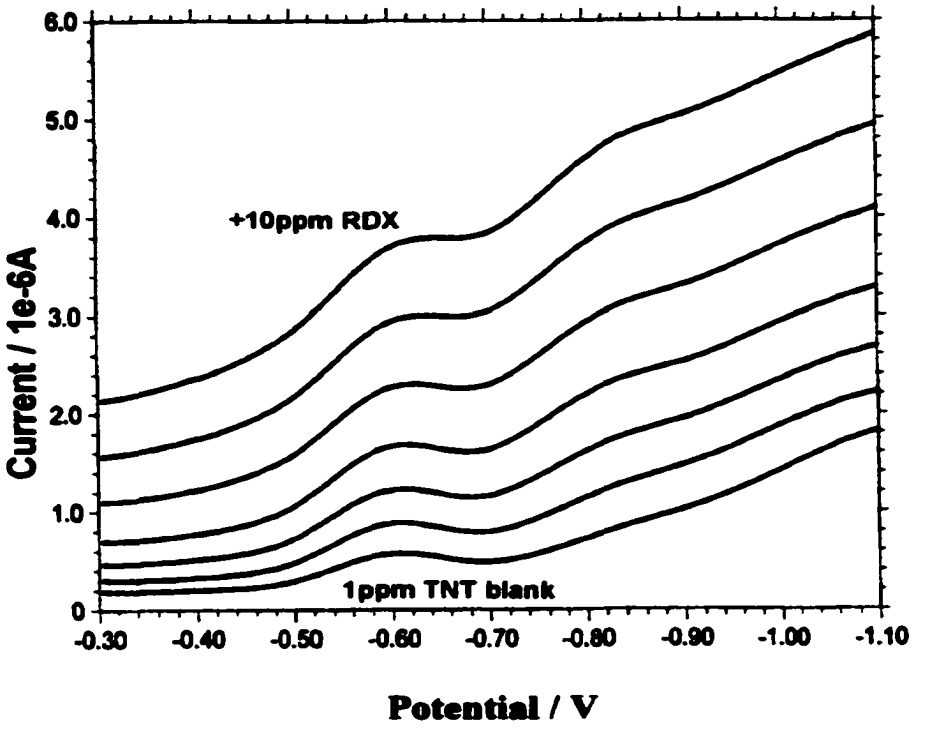


Figure 18 SWV of RDX Concentration Spiked into a 1ppm TNT Solution in 10% Acetonitrile and 1% HCl

In order to reduce the interference problems associated with the presence of RDX and TNT together, we acidified the solution using 1M HCl. When TNT and RDX were analyzed together and then in the presence of a higher acidic solution, the RDX signal disappeared, leaving only a signal from TNT. However, since the reduction potential is dependent on the pH of the solution, the TNT reduction peak was now at –0.42 Volts, instead of –0.61 Volts. Figure 19 shows an overlapping SWV scan of 2 ppm TNT, 2 ppm TNT with 2 ppm RDX, and after acidification of the solution. After acidification, the SWV for TNT and RDX was identical to the signal produced earlier by only TNT (tracing not shown due to direct overlap).

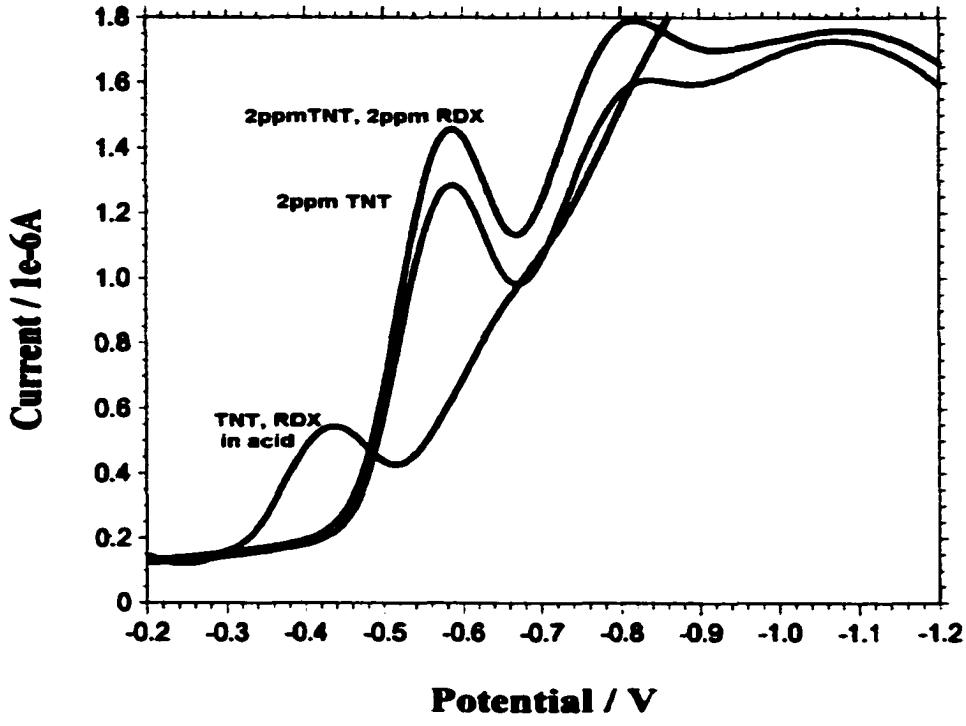


Figure 19 SWV Comparing TNT and RDX Signals With and Without Acidification

Analysis of Breakdown Products Using Electrodes

Out of the five compounds tested for possible interference with TNT analysis, only 2-amino-dinitrotoluene (2-aDNT) appeared to interfere. The first reduction potential peak appeared at –0.58 Volts, which was very close to the potential for TNT found at –0.42 Volts. Also, as seen from the overlapping scan (Figure 20) the peak for 2-aDNT was very high and started its ascent before the TNT peak finished descending, suggesting that if the two were found together, they would interfere with each other, creating one large peak. The only other compound that showed up on the SWV scan was 4-amino-dinitrotoluene, with a reduction potential of –0.80 Volts. The three other compounds tested, p-dinitrobenzene, 2,4-dinitrotoluene, and 1,3,5-trinitrobenzene, did

not show a reduction potential peak in these parameters, suggesting no significant interference with TNT.

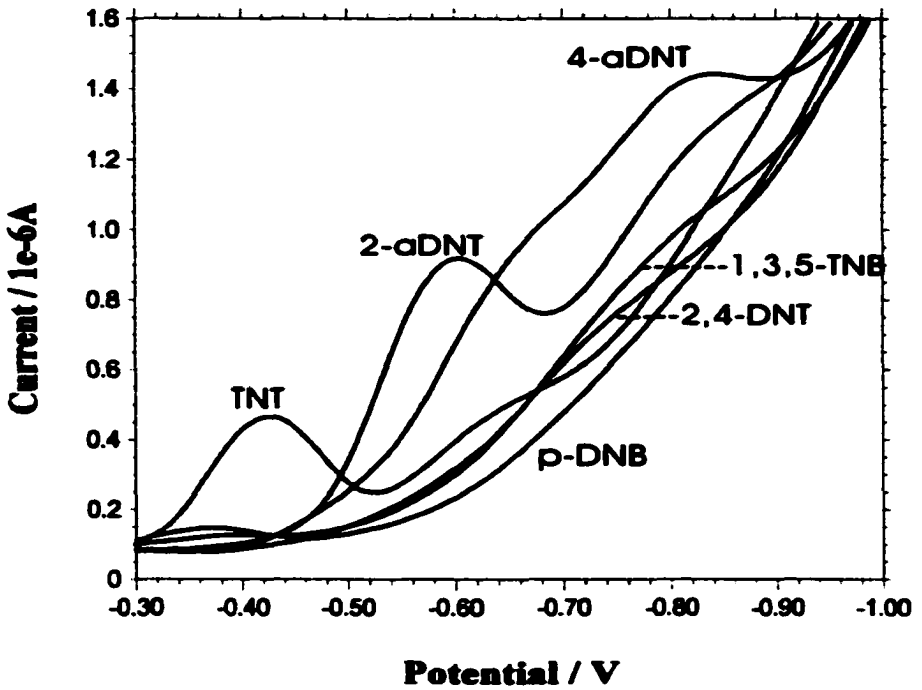


Figure 20 Overlapping SWV scans of TNT and Various Breakdown Products in 1M HCl

TNT Extraction Method

Samples collected from the extraction of TNT from diluted stock solutions in water were analyzed on SPC electrodes. Figure 21 is an example of the SWV scans of the extracted standard curve, with original concentrations ranging from 0 to 50 ppb. This procedure was repeated three times. Appendix 2 lists the complete table of collected data. When concentration was plotted against the average current, the graph resulted in a linear relationship with an R^2 value of 0.9909. Figure 22 shows the plotted concentration vs average current of the TNT standard curve using the screen-printed carbon electrodes (SPCE), made from stock solution and tested with each extraction curve (Appendix 2).

Using the stock solutions, the average percent recovery was calculated and graphed in Figure 23.

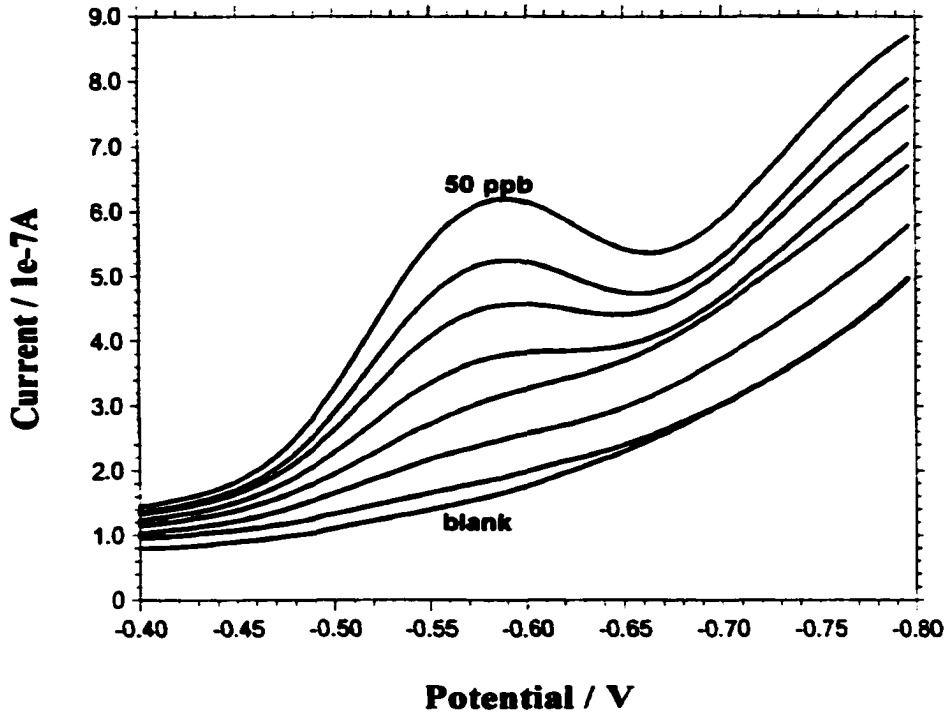


Figure 21 SCV Scans of Extracted TNT Samples on SPCE in 10% Acetonitrile and 1% HCl

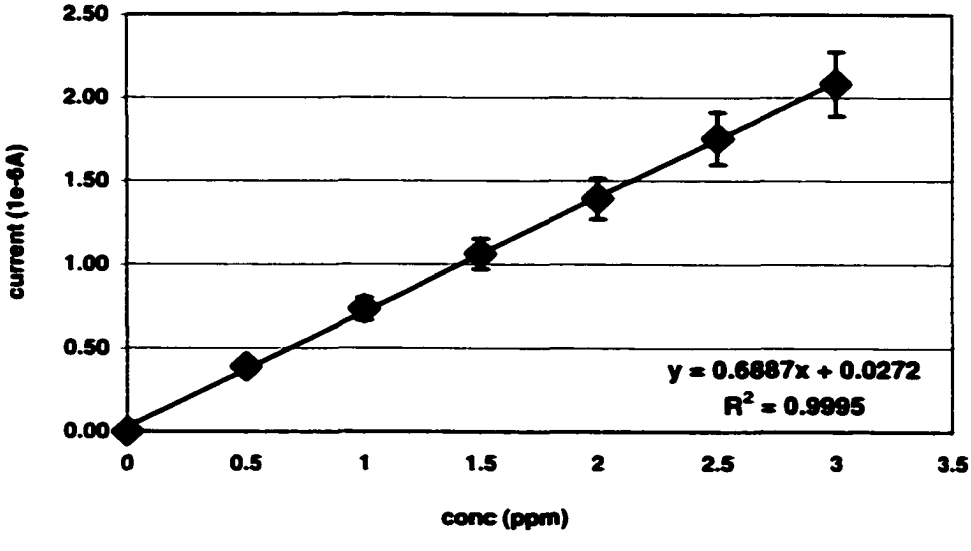


Figure 22 Concentration vs Average Current of TNT Stock Solution on SPCE

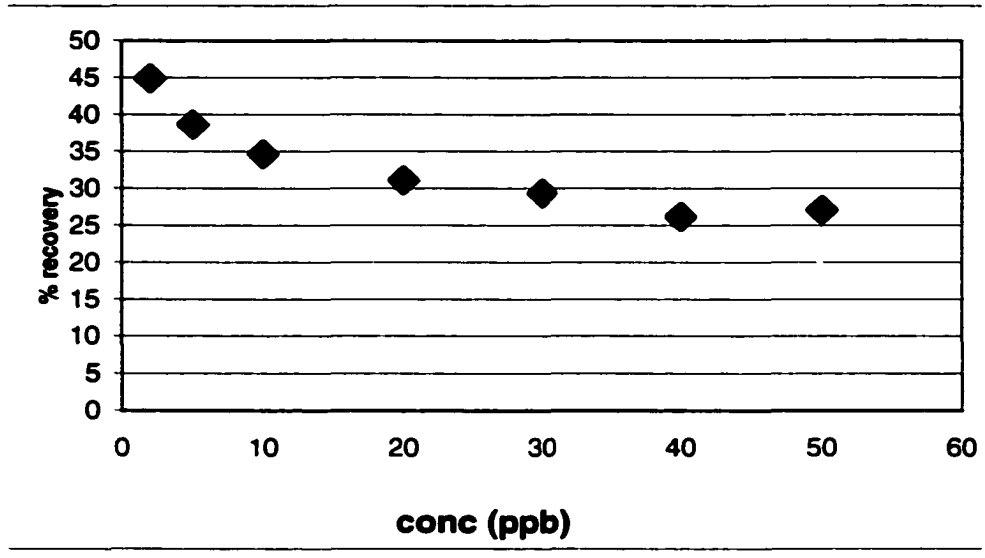


Figure 23 Percent Recovery of TNT Concentration from Extraction Process on SPCE

The TNT extracts were also analyzed using HPLC to verify the linear relationship of the final samples analyzed by the SPC electrodes and the percent recovery. Figure 24 shows the graph of original concentration plotted against average peak area for the extracted samples. Figure 25 shows the concentration plotted against average peak area of the TNT stock solution tested with each trial of extraction samples. Appendix 2 lists the table for the entire data collected from the HPLC trials. Figure 26 is a graph of the average percent recovery as calculated using the data from the HPLC analyzed standard curves and extracted samples. The average current results from the electrode data was plotted against the average peak area results form the HPLC data to show that both suggested a linear relationship from the extraction procedure. (Figure 27)

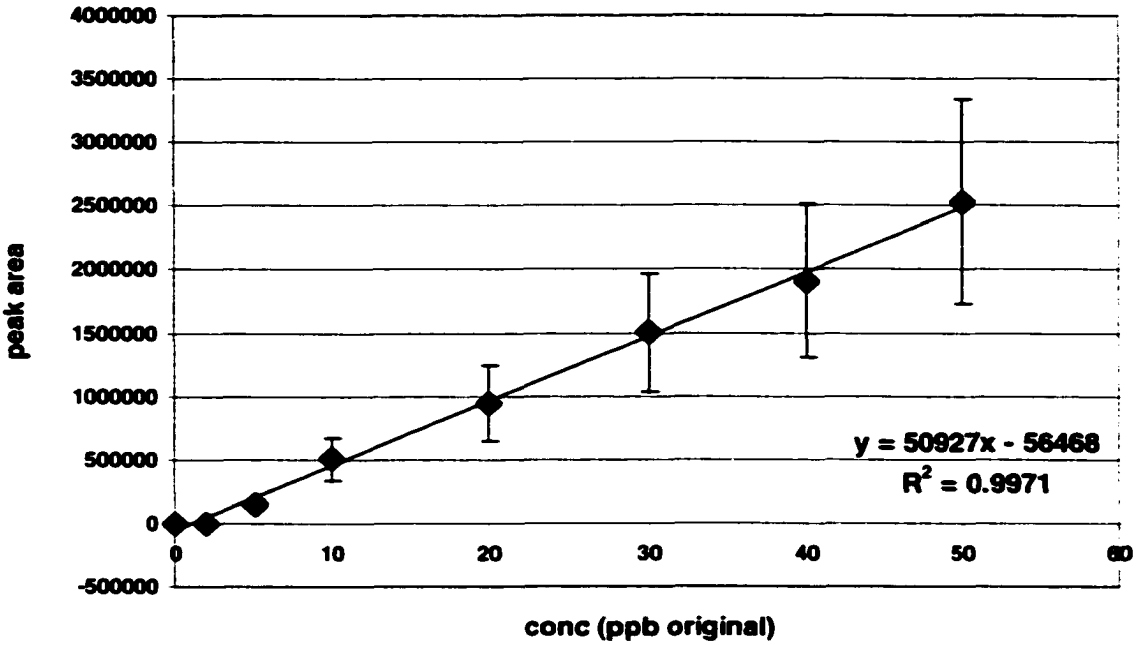


Figure 24 Concentration vs Average Peak Area of Extracted Samples on HPLC

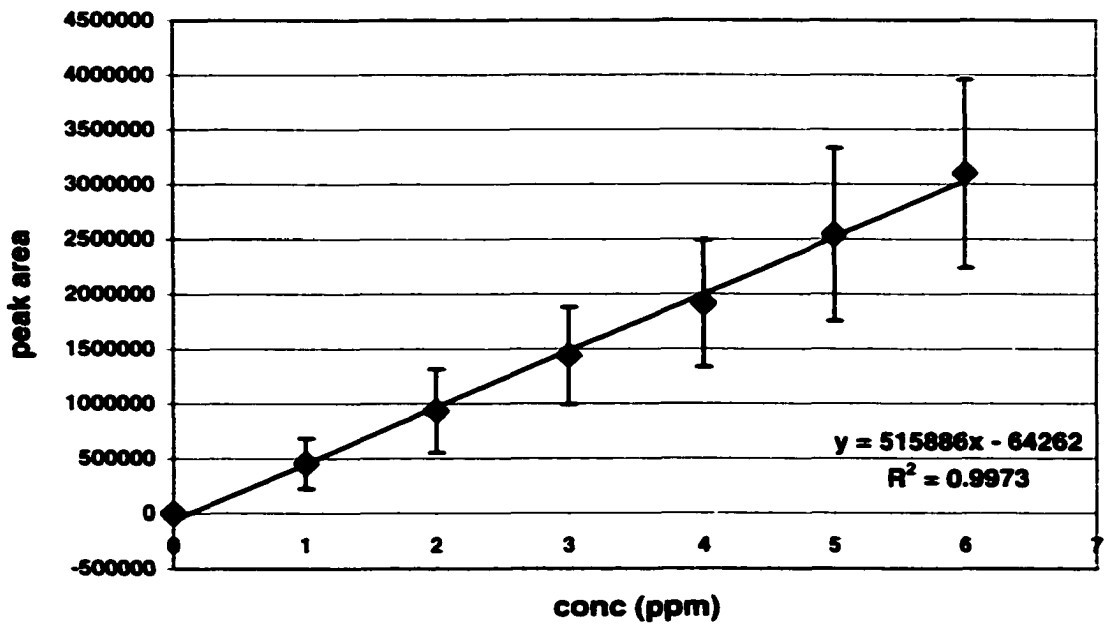


Figure 25 Concentration vs Average Peak Area of TNT Stock Solution on HPLC

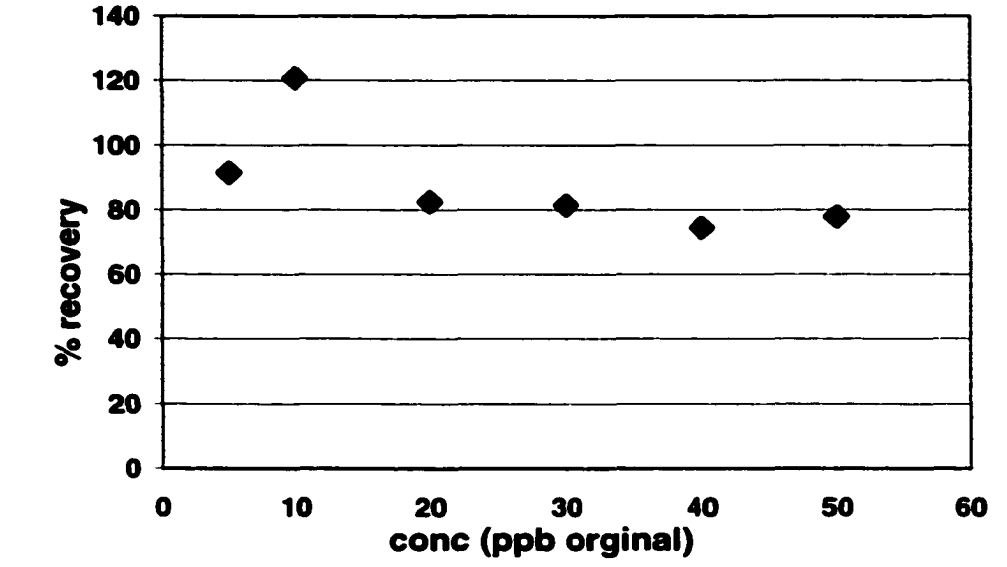


Figure 26 Average Percent Recovery Calculated form HPLC Data

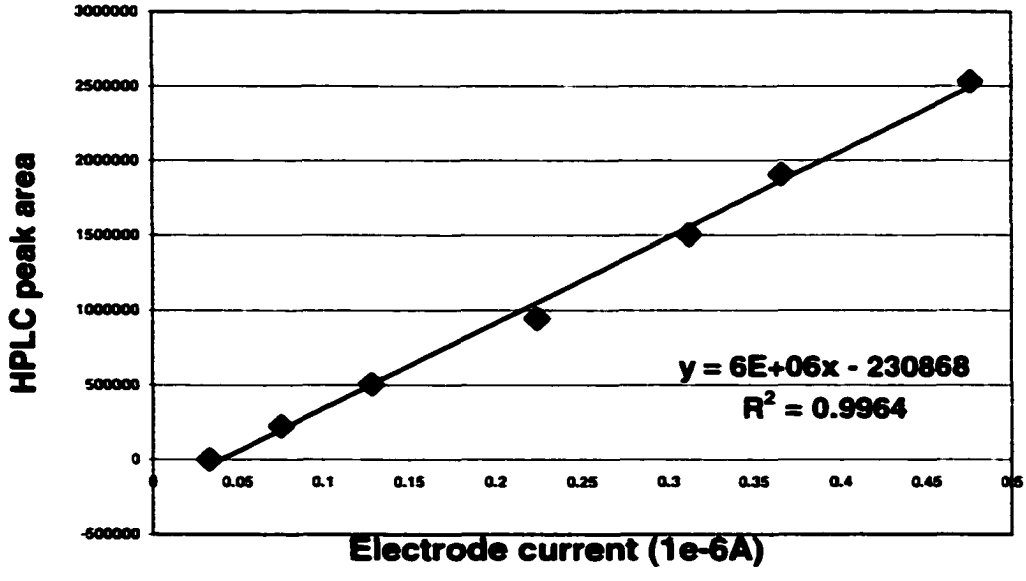


Figure 27 Electrode vs HPLC Results of Extracted Samples

DNT Extractions

A 2-amino-dinitrotoluene (DNT) extraction curve was done to test if the same extraction procedure used for TNT might be useful for the identification of DNT in a sample. It was also done to see if the loss of a nitro group for an amine group would result in a different affinity for the 3M Empore filters leading to altered percent recoveries compared to the TNT recoveries. A trial was run using the same technique as in the TNT extractions, except a stock solution of 2-amino-dinitrotoluene was used for the dilutions and standard curve. Figure 28 shows the results of the extracted samples. The graph of original concentration against current shows an R^2 value of 0.996. Also tested was a standard curve, which when plotted in Figure 29, shows an R^2 value of 0.9968. Using these graphs percent recovery of extracted 2-aDNT was calculated (Figure 30).

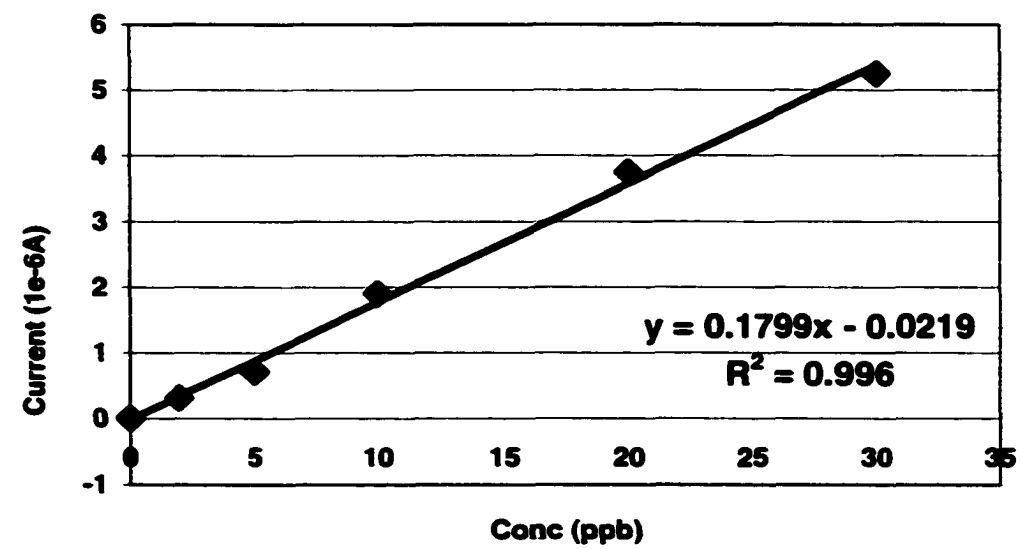


Figure 28 DNT Extraction Curve on SPCE

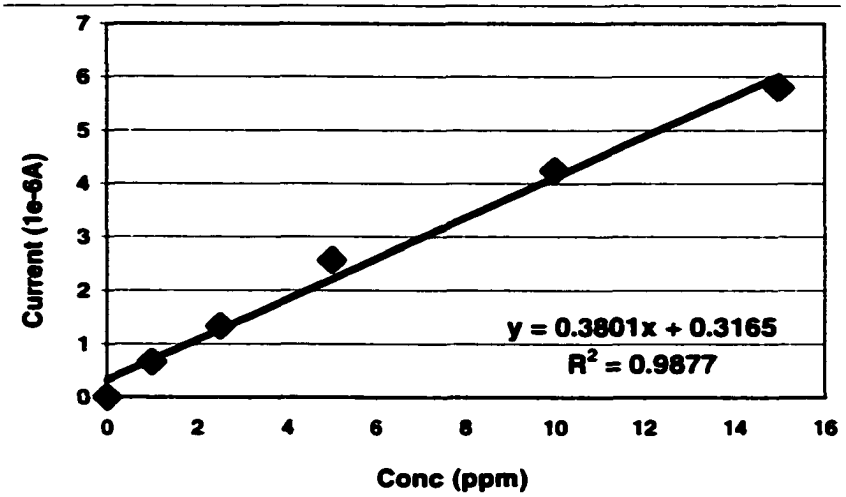


Figure 29 DNT Stock Standard Curve on SPCE

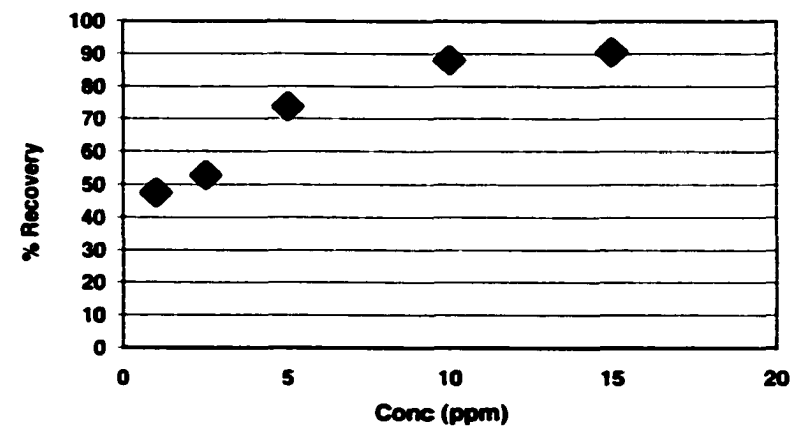


Figure 30 Average DNT Percent Recoveries from SPCE

Plant Tissue and Soil Extractions

To test the previous method developments, TNT and DNT extractions were performed on environmental samples, which included plant tissue, soil and water samples. The plant tissue was obtained from EPA in Athens, Georgia. Table 4 lists the final calculated concentrations for TNT and DNT extractions from both plant tissue and soil samples (*Yucca filamentosa* and *Platanus occidentalis*). Not all plant tissue was

reported in the final analysis, because sample size was inadequate, or tissue was consumed during experimental trials. All samples were done in triplicate except for the Yucca root, which only had enough weight for one trial. Appendix 3 lists the complete data for the plant tissue and soil samples from electrode analysis.

Table 4

TNT and DNT Concentrations for Plant Tissue and Soil Extractions

TNT Concentrations

Sample	Average Concentration (mg/kg)	Recovery Adjusted Concentration (mg/kg)	Previously Reported Value	Percent Difference
Sycamore Root	2.69	2.72	8.00	66
Sycamore Stem	1.71	1.82	N/R	N/A
Sycamore Soil	1.23	1.34	2.10	59
Yucca Root	2.04	2.13	5.00	41
Yucca Soil	1.22	1.34	1.00	18

DNT Concentrations

Sample	Average Concentration (mg/kg)	Recovery Adjusted Concentration (mg/kg)	Previously Reported Value	Percent Difference
Sycamore Root	5.95	7.34	14.00	47
Sycamore Stem	4.84	6.23	8.00	22
Sycamore Soil	2.89	4.04	5.20	22
Yucca Root	4.70	6.09	13.00	53
Yucca Soil	3.05	4.24	6.10	30

Blank Extractions

Blank extractions were done to test the extraction method and analysis for matrix interference and baseline noise. Although the Yucca species used in the blank was different than the one tested, the procedure was the same and should have a similar

matrix. Table 5 lists the average results of the blank extractions, while Appendix 3 lists the entire data collected.

Table 5

TNT and DNT Concentrations for Blank Extractions

TNT Concentrations		
Sample	Average Concentration (mg/kg)	Actual Concentration (mg/kg)
Yucca Leaf	2.65	0.00
Yucca Root	2.40	0.00
Yucca Soil	0.160	0.00

DNT Concentrations		
Sample	Average Concentration (mg/kg)	Actual Concentration (mg/kg)
Yucca Leaf	4.86	0.00
Yucca Root	5.70	0.00
Yucca Soil	0.98	0.00

Environmental Water Samples

Four water samples collected from EPA monitoring wells were tested for TNT to see if results from HPLC analysis at EPA in Athens, Georgia compare with results from the methods tested here. The concentrations of the water samples were plotted against their resulting current, along with two known spiked concentrations, resulting in a 6-point test. Figure 31 shows the graph of these six points and a regression curve with R^2 value of 0.8322. Using this equation, a calculated concentration can be found for each of the samples as if their concentrations were unknown. Table 6 lists known and the calculated

values. Electrode data for all environmental water sample experiments are listed in Appendix 3.

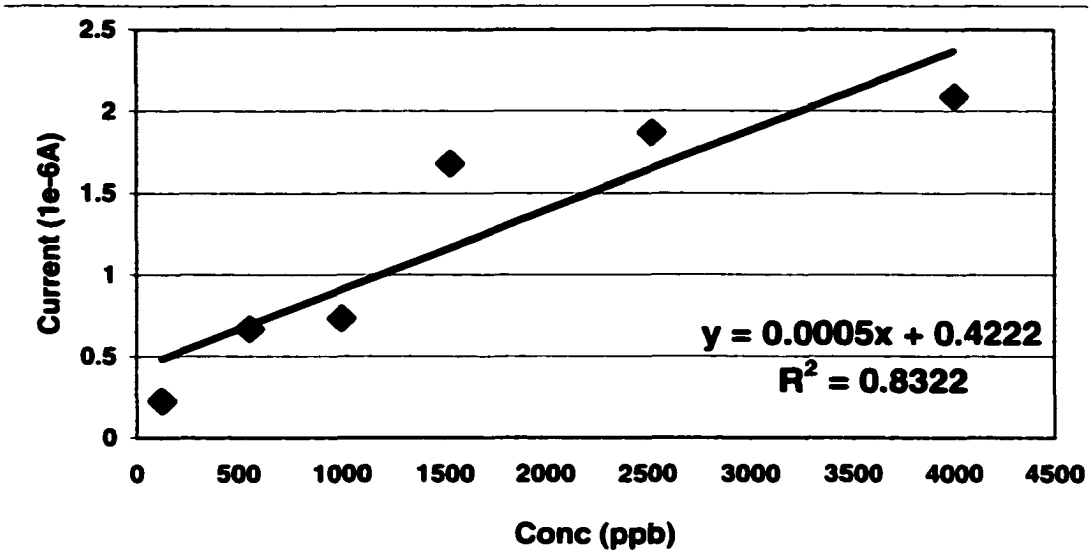


Figure 31 Regression Plot of Environmental Water Samples

Table 6

Calculated and Reported Concentrations for Environmental Water Samples

Sample Code	Known HPLC Concentration (ppb)	Calculated Concentration (ppb)	Percent Difference
Blank	0	-712 (0)	>100
Milan 005-99228	156	-170 (0)	>100
LAAP Well 12	694	896	22
Spike	1000	1050	5
LAAP Well 141	1908	3320	42
Milan 006-99228	3152	3776	16
Spike	4000	4302	7

One environmental sample (LAAP Well 168) was tested using a standard addition method with TNT. Figure 32 shows the resulting SWV scan of this experiment. Using a linear fit regression curve ($R^2 = 0.9961$), the unknown concentration was calculated to be 3417 ppb when the actual value was reported as 1516 ppb. This was more than double the reported value (approximately a 55% difference). A second calculation was tested, by graphing the TNT concentration against the difference in current between the first reduction peak and the following trough, to see if this was a better indication of concentration. This resulted in a linear curve fit with an R^2 value of .9995 and had a 983 ppb calculated TNT concentration of the environmental sample. This was a closer value to the known with an approximate difference of only 35%.

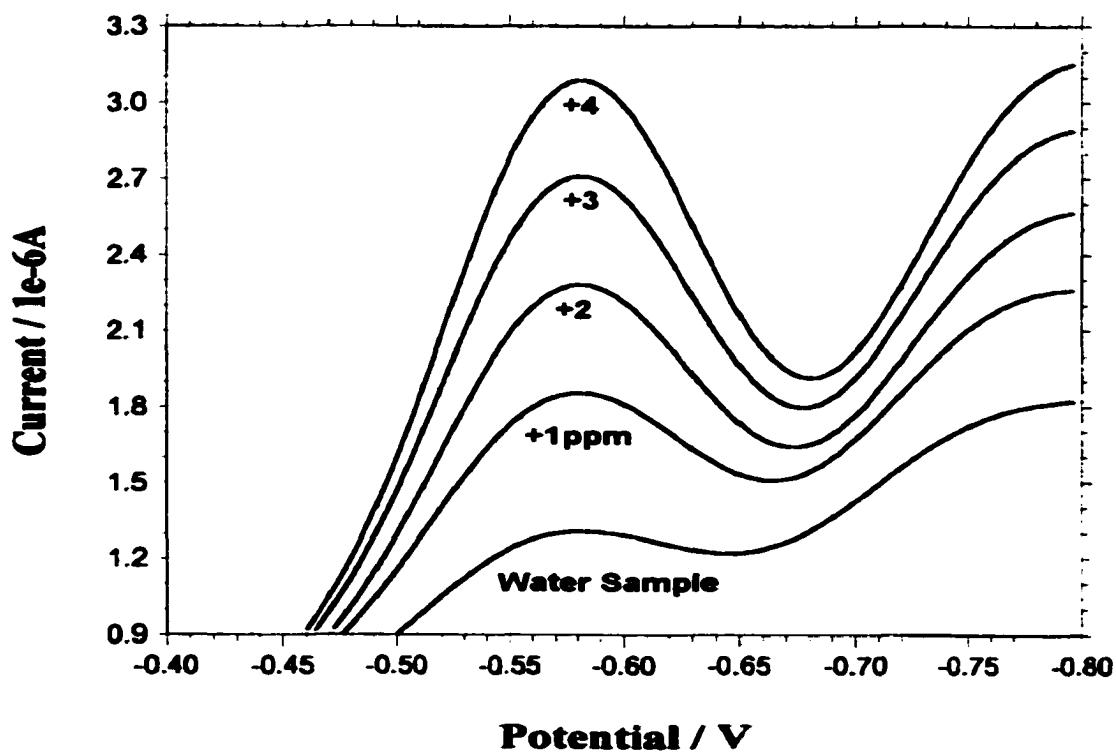


Figure 32 SWV Scans for Standard Addition of Environmental Water Sample

CHAPTER 5

DISCUSSION

Standardization and Optimization

The screen-printed carbon electrodes showed high sensitivity to TNT. Although the amount of change in current between increasing concentrations varied slightly from one electrode to another, the linear relationship was reproducible with each new standard curve. The linear range for TNT, as measured by the first reduction peak, ranged between 0.5 ppm and 15 ppm. A second reduction peak was detected down to 1.5 ppm, but was not detectable in lower amounts. Concentrations above this limit are not useful, so no testing was done beyond the 15 ppm concentration. HPLC analysis confirmed the linear relationship resulting from electrode analysis of TNT standard curves.

The initial phosphate solution containing 1M HCl was altered to see if current changes could be enhanced. Trials were done using acetonitrile in varying concentrations in a phosphate buffer solution keeping a constant 1% HCl in the final solution. The optimization tests revealed that a slightly acidic solution (pH 5) is better for clean baselines; however, if too acidic (pH 2) the current is decreased. A linear relationship can still be observed for a standard curve, but the difference in current between peak potential of the tested concentrations were small, leaving little room for variance. In basic buffer solutions (above pH 7), the baseline increased rapidly causing the reduction potential peaks to become non-detectable. Different pHs also lead to a shift in

reduction peak potentials. A decrease in pH shifted the peak potential to a more positive potential voltage, while an increase in pH shifted the peak potential to a more negative potential.

Tests on RDX standard curves also showed a linear relationship for change in current up to 10 ppm. The peak definition was poorer than TNT for the first reduction peak, and a second reduction peak was not visible. The RDX peaks were small, broad, and resulted in a smaller change in current. Because the peak for RDX is not very distinct, it would be hard to detect RDX in a sample that is co-contaminated with TNT. When TNT is present with RDX, the TNT reduction peak is seen, however, the RDX is not. The result is an overestimation of the TNT concentration. To try to eliminate the RDX signal, acidification was applied. At low pH, the signal from the RDX was lost leaving only the TNT signal. This method could be used to estimate TNT and RDX concentrations from a co-contaminated sample by running one sample in high pH buffer (pH 7) and a second in low pH buffer (pH 2). The high pH would yield overestimated TNT concentrations while the low pH would yield a more accurate TNT concentration. The difference between the two peak currents would be due to the contribution from the RDX concentration. This would allow TNT and RDX to be measured from one sample using only one electrode, in just a few minutes.

Since TNT readily breaks down due to photo- and microbial degradation, large amounts of degradation products could be present in samples and potentially interfere with the detection of TNT on the electrodes. Selected degradation products were tested for electrode sensitivity and reduction peak potential. Analysis of the electrochemical behavior by the TNT breakdown products suggests that 2-amino-dinitrotoluene (DNT)

could be a potential interference with TNT since it has a reduction peak potential close to TNT and overlapping peak tails. Analysis also shows that the electrodes are sensitive to both 2-aDNT and 4-aDNT. Their reduction potential was not thought to be interference to TNT since they had values more negative than TNT and only a small amount of peak overlap. The three other compounds tested (2,4-dinitrotoluene, para-dinitrobenzene, and 1,3,5-trinitrobenzene) did not interfere with TNT, as the electrodes showed essentially no sensitivity towards them using the method and parameters tested in this research.

Coupling the electrode analysis with the solid phase extraction using the 3M Empore SDB-RPS filters resulted in a detection limit of 2 ppb TNT. These filters show excellent efficiency in binding and releasing TNT. Electrode analysis and HPLC analysis of the extracted samples both showed linear results. The extraction method has some variability in the percent recovery. However, even though the electrode average recovery was approximately 30%, the concentration factor of 1:500 was great enough to allow for a significant improvement in the detection limit. The HPLC yielded higher percent recoveries than the electrodes, but had poor reproducibility. It is possible that the HPLC is a more sensitive technique than the screen-printed carbon electrodes.

The DNT extractions showed similar results to that of TNT, but with slightly better percent recoveries. One possible reason for this could be if the filter had a higher affinity for the DNT molecule, which has two nitro groups and one amine group. Another reason could simply be due to a more efficient solvent release from improvement in the extraction method and laboratory techniques, acquired from numerous trials done before in the TNT extraction method development.

Environmental Applications

The screen-printed carbon electrodes had mediocre usefulness for analysis of plant tissue. The calculated concentrations resulting of plant extractions were only about 50% of the reported HPLC values for both TNT and DNT. The values for the soil extractions, however, were closer to 75% of the reported HPLC values. Although the soil results were better, they were still somewhat problematic. When extractions were performed, the solutions had a noticeable amount of impurities in the matrix. The extract had a green cloudy appearance, suggesting that a significant amount of plant material was extracted into the acetonitrile solvent. Blank extractions were performed to test for the possibility of matrix interference. These results showed high and variable current values resulting from matrix interference. Consequently, the results from the soil and plant extractions were inaccurate and unreliable. The soil blanks appeared to have a cleaner matrix and give better results than the plant tissue blanks, suggesting that interferences in the matrix of the plant tissue contributed to poorer results for the plant samples.

The water samples tested had calculated concentrations which closely approximate the reported value. These samples possessed cleaner matrices, although there appeared to still be some interference. These interferences with TNT could be due to breakdown products, as the samples were collected 6 months prior to analysis. However, even with the amount of error between the known and predicted values, the electrode analysis still shows promise as a screening technique for estimates of TNT concentrations in environmental ground water and surface water samples.

The well water sample tested by standard addition techniques had an initial concentration of twice the reported amount when the regression curve, used to calculate

the concentration, was from concentration vs total current. After using peak to trough difference instead of peak current for the Y-axis, the final calculation resulted in a concentration closer to the reported value, but still had about 40% less than the reported HPLC value. This data handling technique could show potential for screening water samples for TNT. All of the environmental applications need more repetitions before making any final conclusions.

General Comments and Applicability of Techniques

During the development of these methods, there existed some potential problems/errors that could have had negative influences on the results. Most of this research included the characterization of screen-printed carbon electrodes, however these electrodes showed some variability in their fabrication. When electrodes were tested with a voltmeter, there were considerable differences in resistance across the carbon and silver strips between electrodes. (Appendix 4) This initial variance would lead to differences in results. Another source of error was the use of HPLC for confirmation of electrode results. Verification experiments done on the HPLC were performed using techniques that were optimal to the best of my knowledge, however it takes a long time to perfect the techniques needed to conduct experiments that result in reliable and reproducible data. I had limited operating experience with the HPLC and had difficulties with noisy baselines and reproducible peak areas, although retention times remained constant for peak identification.

Future Experiments

For future research I would like to look into better techniques for the detection of RDX and TNT. The acidification process had some positive potential as a quick method for the quantification of both TNT and RDX, but I would like to find a possible way to separate and isolate the compounds for better individual analysis.

Also for future research, the extraction of TNT and DNT for concentration of dilute samples could be better optimized and perfected for higher percent recoveries. This could lead to detection limits below the 2 ppb level reported here. Also research for a separation and detection method for TNT and DNT from a co-contaminate sample could be used in screening of environmental samples. This could possibly lead to a method which would separate the other breakdown products from TNT. The DNT extraction experiment was only an initial test to see what potential the 3M Empore filters had on other compounds. Not only do more repetitions of DNT need to be done, other experiments on RDX and other TNT breakdown products are also needed.

Most importantly, for these electrodes to be used in analysis of plant and soil extractions, more research needs to be done to isolate TNT from the matrix. The plant and soil matrices have a lot of interference when analyzed by the electrode method. Perhaps a separation technique could be applied first to reduce matrix interference. Better results were obtained with the water samples, possibly due to the simpler matrices of the sample. However, this screening technique could be useful in research using plants for phytoremediation of TNT and other explosives from the environment. This would be a fast method to test the water effluent for decreasing TNT concentrations or to test various plant tissues for uptake of TNT.

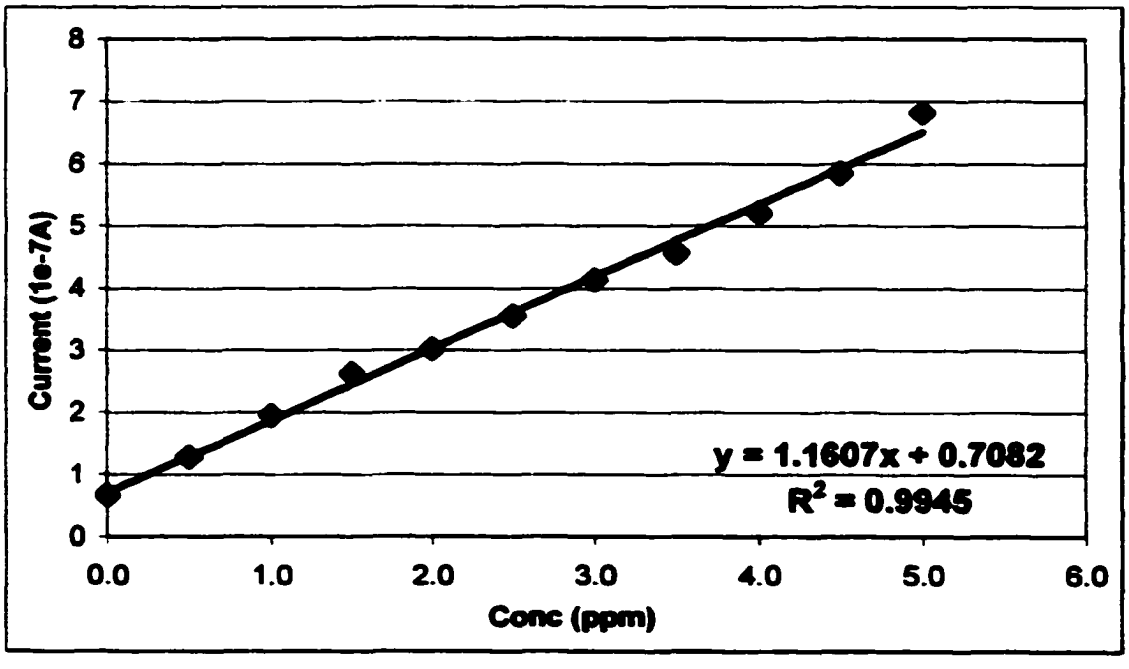
In conclusion, the use of screen-printed carbon electrodes shows great promise as an electrochemical detection method. They are inexpensive, fast, simple and sensitive to the compounds tested here. Detection methods using these electrodes require minimal supplies and solvents, and generate small amounts of waste in the process. Another valuable area of research could include the use of the electrodes for the detection of other environmental contaminants. An important benefit of these detection methods is the ability to analyze samples in the field and at contaminated sites, minimizing the time and cost of lab analysis.

APPENDIX 1

STANDARDIZATION AND OPTIMIZATION EXPERIMENTAL DATA

Data for Characterization of TNT on Screen-Printed Carbon Electrodes (Standard Curve in 1M HCl)

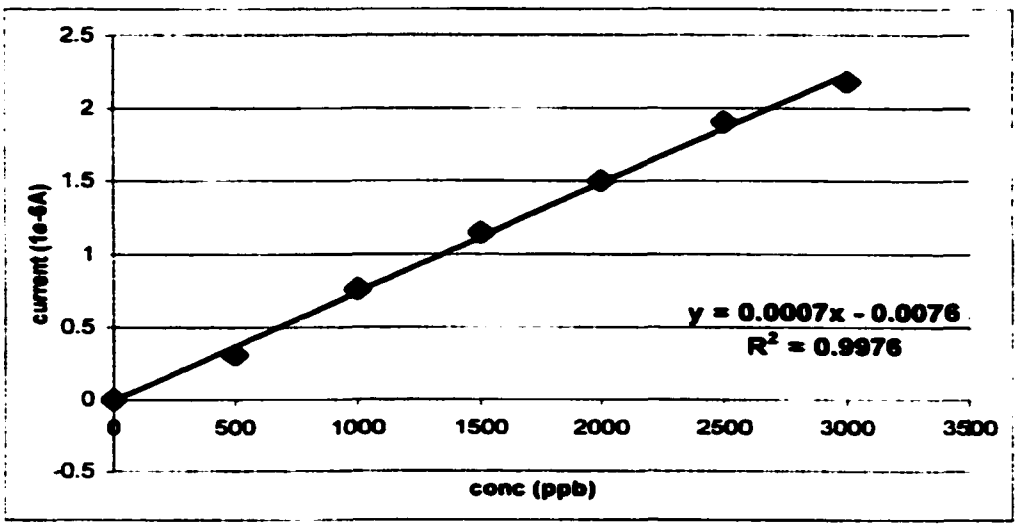
Conc (ppm)	Current (1e-7A)
0.0	0.67
0.5	1.28
1.0	1.95
1.5	2.63
2.0	3.02
2.5	3.56
3.0	4.14
3.5	4.57
4.0	5.22
4.5	5.85
5.0	6.82



Data for TNT Optimization in 10% Acetonitrile and 1%HCl in Phosphate Buffer

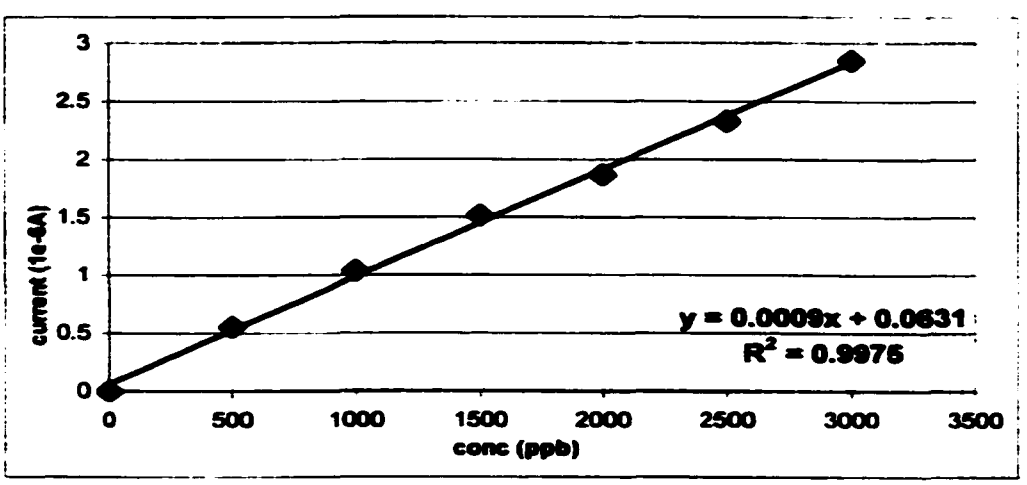
TNT curve A

conc TNT (ppb)	current (1e-6A)	current - blank
0	0.6278	0
500	0.9386	0.3108
1000	1.388	0.7602
1500	1.772	1.1442
2000	2.129	1.5012
2500	2.532	1.9042
3000	2.81	2.1822



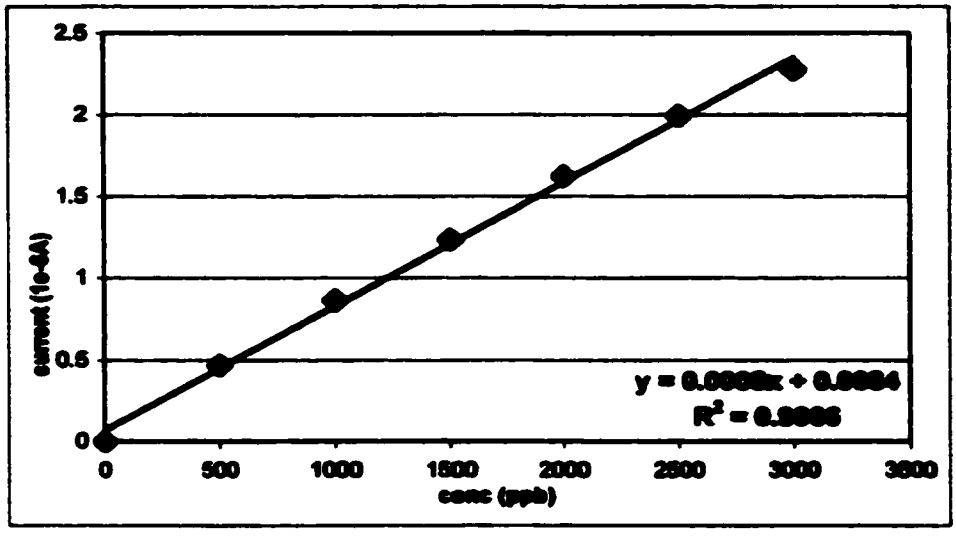
TNT curve B

conc TNT (ppb)	current (1e-6A)	current - blank
0	0.5802	0
500	1.114	0.5538
1000	1.593	1.0328
1500	2.073	1.5128
2000	2.428	1.8678
2500	2.891	2.3308
3000	3.412	2.8618



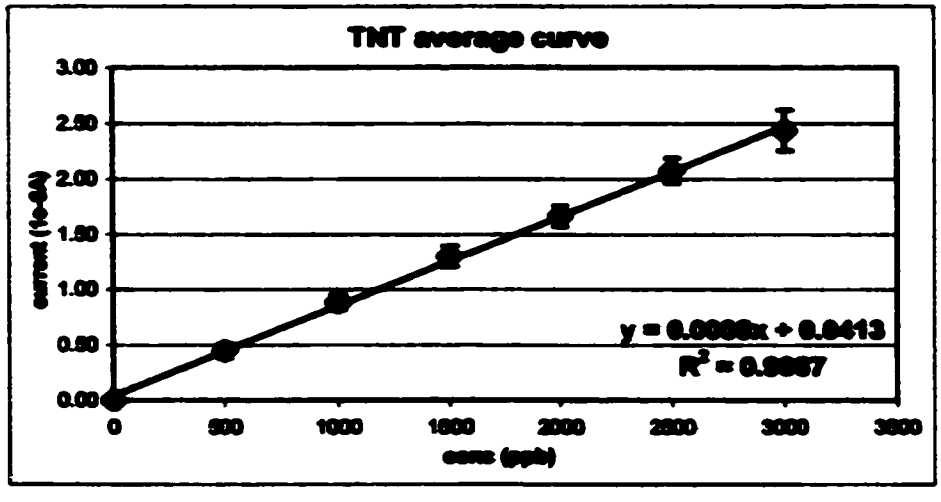
TNT curve C

conc TNT (ppb)	current (1e-6A)	current - blank
0	0.0084	0
500	1.076	0.4666
1000	1.469	0.8626
1500	1.841	1.2348
2000	2.226	1.6216
2500	2.6	1.9838
3000	2.883	2.2768



TNT average curve

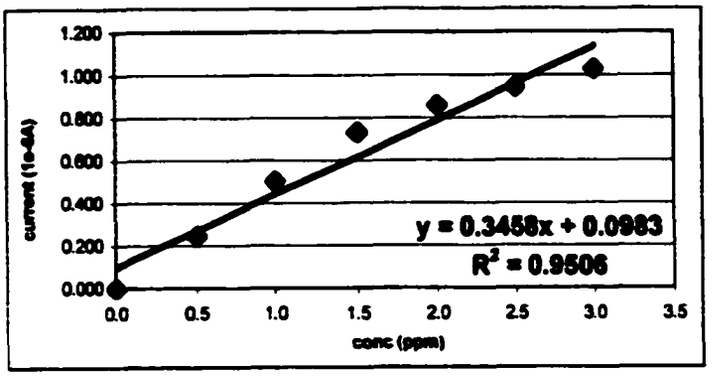
conc TNT (ppb)	curve A current	curve B current	curve C current	average current	standard deviation	standard error	stnd dev %
0	0	0	0	0.0000	0.00000	0.00000	0.00000
500	0.3108	0.5638	0.4666	0.4444	0.12328	0.07118	0.09185
1000	0.7602	1.0328	0.8626	0.8852	0.13770	0.07950	0.08986
1500	1.1442	1.5128	1.2348	1.2972	0.18211	0.11091	0.08806
2000	1.5012	1.8578	1.6216	1.6935	0.18588	0.10729	0.06843
2500	1.9042	2.3308	1.9838	2.0762	0.22468	0.12969	0.11249
3000	2.1822	2.8518	2.2768	2.4369	0.38243	0.20825	0.16121



RDX Characterization Standard Curves in 10% Acetonitrile and 1% HCl on Screen-Printed Carbon Electrodes

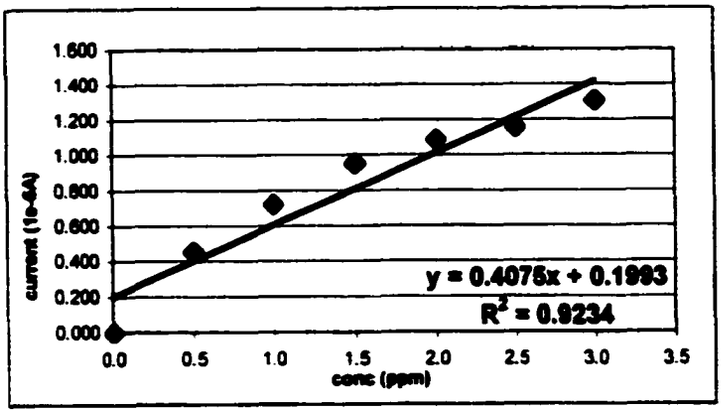
Trail 1

conc (ppm)	current	current - blank
0.0	2.123	0.000
0.5	2.371	0.248
1.0	2.626	0.503
1.5	2.856	0.733
2.0	2.983	0.860
2.5	3.068	0.945
3.0	3.153	1.030



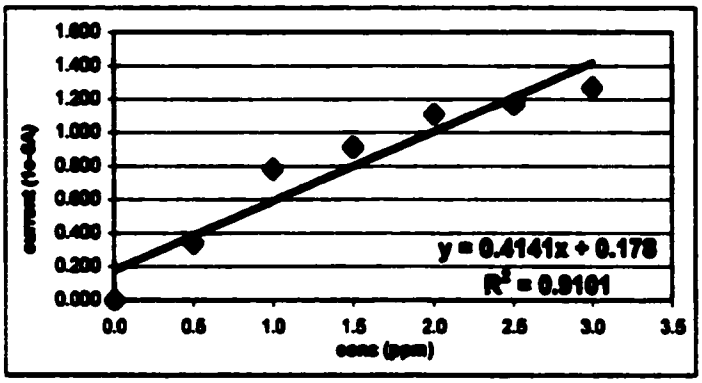
Trail 2

conc (ppm)	current	current - blank
0.0	2.473	0.000
0.5	2.923	0.450
1.0	3.194	0.721
1.5	3.425	0.952
2.0	3.558	1.085
2.5	3.630	1.157
3.0	3.782	1.309



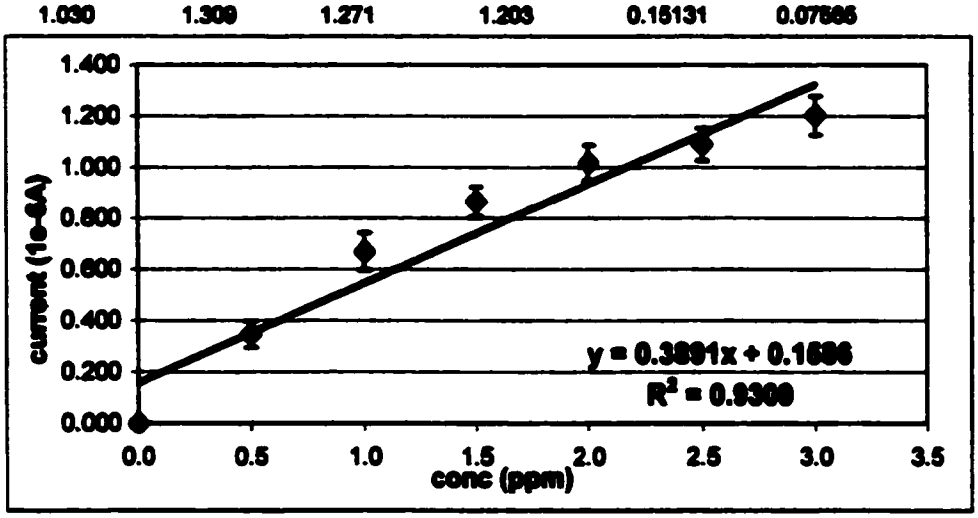
Trail 3

conc (ppm)	current	current - blank
0.0	2.972	0.000
0.5	3.315	0.343
1.0	3.756	0.784
1.5	3.885	0.913
2.0	4.084	1.112
2.5	4.143	1.171
3.0	4.243	1.271



RDX Averages

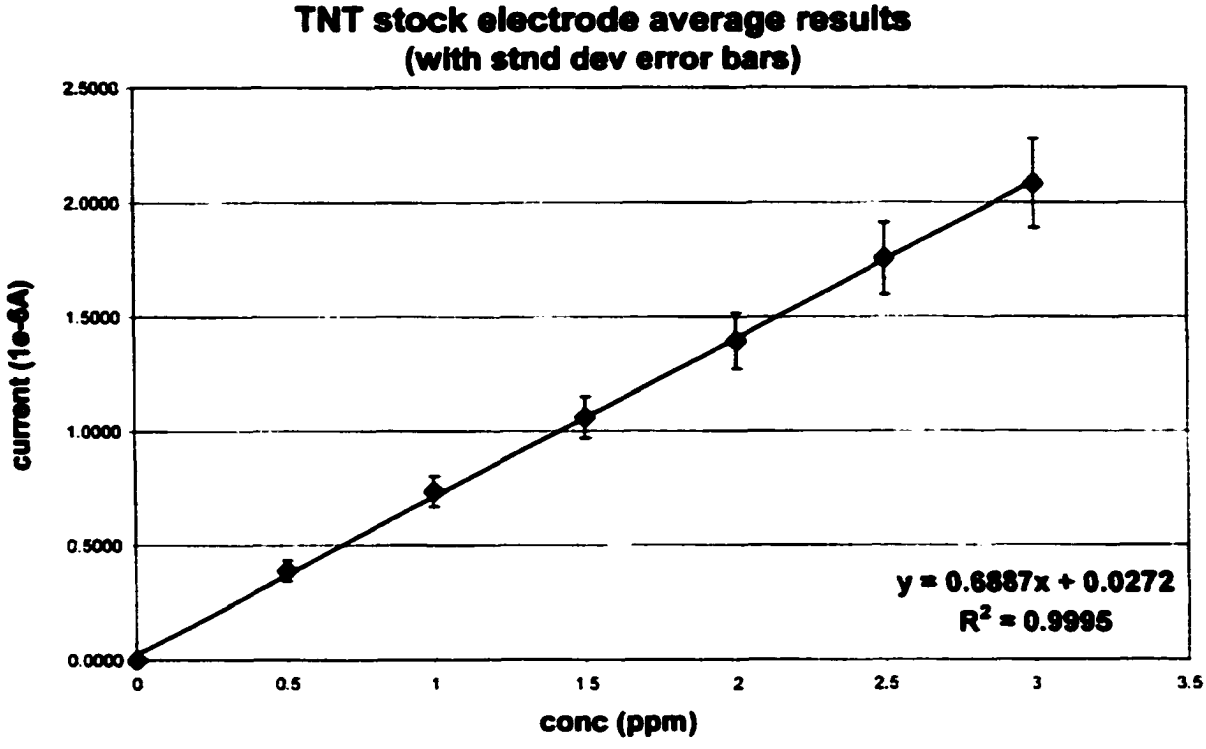
conc	trial 1	trial 2	trial 3	average	stnd dev	stnd dev/2
0.0	0.000	0.000	0.000	0.000	0.00000	0.00000
0.5	0.246	0.460	0.343	0.347	0.10106	0.05053
1.0	0.503	0.721	0.784	0.669	0.14745	0.07373
1.5	0.733	0.952	0.913	0.866	0.11682	0.05841
2.0	0.860	1.086	1.112	1.019	0.13536	0.06918
2.5	0.946	1.157	1.171	1.091	0.12663	0.06332
3.0	1.030	1.309	1.271	1.203	0.15131	0.07566

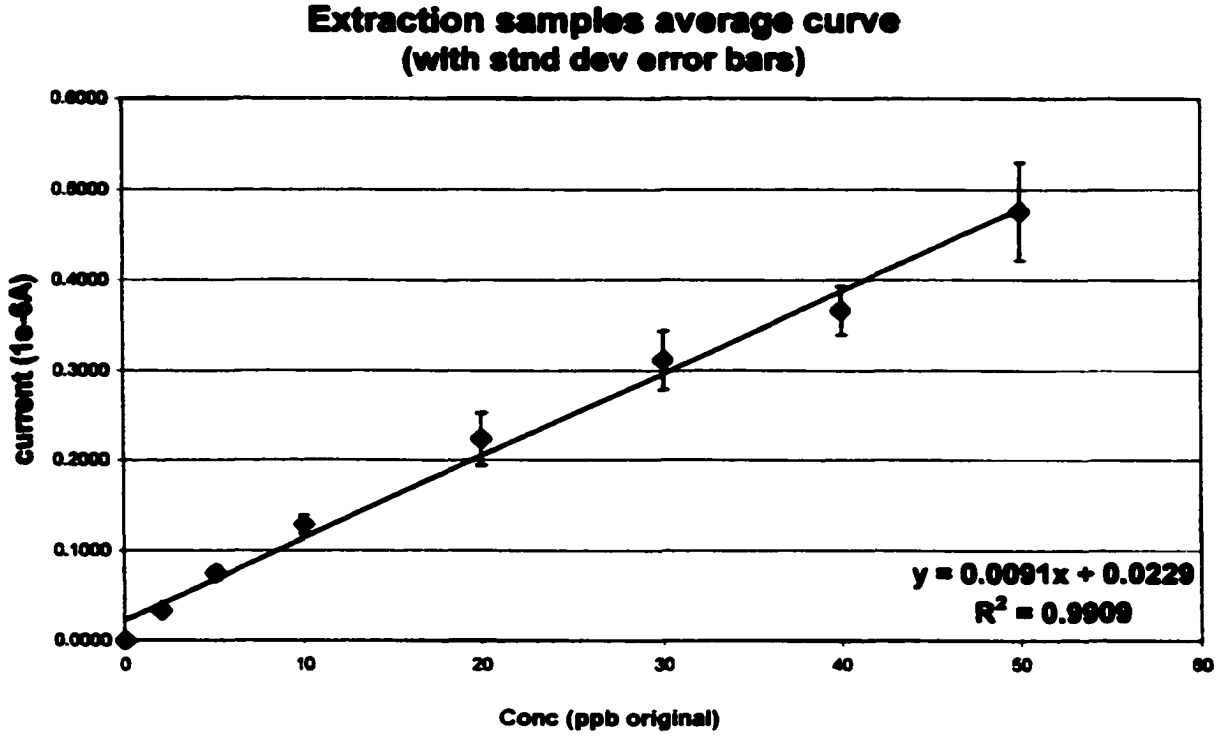


APPENDIX 2

EXTRACTION METHOD DATA

Graphs and Data for TNT Extractions on Screen-Printed Carbon Electrodes in 10% Acetonitrile and 1% HCl in Phosphate Buffer





Electrode Results

TNT stock

	blank = 0.3064		blank = 0.3136		blank = 0.4142					
conc (ppm)	trial 1	trial 1-blank	trial 2	trial 2-blank	trial 3	trial 3-blank	average	stnd dev	stand error	std dev /2
0	0.3064	0	0.3136	0	0.4142	0	0.0000	0.000000	0.000000	0
0.5	0.7751	0.4687	0.6086	0.295	0.8189	0.4047	0.3895	0.087846	0.050718	0.043923124
1	1.132	0.8256	0.8973	0.5837	1.214	0.7998	0.7364	0.132841	0.076688	0.066420623
1.5	1.444	1.1376	1.167	0.8534	1.609	1.1948	1.0619	0.182846	0.105566	0.091422662
2	1.75	1.4436	1.443	1.1294	2.024	1.8098	1.3943	0.243970	0.140856	0.121985013
2.5	2.099	1.7926	1.736	1.4244	2.466	2.0518	1.7563	0.315274	0.182024	0.157637062
3	2.359	2.0526	2.027	1.7134	2.899	2.4848	2.0836	0.386633	0.223223	0.193316606

Extractions

	blank = 0.1696		blank = 0.1527		blank = 0.2292					
conc (ppb)	trial 1	trial 1-blank	trial 2	trial 2-blank	trial 3	trial 3-blank	average	stnd dev	stand error	std dev /2
0	0.1696	0	0.1527	0	0.2292	0	0.0000	0.000000	0.000000	0
2	0.193	0.0232	0.1855	0.0328	0.2733	0.0441	0.0334	0.010462	0.006040	0.005230758
5	0.2527	0.0829	0.2125	0.0598	0.3119	0.0827	0.0751	0.013279	0.007667	0.006639716
10	0.3183	0.1485	0.2588	0.1061	0.3587	0.1295	0.1280	0.021238	0.012262	0.010619008
20	0.3838	0.214	0.3243	0.1716	0.5157	0.2865	0.2240	0.058103	0.033546	0.029061692
30	0.4591	0.2893	0.4131	0.2604	0.6149	0.3857	0.3118	0.065610	0.037880	0.032805144
40	0.5285	0.3587	0.4709	0.3182	0.6535	0.4243	0.3664	0.053711	0.031010	0.026855493
50	0.6211	0.4513	0.5345	0.3818	0.6243	0.5951	0.4761	0.108785	0.062807	0.0543927

Data for Percent Recovery Calculations for TNT Extractions

% recovery

trial 1

original conc (ppb)	theoretical concentrated ppm	electrode dilution 1:10 (ppm)	trial 1-blank values	what theor values should say	fraction recovered	% recovery
0	0	0	0	0.0033	0	0.00
2	1	0.1	0.0232	0.16061	0.144449287	14.44
5	2.5	0.25	0.0829	0.281575	0.318928312	31.89
10	5	0.5	0.1485	0.42665	0.345468835	34.55
20	10	1	0.214	0.7684	0.276227557	27.62
30	15	1.5	0.2893	1.10295	0.262298568	26.23
40	20	2	0.3567	1.4395	0.247794373	24.78
50	25	2.5	0.4513	1.77605	0.254103207	25.41

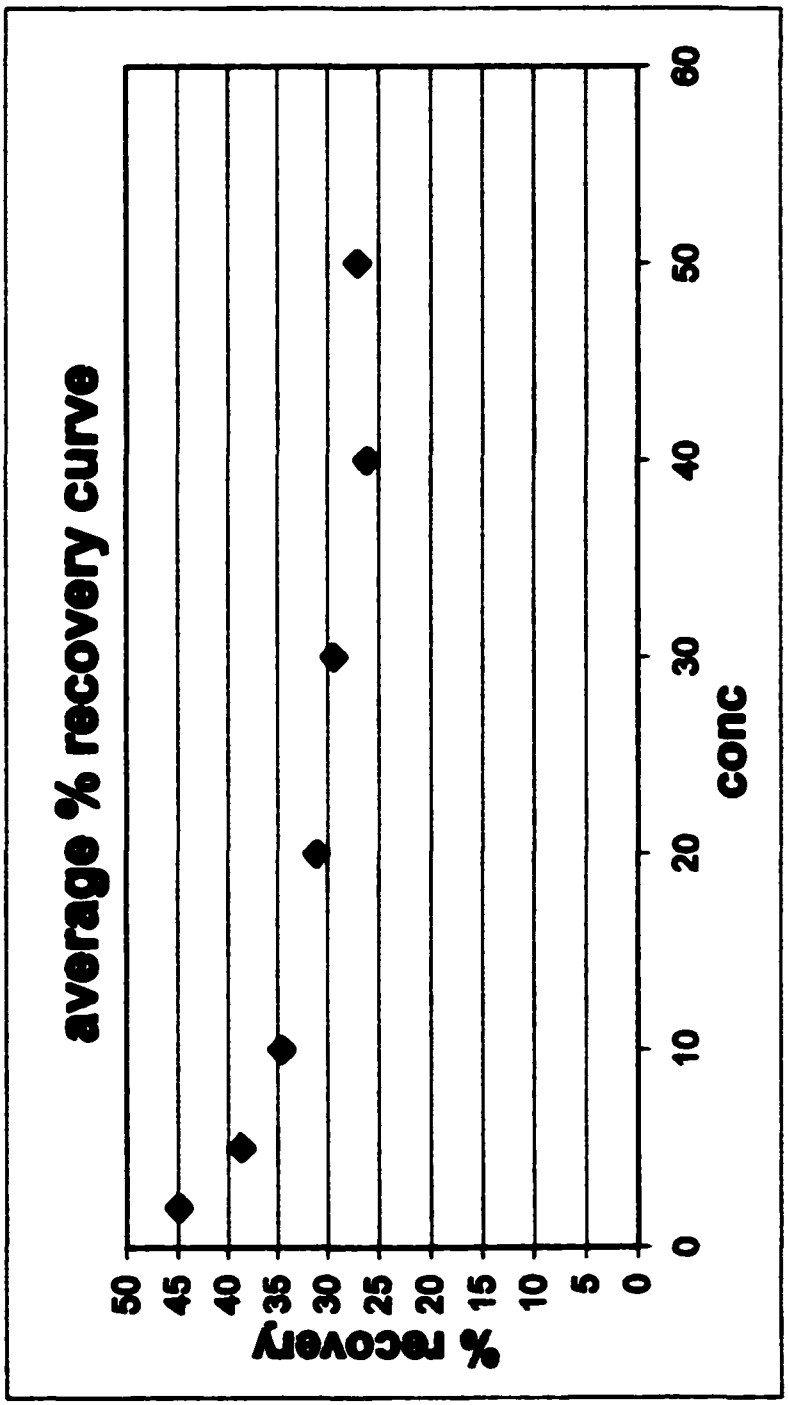
trial 2

original conc (ppb)	theoretical concentrated ppm	electrode dilution 1:10 (ppm)	trial 2-blank values	what theor values should say	fraction recovered	% recovery
0	0	0	0	0.0058	0	0.00
2	1	0.1	0.0326	0.06255	0.524360466	52.44
5	2.5	0.25	0.0586	0.147675	0.404943288	40.49
10	5	0.5	0.1061	0.28955	0.366430868	36.64
20	10	1	0.1716	0.5733	0.299319728	29.93
30	15	1.5	0.2604	0.85705	0.303832915	30.38
40	20	2	0.3182	1.1408	0.278927089	27.89
50	25	2.5	0.3818	1.42455	0.268014461	26.80

trial 3

original conc (ppb)	theoretical concentrated ppm	electrode dilution 1:10 (ppm)	trial 3-blank values	what theor values should say	fraction recovered	% recovery
0	0	0	0	-0.0176	0	0.00
2	1	0.1	0.0441	0.06496	0.67867831	67.86
5	2.5	0.25	0.0827	0.1888	0.438029661	43.80
10	5	0.5	0.1295	0.3952	0.327682186	32.77
20	10	1	0.2065	0.808	0.354579208	35.46
30	15	1.5	0.3857	1.2208	0.315940367	31.59
40	20	2	0.4243	1.6336	0.259733105	25.97
50	25	2.5	0.5951	2.0464	0.290803382	29.08

original conc (ng/mL)	trial 1 % recovery		trial 2 % recovery		trial 3 % recovery		average % recovery	
0	0		0		0		0.00	
2	14.44		62.44		67.89		44.92	
5	31.89		40.49		43.8		38.68	
10	34.85		39.04		32.77		34.65	
20	27.82		28.83		36.48		31.10	
30	28.23		30.38		31.59		29.40	
40	24.78		27.69		28.97		28.21	
60	25.41		28.8		29.08		27.10	



Data for HPLC Analysis of TNT Extractions

HPLC Results

TNT stock

conc (ppm)	trial 1	trial 2	trial 3	average	stnd dev	stand error	stnd dev /2
0	0	0	0	0.00	0.000	0.000	0
1	783764	130011	0	456887.50	462273.180	326877.323	231136.5898
2	1474004	0	397525	935764.50	761185.601	538240.856	380592.8004
3	2375294	1334086	602641	1437340.33	890825.885	514318.804	445412.9426
4	3159260	1708742	869735	1912579.00	1158293.280	668741.249	579146.6402
5	4186961	2387346	1049196	2541834.33	1575573.244	909658.061	787786.6221
6	4805670	3118484	1373947	3099367.00	1715941.369	990899.673	857970.6845

Extractions

conc (ppb)	trial 1	trial 2	trial 3	average	stnd dev	stand error	stnd dev /2
0	0	0	0	0.00	0.000	0.000	0
2	0	0	0	0.00	0.000	0.000	0
5	273961	175024	0	224502.50	69973.166	49476.625	34986.58287
10	854642	476902	184687	505410.33	335886.096	193924.016	167943.0479
20	1520731	969389	347187	945769.00	587128.443	338878.923	293564.2214
30	2441649	1466000	584074	1503907.67	928916.968	536310.712	464458.484
40	3155598	1831630	735639	1907622.33	1211767.930	699814.867	605883.9651
50	4210118	2370738	1013204	2531353.333	1604497.661	926357.5885	802248.8306

% recovery

trial 1

original conc (ppb)	theoretical concentrated ppm	electrode dilution 1:4 (ppm)	trial 1 peak area values	what theor values should say	fraction recovered	% recovery
0	0	0	0	-56792	0.000	0.00
2	1	0.25	0	147785.25	0.000	0.00
5	2.5	0.625	273961	454651.125	0.603	60.26
10	5	1.25	854642	966094.25	0.885	88.46
20	10	2.5	1520731	1986980.5	0.765	76.46
30	15	3.75	2441649	3011866.75	0.811	81.07
40	20	5	3155598	4034753	0.782	78.21
50	25	6.25	4210118	5057639.25	0.832	83.24

Trial 2 original conc (mM)	theoretical concentrated conc (mM)	electrode dilution 1:4 (mM)	trial 2 peak area values	what theor values should be	fraction recovered	% recovery
0	0	0	0	-439984	0.000	0.00
2	1	0.25	0	-360257	0.000	0.00
5	2.5	0.625	170034	-91611.5	-2.146	-214.46
10	5	1.25	476802	269131	1.782	178.20
20	10	2.5	888889	881619	1.008	100.81
30	15	3.75	1666666	1657101	0.897	89.67
40	20	5	1831630	2362886	0.770	77.66
60	25	6.25	2370736	3048071	0.778	77.78

Trial 3 original conc (mM)	theoretical concentrated conc (mM)	electrode dilution 1:4 (mM)	trial 3 peak area values	what theor values should be	fraction recovered	% recovery
0	0	0	0	-103795	0.000	0.00
2	1	0.25	0	-44001	0.000	0.00
5	2.5	0.625	0	48830	0.000	0.00
10	5	1.25	164667	186016	0.947	94.70
20	10	2.5	347187	493786	0.703	70.31
30	15	3.75	884074	782585	0.737	73.70
40	20	5	736639	1091328	0.674	67.41
60	25	6.25	1013204	1390036	0.729	72.89

original conc (mM)	trial 1 % recovery	trial 2 % recovery	trial 3 % recovery	average % recovery
0	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00
5	60.26	214.46	0.00	91.57
10	88.49	178.20	94.70	120.79
20	76.46	100.81	70.31	82.53
30	81.07	89.67	73.70	81.48
40	78.21	77.66	67.41	74.43
60	83.24	77.78	72.89	77.97

Data for DNT Extraction Percent Recovery on Screen-Printed Carbon Electrodes

% Recovery for 2-aDNT Extraction

Extracted Curve

conc (ppm)	current (1e-6A)	blank
0	1.067	0.000
1	1.380	0.313
2	1.778	0.711
5	2.970	1.903
10	4.811	3.744
15	6.317	5.250

Standard Curve

conc (ppm)	current (1e-6A)	blank
0	0.688	0.000
1	1.348	0.660
2	2.032	1.344
5	3.266	2.578
10	4.941	4.253
15	6.484	5.796

% Recoveries

conc	standard	extraction	standard	recovery
0	0.000	0.000	0.000	0.00
1	0.660	0.313	0.474	47.42
2	1.344	0.711	0.529	52.90
5	2.578	1.903	0.738	73.82
10	4.253	3.744	0.880	88.03
15	5.796	5.250	0.906	90.58

APPENDIX 3

ENVIRONMENTAL APPLICATION DATA

Data for Plant Tissue and Soil Extractions on Screen-Printed Carbon Electrodes

Explosive Concentrations in Soil

TNT

sample	rep	calculated ppm value for x	dilution factor (1:0.2)	conc in mg	sample weight(g)	conc mg/kg	average conc	reported value mg/kg
Sycamore	1	0.525	0.10496	0.0010496	1.0325	1.0166	1.2304	2.10
Soil	2	0.506	0.10112	0.0010112	1.0033	1.0079		
	3	0.845	0.16908	0.0016908	1.0145	1.6666		
Yucca	1	0.842	0.16836	0.0016836	1.0206	1.6496	1.2235	1.00
Soil	2	0.263	0.05262	0.0005262	1.0063	0.5219		
	3	0.757	0.15148	0.0015148	1.0105	1.4991		

2-aDNT

sample	rep	calculated ppm value for x	dilution factor (1:0.2)	conc in mg	sample weight(g)	conc mg/kg	average conc	reported value mg/kg
Sycamore	1	1.520	0.304	0.00304	1.0325	2.9443	2.8883	5.20
Soil	2	1.588	0.3176	0.003176	1.0033	3.1656		
	3	1.296	0.2592	0.002592	1.0145	2.5550		
Yucca	1	1.722	0.3444	0.003444	1.0206	3.3745	3.0515	6.10
Soil	2	1.514	0.3028	0.003028	1.0083	3.0031		
	3	1.403	0.2806	0.002806	1.0105	2.7768		

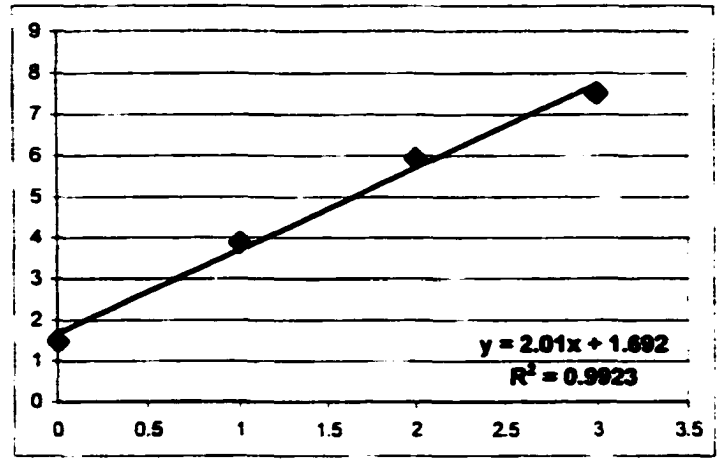
Soil Extractions

TNT

Yucca -1

conc (ppm)	current(1e-6A)
0	1.501
1	3.88
2	5.929
3	7.518

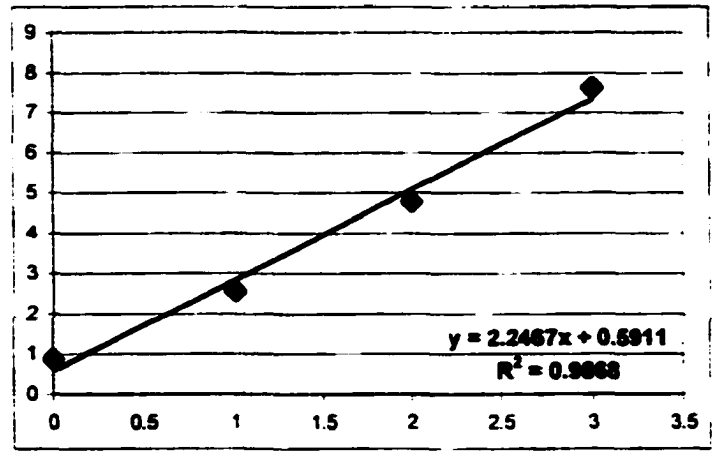
when y =0 linear fit
x = 0.8418



Yucca -2

conc (ppm)	current(1e-6A)
0	0.8784
1	2.557
2	4.784
3	7.625

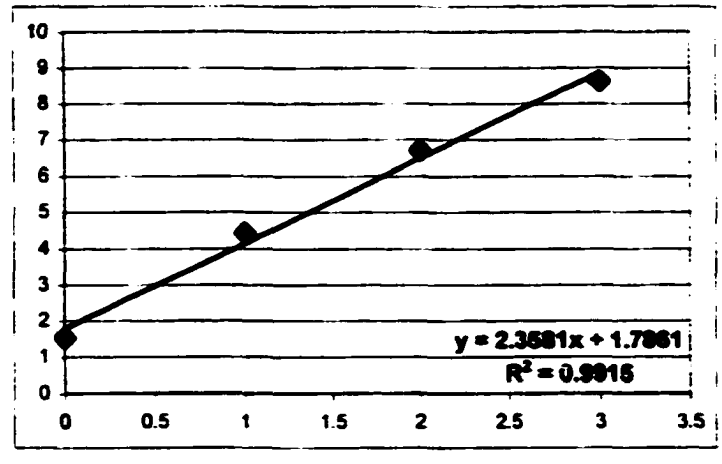
when y =0 linear fit
x = 0.2631



Yucca - 3

conc (ppm)	current(1e-6A)
0	1.531
1	4.423
2	6.71
3	8.629

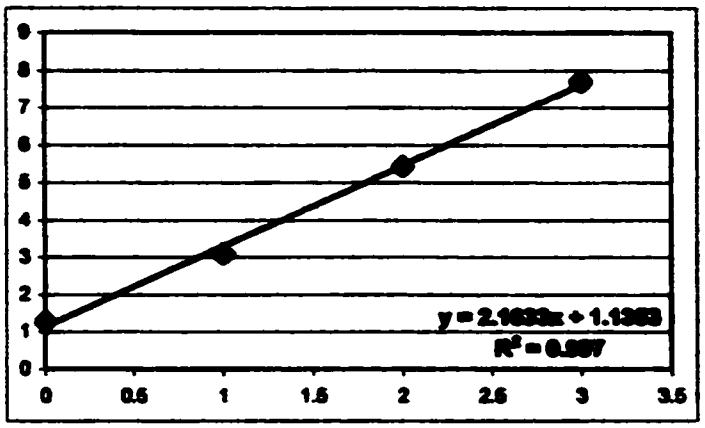
when y =0 linear fit
x = 0.7574



Sycamore - 1

conc.(ppm)	current(1e-6A)
0	1.281
1	3.093
2	5.436
3	7.711

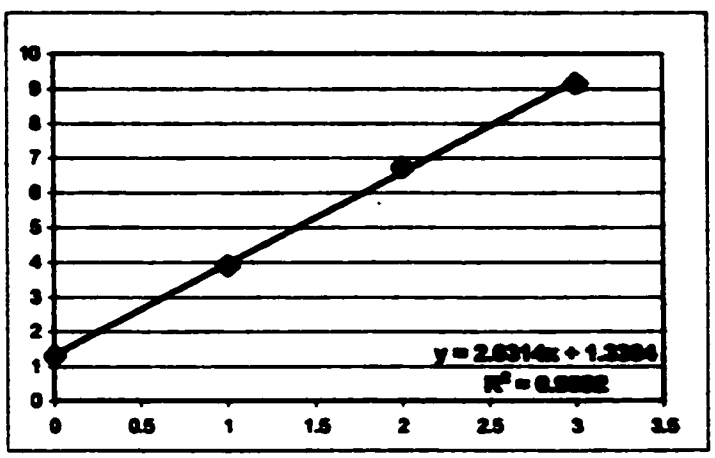
when y =0	linear fit	poly fit
x =	0.5246	0.72, 14.98



Sycamore - 2

conc.(ppm)	current(1e-6A)
0	1.317
1	3.911
2	6.735
3	9.147

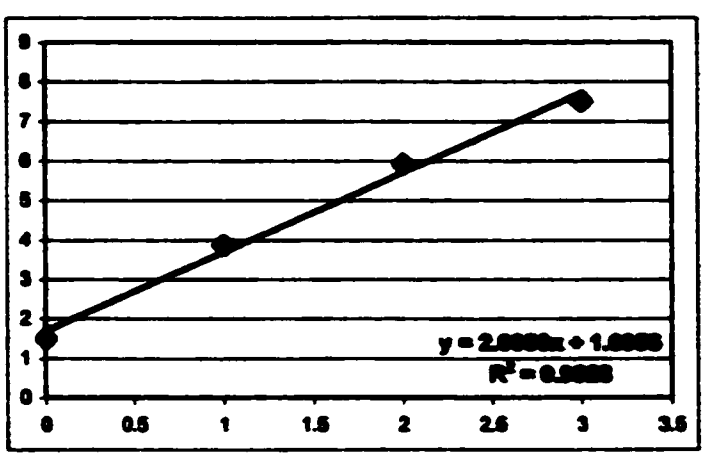
when y =0	linear fit	poly fit
x =	0.5056	0.46, 61.29



Sycamore - 3

conc.(ppm)	current(1e-6A)
0	1.514
1	3.868
2	5.922
3	7.514

when y =0	linear fit	poly fit
x =	0.8464	0.88, 14.12



Explosive Concentrations in Plants

TNT

sample	rep	calculated ppm value for x	dilution factor (1:10)	conc in mg	sample weights(g)	sample weights(kg)	conc mg/kg	average	reported value mg/kg
Sycamore Root	1	0.7893	0.07893	0.0007893	0.2710	0.0002710	2.9125	2.6907	8.00
	2	0.5412	0.05412	0.0005412	0.2719	0.0002719	1.9904		
	3	0.9111	0.09111	0.0009111	0.2875	0.0002875	3.1690		
Sycamore Stem	1	0.4936	0.04936	0.0004936	0.2638	0.0002638	1.8711	1.7131	1.00
	2	0.4044	0.04044	0.0004044	0.2665	0.0002665	1.5174		
	3	0.5044	0.05044	0.0005044	0.2881	0.0002881	1.7508		
Yucca Root	1	0.6894	0.06894	0.0006894	0.3381	0.0003381	2.0390	2.0390	5.00

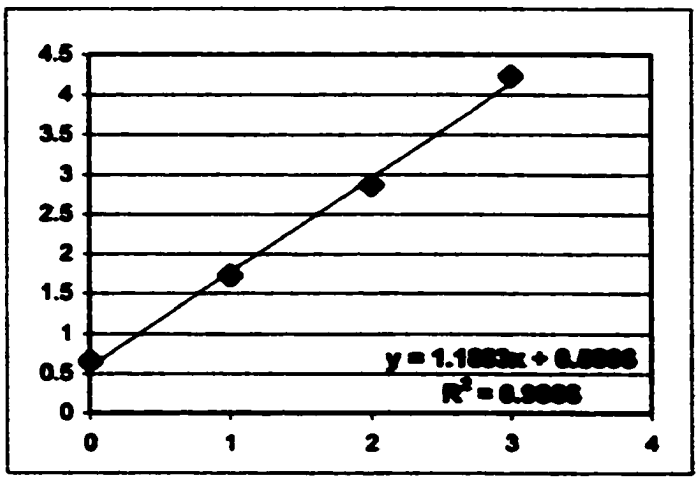
2-aDNT

sample	rep	calculated ppm value for x	dilution(1:10) for electrode	conc in mg	sample weights(g)	sample weights(kg)	conc mg/kg	average	reported value mg/kg
Sycamore Roots	1	1.479	0.1479	0.001479	0.2710	0.0002710	5.4576	5.9495	14.00
	2	1.906	0.1906	0.001906	0.2719	0.0002719	7.0099		
	3	1.547	0.1547	0.001547	0.2875	0.0002875	5.3809		
Sycamore Stem	1	1.35	0.135	0.00135	0.2638	0.0002638	5.1175	4.8427	8.00
	2	1.458	0.1458	0.001458	0.2665	0.0002665	5.4709		
	3	1.135	0.1135	0.001135	0.2881	0.0002881	3.9396		
Yucca Root	1	1.59	0.159	0.00159	0.3381	0.0003381	4.7028	4.7028	13.00

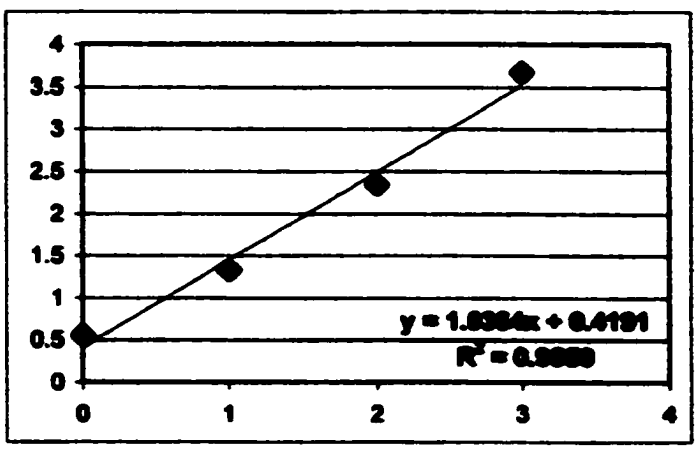
Stem Extraction

TNT

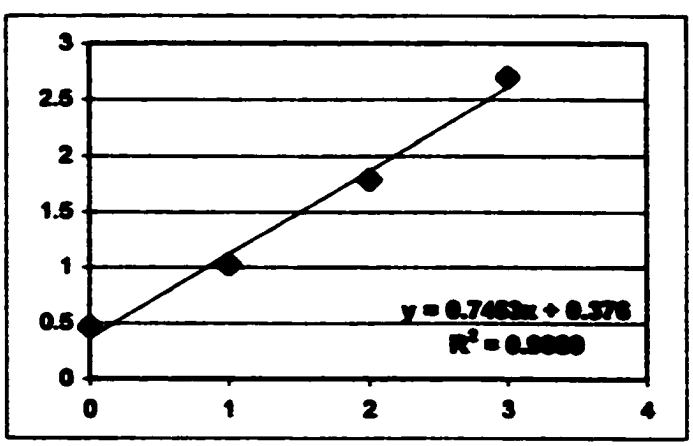
Sycamore Stem-1 conc (ppm added)	peak (1e-6A)
0	0.6533
1	1.725
2	2.863
3	4.235
linear fit x value =	0.4936



Sycamore Stem-2 conc (ppm added)	peak (1e-6A)
0	0.5532
1	1.33
2	2.341
3	3.671
linear fit x value =	0.4044



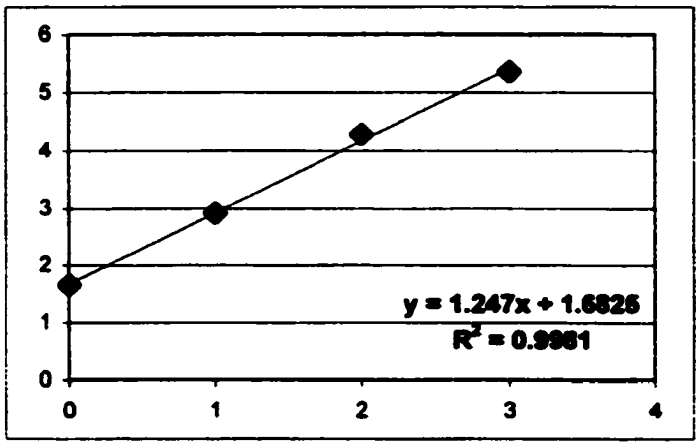
Sycamore Stem-3 conc (ppm added)	peak (1e-6A)
0	0.4667
1	1.025
2	1.787
3	2.667
linear fit x value =	0.5044



DNT

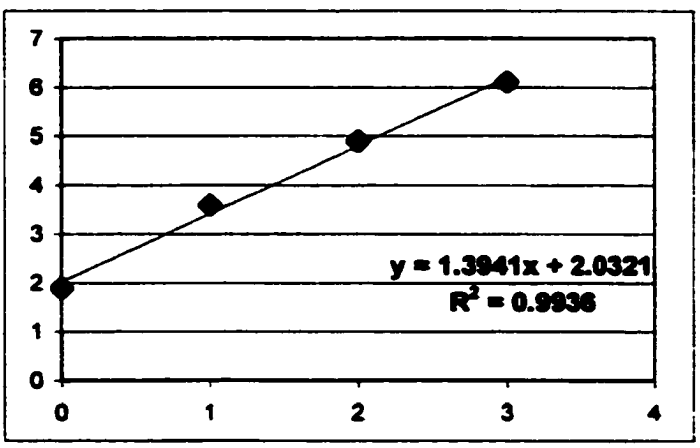
Sycamore Stem-1

conc (ppm added)	peak (1e-6A)
0	1.659
1	2.914
2	4.278
3	5.361
linear fit x value =	1.35



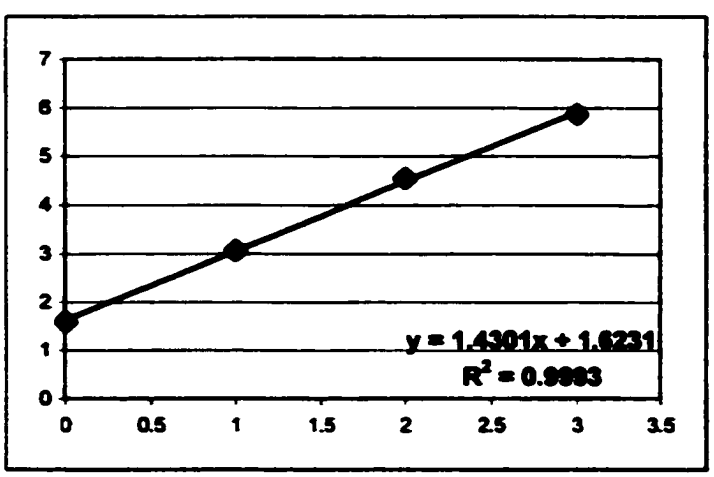
Sycamore Stem-2

conc (ppm added)	peak (1e-6A)
0	1.898
1	3.586
2	4.903
3	6.106
linear fit x value =	1.596



Sycamore Stem-3

conc (ppm added)	peak (1e-6A)
0	1.594
1	3.065
2	4.547
3	5.867
linear fit x value =	1.135

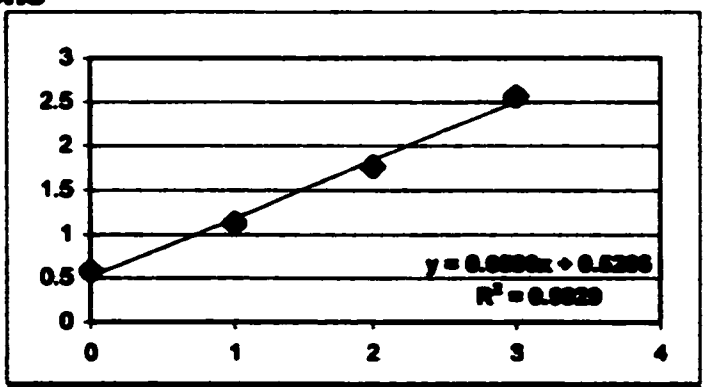


Plant Root Tissue Extractions

TNT

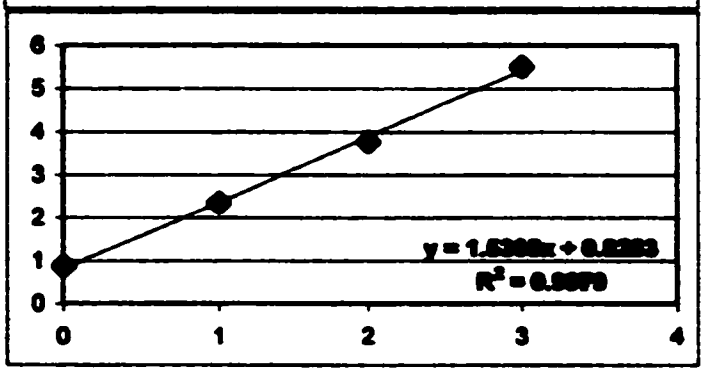
Sycamore Root-1

conc (ppm added)	peak (1e-6A)
0	0.58
1	1.128
2	1.77
3	2.584
linear fit x value =	0.7883



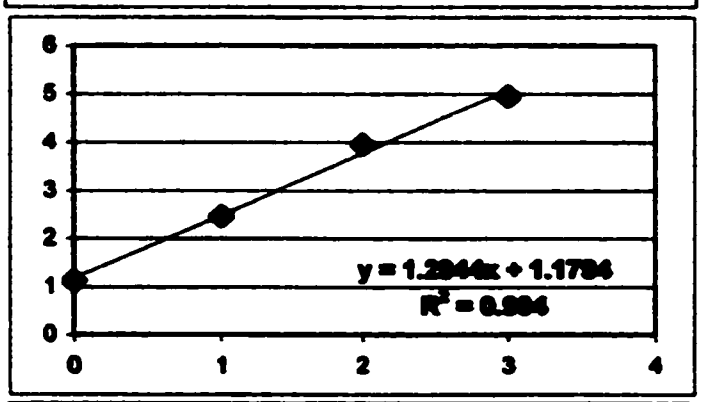
Sycamore Root-2

conc (ppm added)	peak (1e-6A)
0	0.8783
1	2.343
2	3.788
3	5.506
linear fit x value =	0.5412



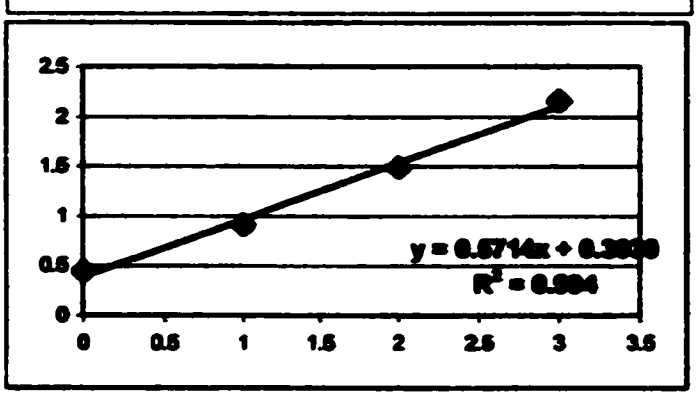
Sycamore Root-3

conc (ppm added)	peak (1e-6A)
0	1.127
1	2.461
2	3.951
3	4.945
linear fit x value =	0.9111



Yucca Root-1

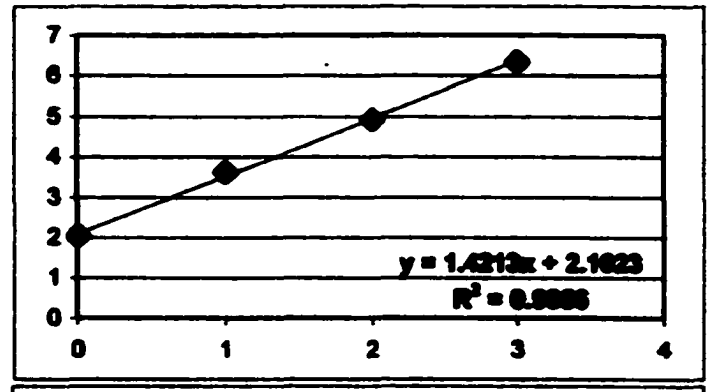
conc (ppm added)	peak (1e-6A)
0	0.4442
1	0.9136
2	1.469
3	2.157
linear fit x value =	0.6894



DNT

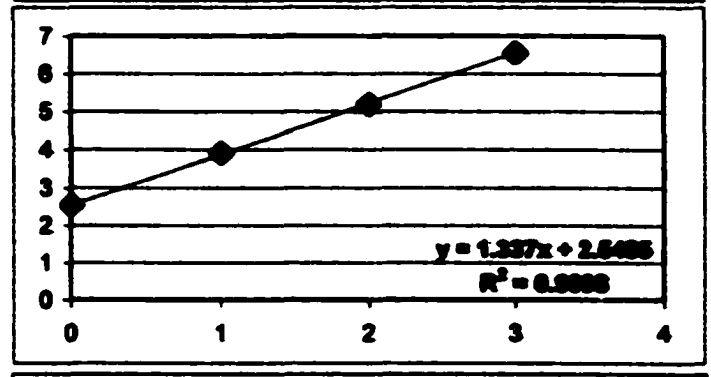
Sycamore Root-1

conc (ppm added)	peak (1e-6A)
0	2.042
1	3.621
2	4.931
3	6.343
linear fit x value =	1.479



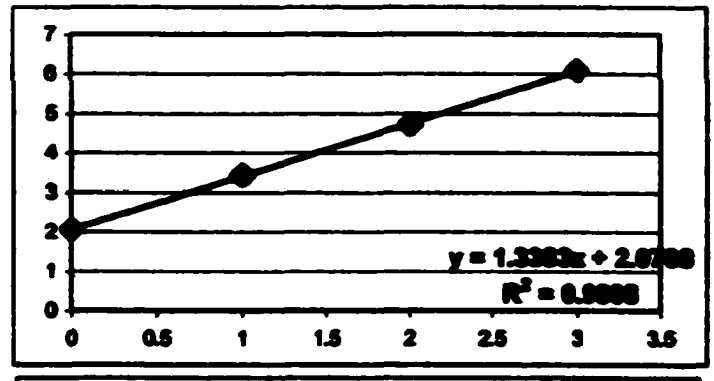
Sycamore Root-2

conc (ppm added)	peak (1e-6A)
0	2.543
1	3.908
2	5.194
3	6.571
linear fit x value =	1.906



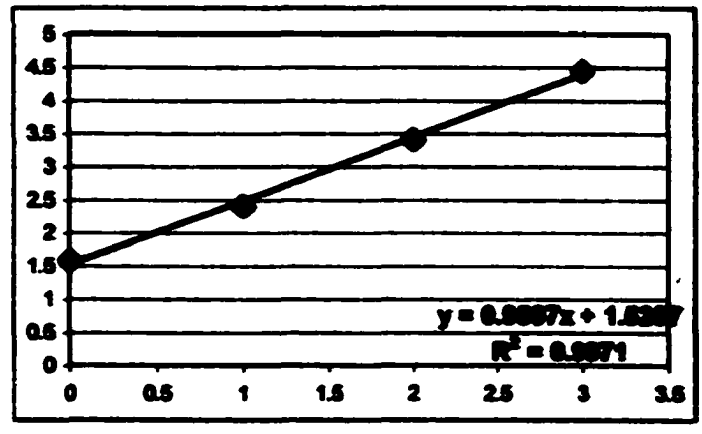
Sycamore Root-3

conc (ppm added)	peak (1e-6A)
0	2.086
1	3.431
2	4.718
3	6.098
linear fit x value =	1.547



Yucca Root-1

conc (ppm added)	peak (1e-6A)
0	1.589
1	2.407
2	3.412
3	4.463
linear fit x value =	1.59



Blank Explosive Concentrations

TNT

sample	rep	calculated ppm value for x	dilution factors	conc in mg	sample weights(g)	sample weights(kg)	conc mg/kg	average	reported value mg/kg
Yucca Leaf	1	0.631	0.0631	0.000631	0.2618	0.0002618	2.4102	2.65	0.00
	2	0.748	0.0748	0.000748	0.2593	0.0002593	2.8847		
	3	0.726	0.0726	0.000726	0.2732	0.0002732	2.6574		
Yucca Root	1	0.384	0.0384	0.000384	0.1151	0.0001151	3.3362	2.40	0.00
	2	0.273	0.0273	0.000273	0.1240	0.0001240	2.2016		
	3	0.234	0.0234	0.000234	0.1411	0.0001411	1.6584		
Soil	1	0.135	0.027	0.00027	1.0379	0.0010379	0.2601	0.16	0.00
	2	0.029	0.0058	0.000058	1.1337	0.0011337	0.0512		
	3	0.108	0.0216	0.000216	1.1936	0.0011936	0.1810		

2-aDNT

sample	rep	calculated ppm value for x	dilution factors	conc in mg	sample weights(g)	sample weights(kg)	conc mg/kg	average	reported value mg/kg
Yucca Leaf	1	1.13	0.113	0.00113	0.2618	0.0002618	4.3163	4.86	0.00
	2	1.07	0.107	0.00107	0.2593	0.0002593	4.1265		
	3	1.68	0.168	0.00168	0.2732	0.0002732	6.1493		
Yucca Root	1	0.784	0.0784	0.000784	0.1151	0.0001151	6.8115	5.70	0.00
	2	1.06	0.106	0.00106	0.1240	0.0001240	8.5484		
	3	0.245	0.0245	0.000245	0.1411	0.0001411	1.7364		
Soil	1	0.333	0.0666	0.000666	1.0379	0.0010379	0.6417	0.98	0.00
	2	0.483	0.0966	0.000966	1.1337	0.0011337	0.8521		
	3	0.863	0.1726	0.001726	1.1936	0.0011936	1.4460		

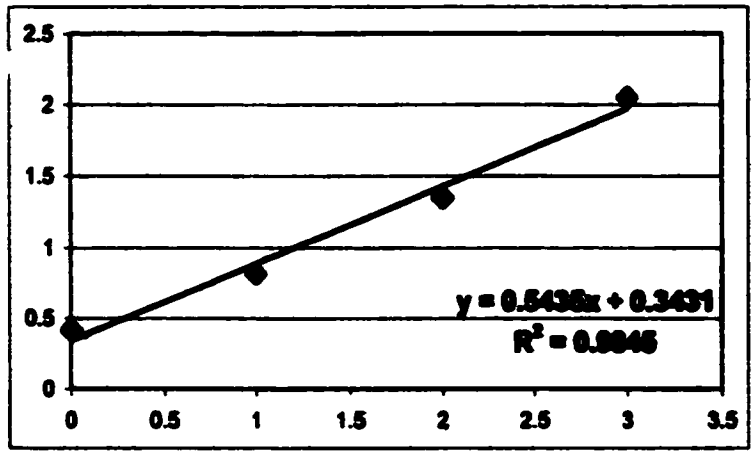
Blank Extractions

TNT

Yucca Leaf-1

conc.(ppm)	current(1e-6A)
0	0.4179
1	0.8144
2	1.35
3	2.051

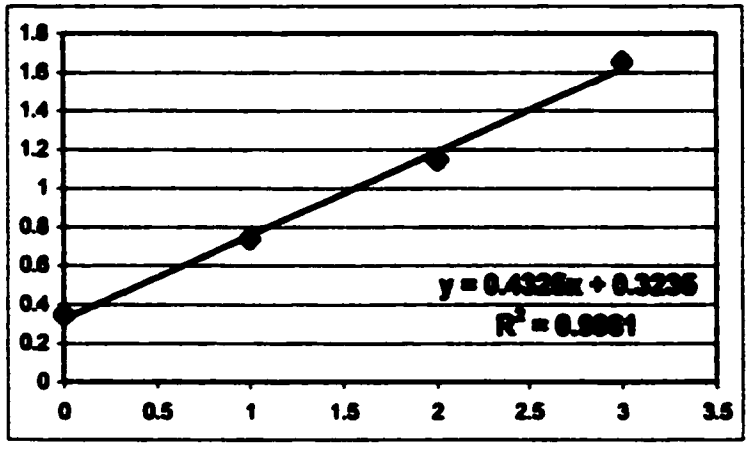
when y =0 linear fit
x = 0.631



Yucca Leaf-2

conc.(ppm)	current(1e-6A)
0	0.3463
1	0.7396
2	1.147
3	1.654

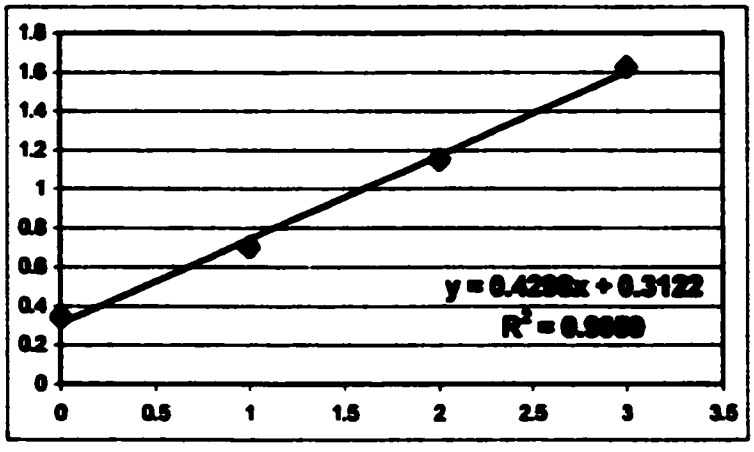
when y =0 linear fit
x = 0.748



Yucca Leaf-3

conc.(ppm)	current(1e-6A)
0	0.3463
1	0.7021
2	1.152
3	1.628

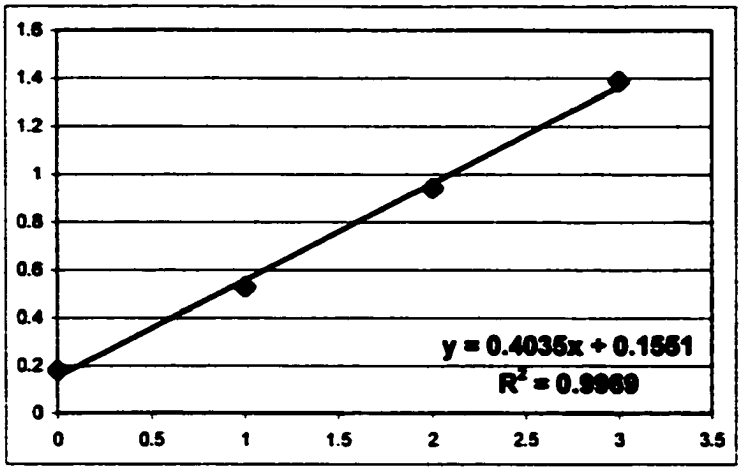
when y =0 linear fit
x = 0.726



Root -1

conc (ppm)	current(1e-6A)	current - solvent
solvent	0.2992	0
0	0.4808	0.1816
1	0.828	0.5288
2	1.241	0.9418
3	1.688	1.3888

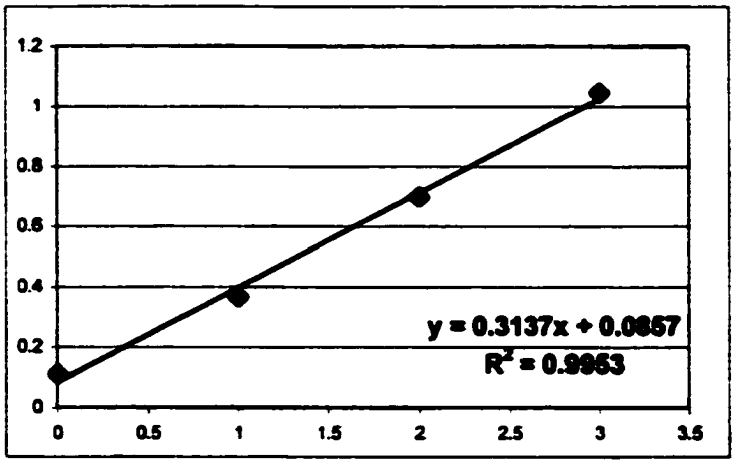
when y =0 linear fit
x = 0.384



Root -2

conc (ppm)	current(1e-6A)	current - solvent
solvent	0.2191	0
0	0.331	0.1119
1	0.5861	0.367
2	0.9182	0.6991
3	1.266	1.0469

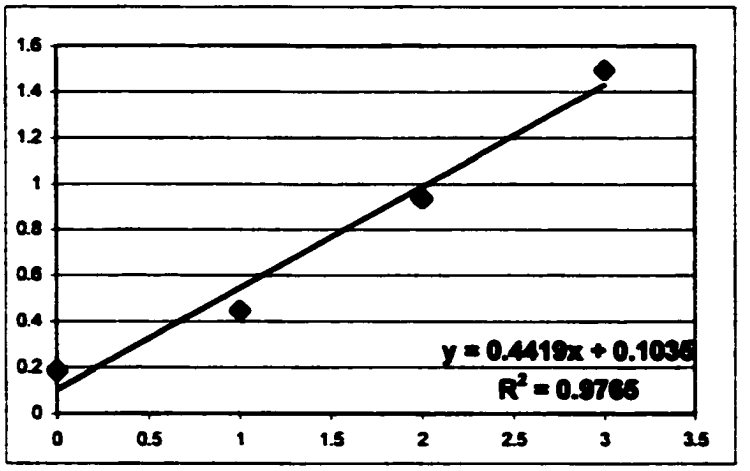
when y =0 linear fit
x = 0.273



Root -3

conc (ppm)	current(1e-6A)	current - solvent
solvent	0.3287	0
0	0.5148	0.1861
1	0.7751	0.4464
2	1.266	0.9373
3	1.824	1.4953

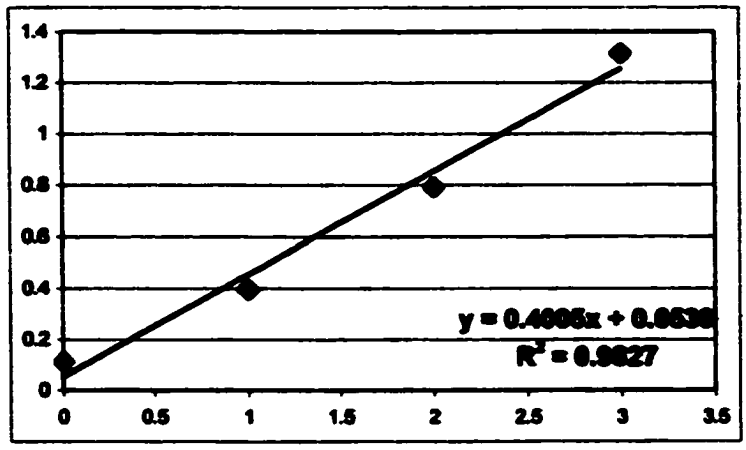
when y =0 linear fit
x = 0.234



Soil -1

conc.(ppm)	current(1e-6A)	current - solvent
solvent	0.2326	0
0	0.3453	0.1127
1	0.6294	0.3968
2	1.026	0.7934
3	1.548	1.3154

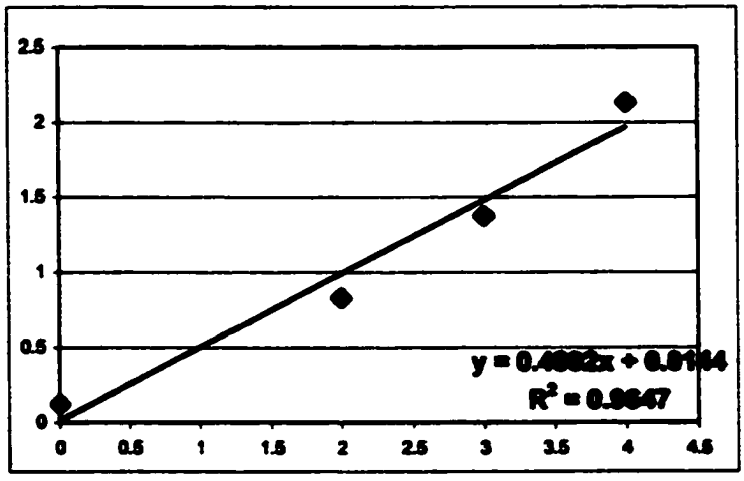
when y =0 linear fit
x = 0.135



Soil -2

conc.(ppm)	current(1e-6A)	current - solvent
solvent	0.2133	0
0	0.3366	0.1233
2	1.042	0.8287
3	1.588	1.3747
4	2.347	2.1337

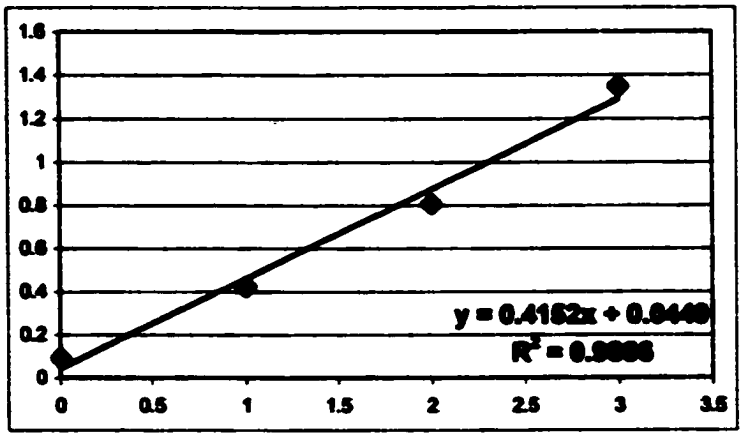
when y =0 linear fit
x = 0.029



Soil-3

conc.(ppm)	current(1e-6A)	current - solvent
solvent	0.2084	0
0	0.2909	0.0825
1	0.6294	0.423
2	1.013	0.8096
3	1.565	1.3466

when y =0 linear fit
x = 0.108



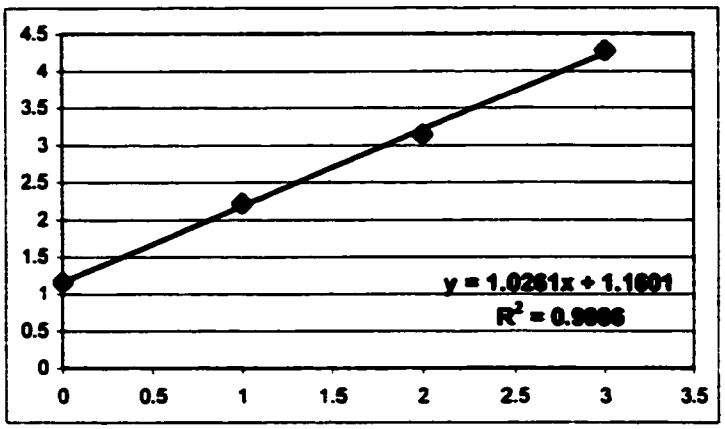
Blank Extractions

DNT

Yucca Leaf-1

conc (ppm)	current(1e-6A)
0	1.16
1	2.221
2	3.143
3	4.273

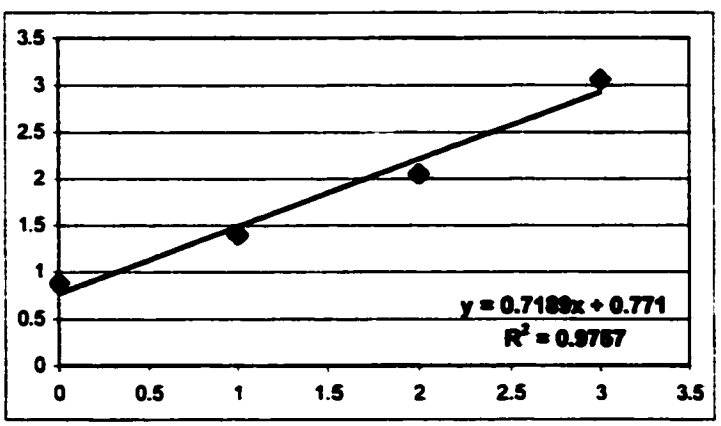
when y =0 linear fit
x = 1.13



Yucca Leaf-2

conc (ppm)	current(1e-6A)
0	0.8626
1	1.403
2	2.048
3	3.064

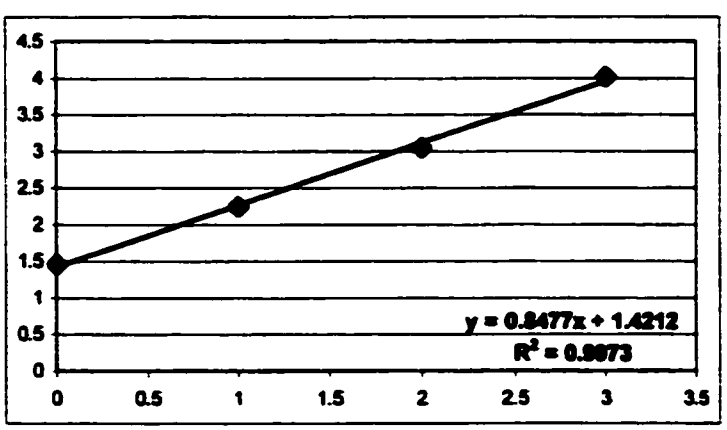
when y =0 linear fit
x = 1.07



Yucca Leaf-3

conc (ppm)	current(1e-6A)
0	1.46
1	2.245
2	3.048
3	4.018

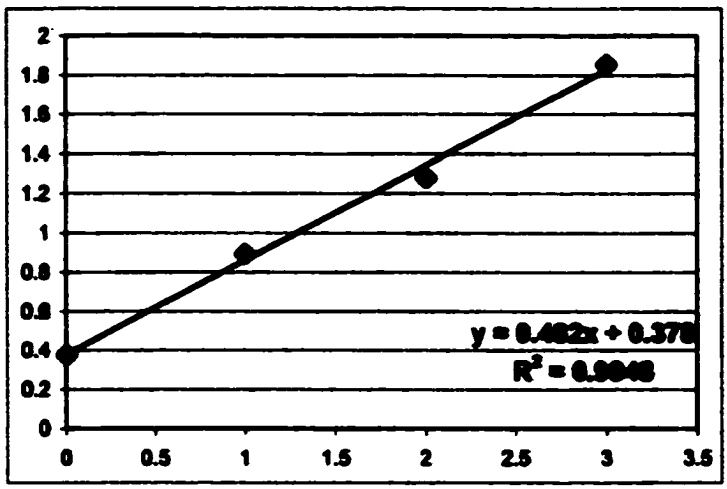
when y =0 linear fit
x = 1.68



Root -1

conc.(ppm)	current(1e-9A)	current - solvent
solvent	1.073	0
0	1.45	0.377
1	1.966	0.893
2	2.352	1.279
3	2.928	1.855

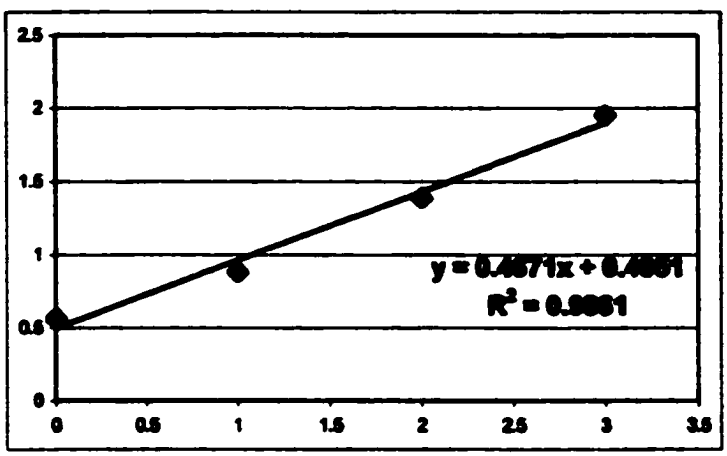
when y =0 linear fit
x = 0.784



Root -2

conc.(ppm)	current(1e-9A)	current - solvent
solvent	1.137	0
0	1.699	0.562
1	2.019	0.882
2	2.526	1.389
3	3.087	1.95

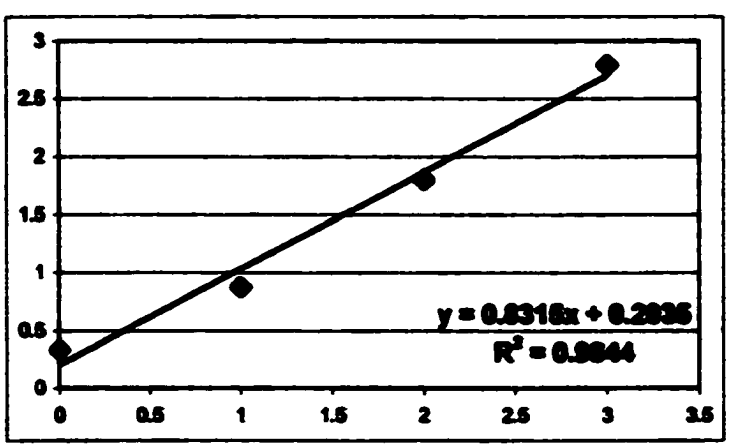
when y =0 linear fit
x = 1.08



Root -3

conc.(ppm)	current(1e-9A)	current - solvent
solvent	1.97	0
0	2.301	0.331
1	2.846	0.876
2	3.772	1.802
3	4.764	2.794

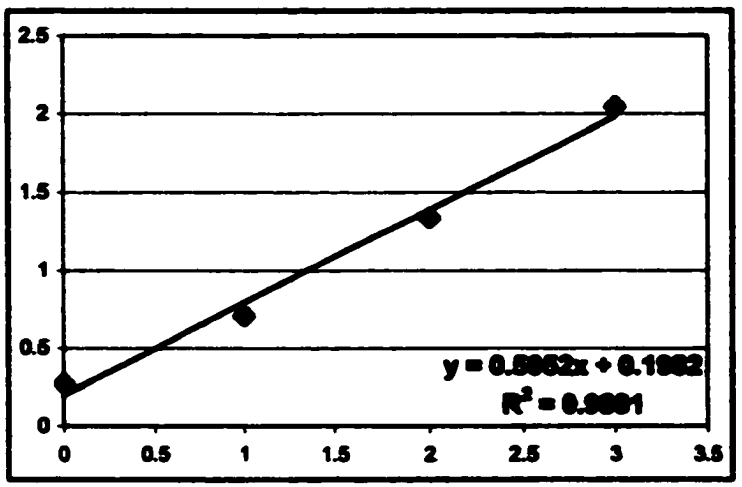
when y =0 linear fit
x = 0.245



Soil -1

conc.(ppm)	current(1e-6A)	current - solvent
solvent	1.463	0
0	1.736	0.273
1	2.169	0.706
2	2.792	1.329
3	3.469	2.046

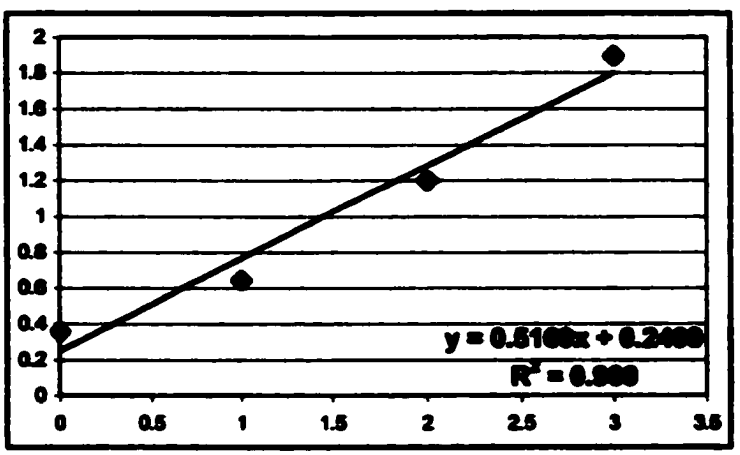
when y =0 linear fit
x = 0.333



Soil -2

conc.(ppm)	current(1e-6A)	current - solvent
solvent	1.379	0
0	1.738	0.359
1	2.023	0.644
2	2.581	1.202
3	3.275	1.896

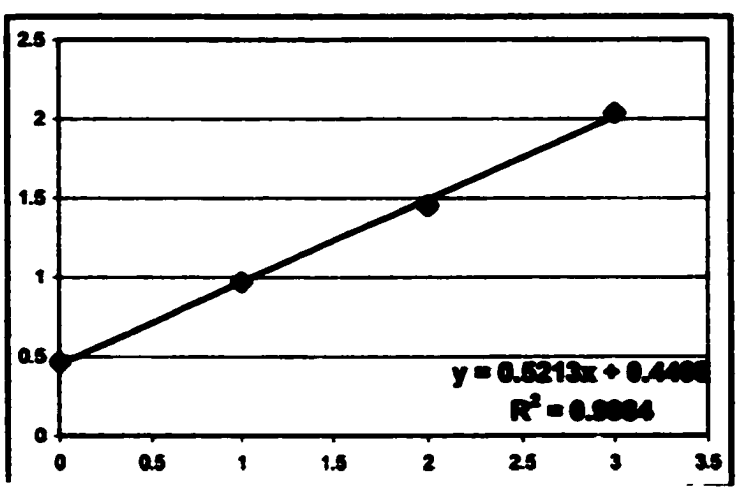
when y =0 linear fit
x = 0.483



Soil -3

conc.(ppm)	current(1e-6A)	current - solvent
solvent	1.236	0
0	1.699	0.463
1	2.206	0.97
2	2.691	1.455
3	3.275	2.039

when y =0 linear fit
x = 0.863

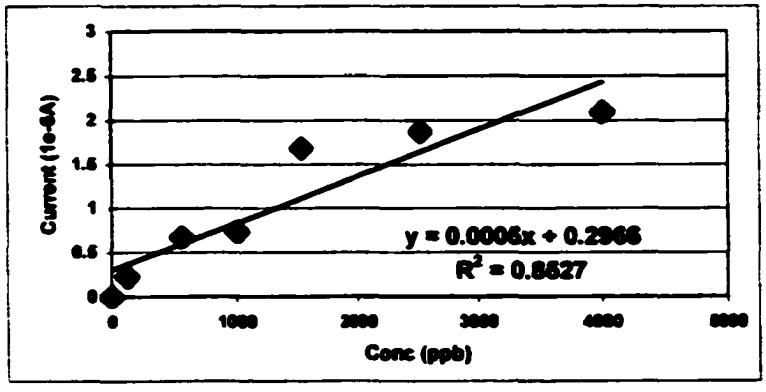


Data for Environmental Water Samples on Screen-Printed Carbon Electrodes

Environmental Water Samples Electrode Data

Standard Curve Method

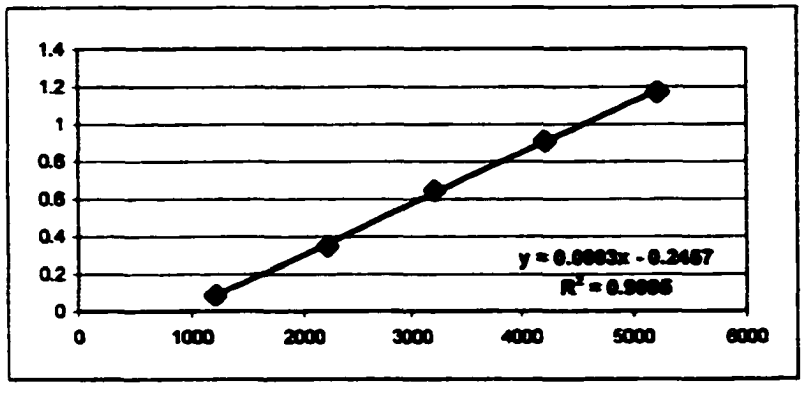
Original Conc (ppb)	Conc After Dilution (ppb)	Current (1e-6A)	current - blank	calculated concentration	final conc after dilution error (ppb)
0	0	0.3319	0	-583.2	-711.84
156	124.8	0.5576	0.2257	-141.8	-170.16
694	555.2	1.002	0.6701	747	896.4
1000	1000	1.066	0.7341	875	1050
1908	1526.4	2.012	1.6801	2767	3320.4
3152	2521.6	2.202	1.8701	3147	3776.4
4000	4000	2.421	2.0891	3585	4302



Standard Additon Method

Conc TNT (ppb)	Peak Current (1e-6A)	Trough Current (1e-6A)	Difference
1213	1.309	1.222	0.087
2213	1.855	1.507	0.348
3213	2.282	1.638	0.644
4213	2.709	1.798	0.911
5213	3.087	1.915	1.172

original conc =	1516 ppb TNT
after dilution =	1213 ppb
calculated conc =	819
final conc =	983



APPENDIX 4

ELECTRODE RESISTANCE DATA

Data for Electrode Resistance Analysis of Screen-Printed Carbon Electrodes

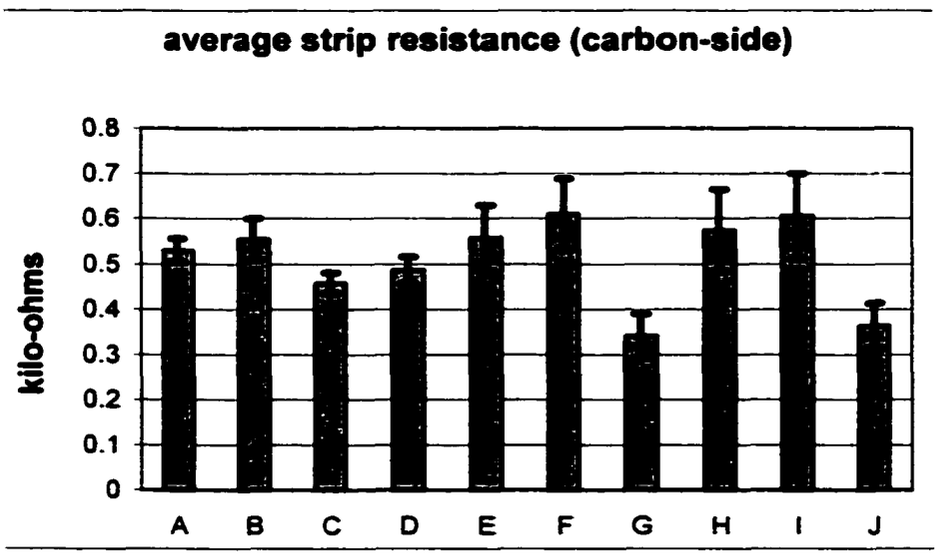
Analysis of Screen-Printed Carbon Electrodes

Received 7-10-00

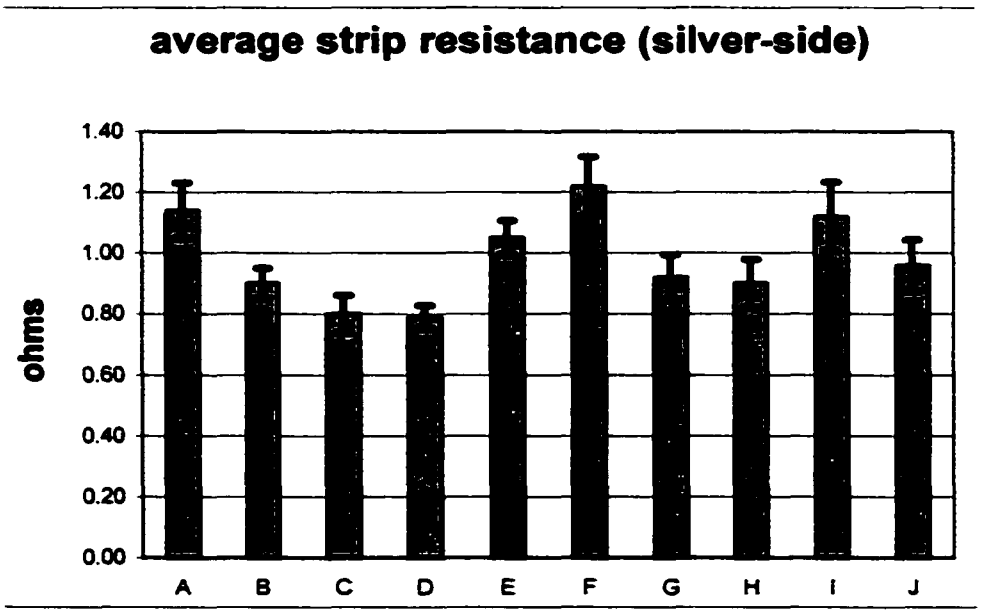
slide	electrode	Resistance (K-ohms) carbon-slide	average per slide	standard deviation	Resistance (ohms) silver-slide	average per slide	standard deviation
A	1	0.517	0.530	0.049	1.10	1.14	0.162
	3	0.488			1.10		
	5	0.609			1.40		
	7	0.544			1.20		
	10	0.486			0.90		
B	1	0.469	0.554	0.091	0.80	0.90	0.100
	3	0.519			0.90		
	5	0.629			1.00		
	7	0.671			1.00		
	10	0.480			0.80		
C	1	0.432	0.469	0.044	0.70	0.80	0.122
	3	0.468			0.80		
	5	0.499			1.00		
	7	0.505			0.80		
	10	0.401			0.70		
D	1	0.470	0.497	0.059	0.70	0.79	0.074
	3	0.498			0.75		
	5	0.572			0.90		
	7	0.500			0.80		
	10	0.469			0.80		
E	1	0.491	0.557	0.146	1.05	1.05	0.112
	3	0.428			1.10		
	5	0.754			1.20		
	7	0.657			1.00		
	10	0.465			0.90		
F	1	0.573	0.610	0.166	1.05	1.22	0.196
	3	0.554			1.10		
	5	0.815			1.50		
	7	0.702			1.35		
	10	0.405			1.10		
G	1	0.337	0.341	0.098	0.90	0.92	0.148
	3	0.371			1.00		
	5	0.462			1.10		
	7	0.343			0.90		
	10	0.190			0.70		
H	1	0.472	0.574	0.180	0.80	0.90	0.158
	3	0.632			1.00		
	5	0.819			1.10		
	7	0.605			0.90		
	10	0.340			0.70		
I	1	0.491	0.605	0.167	1.00	1.12	0.228
	3	0.738			1.20		
	5	0.785			1.40		
	7	0.575			1.20		
	10	0.336			0.80		

J	1	0.352	0.364	0.099	0.90	0.96	0.167
	3	0.419			1.00		
	5	0.441			1.10		
	7	0.413			1.10		
	10	0.197			0.70		

strip	average	stnd dev/2
A	0.53	0.0247
B	0.554	0.0456
C	0.459	0.0221
D	0.487	0.0295
E	0.557	0.0723
F	0.61	0.0779
G	0.341	0.0490
H	0.574	0.0900
I	0.605	0.0937
J	0.364	0.0496



strip	average	stnd dev/2
A	1.14	0.0908
B	0.90	0.0500
C	0.80	0.0612
D	0.79	0.0371
E	1.05	0.0559
F	1.22	0.0978
G	0.92	0.0742
H	0.90	0.0791
I	1.12	0.1140
J	0.96	0.0837



BIBLIOGRAPHY

Agency for Toxic Substance and Disease Registry. (1995). Toxicological Profile for Dinitrophenols. Atlanta, GA: U.S. Department of Health and Human Services.

Agency for Toxic Substance and Disease Registry. (1998). Toxicological Profile for 2,4-Dinitrotoluene and 2,6-Dinitrotoluene. Atlanta, GA: U.S. Department of Health and Human Services.

Agency for Toxic Substance and Disease Registry. (1998). Toxicological Profile for 2,4,6- Trinitrotoluene. Atlanta, GA: U.S. Department of Health and Human Services.

Agency for Toxic Substance and Disease Registry. (1998). Toxicological Profile for RDX. Atlanta, GA: U.S. Department of Health and Human Services.

Best, E.P.H., Sprecher, S.L., Larson, S.L., Fredrickson, H.L, & Badre, D. (1999). Environmental behavior of explosives in groundwater from the Milan army ammunition plant in aquatic and wetland plant treatments: Uptake and fate of TNT and RDX in plants. Chemosphere, 39(12), 2057-2072.

Bose, P., Glaze, W.H., & Maddox, D.S. (1998). Degradation of RDX by various advanced oxidation processes: Reaction rates. Wat. Res., 32(4), 997-1004.

Bouvier, E. & Oehrle, S.A. (1995). Analysis and identification of nitroaromatic and nitramine explosives in water using HPLC and photodiode-array detection. LC-GC, 13(2), 120-130.

Christian, G. (1994). Analytical Chemistry. New York: John Wiley and Sons, Inc.

Coleman, N.V., Nelson, D.R., & Duxbury, T. (1998). Aerobic biodegradation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) as a nitrogen source by a *Rhodococcus* sp. Strain DN22. Soil. Biol. Biochem., 30(8/9), 1159-1167.

CRC Handbook (1998-1999). CRC Handbook of Chemistry and Physics, Seventy Ninth Edition. Washington, D.C.: CRC Press.

Crosby, D. (1998). Environmental Toxicology and Chemistry. New York: Oxford University Press.

Drzyzga, O., Bruns-Nagel, D., Gorontzy, T., Blotevogel, K., & von Low, E. (1999). Anaerobic incorporation of the radiolabeled explosive TNT and metabolites intothe organic soil matrix of contaminated soil after different treatment procedures. Chemosphere, 38(9), 2081-2095.

Elovitz, M.S., & Weber, E.J. (1999). Sediment mediated reduction of 2,4,6-trinitrotoluene and fate of the resulting aromatic (poly)amines. Environ. Sce. Technol., 33, 2617-2625.

Galus, Z. (1994). Fundamentals of Electrochemical Analysis. Warshaw: Polish Scientific Publishers PWN.

Godejohann, M., Astratov, M., Preiss, A., & Levsen, K. (1998). Application for continuous-flow HPLC-proton nuclear magnetic resonance spectroscopy and HPLC-thermospray mass spectroscopy for structural elucidation of phototransformation products of 2,4,6-trinitrotoluene. Analytical Chemistry, 70, 4104-4110.

Godejohann, M., Preiss, A., Mugge, C., & Wunsch, G. (1997). Application on on-line HPLC-^{1}H NMR to environmental samples: Analysis of groundwater near former ammunition plants. Anal Chem, 69, 3832-3839.

Hamann, C., Hamnett, A., & Vielstich, W. (1998). Electrochemistry. Weinheim: Wiley-VCH.

Harvey, S.D., &Clauss, T.R.W. (1996) Rapid on-line chromatographic determination of trace-level munitions in aqueous samples. Journal of Chromatrography, 753, 81-89.

Hilmi, A., Luong, J.H.T., & Nguyen, A. (1999). Determination of explosives in soil and groundwater by liquid chromatography-amperometric detection. Journal of Chromatography, 844, 97-110.

Hughes, J., Shanks, J., Vanderford, M., Lauritzen, J., & Bhadra, R. (1997). Transformation of TNT by aquatic plants and plant tissue cultures. Environ. Sci. Technol., 31, 266-271.

Jenkins, T., & Schumacher, P.W. (1990). Evaluation of a Field Kit for Detection of TNT in Water and Soils. U.S. Army CRREL Special Report, 90-20.

Jenkins, T., & Thorne, P. (1995). Evaluation of the New Clean Solid Phases for Extraction of Nitroaromatics and Nitramines from Water. U.S. Army Cold Regions Research and Engineering Laboratory Special Report.

Jenkins, T.F., Thorne, P.G., & Walsh, M.E. (1994). Field Screening Method for TNT and RDX in Groundwater. U.S. Army CRREL Special Report 94-14.

Kissenger, P., & Heineman, W. (1996). Laboratory Techniques in Electroanalytical Chemistry. New York: Marcel Dekker.

Krausa, M., & Schorb, K. (1999). Trace detection of 2,4,6-trinitrotoluene in the gaseous phase by cyclic voltammetry. Journal of Electroanalytical Chemistry, 461, 10-13.

Lund, H., & Hammerich, O. (2001). Organic Electrochemistry. New York: Marcel Dekker, Inc.

Merck Index (1996). The Merck Index, Twelfth Edition: Merck and Co., Rahway, NJ.

Merrifield, R., Moreton, P.A. (1998). An examination of the major-accident record for explosives manufacturing and storage in the UK. Journal of Hazardous Materials, 63, 107-118.

Moore, D., & McCabe, G. (1998). Introduction to the Practice of Statistics. New York: W.H. Freeman and Company.

Oldman, K., & Mylank, J. (1994). Fundamentals of Electrochemical Science. San Diego: Academic Press, Inc.

Pfortner, P., Weller, M., & Niessner, R. (1998). Detection of bound nitroaromatic residues in soil by immunoassay. Anal Chem, 360, 781-783.

Qaisi, K.M., Ro, K.S., Reible,D., Thibodeaux, L.J., Valsaraj, K.T., & Constant, W.D. (1996). Transport process of TNT from flooded highly contaminated surface soil bed. Environ. Sci. Health., A31(10), 2515-2532.

Rivera, R., Medina, V.F., Larson, S.L., & McCutcheon, S. (1998). Phytotreatment of TNT-contaminated groundwater. Journal of Soil Contamination, 7(4), 511-529.

Sawyer, S., Sobkowiak, A., & Roberts, J. (1995). Electrochemistry for Chemists. New York: John Wiley and Sons, Inc.

Skoog, D., Holler, F., & Nieman, T. (1998). Principles of Instrumental Analysis. Philedelphia: Harcourt Brace College Publishers.

Thompson, P., Ramer, L., & Schnoor, J.L. (1998). Upatake and Transformation of TNT by hybrid poplar trees. Environ. Sci. Technol., 32, 975-980.

Thompson, P., Ramer, L., Guffey, A., & Schnoor, J.L. (1998). Decreased transpiration in poplar trees exposed to 2,4,6-trinitrotoluene. Environmental Toxicology and Chemistry, 17(5), 902-906.

Valsaraj, K.T., Qaisi, K.M., Constant, W.D., Thibodeaux, L.J., & Ro, K.S. (1998). Diffusive transport of 2,4,6-trinitrotoluene (TNT) from contaminated soil to overlaying water. Journal of Hazardous Materials, 59, 1-12.

Wallenborg, S., & Bailey, C. (2000). Separation and detection of explosives on a microchip using micellar electrokinetic chromatography and indirect laser-induced fluorescence. Anal Chem, 72, 1872-1878.

Walsh, M., Jenkins, T.F., Schnitker, P.S., Elwell, J.W., & Stutz, M.H. (1993). Evaluation of SW846 Method 8330 for Characterization of Sites Contaminated with Residues of High Explosives. U.S. Army CRREL Special Report 93-5.

Walsh, M.E., & Ranney, T. (1998). Determination of Nitroaromatic, nitramine, and nitrate ester explosives in water using solid-phase extraction and gas chromatography-electron capture detection: Comparison with high-performance liquid chromatography. Journal of Chromatographic Science, 36, 406-416.

Wang, J. (1994). Analytical Electrochemistry. Weinhiem: VCH Publishing.

Wang, J., Lu, F., MacDonald, D., Lu, J., Ozsoz, M.E.S., & Rogers, K.R. (1998). Screen-printed voltammetric sensor for TNT. Talanta, 46, 1405-1412.

Wang, J., Tian, B., & Rogers,K. (1998). Thick-film electrochemical immunosensor based on stripping potentiometric detection of a metal ion label. Analytical Chemistry, 70(9), 1682-1685.

Watts, R. (1998). Hazardous Wastes: Sources, Pathways, Receptors. New York: John Wiley and Sons, Inc.

Weissmahr, K., Hildenbrand, M., Schwarzenbach, R., & Haderlein, S. (1999). Laboratory and fiel scale evaluation of geochemical controls on groundwater transport of nitroaromatic ammunition residues. Environ. Sci. Technol., 33, 2593-2600.

Williford, C.W., & Bricka, R.M. (1999). Extraction of TNT from aggregate soil fraction. Journal of Hazardous Materials, 66, 1-13.

VITA

Graduate College
University Nevada, Las Vegas

Rebecca Pearson

Home Address:
3703 Laguna Veneta Ave
Las Vegas, NV 89141

Degrees:

Bachelor of Science, Chemistry, 1999
University Nevada, Las Vegas

Bachelor of Science Minor, Biology, 1999
University Nevada, Las Vegas

Special Honors and Awards:

National Network for Environmental Management Studies Fellowship, 1999
Undergraduate Research Award, 1998

Publications:

Mercury Concentrations in Bullfrogs (Rana Castebiena) Collected from a Southern Nevada Wetland. Bulletin of Environmental Contamination and Toxicology. Shawn Gerstenberger SL and Pearson R (Accepted).

Thesis Title: Electrochemical Techniques and Explosive Detection Using Screen-Printed Carbon Electrodes

Thesis Examination Committee:

Chairperson, Dr. Shawn Gerstenberger, Ph.D.
Committee Member, Dr. Kim Rogers, Ph.D.
Committee Member, Dr. Brian Johnson, Ph.D.
Graduate Faculty Representative, Dr. Spencer Steinberg, Ph.D.