

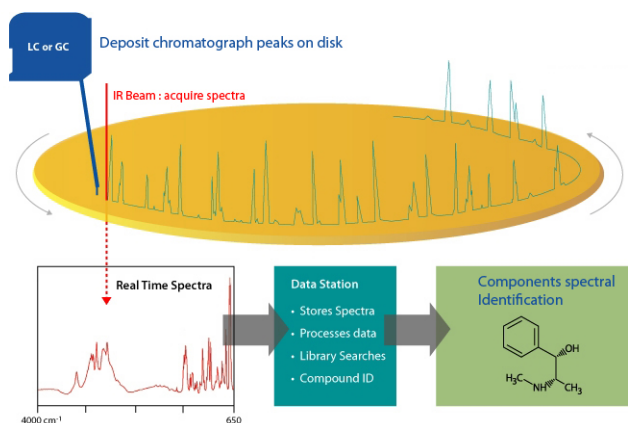


## DiscovIR-GC<sup>TM</sup> Deposition and Detection System

Application Note 029  
October 2008

### Identification of explosive components and isomers

The DiscovIR-GC<sup>TM</sup> is a powerful new tool for materials analysis. When connected to the outlet of a GC column, the DiscovIR deposits chromatographic eluants as a continuous track on an infrared transparent substrate. The built-in interferometer simultaneously captures a set of time-ordered infrared spectra from the deposited track. The result is a map of molecular structure of all sample components.



### Summary

The analysis of explosives is an important tool, both for the producers of explosive products and for forensics. This application note illustrates the use of combined Gas Chromatography and FT-IR spectrometry to analyse multi-component explosive material. The ability of FTIR to detect molecular structural variations enables the direct identification of positional isomers frequently found in explosive products.

### Introduction

#### Uses

Chemical explosives are regularly employed in mining, demolition, military weapons, and firearms. There is a broad array of chemical materials synthesized for explosives. Most explosive products are multi-component mixtures of chemical entities. Black powder, for example, is based on a mixture of three inorganic materials; a nitrate, sulfur, and carbon. Explosive products can consist of organic materials, inorganics, and polymeric. Explosive products are also mixtures of differing explosive compounds plus non-explosive components. Non-explosive components of an explosive product may include plasticizers (plastic explosives), polymers (Styrene-butadiene) incorporated in materials such as Semtex-H, antioxidant stabilizers, and wax (a desensitizer).



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Chemical synthesis of explosive materials often results in the production of a mix of positional isomers. IR spectroscopy can readily identify many of these materials.

### **Analytical needs**

There are various needs for chemical identification of the components of explosive products. These include:

- Explosives development, manufacturing, and quality control
- Forensics – crime and terrorism  
Forensic analysis of explosives and/or their degradation products is also increasingly important for analysis of civil criminal incidents and for investigation of terrorist activities. The determination of origin of an explosive is based in part on identification of explosives composition, and on chemical tags in an explosive or post-explosion residue.
- Environmental contaminants  
The persistence and toxicity of explosive compounds is a concern for the safety of the environment surrounding military firing ranges, bombing ranges, and munitions plants. The EPA establishes procedures for the measurement explosives residues.

### **Analytical methodologies**

A variety of methods is used in the analysis of explosive materials. Because most explosive products are comprised of a mixture of materials, chromatography is frequently employed to separate components. Characteristic elution times are used for initial identification, but this is generally regarded as inadequate confirming identification.

Specific detection systems, such as TLC plus selective color reagents identify groups of explosive types, but not specific components. Preferred protocols are the use of chromatography plus species-specific techniques such as IR, NMR, and MS. The information obtained from these spectrometric methods is more directly related to the molecular structures of the analytes than the information obtained from chromatographic data.

## ***Experimental***

### **Sample** Restek 31451

Sample material was obtained from Restek Corp. The sample is commonly used as a reference standard for tests in accordance with EPA method 8330 (monitoring the disposal of expired or deteriorated munitions). The sample consisted of a mixture of seven explosive components dissolved in acetonitrile. Concentration of each component was 1 mg/ml.

### **Instrumentation**

Gas Chromatograph: Agilent 6890N. GC column was a Varian VF-1ms 15m 0.25mm i.d., 0.25 $\mu$ m film

IR Detection System: DiscovIR-GC

### **Experimental conditions-GC**

Sample 1  $\mu$ l split 1/30



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Carrier Gas: Helium, 1 cc/min  
Injector: 150°C  
Column oven: 50°C (1 min), 10°/min to 250°C  
**Experimental conditions: DiscovIR-GC**  
Restrictor, oven, transfer line: 250°C  
Disk speed: 3 mm/min  
Disk temp: -40°C  
Chamber Pressure:  $2.24 \times 10^{-4}$  torr

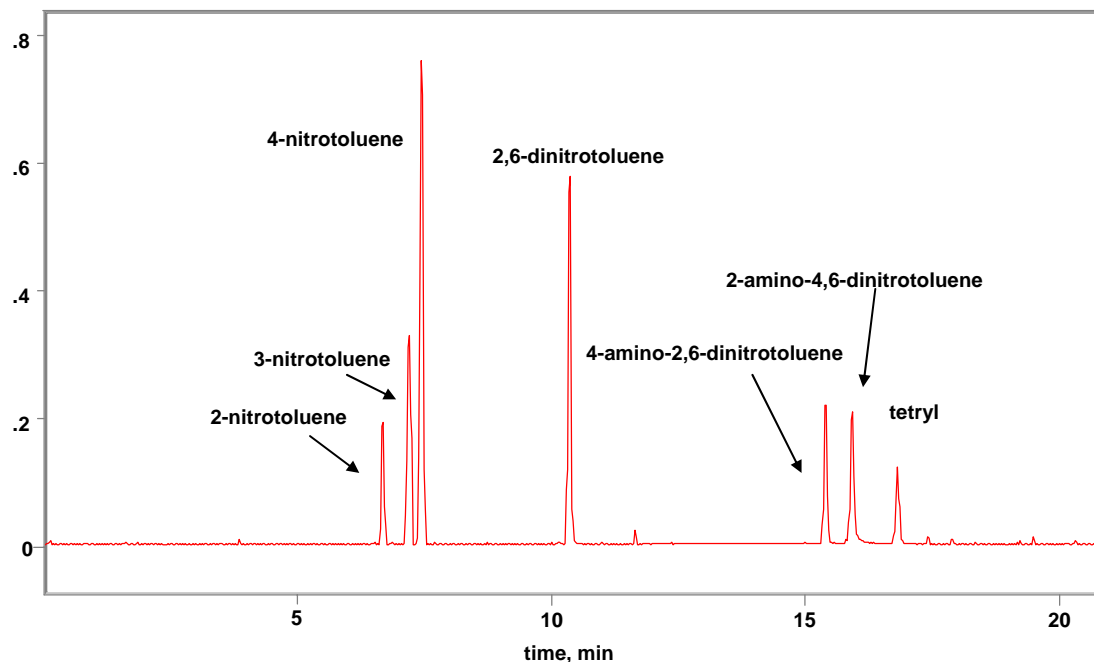
## Results

Unlike the traditional light-pipe GC-IR configurations, the DiscovIR-GC deposits solutes as solid-phase samples within the FT-IR optical path. This provides several advantages.

- Solid-phase spectra present sharp spectral bands, with none of the broadening characteristics of the free movement of molecules in the vapor phase. Higher information content than provided by vapor phase spectra.
- Typically a 200-fold increase in sensitivity of vapor phase.
- Sensitivity is not effected by temperature increase of the sample.

The figure below is the infrared chromatogram of the solutes deposited on the DiscovIR Zn-Se sample collection disk. Each peak represents a mass of ca. 33 ng.

### GC chromatogram of sample 31451

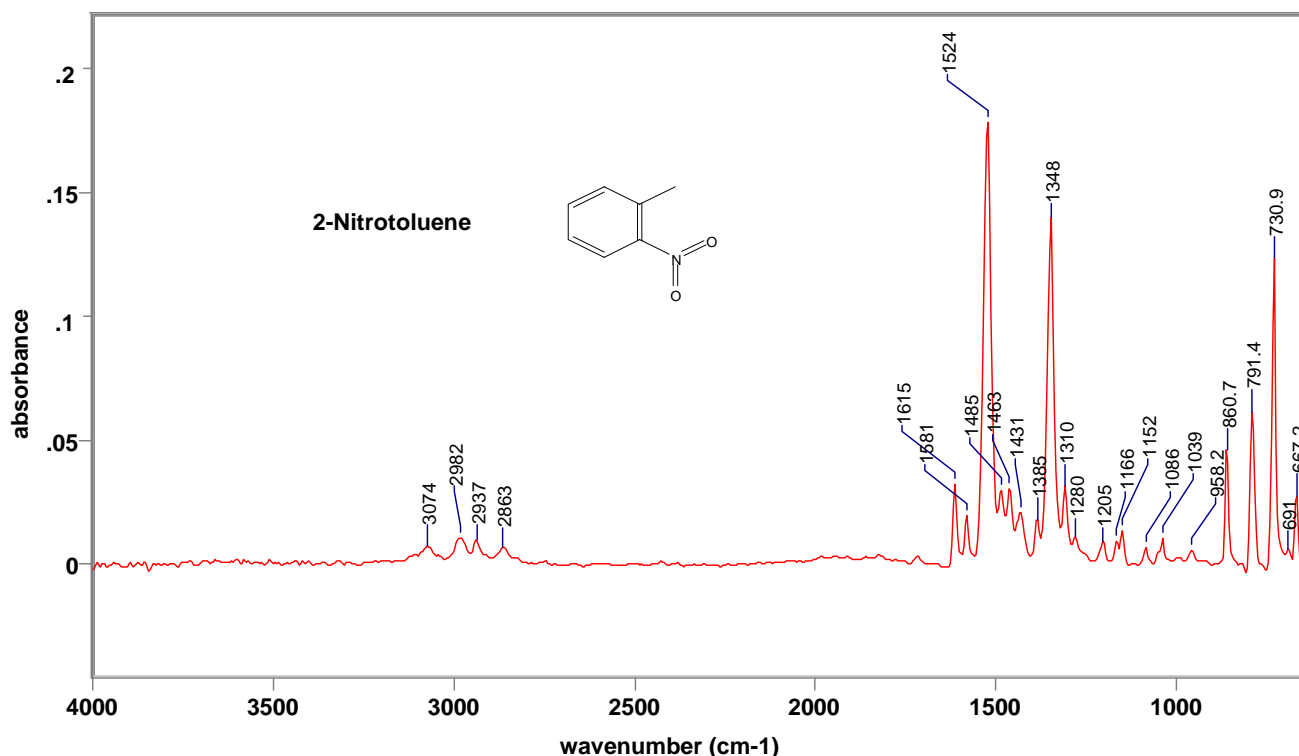


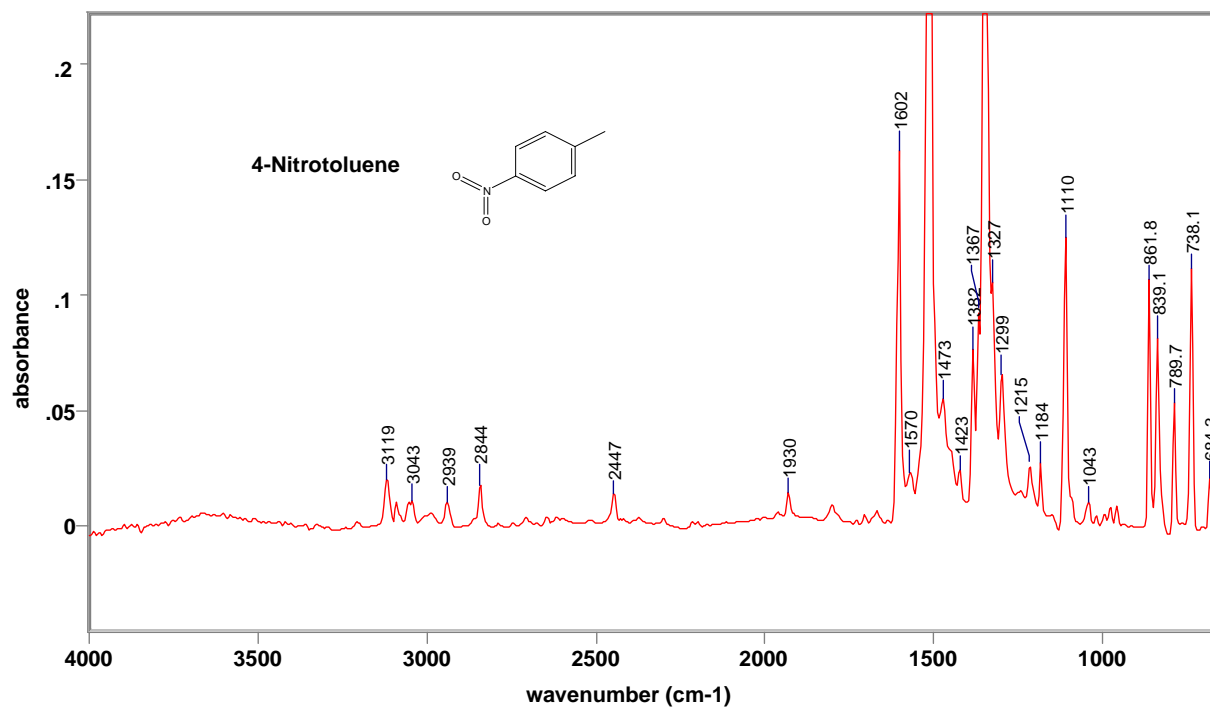
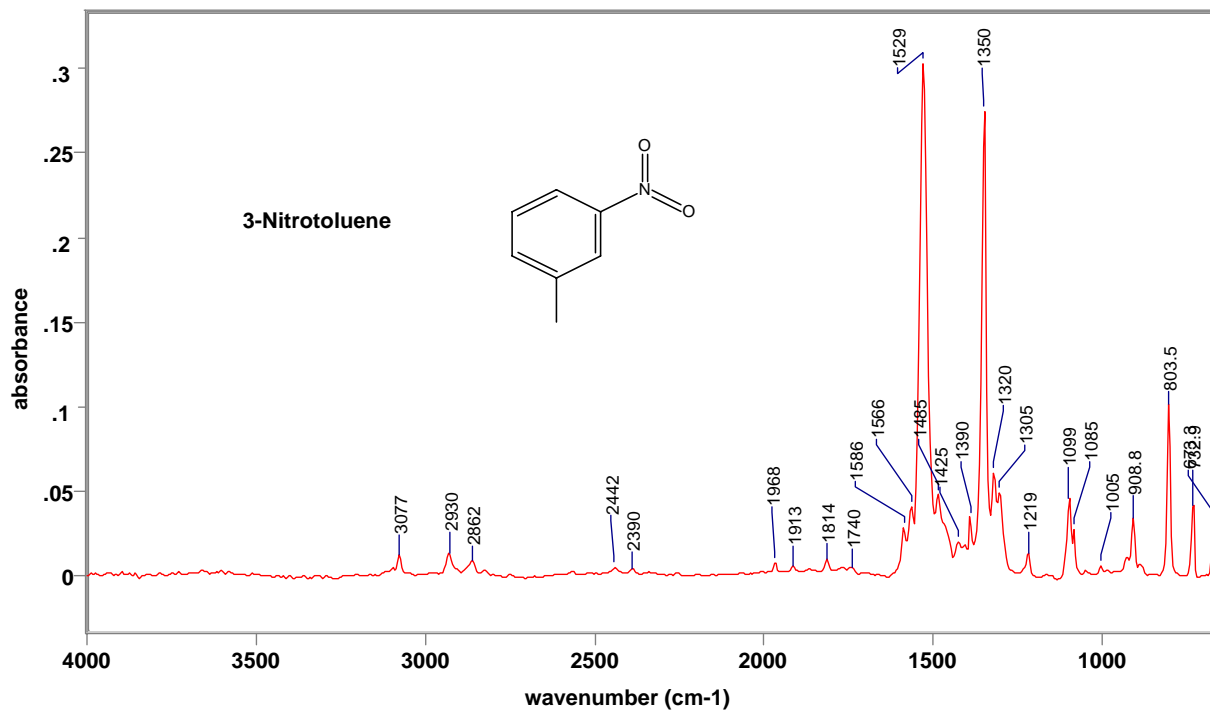
The seven spectra collected from each peak are displayed on the following pages. All of the compounds in the sample are nitro aromatics. The first three eluant peaks are positional

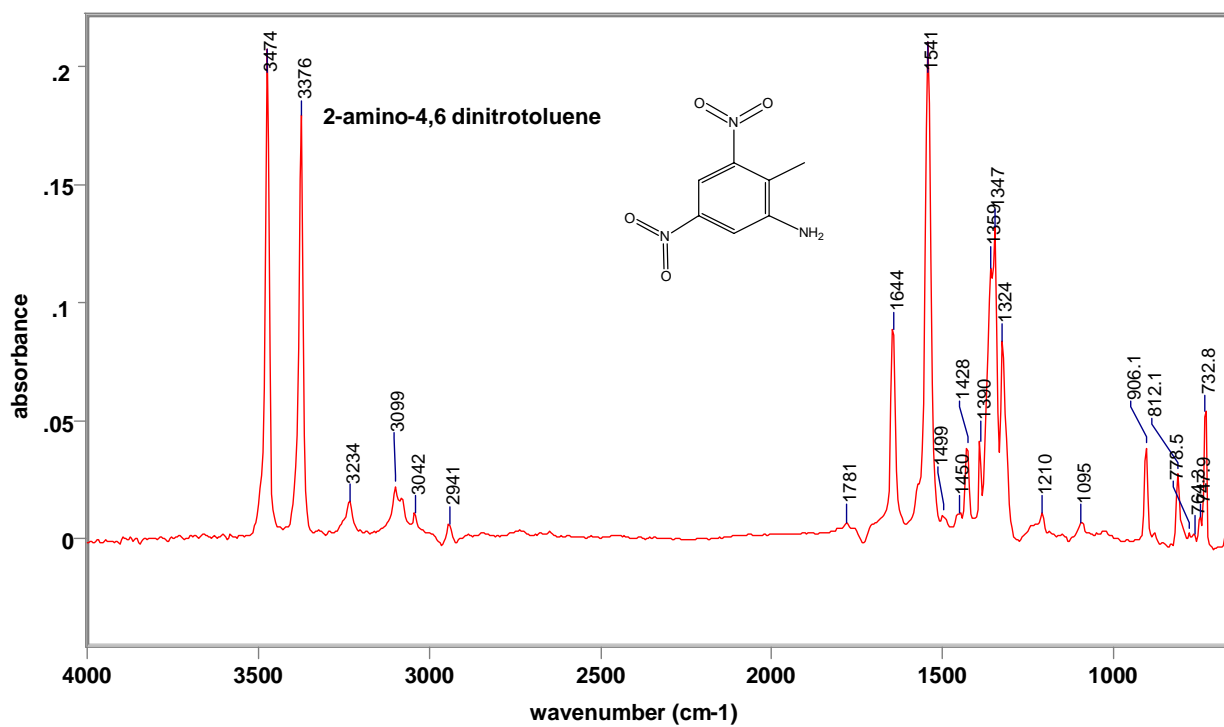
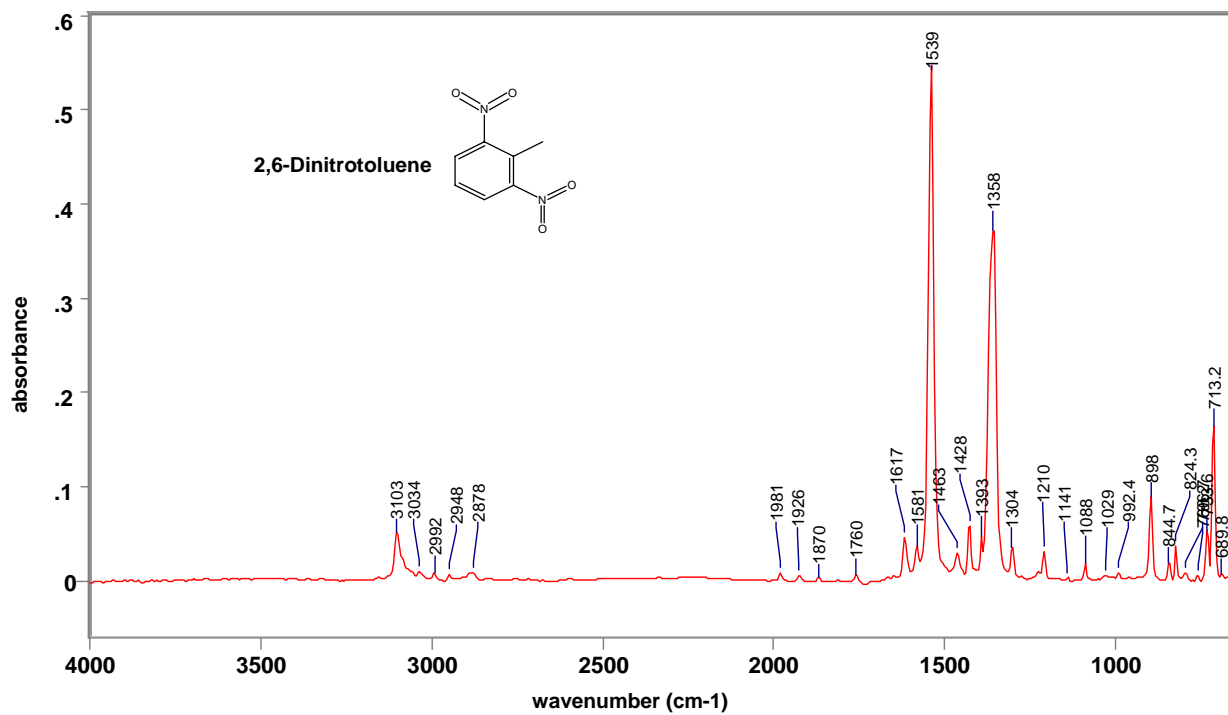


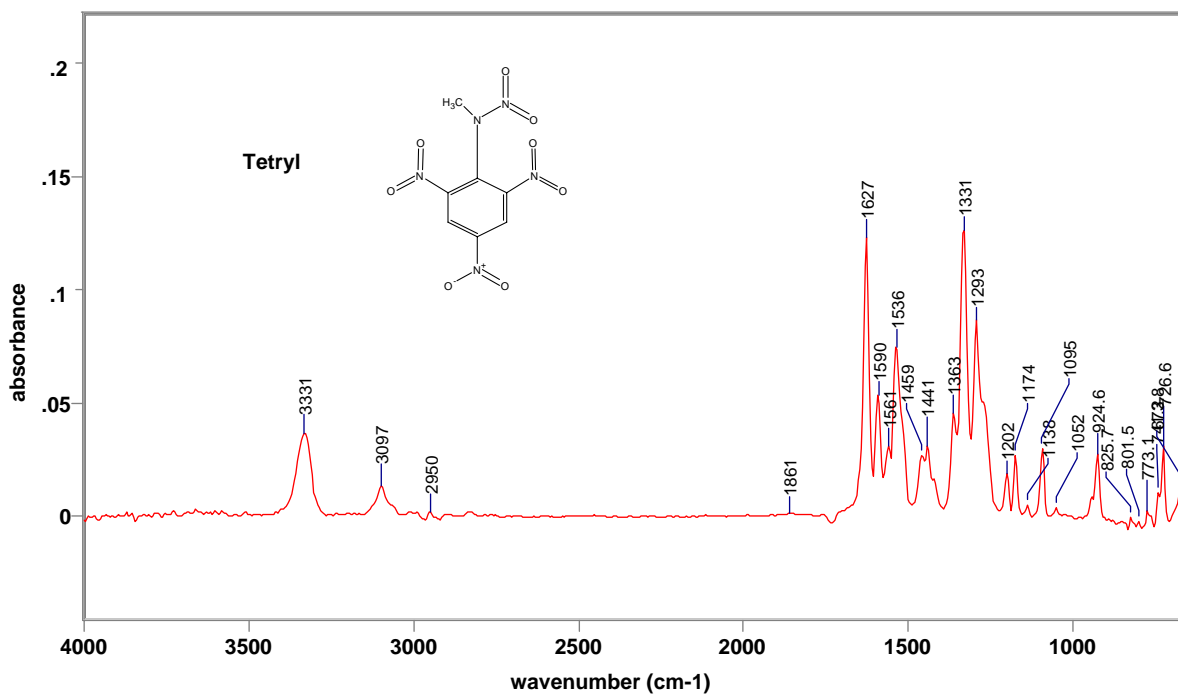
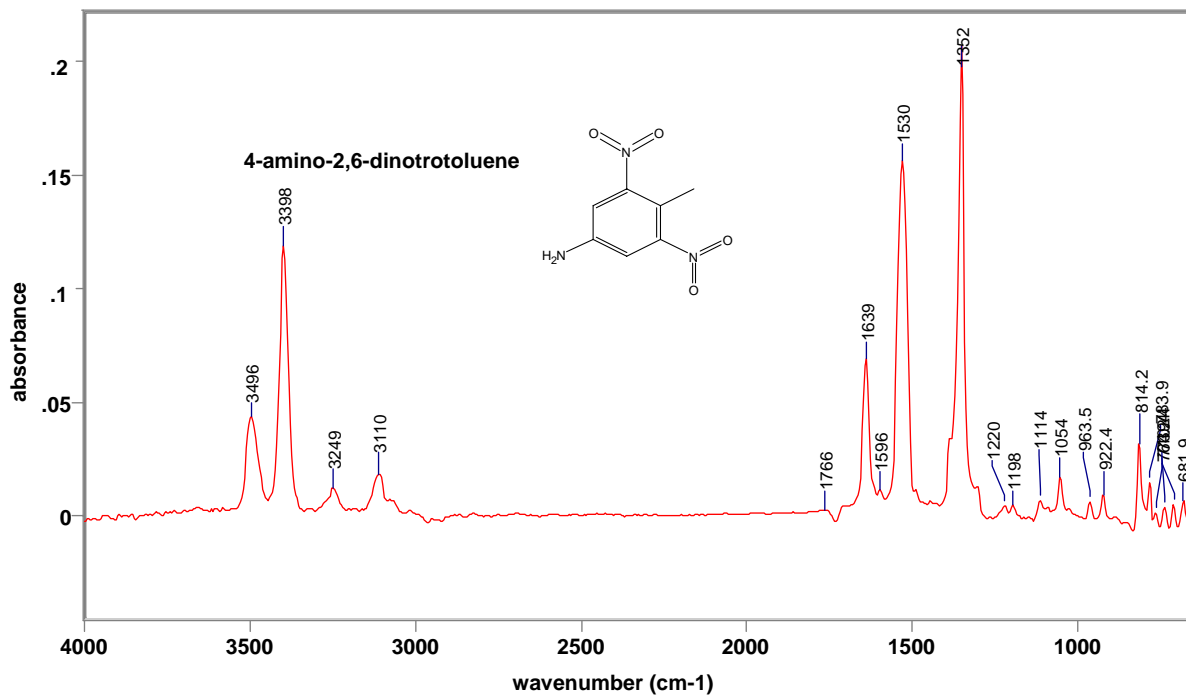
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isomers of identical molecular weight eluants, as are the 5<sup>th</sup> and 6<sup>th</sup> peaks. The O=N=O stretching of the nitro aromatics appear in the 1590 – 1510 range ( $\nu_{as}$ ) and the 1370-1320  $\text{cm}^{-1}$  range ( $\nu_s$ ). These frequencies are shifted somewhat higher in the dinitro compounds. The amino group on the 5<sup>th</sup> and 6<sup>th</sup> eluants generates a pair of stretching vibrations in the 3500 – 3400  $\text{cm}^{-1}$  region characteristic of aromatic primary amines. Aromatic ring stretch bands around 1600  $\text{cm}^{-1}$  and 1500  $\text{cm}^{-1}$  are found in all analytes. The numerous additional sharp bands in the fingerprint region reflect whole molecule absorbances arising from configuration of the molecules.



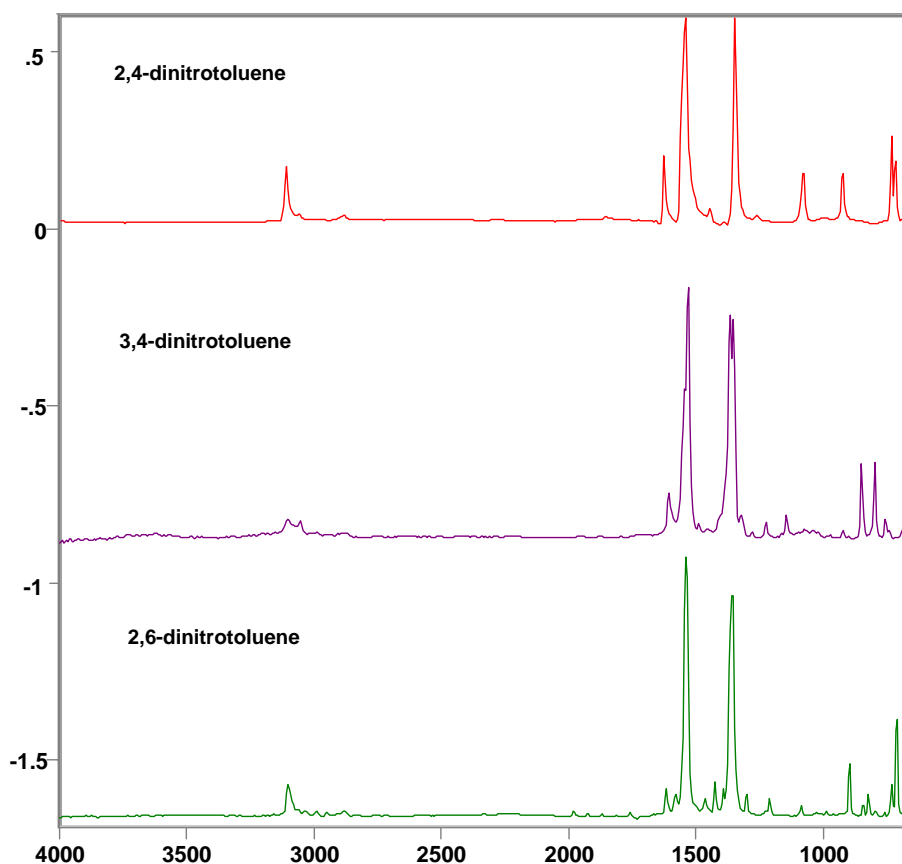






## Isomerism

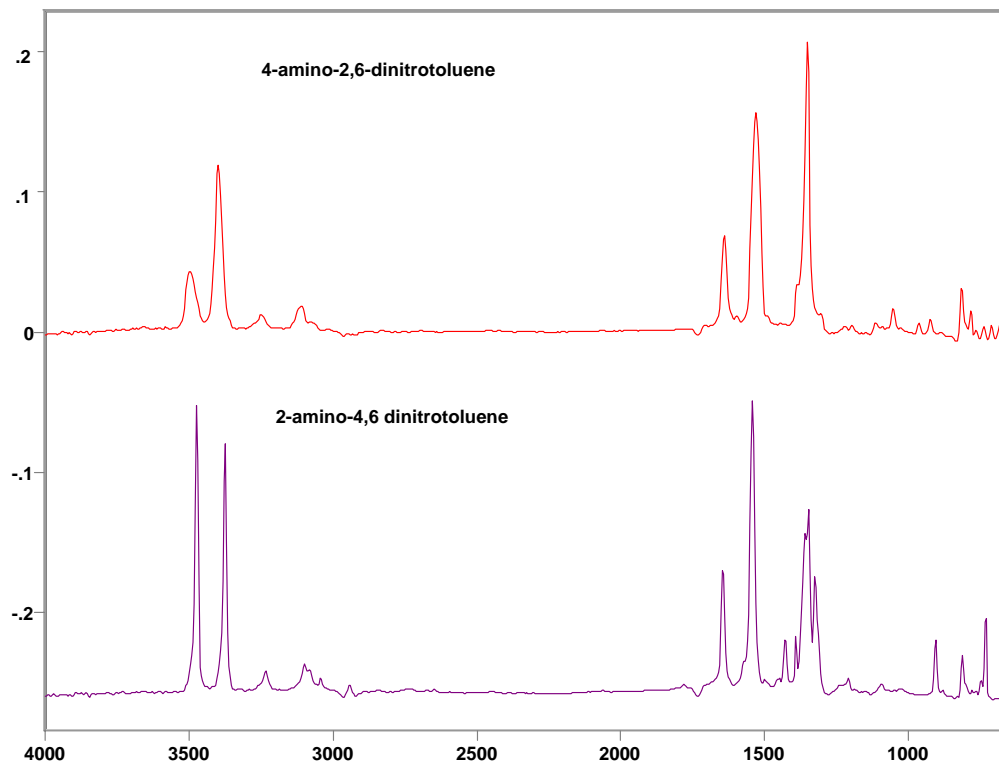
FTIR is a premier tool for ready identification of isomers of explosive compounds. Many explosive materials can exist as positional isomeric forms of identical molecular weight. IR spectral differences between isomers are usually distinctive. Aromatic nitro compounds will manifest primary infrared bands characteristic of the stretch vibrations. The position of the nitro group(s) on the aromatic ring will also give rise to varying intra-molecular interactions. These interactions can result in additional spectral bands, as well as changes of frequency and intensity of the functional group bands. This is a result of whole molecule induced vibrations, and is usually unique to the molecule in question (with the exception of enantiomers). Identification by IR is especially powerful in identification of isomeric forms of a compound. The figure below illustrates the spectral differences of the three dinitrotoluene analytes in the sample. By use of library matching one can readily obtain unequivocal identification of these three positional isomers.



The following pair of spectra similarly provide ready identification of the amino-dinitrotoluene isomers.







## Conclusions

- Identification of explosives components is greatly assisted by the combination of chromatography and spectroscopy. Chromatography resolves a mixed sample into its individual pure components, enabling unequivocal identification of the individual solutes.
- Interface of the chromatograph to FT-IR provides direct real-time identification of each component, and immediate presentation of results.
- The condensed-phase spectra produced by this system are superior to infrared data generated by GC light pipe instrumentation. Spectra are readily searched and identified within commercially available condensed-phase libraries, or user prepared libraries.
- Chromatography integrated with the DiscovIR provides an integrated, single-step instrument configuration. The control software provided combines data collection and data analysis control in a single operating package. Results are available immediately upon completion of the chromatography separation.
- The ability of FT-IR to characterize compounds based on structure facilitates the ready identification of positional isomers commonly found in explosives products.

