Appendix A. Multi-Dimensional Detection of Nitro-Organic Explosives by Gas Chromatography-Pyrolysis-Ultraviolet Detection (GC-PUD)

A.1. Abstract

We describe a new methodology for the trace detection of organic explosives containing nitro functionalities. Conventional gas chromatography separates the components of an explosive mixture. Effluent from the gas chromatograph is pyrolyzed by passage over a heated nichrome wire. Nitric oxide produced on pyrolysis of a nitro-organic compound is then detected by ultraviolet absorption spectroscopy between 180 and 240 nm, using a deuterium lamp as the light source. Nitric oxide exhibits a sharply banded, characteristic spectrum in this region, enabling detection of nitro-organics. The system is tested using the explosive simulants nitrobenzene and 2,4-dinitrotoluene, and with the nitramine explosive tetryl. Detection limits are 25 ng for nitrobenzene, and 50 ng for 2,4-dinitrotoluene. Tetryl is detected with a detection limit of 50 ng. The system is both easy to implement and could be built as a compact, low power device.

A.2. Introduction

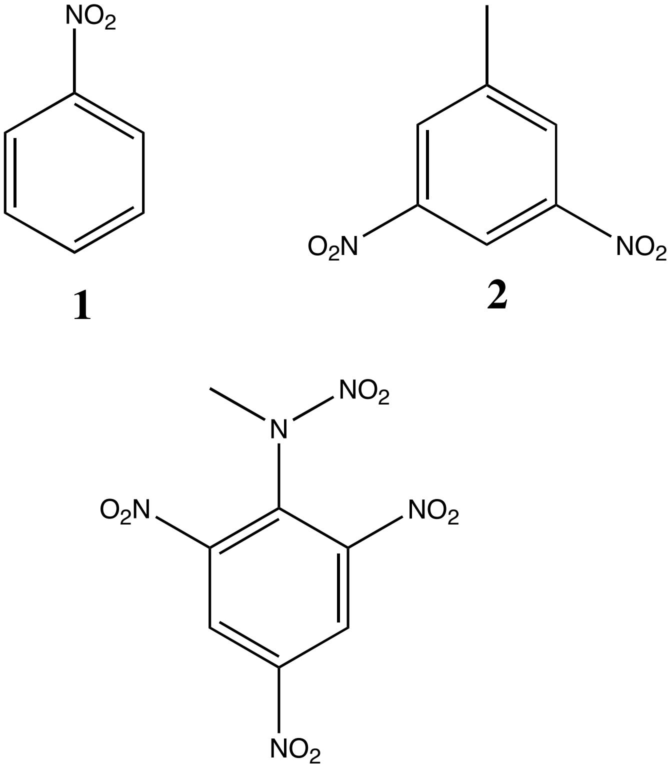
Explosives detection is an urgently needed capability that is now at the forefront of many research efforts. An ideal explosives detection system would be reliable, simple and provide an unambiguous signal when explosives are detected. We report here a new methodology for the detection of nitro-organic explosives based on the ultraviolet detection of NO produced in the thermal decomposition of explosive compounds separated by gas chromatography.

Trace explosives detection methodologies commonly make use of the fragmentation of the target molecules (with the notable exception of ion mobility spectrometry systems[1]), followed by sensitive detection of the released gaseous products. Since many explosive compounds are based on nitro-organics, NO is a common product of decomposition, and a good target for sensitive detection. Both Steinfeld[2] and Moore[3] have recently reviewed the wide variety of techniques used to detect explosives. NO has been detected as the product of thermal decomposition of nitro-organics by IR spectroscopy, microwave spectroscopy, and fluorescence. A number of non-optical techniques, such as mass spectrometry, have also been used.

One of the more successful techniques to detect NO is the use of chemiluminescence. The EGIS system, manufactured by Thermo Electron Corporation, utilizes this type of detector[4]. The chemiluminescence detector, also known as a thermal energy analyzer[5], operates by pyrolyzing the sample in a catalytic reactor to release NO. The NO is subsequently reacted with ozone to produce excited NO_2 which emits infrared radiation that is detected with a photomultiplier. The EGIS system is selective for nitro-organics and is highly sensitive, able to respond to a few picograms of analyte.

The coupling of gas phase ultraviolet absorption with gas chromatography has been practiced sporadically for the past 40 years. Kaye reported the first GC-UV system in 1962[6], which used ultraviolet absorption at 170 nm for the analysis of a chromatographic separation of gasoline. GC-UV systems have since been used for the analysis of wine[7], indoor dust[8], and proposed as a means for functional group analysis[9].

The nitro-organic explosives possess strong absorptions in the UV[10,11,12], and their direct detection by GC-UV is possible. However, the spectra are broad and featureless, and overlap with the absorptions of many other organic compounds. The ultraviolet absorption spectra of the nitro-organic explosives themselves cannot provide unambiguous detection of explosives in the presence of other organics.



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Scheme A.1. Nitrobenzene (**1**), 2,4-dinitrotoluene (**2**), and tetryl (**3**).

The multidimensional[13] technique employed here, gas chromatography-pyrolysis-ultraviolet detection (GC-PUD), overcomes this limitation. After separation by gas chromatography, explosive vapors are pyrolysed on a heated nichrome wire. NO produced in the pyrolysis is subsequently detected by ultraviolet spectroscopy. Explosive simulants nitrobenzene and 2, 4-dinitrotoluene, as well as the explosive tetryl, all yield detectable NO on pyrolysis (Scheme A.1). Linearity of response and sensitivity are good, with a limit of detection of ~50 ng for tetryl. GC-PUD is technically simple, and provides a clear signal for the presence of explosives.

A.3. Experimental

A block diagram of the experimental apparatus is shown in Figure A.1. The gas chromatograph (SRI Model 8610C) is connected to the pyrolysis tube via a heated stainless steel transfer line, usually held at 250 °C. The homemade pyrolysis tube is comprised of a Kimax glass envelope, ~5 mm in diameter, inside of which is a coil of nichrome wire. The tube is sealed using a high temperature ceramic putty. A current of 2-2.5 A is passed through the coil, heating it to a temperature of 900-1200 °C. The temperature was measured with a Micro-Optical Pyrometer, Pyrometer Instrument Co., Inc., Bergenfield, NJ. The gaseous products from pyrolysis flow to a heated absorption cell. The cell consists of two aluminum blocks supporting a quartz tube (3 mm OD) between them, with silica windows on either side. The tube serves as both a light pipe and a conduit for the pyrolysis products. The cell has a pathlength of ~6 cm, and is typically heated to 150 °C. Residence time in the cell is approximately 3 s, so no peak broadening due to the cell is expected.

The light from a 30 W deuterium lamp (Oriel 63163) is coupled into the cell using silica lenses. Unfocused light exiting the cell is directed into a Chromex 250is imaging spectrograph equipped with an Apex SPH-5 CCD detector. The resolution of the system is approximately 0.5 nm. The entire optical path, including the spectrometer, is purged with nitrogen to allow operation below 200 nm. Spectra from 180-240 nm are acquired approximately every 1.5 seconds, with an integration time of 1 s.

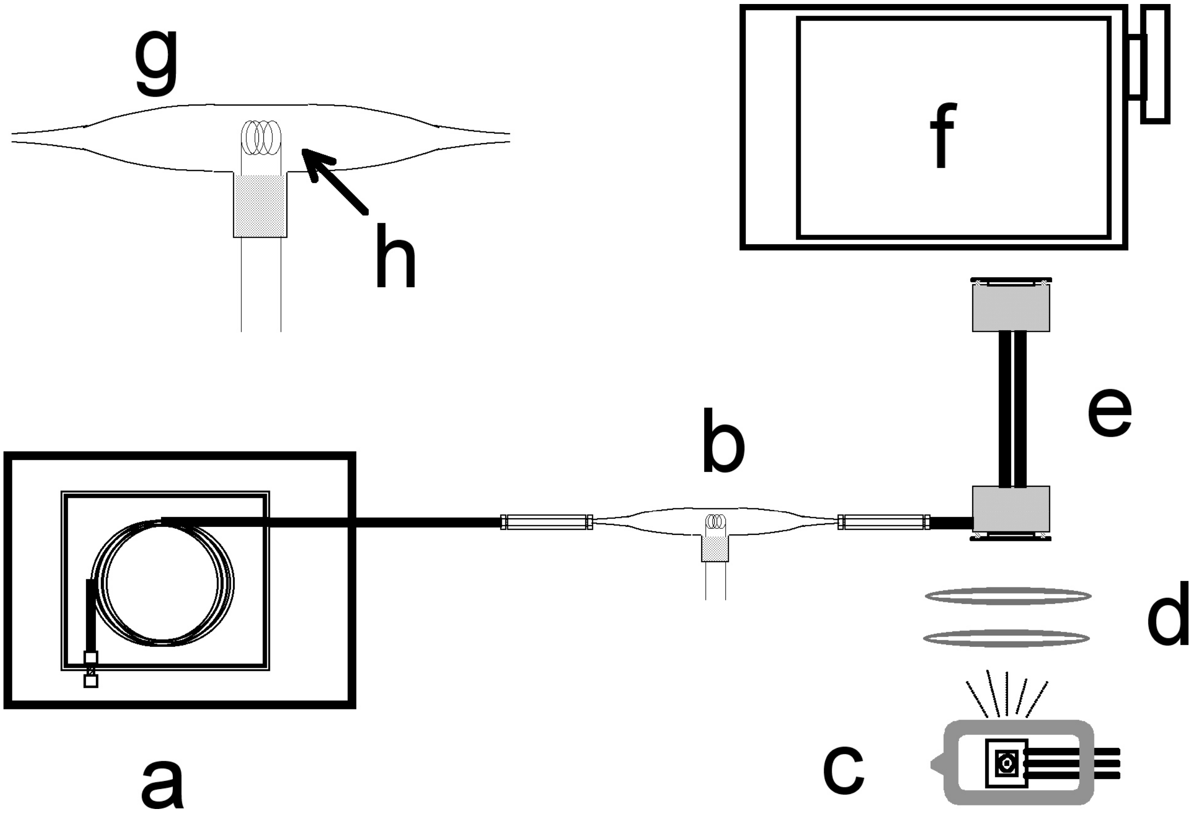

Figure A.1. Block diagram of GC-PUD system. a) SRI 8610C gas chromatograph. b) pyrolyzer tube. c) D_2 lamp. d) silica lenses. e) ultraviolet absorption cell. f) Chromex 250 is/sm spectrometer. Inset shows details of the pyrolyzer. g) Kimax evelope. h) Nichrome coil.

The gas chromatograph uses a 100% methyl polysiloxane column (MXT-1 15m × 0.53mm × 5µm film) with on-column injection. For nitrobenzene and 2,4-dinitrobenzene, the temperature of the GC oven was ramped from 50 °C to 250 °C at 15 °C/min. The temperature program for tetryl was as follows: 100 °C for 2 minutes, then ramped at 10 °C/min to 200 °C, then ramped at 20 °C/min to 250°C, and held for 5 minutes. Helium was used as the carrier gas with a source pressure of 5 psig.

Nitrobenzene and 2, 4-dinitrobenzene (Aldrich) are used without further purification. Acetonitrile was obtained from EM Science. Tetryl was acquired as a 1mg/mL solution in acetonitrile from Supelco.

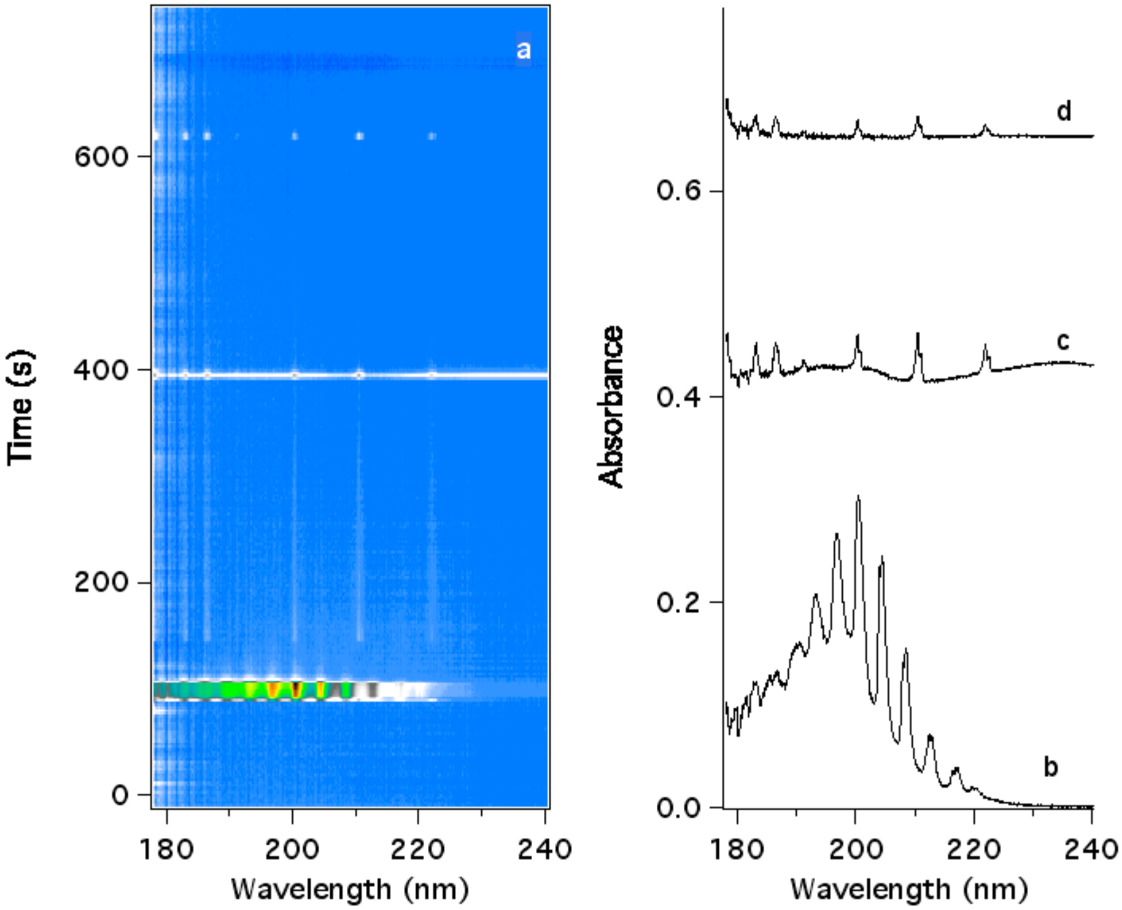

Figure A.2. a) 3-D GC-PUD chromatogram 500 ng each of nitrobenzene (elutes at 395 s) and 2, 4-dinitrotoluene (620 s). Acetonitrile elutes at 100 s. b) Ultraviolet spectrum obtained at 100 s, showing ammonia formed on the pyrolysis of acetonitrile. c) Ultraviolet spectrum obtained at 395 s, showing NO formed on the pyrolysis of nitrobenzene. d) Ultraviolet spectrum obtained at 620 s, showing NO formed on the pyrolysis of 2, 4-dinitrotoluene. Spectra b, c, and d have the same scale and have been shifted vertically for clarity.

A.4. Results and discussion

Figure A.2a shows a representative 3-D chromatogram of 500 ng each of nitrobenzene (NB) and 2,4-dinitrotoluene (2,4-DNT) obtained by GC-PUD. The sample was injected as 1 μL of a 1 mg/mL solution of NB and 2,4-DNT in acetonitrile. Clear signals are visible due to acetonitrile, NB, and 2,4-DNT at retention times of 100 s, 395 s, and 620 s, respectively. Figures A.2b, c, and d show horizontal slices through the chromatogram at these retention times. The spectrum shown in Figure A.2b is identical to that of ammonia, indicating that ammonia is a product of the pyrolysis of acetonitrile. The spectra in Figures A.2c and A.2d match the spectrum of NO[14], indicating that NO is produced by the pyrolysis of NB and 2,4-DNT.

Figure A.3 shows the relationship between peak area and the mass of analyte injected into the gas chromatograph for NB, 2,4-DNT and tetryl. Peak areas were determined by taking a vertical slice through the 3-D chromatogram at the maximum of the 215 nm band of NO. This generates a chromatogram equivalent to an experiment where one monitors the absorbance of the eluent at 215 nm only. The 215 nm band was chosen because it has the largest absorbance in our experiment. The area of the peak representing the eluted compound was then determined for several injections of different masses of each compound.

The peak areas for all three analytes tested are linear with mass below approximately 5 micrograms. At higher concentrations, NB and 2,4-DNT showed a small negative deviation from linearity. The slope of the curves for NB and 2,4-DNT are essentially identical, while the slope for tetryl is significantly greater. The correspondence between the slopes of NB and 2,4-DNT shows that the number of nitro groups on the molecule is not related to the amount of NO generated by pyrolysis in our system. The steeper slope of the curve for tetryl may be due to the presence of both nitro and nitramine functionalities in this compound, altering its pyrolysis behaviour. Limits of detection (LOD), determined as three times the noise, were 50 ng for tetryl and 2,4-DNT, and 25 ng for nitrobenzene.

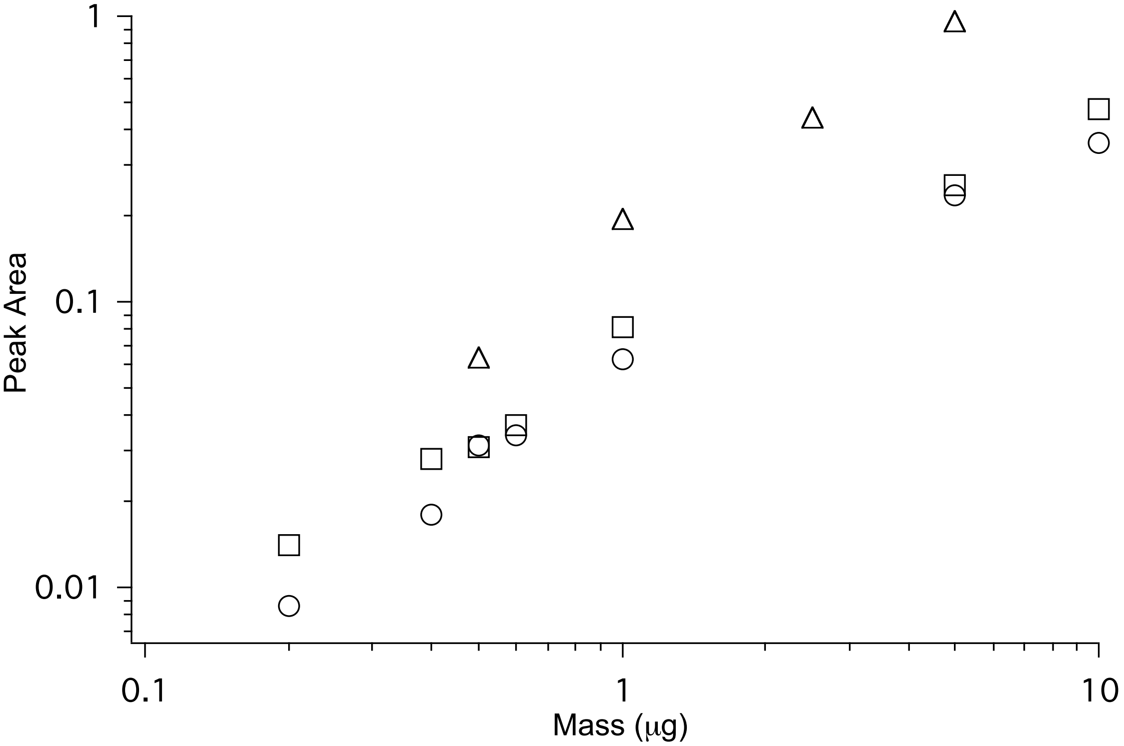

Figure A.3. Peak area vs. mass of analyte injected for NB (circles), 2,4-DNT (squares) and tetryl (triangles). Note the log scale.

Two major factors contribute to the observed LODs. The most important issue is the efficiency of the pyrolyzer. The current delivered to the pyrolyzer, and thus its temperature, is set by increasing the temperature until no absorbance due to the analyte remains, and only NO absorbance is observed. This was found to occur at temperatures between 900 °C and 1200 °C, depending on the amount of analyte injected. These temperatures are much higher than those required for pyrolysis of most nitroarenes[15]. This suggests that much of the analyte is not passing close enough to the nichrome wire to be pyrolyzed, necessitating a high temperature in order to completely pyrolyze the analyte.

A second issue is that of peak width in the chromatogram. Since the detector is measuring the instantaneous concentration of NO in the cell, broad peaks will lead to less signal than narrow peaks, even though the total amount of analyte in each peak is the same. This accounts for the lower LOD for nitrobenzene, which elutes early and has a rather narrow peak, compared to 2,4-DNT, which exhibits a broader peak under these chromatographic conditions.

Organic compounds containing both nitrogen and oxygen, such as amides, will also produce NO on pyrolysis, leading to possible interferences. These interferences can be reduced by the use of sampling techniques that pre-select for explosives, or by using a catalytic pyrolyzer[5], as is used in the EGIS system. The catalytic pyrolyzer operates at much lower temperatures (275 °C), and produces NO only from nitro-organic compounds.

A.5. Conclusions

We have developed a system, gas chromatography-pyrolysis-ultraviolet detection, for the selective detection of nitro-organic explosives in the presence of other organics. After separation by gas chromatography, explosive compounds are pyrolyzed by passage over a hot wire, and the resulting NO is detected by its characteristic ultraviolet absorption spectrum. Nitrobenzene, 2,4-dinitrotoluene and tetryl are all detected with a linear response, and limits of detection of 25 ng for nitrobenzene, and 50 ng for tetryl and 2,4-dinitrotoluene.

The GC-PUD system is technically simple and provides a clear signal of the presence of nitro-organics. While the current detection limits are not sufficient for the detection of common real-world samples, optimization of the system would provide the necessary sub-nanogram to picogram sensitivity. Increases in sensitivity could be achieved by using a multi-pass cell, a more sensitive UV spectrometer, and by improving the efficiency of the pyrolyzer. The use of fast GC techniques[16] would improve the speed of the analysis.

Other diagnostic pyrolytic reactions may exist that can be probed with this technique. For instance, the production of ammonia from acetonitrile on pyrolysis suggests that all nitriles may form ammonia when pyrolyzed. The study of the pyrolysis products from a wide variety of compounds would enable the GC-PUD technique to be used for the functional group analysis of complex mixtures.

A.6. Acknowledgements

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