A Quantitative Method to Detect Explosives and Selected Semivolatiles in Soil Samples by Fourier Transform Infrared Spectroscopy*

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A Quantitative Method To Detect Explosives And Selected Semivolatiles In Soil Samples By Fourier Transform Infrared Spectroscopy

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Abstract

This paper describes a novel Fourier transform infrared (FTIR) spectroscopic method that can be used to rapidly screen soil samples from potentially hazardous waste sites. Samples are heated in a thermal desorption unit and the resultant vapors are collected and analyzed in a long-path gas cell mounted in a FTIR. Laboratory analysis of a soil sample by FTIR takes approximately 10 minutes. This method has been developed to identify and quantify microgram concentrations of explosives in soil samples and is directly applicable to the detection of selected volatile organics, semivolatile organics, and pesticides.

Introduction

Semivolatile organics, volatile organics, and pesticides are ubiquitous environmental contaminants, the sources of which are almost as diverse as the types of contaminants. For example, pesticides and related residues result from agriculture, and explosives and related contaminants result from the defense sector. A common factor to all is the need for methods to accurately and efficiently detect the presence of these compounds. In particular, contamination of soil with explosives and their related impurities and degradation products is a serious environmental concern for government and industry laboratories. The testing, production, storage, and use of explosives contribute to the potential of environmental contamination by these chemicals. Although the contaminants associated with explosives may not be considered explosive hazards themselves, toxicologically they may be of equal danger (e.g., owing to the hepatocarcinogenicity of 2,6-dinitrotoluene)¹. It has become increasingly important to quickly identify sites contaminated by these chemicals in order to successfully monitor the remediation process.²

The current methods for characterizing hazardous waste sites are time-consuming, cumbersome, and expensive. Typically, site characterization requires a preliminary site assessment, followed by sampling of potentially contaminated soils and waters. The samples are sent to laboratories for analysis using EPA-certified methods. It is often necessary to repeat the entire sampling-analysis cycle to characterize a site completely and accurately. For these reasons, new methods of site assessment and characterization are continually being researched.

This paper presents a new method of near-real-time soil analysis for explosives and selected contaminants by Fourier transform infrared (FTIR) spectroscopy. The method is currently being developed in the laboratory with a future goal for adaptation as a field or mobile laboratory method. In the laboratory, this method has been tested on pesticides, pesticide intermediates, explosives, and explosive-related contaminants. The focus of this paper, however, will be on the analysis of explosives and their related

contaminants.

Fourier transform infrared spectroscopy has several advantages in performing soil sample analysis for organics. For example, organic compounds possess unique absorbances in the 1200-700 cm^{-1} region, commonly referred to as the "fingerprint region." Based upon the detection of these specific absorbances, classical least squares (CLS) and partial least squares (PLS) software may then be used for quantitative identification of target analytes. More sophisticated software may be used to digitally filter the data and thereby enhance the analyte signal prior to quantitative analysis³⁻⁴. This advanced technology should allow users to rapidly and accurately characterize soil samples from hazardous waste sites. Since the time-consuming liquid/solid sample extractions normally associated with organic analyses are not necessary with this method, sample preparation is minimal. A typical analysis requires no more than ten minutes per sample.

Equipment

All spectral data in this report were obtained using a Nicolet 60SX FTIR spectrometer equipped with a MCT-A detector. A personal computer with PCIR (Nicolet Instrument Corp.) and LabCalc CLS software (Galactic Industries) was used to analyze the data. A long-path gas cell (Infrared Analysis, Anaheim, CA) was used for sample collection. The cell has a pathlength range of 4 to 26 m and was set at 13.2 m for data collection. The cell has a 5-L capacity and sits vertically in the FTIR bench. Located atop the cell is a stainless steel transfer line joined to a thermal desorption unit (TDU) (CDS 122 Pyroprobe, Oxford, PA). The TDU is a heated sample port that allows introduction of either liquid or solid samples. The majority of data in this paper was collected with the transfer line connected in an elbow, or 90 degree, configuration. However, it was later discovered that a straight transfer line provided more consistent results, and this design of transfer line will be used in all succeeding experiments with this equipment.

A general schematic of the gas cell and TDU system is shown in Figure 1. The gas cell has three temperature probes along its vertical exterior. A cylindrical brass jacket covers the glass cell, and three heating tapes are wrapped around the jacket from the bottom up. The temperature probes and heating tapes are connected to temperature controllers that keep the cell temperature between 175 and 180° C from top to bottom. Layers of insulation are wrapped and secured around the modified cell to stabilize the temperature. The transfer line is also wrapped with a heating tape and covered with insulation to prevent the development of cold spots, which could cause condensation of the sample and consequently decrease analytical accuracy. The transfer line is kept at 200°C. The TDU is temperature programmed, starting at 240°C and rapidly increasing to a final probe temperature of 300°C.

The TDU is equipped with an inlet line connected to a nitrogen tank. An on-off valve, located to the rear of the TDU, controls the release of nitrogen into the system. The nitrogen gas is used to flush out the TDU and cell between analyses. Two valves are located on top of the cell, one to control the nitrogen entering the cell and the other to control the outflow of gas and sample from the cell. The outflow line is connected to a mechanical vacuum pump in order to evacuate the cell between analyses.

Experimental Method

Uncontaminated soil, used as background blanks and as the matrix for spiking target contaminants, was supplied by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA). The USATHAMA and ChemService (West Chester, PA) supplied 2,4,6-trinitrotoluene (TNT), while 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Standards of each contaminant were prepared in acetone and stored in amber glass vials with Teflon-lined septa. Mixtures of TNT, 2,4-DNT, and 2,6-DNT were prepared by carefully adding measured aliquots of the single components to amber vials. The concentration of each contaminant was calculated, marked

on the vials, and recorded.

Injections of the single-component liquid standards were used to develop the computer-based spectral library and to assess quantitative accuracy. These pure standards were also used as reference standards in the CLS software program. Injections could be made directly into the TDU through a septum covering the probe injection port, or the liquid could be injected onto the platinum ribbon of the probe and then inserted into the TDU. The latter technique allows evaporation of the solvent from the sample by briefly raising the temperature of the probe to 100°C prior to its placement in the TDU. For obvious reasons, this technique may not be used with volatiles. Once inserted into the TDU, the probe temperature may then be elevated to the setting required to volatilize the sample.

Prior to all sample analyses, a background spectrum of the evacuated cell was collected. The background consisted of 128 scans Fourier processed at 1 wavenumber resolution. For each analysis, the ratio of the sample to background absorbance was determined. Soil samples were prepared by adding approximately 50 mg of soil to a small quartz pyrolysis tube packed at one end with glass wool. A small aliquot of standard was transferred via a Hamilton syringe into the soil. The open end was then packed with glass wool as well. The pyrolysis tube was placed in a coil probe and quickly brought to 100°C or "flashed" to evaporate the solvent.

The probe was then placed inside the TDU, where the sample was rapidly heated to a temperature of 300°C. The evacuated cell was closed off from the vacuum and opened to the TDU. The vapors desorbed from the soil entered into the evacuated cell. Spectral analysis was started after a one-minute equilibration period to allow the sample to fully desorb from the soil and travel into the cell. For each sample, 128 scans were coadded and Fourier processed at 1 wavenumber resolution.

Results

The results demonstrate the identification and quantification of the explosive 2,4,6-trinitrotoluene and of 2,4,6-trinitrotoluene mixed with interfering contaminants in soil samples.

Identification and Analysis of TNT, 2,4-DNT, and 2,6-DNT

Identification of the two DNT isomers and TNT relied upon the difference in peak shape of the two main nitro absorbances, which occur at approximately 1555 and 1350 cm^{-1} . Figures 2 and 3 show the absorbance spectra for 2,4-DNT, 2,6-DNT, and TNT in these regions. The absorbance maxima for 2,4-DNT and 2,6-DNT at 1551.6 and 1553.1 cm^{-1} , respectively, are almost identical. However, 2,4-DNT has a secondary maximum at 1610 cm^{-1} that is not present in 2,6-DNT. Unfortunately, this secondary maximum would not be detected in samples containing "lower" concentrations of 2,4-DNT (e.g., less than 230 ppm with the current experimental conditions and less than 115 ppm with a doubled pathlength). Nevertheless, in the CLS spectral identification of these isomers, the region around this maximum used in combination with the 1550 cm^{-1} region, could help to decrease incidents of false positives or misinterpretation of the isomers. The TNT absorption maximum at 1559.4 cm^{-1} allows the spectral algorithm to more readily identify TNT from the DNT isomers. The absorbances centered at 1350 cm^{-1} were also similar. The maxima were located at 1349, 1358, and 1352 cm^{-1} for TNT, 2,6-DNT, and 2,4-DNT, respectively.

Spectral identification with the CLS software requires only one standard per chemical component. Spectral bands of quantitative interest are entered into the CLS program. The CLS equation takes into account the absorbance and concentration for the reference samples, pathlength of the cell, and component absorptivity at each frequency. On the other hand, the PLS software requires multiple standards of both pure components and mixtures. Nonetheless, PLS may be preferable if significant interference is found

in the spectral regions of interest⁵. Mixtures of components may be entered into PLS software as a training set. Use of PLS algorithms will not be possible, however, until a data base of sufficient size is collected⁶.

Mixture analyses utilized three different previously prepared standards, each containing the two DNT isomers and TNT in varying concentrations. The mixtures were prepared so as to represent a relatively broad range of compositions. The data are presented in Table I. Mixture 1 contained a low concentration of TNT and high concentrations of both DNT isomers. In mixture 2, the concentration of 2,6-DNT was increased. Mixture 3 had higher concentrations of TNT and 2,4-DNT, and a lower concentration of 2,6-DNT. The spectra of all three mixtures are overlaid in Figure 4.

The spectral library offers the advantage of storing spectra of known interfering contaminants so that they may subsequently be subtracted from a sample spectrum. However, under the present laboratory conditions, we rarely found this necessary for two reasons: the unique peak shapes of the target organics in the fingerprint region and the clean background of the laboratory ambient air.

There is a bias in the data toward calculated values which were lower than actual values. A few of the FTIR measurements in Table I are quite accurate, with percent error of less than 5%. However, most are in the 20-30% error range, as supported by the average error (24.4%). Still, a few of the components had percent errors of 40-50%. Reproducibility problems seemed to originate from the angular transfer line configuration. These differences may be attributed to the 90° elbow in the angular transfer line causing difficulty in migration of the sample from the TDU to the cell, or possibly, inconsistencies in temperature of the transfer line due to its angled shape. A straight transfer line has since been installed, and preliminary data analysis (Table II) indicates more-reproducible values.

Detection levels and TDU capacity

Explosives in soil samples are typically measured in ppm, as determined from the micrograms of analyte per gram of soil. The sample tubes for the TDU have a capacity of 50 mg of soil. The sample mass is limited by the size of the pyroprobe unit. The soil samples were spiked at a concentration one may realistically expect to find at a contaminated site, allowing for the sample-size capacity of the TDU. A larger desorption unit which could capably desorb 1 g or more of soil would benefit the method in numerous ways. For example, gram quantities of sample can be weighed out more rapidly and are associated with less analytical error than microscale preparation and analysis.

The current detection limits are approximately 80 μg contaminant with a 13.2-m pathlength cell. This value was derived by collecting data on various quantities of TNT, with the level of 81 μg being the lowest detectable quantity observed while a signal-to-noise (S/N) ratio of at least 3:1 is maintained. With a larger TDU unit, it is plausible to suggest that 80 μg of analyte could be desorbed from 1 g of soil, resulting in a detection limit of approximately 80 ppm. This value would be lowered to 40-50 ppm if the pathlength of the cell were increased to 26.4 m, which is possible with the long-path gas cell.

A scaled-up model of the pyroprobe used in this research was ordered and tested. The unit held approximately 0.5 g of soil, but the contents consistently blew out of the quartz tube upon heating. Thus, other means of soil sample desorption are being pursued.

Through the use of CLS software, it is possible to correctly identify 2,4-DNT, 2,6-DNT, and TNT, either as pure components or as mixtures, in a soil sample. Samples are analyzed over operator-specified spectral regions. The software identifies peak shape and intensity for a specific region. For the analytes studied in this paper, the primary region of interest is the 1632-1514 cm^{-1} region. The region of

1420-1300 cm^{-1} may also be used, either by itself or in combination with the primary region. Data analysis was performed using both single- and dual-peak range methods. The results were virtually identical, but only those for the single-peak region are presented here. There were no false negatives. Precision of the instrument and method is indicated in Figure 5, which shows the spectral agreement obtained from three soil samples spiked with equal amounts of 2,4-DNT.

Reproducibility of Standards

Reproducibility between successively run standards was very good, particularly for data collected with the straight transfer line. Table II shows the results from a series of measurements with three equivalent volumes (3 μL) of the 2,4-DNT standard spiked into soil samples (118 $\mu\text{g}/\mu\text{L}$). Peak areas were integrated using LabCalc software. The data set is being expanded to generate a larger set of numbers for more comprehensive statistical analyses.

Table I. Identification and quantitation of 2,4-DNT, 2,6-DNT, and TNT mixtures at 1 cm^{-1} resolution (elbow transfer line).

Sample Number	Component	Quantity Injected (μg)	Quantity Detected (μg)	% Error
Mixture 1				
T4059	2,4-DNT	192	183	4.7
	2,6-DNT	261	199	23.8
	TNT	75	73	2.7
T5010	2,4-DNT	276	216	21.7
	2,6-DNT	366	258	29.5
	TNT	105	64	39.0
Mixture 2				
T4056	2,4-DNT	89	90	1.1
	2,6-DNT	147	113	23.1
	TNT	67	71	6.0

T4051	2,4-DNT	148	116	21.6
	2,6-DNT	245	239	2.4
	TNT	112	148	32.1
T4057	2,4-DNT	148	119	19.6
	2,6-DNT	245	155	36.7
	TNT	112	54	51.8
T4052	2,4-DNT	207	163	21.2
	2,6-DNT	343	301	12.2
	TNT	157	117	25.5
T4058	2,4-DNT	207	180	13.0
	2,6-DNT	343	272	20.7
	TNT	157	115	26.7
Mixture 3				
T5013	2,4-DNT	268	197	26.5
	2,6-DNT	106	50	52.8
	TNT	225	159	29.3
T5015	2,4-DNT	268	144	46.3
	2,6-DNT	106	62	41.5
	TNT	225	166	26.2
Average Error = 24.4%				

Table II. Reproducibility of soil standards spiked with 2,4-dinitrotoluene (straight transfer line).

Run	Peak Area	Results
T3054	7.80	Average = 7.74
T3055	7.89	Percent Deviation = 1.98%
T3056	7.53	

Conclusion

Qualitative and quantitative analysis of explosives and selected contaminants in soil samples was successfully performed by FTIR. The experiments demonstrate that analyses may be performed at high temperatures without too significant a loss of data quality, and that semivolatile liquids and solids can be thermally desorbed into a heated gas cell and rapidly analyzed by FTIR. Precision of results was very

good, approximating 2% for sequentially spiked standards. Quantitation of single contaminants from soil samples proved more accurate than quantitation of the liquid mixes; however, adaptations to the method that will decrease or eliminate these discrepancies are being investigated.

Future Work

The next phase of work will involve (1) lowering the detection levels through modification of the desorption system and (2) broadening the target analyte list to both increase the number of semivolatiles studied and to include volatiles as well. Development of a custom-designed desorption system will enable us to analyze larger soil samples and may be the key to reaching the desired decrease in detection level of two orders of magnitude. Since larger samples are generally more homogenous in nature, a larger sample will also be more representative of the actual concentrations of explosives in soil from contaminated sites. As mentioned previously, the pathlength of the gas cell may also be adjusted to help decrease the detection levels. Also, supercritical fluid extraction (SFE) as a means of extracting the target analyte would likely prove beneficial, several research groups have found an advantage in applying this extraction method prior to analytical detection⁷⁻⁹. Moreover, SFE offers the opportunity to use environmentally safe solvents for sample extraction. This would have the further advantage of minimizing waste solvent generation for the field method and in the laboratory.

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Figure 1. Schematic diagram of cell and inlet system.

Figure 2. Comparison of 2,4-DNT, 2,6-DNT, and TNT absorption in the spectral region of 1640-1400 cm⁻¹.

Figure 3. Absorption of 2,4-DNT, 2,6-DNT, and TNT in the spectral region of 1400-1300 cm⁻¹.

Figure 4. Comparison of spectra for three different mixtures of 2,4-DNT, 2,6-DNT, and TNT

Figure 5. Comparison of three soil samples spiked with 2,4-DNT in acetone in the spectral region 1630-1450 cm⁻¹.