Document Title: Technology Development, Implementation and Evaluation for Collection and Analysis of Explosives Trace Chemical Evidence

Author(s): M. E. Sigman

Document No.: 189913

Date Received: August 28, 2001

Award Number: 1997-LB-VX-A063

189913
c.2

Grant No. 97-LB-VX-A063

Technology Development, Implementation and Evaluation for Collection and Analysis of Explosives Trace Chemical Evidence

M. E. Sigman

Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6100

National Institute of Justice
Office of Justice Programs

August 2000

Report Contents

Abstract

A method has been developed for sampling surfaces and analyzing for the presence of trace amounts of organic explosives. The method entails the use of a Teflon™ dry surface-wiping material for sample collection, and a common laboratory instrument (a gas chromatograph) suitable for explosives analysis. Minimal instrument modifications are required, making the implementation of this method fast, inexpensive, and easily accomplished in any forensics laboratory. Applications of the method range from investigating debris left after a bomb detonation to surface testing baggage in airports. The method has been tested in the laboratory and published in peer-reviewed journals. Documentation of this work has been provided to local, state and federal law enforcement officials.

Executive Summary

In the course of an investigation involving a suspected or known bombing incident, samples of debris are collected at the scene for later analysis in a laboratory. The laboratory analysis for explosives residue typically involves visual microscopic interrogation as well as chemical testing. Ignition testing of microscopic particles retrieved under visual inspection yields some clues as to the identity of explosive components present in the debris. Further chemical testing can involve washing the debris with water and organic solvents to remove traces of inorganic and organic explosives, respectively. Typically, only a fraction of the total volume of wash solution is analyzed for explosives.

An investigator is likely to encounter several obstacles when following the general methodology described above. For example, a piece of debris may be too large to conveniently transport to a laboratory. Debris that can not be transported must be sampled in the field, which requires the use of solvents or solvent-wetted wipes. Conventional cotton wipes may easily snag and tear on the rough surfaces and edges of post-blast debris, resulting in some loss of sample. Back at the laboratory, the wipes must be individually extracted to obtain trace quantities of explosives. The requirement for using solvents in the sampling and analysis of explosives imposes an additional obstacle in cases where the investigator wishes to do a rapid analysis or survey of debris on-site. As solvent processing methods generally do not lend themselves to convenient field analysis, a sampling and analysis method is needed that obviates the use of solvent and provides for rapid on-site testing.

The goal of this research project was to provide scene investigators and forensic chemists with an alternative method for organic explosives sampling and analysis that did not require the use of solvents. The research has resulted in the development of a dry surface-wipe method of debris sampling that utilizes abraded Teflon as the sample collection material. Teflon was identified as the wipe material-of-choice after surveying a number of commercial polymers. The resistance of Teflon to tearing on rough surfaces and edges of debris from a bomb blast and its stability under gentle heating made Teflon the ideal material for this application. For analysis, an innovative approach has been developed where the Teflon wipe is heated to 170°C in the sample inlet of the instrument. This allows the explosives to be removed from the wipe and introduced directly into a conventional gas chromatograph. We have referred to this method of sample introduction as "in-injection port thermal desorption." The method developed under this research program uses commercially available polymers and laboratory instruments and requires only the addition of a single inexpensive valve onto the chromatograph's exterior ($20 and 5 minutes to install). This allows any existing forensic laboratory already possessing a gas chromatograph to utilize the method without a large investment of dollars that could be better spent in other areas of law enforcement.

The work resulted in one peer-reviewed publication in the journal *Analytical Chemistry* in 1999 (attached as **Appendix I**). A detailed operational procedure of the method was published as an Oak Ridge National Laboratory Technical Manuscript (*ORNL-TM*) in 1999 (attached as **Appendix II**) This document contains more explicit details on implementing the method. A manuscript giving rigorously determined detection limits for a series of explosives and explosives-related chemicals was submitted to the *Journal of Forensic Science* (attached as **Appendix III**). The manuscript for publication in *Journal of Forensic Science* has been accepted for publication pending minor changes in the manuscript. The review of this manuscript states; ***"The paper is well done. It is well documented and provides a useful reference for future explosives detection work."*** Copies of the *Analytical Chemistry* paper and the *ORNL-TM* were distributed to members of local, state and federal law enforcement agencies. A distribution list can be found at the end of the *ORNL-TM* in Appendix II. In response to these documents, Dr. Antonio Cantu, US Secret Service, requested that copies be sent to Dr. Joseph Almog, Investigations Department, Division of Identification and Forensic Science, Israel Police. In addition, copies of these materials have been given to Dr. F. Wayne Barte, Office of Law Enforcement Technology Commercialization (OLETC), Wheeling, WV.

Leveraging NIJ's Investment; The "in-injection port thermal desorption" method of explosives sample introduction, developed under this grant, has also proven useful as a method of introducing explosives samples collected by other means. Explosives vapors can be collected onto adsorbent traps and then introduced into an analytical system by the "in-injection port thermal desorption" method. ORNL has leveraged NIJ's investment by utilizing the sample introduction method as part of a DARPA-sponsored program. The DARPA program, entitled "Engineered Bee Colonies: A Platform for Detecting Agents of Harm," focuses on the use of honeybees for environmental sampling, with an emphasis on explosives detection. We have also utilized the technology to determine nitroglycerine concentrations in the headspace above smokeless gunpowder in support of an ATF-sponsored research program at ORNL.

Appendix I: Research Article, published in *Analytical Chemistry*, **1999**.

Anal. Chem. **1999,** *71,* 4119-4124

Articles

In-Injection Port Thermal Desorption for Explosives Trace Evidence Analysis

Michael E. Sigman* and Cheng-Yu Ma

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS 6100, Oak Ridge, Tennessee 37831-6100

A gas chromatographic method utilizing thermal desorption of a dry surface wipe for the analysis of explosives trace chemical evidence has been developed and validated using electron capture and negative ion chemical ionization mass spectrometric detection. Thermal desorption was performed within a split/splitless injection port with minimal instrument modification. Surface-abraded Teflon tubing provided the solid support for sample collection and desorption. Performance was characterized by desorption efficiency, reproducibility, linearity of the calibration, and method detection and quantitation limits. Method validation was performed with a series of dinitrotoluenes, trinitrotoluene, two nitroester explosives, and one nitramine explosive. The method was applied to the sampling of a single piece of debris from an explosion containing trinitrotoluene.

Traces of some chemical components from an explosive device are not consumed in an explosion, and some components are vaporized upon detonation and can later be found condensed on debris.[1,2] Multiple physical and chemical techniques are utilized to collect and analyze explosive trace chemical evidence from postblast debris.[2-4] One method of analysis involves extracting the debris with organic solvents and water. Organic solvents may extract plasticizers, oils, and paint components, in addition to organic explosives, thus necessitating cleanup prior to instrumental analysis. The use of organic solvents, including solvent-wetted cotton wipes, can require extraction and volume-reduction steps in processing the sample. These processing steps typically require a laboratory and prevent on-site analysis. Rapid analysis may be beneficial in cases where microbial populations and other environmental factors may accelerate analyte decomposition.[5] A dry sampling method may also be highly useful in cases where pieces of debris are too large for efficient solvent extraction or microscopic investigations. Rapid field analysis of a dry surface wipe would be possible utilizing a thermal desorption method with a portable gas chromatograph. This paper reports the first such dry sampling method as an additional tool for forensic investigators. The need for thermally desorbable dry wipes, to assist in the detection of hidden explosives, has previously been recognized.[6,7] A solvent-wetted wipe analysis for trace explosives evidence has also been reported.[8] That method also requires solvent extraction of the wipe, followed by sample concentration and analysis. The method presented here seeks to circumvent the wet chemistry workup step by providing a material and method for performing dry surface wipes which are followed by thermal desorption and gas chromatographic analysis.

Selection of an appropriate material for a dry surface wipe is subject to several considerations. The material must be resistant to shredding by sharp or rough surfaces often encountered on postblast debris; however, it must be compliant enough to give good surface contact. In addition, thermal desorption of explosives residue requires that the material be stable to approximately 200 °C. Furthermore, the wipe must release the explosives residue in good yield upon thermal desorption. Ease of processing for initial preparation of the wipe is also an important consideration. This paper explores the use of Teflon tubing as a dry surface wipe. Teflon is shred-resistant and has the required thermal stability. Abrading the Teflon enhances surface contact. Several organic explosives have previously been shown to thermally desorb from Teflon.[9,10] Initial processing of the Teflon to produce an acceptable surface-wipe material is easy and conveniently done with readily available laboratory equipment.

Gas chromatographic methods of analysis for trace explosives and incendiary chemicals has recently been reviewed.[2,11,12] The three most sensitive detection methods for gas chromatographic

---

* To whom correspondence should be addressed. Tel.: (423) 576-2173. Fax: (423) 574-4902. E-mail: sigmanme@ornl.gov

(1) Bender, E.; Hogan, A.; Leggett, D.; Miskolczy, G.; MacDonald, S. *J. Forensic Sci.* **1992**, *37*, 1673-8.
(2) Steinfeld, J. I. *Annu. Rev. Phys. Chem.* **1998**, *49*, 203-32.
(3) Beveridge, A. D. *Forensic Sci. Rev.* **1992**, *4*, 17.
(4) Garner, D. D.; Fultz, M. L. *J. Energ. Mater.* **1986**, *4*, 133-48.
(5) Dr. John Caton, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, personal communication.
(6) Kolla, P. *Anal. Chem.* **1995**, *67*, 184A.
(7) Feterolf, D. D.; Clark, T. D. *J. Forensic Sci.* **1993**, *38*, 28.
(8) Kolla, P.; Sprunkel, A. *J. Forensic Sci.* **1995**, *40*, 406-11.
(9) Peterson, P. K.; Conrad, F. J. *Proc. – New Concepts Symp. Workshop Detect. Identif. Explos.*, NTIS, Springfield, VA.; **1978**, pp 85-8.
(10) Petersen, P. K. *Proc. Int. Symp. Anal. Detect. Explos.*, Federal Bureau of Investigation, Washington, DC.; **1983**, pp 391-5.
(11) Fultz, M. A.; DeHaan, J. D. Gas Chromatography in Arson and Explosives Analysis. In *Gas Chromatography In Forensic Science*; Tebbett, I., Ed.: E. Horwood: New York, 1992, Chapter 5, pp 109-63.
(12) Walsh, M. E.; Ranney, T. *J. Chromatogr. Sci.* **1996**, *36*, 406-16.

10.1021/ac9901079 CCC: $18.00 © 1999 American Chemical Society
Published on Web 08/20/1999

analysis of explosives are electron capture detection (ECD),[13] thermal energy analyzer (TEA),[13] and negative ion chemical ionization mass spectrometry (NICI).[14–17] In this paper, both ECD and NICI detection are employed.

Trace analysis of picogram quantities of explosives, by injection of standard mixtures, has previously been demonstrated using a gas chromatography/electron capture detection (GC/ECD) method.[18] Notably, the method utilized a 165 °C injection-port temperature to prevent degradative losses of the analytes. An injection port temperature of 170 °C was later reported to be the optimum for giving the minimal degradation and maximum analytical sensitivity for a series of explosives.[19] In addition to a 170 °C injection port temperature, it was reported that thin-film moderate-polarity stationary phases ($<0.25\ \mu$m) and high-carrier gas flow rates (up to tens of mL min^{-1}) are required for optimum analyte separation and recovery.

Gas chromatography with negative ion chemical ionization mass spectrometric detection (GC/NICI) has been shown by Martz to exhibit nanogram sensitivity levels for explosives when scanning a range of ions.[20] It was also shown that picogram detection levels could be obtained with selected-ion monitoring. Ion-scanning techniques are employed in this work. The advantage of scanning a range of ions is that it allows for the identification of a suite of explosives without a priori knowledge of the sample composition.

EXPERIMENTAL SECTION

Apparatus. GC/ECD analysis was performed on a Hewlett-Packard 5890 Series II Gas Chromatograph, equipped with an electron-capture detector. The auxiliary flow was set at 124 mL min^{-1}, and the detector temperature was set at 250 °C. GC/NICI analysis was performed on a Hewlett-Packard 5989 Gas Chromatograph/Mass Spectrometer operating in electron capture negative ion chemical ionization (NICI) mode. With reagent gas (methane) optimized at 0.8 Torr, the instrument was tuned using the manufacturer's procedure. Source temperature was set at 150 °C, and the quadrapole temperature was set at 100 °C. The electron energy was set at 230 eV and the emmision current at 300 μA. Full-scan (100–550 amu) spectral data were acquired at a rate of 0.72 scan s^{-1}. To check the instrument performance, 320 pg of decachlorobiphenyl and 92 pg of hexachlorobenzene were injected and analyzed with a column temperature program as follows: 100 °C held for 3 min, raised to 280 °C at 20 °C min^{-1}. The resulting spectra were then compared with reference spectra:[21] for decachlorobiphenyl m/z 498 (100%), 464 (>27%), and 430 (>5%) and for hexachlorobenzene m/z 284 (100%), 286 (>70%), 250 (>10%). If the relative abundance was out of range, the instrument was retuned. The GC peak heights for both compounds acquired over the full-scan mass range must be at least three times greater than the noise.

Figure 1. Optical micrograph of the Teflon tubing used for surface wiping and thermal desorption. The tube on the left is as provided by the vendor, and the tube on the right has been roughened with a 240-grit emory cloth.

The gas chromatograph was modified by attaching an on/off valve to the split vent on the front of the instrument. The gas chromatograph was fitted with a 12-m HT5 column (5% phenyl polycarborane siloxane, Scientific Gas Engineering, Inc., Austin, TX) with a 0.22-mm i.d. and a 0.1-μm film thickness. For GC/ECD analysis, a He carrier flow rate of 2.6 mL min^{-1} on the column with a vent flow of 50 mL min^{-1} was used. For GC/NICI analysis, a He flow of 1.2 mL min^{-1} was used. Slower flow rates or a longer column length were found to lead to degradation of PETN on the column.

Reagents. Teflon tubing, 1/8 in o.d. and 1/16 in i.d. (Upchurch Scientific, Oak Harbor, WA), was use as the surface-wipe/thermal-desorption material. The tubing was cut to 55 mm in length and abraded by lightly sanding with a 240-grit emory cloth. The tubing was held in a standard drill chuck attached to a laboratory stirrer motor and gently sanded at several hundred revolutions per minute to give a material as shown in Figure 1. Roughening the tube allows for better surface contact when wiping debris. The abraded Teflon tubes were heated at 220 °C under a flow of argon, 360 mL min^{-1}, for at least 5 h. The resulting tubes had little or no detectable background signal on the ECD or NICI when thermally desorbed by the method described here.

All explosives were used as received. Diethyleneglycol dinitrate (DEGN [693-21-0]) was obtained from Trojan Corp. (Spanish Fork, UT). 2,6-Dinitrotoluene (2,6-DNT [606-20-2]); 2,4-dinitrotoluene (2,4-DNT [121-14-2]); 2,3-dinitrotoluene (2,3-DNT 602-01-7]); 3,4-dinitrotoluene (3,4-DNT [610-39-9]); and 1,3-dinitronaphthalene (DNN 606-37-1]) were purchased from Aldrich Chemical Co. (Milwaukee, WI). 2,5-Dinitrotoluene (2,5-DNT [619–15–8]) and benzene were obtained from Fisher Scientific Co. (Pittsburgh, PA). 2,4,6-Trinitrotoluene (TNT [118-96-7]) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX [121-82-4]) were supplied by the Naval Explosive Ordnance Disposal Technical Division at the Naval Surface Warfare Center (Indian Head, MD). Pentaerythritol tetranitrate (PETN [00078-11-5]) was obtained from the US Army Standard Analytical Reference Material respository, US Army Environmental Center (Aberdeen Proving Ground, MD). Acetonitrile was obtained from EM Science (Gibbstown, NJ). Stock solutions containing DEGN (0.85 mg mL^{-1}); 2,6-DNT (6.30 mg mL^{-1}); 2,5-DNT (11.90 mg mL^{-1}); 2,4-DNT (16.20 mg mL^{-1}); 2,3-

---

(13) Douse, J. M. F. *J. Chromatogr.* **1985**, *328*, 155–65.
(14) Barshick, S. A.; Griest, W. H.; *Anal. Chem.* **1998**, *70*, 3015–20.
(15) Yinon, J. *J. Forensic. Sci.* **1980**, *25*, 401–7.
(16) Echenrode, B. A.; Glish, G. L.; McLuckey, S. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *99*, 151–67.
(17) Yinon, J. *Forensic Mass Spectrometry*; Yinon, J., Ed.; CRC Press: Boca Raton, FL.; 1987, pp 106–30.
(18) Douse, J. M. F. *J. Chromatogr.* **1981**, *208*, 83–8.
(19) Kolla, P. *J. Chromatogr., A* **1994**, *674*, 309–18.
(20) Martz, R. M.; Munson, T. O.; Lassel, L. D. In *Proc. Int. Symp. Anal. Detect. Explos.*, FBI Academy, Quantico, VA, Mar. 29–31, 1983; United States Federal Bureau of Investigation: Washington, D.C., 1983; p 245.
(21) Stemmler, E. A.; Hites, R. A. *Electron Capture Negative Ion Mass Spectra of Environmental Contaminants and Related Compounds*, VCH Publisher: New York; 1988; pp 39, 253.

DNT (6.00 mg mL^{-1}); 3,4-DNT (7.80 mg mL^{-1}); TNT (6.60 mg mL^{-1}); PETN (2.70 mg mL^{-1}); RDX (5.20 mg mL^{-1}); and 1,3-DNN (3.70 mg mL^{-1}) were prepared in acetonitrile. The stock solutions were used to prepare mixtures of known concentrations in benzene for method development.

Procedure. The injection-port temperature was reduced to less than 50 °C to allow the Teflon tube to be placed into the injection port without loss of more volatile components. In a typical calibration analysis, a 2 μL sample of calibration solution was deposited on a Teflon tube by syringe, and the solvent was allowed to evaporate (approximately 5 min). The Teflon tube was placed inside the injection port, and the port was then closed and heated to 170 °C with the split purge turned off and the exit port blocked by closing the on/off valve. The flow during thermal desorption increased to 6.4 mL min^{-1}, forcing analytes onto the analytical column. Thermal desorption was allowed to proceed for 6 min, including the 3.5–4 min injector heating time. The gas-chromatograph oven was held at ambient temperature during thermal desorption to allow the analytes to condense and focus at the head of the column. A two-tiered thermal program was employed in which the oven temperature was held for 3 min at 70 °C and then heated to 185 °C at a rate of 8 °C min^{-1} in the first part of the program. The temperature was then raised to 250 °C at a rate of 30 °C min^{-1} and held at that temperature for 10 min.

To test the recovery of explosives by the dry-wipe method, simulated post-blast debris was generated. To simulate explosives residue found in post-blast debris it was desirable to prepare a surface containing very small particulates of explosive as opposed to a monomolecular distribution of explosives on the surface. The simulated debris was prepared by addition of an aqueous suspension of RDX to a 1-in. diameter stainless steel disk.[22] The suspension was prepared by placing a small amount, 4.74 mg, of RDX in 20 mL of water (273 ng per μL). The mixture was rapidly stirred on a magnetic stir plate for 1.5 h in an ice bath to generate a suspension of small particles. The stirring procedure was carried out in a fume hood with additional protection of a blast shield. The stirring was stopped, and a 2-μL sample was withdrawn from below the surface using a mechanical pipett. A small amount of RDX could be seen floating on the surface of the water. The withdrawn sample was transferred to the stainless steel disk, and the water was allowed to evaporate. The disk was then wiped with abraded Teflon to remove the explosives particles. The remainder of the explosive was washed from the disk using 200 μL of acetonitrile. Analysis of the Teflon wipe was performed as discussed above using GC/ECD after spiking the tube with 61 ng of 1,3-DNN internal standard. The acetonitrile wash was also analyzed as described above after spiking 20 μL (10% of the sample) onto an abraded Teflon tube along with 61 ng of 1,3-DNN internal standard.

RESULTS AND DISCUSSION

Reproducibility of Sorbent Tube Preparation. Three batches of abraded tubes were prepared. Each batch consisted of three tubes, of which, one was randomly selected and tested. Each tube to be tested was spiked with an analyte mixture and thermally desorbed. Recoveries were determined by GC/ECD. The analysis was repeated in triplicate for each tube, and the average analyte recovery was determined for each tube. The average analyte recoveries were used to determine the %RSD. The results, listed in Table 1, show that the average analyte recoveries from the representative three tubes have a %RSD of less than 7% for every analyte except PETN. The thermal instability of PETN leads to a higher %RSD for this analyte. The demonstrated batch-to-batch reproducibility in the preparation of the surface-wipe material ensures that the method accuracy and precision are independent of the surface-wipe preparation.

Table 1. Average In-Injection Port Thermal Desorption Recoveries for Explosives of Randomly Selected Abraded Teflon Surface Wipes from Independent Wipe Preparations

analyte	average recovery (ng)	%RSD
DEGN	2.38	4.23
2,6-DNT	2.20	3.06
2,5-DNT	3.58	3.77
2,4-DNT	5.71	5.94
2,3-DNT	2.52	4.57
3,4-DNT	2.83	6.80
TNT	5.48	5.90
PETN	11.44	12.41
RDX	9.20	4.61

Accuracy. The accuracy of the method was determined by comparison of the instrument response due to analyte thermal desorption from Teflon relative to the response from a liquid injection (170 °C injection port, splitless for 2 min) of the same quantity of analyte as determined by GC/ECD. The comparison provides a measure of the percent recovery (desorption efficiency) of the spiked analyte. The values reported in Table 2 are the result of at least three successive sets of thermal desorptions and liquid injections. The analyte levels were approximately 20 ng per component. Desorption efficiency for the analytes ranged from 84.6% for 2,5-dinitrotoluene to 112.99% for RDX. The source of increased recovery for RDX is unknown, but the recovery falls within the reproducibility determined for the method (vide infra). The average recovery for DNN, the internal standard used in this study, was 87.37% with a relative standard deviation of 8.44%.

Precision. Eight solutions were prepared, each containing all of the explosives analytes and DNN as an internal standard. Two microliters of a given solution were spiked onto Teflon tubes and the solvent evaporated to give the range of analyte loadings reported in Tables 2 and 3. The loading of the internal standard was 98 ng for each sample analyzed by GC/ECD (Table 2) and 74 ng for each sample analyzed by GC/NICI. At least three replicate thermal desorptions were performed for each of the eight solutions. The average response and the %RSD were determined for each analyte at each loading for both ECD and NICI detection. The observed ranges in %RSD are listed in Tables 2 and 3 as a measure of the precision of the method. The larger %RSD values resulted from analyte loadings that approached the thermal-desorption limit of detection (vide infra). The largest overall %RSD was determined for PETN detection by ECD.

Linearity and Range. The linearity of the method was determined from the same data used for the precision determination. The ratios of the instrument response for each analyte

---

[22] The method described here is a modified version of a method provided by Dr. Tom Chamberlin, FAA Explosives Testing and Analysis Laboratory, Atlantic City, NJ. Personal communication, 1999.

Table 2. Validation Data for the In-Injection Port Thermal Desorption and Analysis of Explosives Residue by GC/ECD

analyte	accuracy (desorption efficiency)	reproducibility (%RSD)	calibration slope	calibration linearity (r^2)	method limit of detection (pg)	method limit of quantitation (pg)	loading range (ng)
DEGN	94.82	8.08–45.44	3.5840	0.9906	229	694	0.15–24.51
2,6-DNT	93.07	4.85–25.83	4.7716	0.9978	29	88	0.11–18.17
2,5-DNT	84.6	5.02–30.06	13.3586	0.9669	78	236	0.14–22.88
2,4-DNT	97.33	4.53–19.20	2.1054	0.9974	174	527	0.29–46.72
2,3-DNT	95.68	2.78–28.78	14.1727	0.9793	39	118	0.11–17.30
3,4-DNT	96.27	3.58–23.22	8.3386	0.9986	59	179	0.14–22.49
TNT	89.35	4.47–24.32	3.4552	0.9978	340	1030	0.20–31.72
PETN	95.48	5.8–71.24	0.9029	0.9882	133	403	0.33–51.91
RDX	112.99	5.0–32.80	2.9120	0.9968	332	1006	0.31–49.98

Table 3. Validation Data for the In-Injection Port Thermal Desorption and Analysis of Explosives Residue by GC/NICI

analyte	reproducibility (%RSD)	calibration slope	calibration linearity (r^2)	method limit of detection (ng)	method limit of quantitation (ng)	loading range (ng)
DEGN	13.14–34.00	0.3978	0.9946	1.770	5.364	2.60–37.76
2,6-DNT	15.07–26.64	2.3417	0.9881	0.480	1.455	0.68–10.04
2,5-DNT	8.71–29.63	2.2989	0.9903	0.510	1.545	0.86–12.64
2,4-DNT	7.19–30.74	1.0827	0.9931	0.677	2.052	1.18–17.22
2,3-DNT	7.2–28.73	3.0132	0.9940	0.503	1.524	0.66–9.56
3,4-DNT	4.55–18.81	1.9484	0.9952	0.113	0.342	0.86–12.44
TNT	1.81–31.95	1.2328	0.9946	0.396	1.200	1.20–17.54
PETN	4.16–38.26	0.1477	0.9971	5.621	17.033	8.25–119.96
RDX	0.99–11.09	0.6375	0.9827	1.839	5.573	4.74–138.18

relative to the response for the internal standard were averaged. The average response ratios were plotted against the analyte to internal standard concentration ratios. The response and concentration ratios were used to perform linear regression to obtain calibration curves. The linearity (r^2) resulting from linear regression are given in Tables 2 and 3 for ECD and NICI detection, respectively. The linear model accounted for greater than 96.7% of the variance in all cases and greater than 99% in most cases.

Limit of Detection and Limit of Quantitation. The data used for the precision and linearity were also employed to determine the method limit of detection (LOD) and limit of quantitation (LOQ) for each analyte using both methods of detection. The method LODs, given in Tables 2 and 3, follow the definition of the lowest analyte concentration in a sample that can be detected, but not quantified.[23] We adopt the definition of limit of detection as equal to 3.3(SD/S), where SD is the standard deviation of the response near the detection limit and S is the slope of the calibration curve. The values in Tables 2 and 3 represent validated limits of detection for the thermal desorption method.[23,24] The instrument limit of detection is substantially lower for each analyte, low picograms by ECD and low nanograms by NICI.[11] In determining *S*, a standard *t*-test was used to determine that the intercept from each calibration curve was not different from zero at the 95% confidence level. The LOD was then calculated from the slopes of each calibration (intercept forced to zero) and the standard deviation for the response, at a level approximating the detection limit.

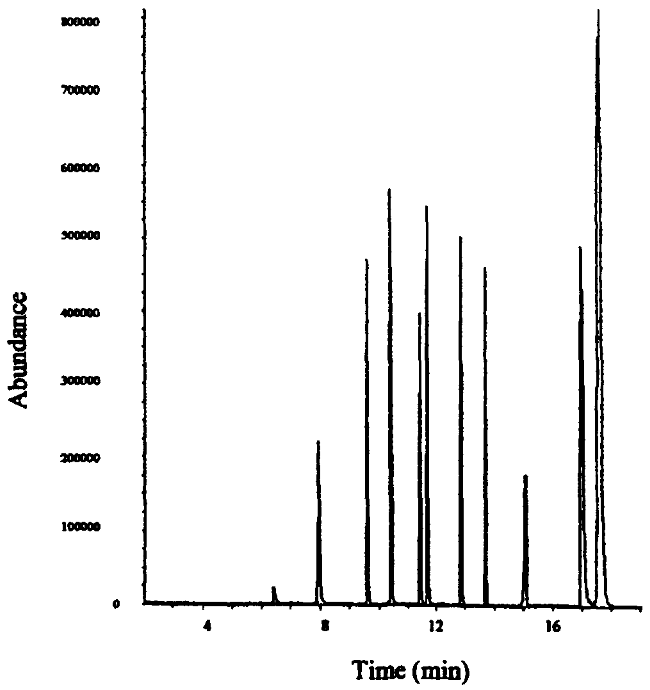


Figure 2. In-injection port thermal desorption GC/NICI chromatogram of a standard mix of explosives. The analytes (quantity) elute in the following order, starting at 8 min: DEGN (12 ng); 2,6-DNT (3.2 ng); 2,5-DNT (4.0 ng); 2,4-DNT (5.4 ng); 2,3-DNT (3.0 ng); 3,4-DNT (4.0 ng); TNT (5.6 ng); PETN (38 ng); RDX (44 ng); and DNN (74 ng).

The method LOQ is defined as the lowest analyte concentration that can be qantified in a sample with acceptable precision and accuracy using a specified method.[23] We subscribe to the use of a 10:1 signal-to-noise ratio to determine the LOQ. The LOQ values given in Tables 2 and 3 follow from the definition, analogous to that for LOD; LOQ = 10(SD/*S*). The largest LOQs determined by ECD (Table 2), for TNT and RDX are approximately 1.0 ng.

---

(23) Krull, I.; Swartz, M. *LC-GC* **1997**, *15*, 535–9.

(24) ACS Committee on Environmental Improvement and Subcommittee on Environmental Analytical Chemstry. *Anal. Chem.* **1980**, *52*, 2242–9.

Figure 3. Postblast debris from a TNT-based explosion. A 1 cm^2 area of the surface was sampled by an abraded-Teflon dry wipe. The resulting in-injection port thermal desorption GC/NICI chromatogram is shown in Figures 4 and 5.

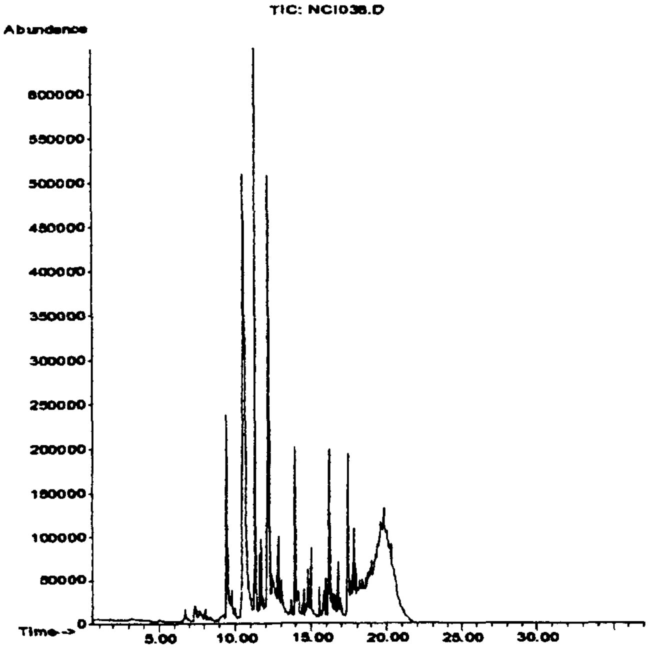


Figure 4. In-injection port thermal desorption GC/NICI chromatogram of a dry surface wipe of postblast debris from a TNT-containing device.

Although these values appear to be large relative to the instrument limit of detection, they are 70–700 times smaller than the amounts of TNT reported postblast on a 1 m^2 steel plate located 10 m from dynamite blasts.[6] The largest LOQs determined by NICI, for DEGN, RDX and PETN, were 5.4, 5.6, and 17.0 ng, respectively. The LOQs for the nitroaromatics were less than 2 ng.

Specificity. The ability to measure explosives-related analytes accurately and specifically in the presence of other components was not rigorously determined for the method using either ECD or NICI detection. However, the peak broadening and tailing from thermal desorption is not significant, as shown for a GC/NICI chromatogram in Figure 2. The analytes (quantity) elute in the following order, starting at 8 min: DEGN (12 ng); 2,6-DNT (3.2 ng); 2,5-DNT (4.0 ng); 2,4-DNT (5.4 ng); 2,3-DNT (3.0 ng); 3,4-DNT (4.0 ng); TNT (5.6 ng); PETN (38 ng); RDX (44 ng); and DNN (74 ng).

Recovery of RDX from Simulated Postblast Debris. Simulated post-blast debris was prepared as described in the Experimental Section of this paper. Analysis of the abraded Teflon wipe and the acetonitrile wash found 206.7 ng of RDX on the wipe and 106.8 ng of RDX in the wash, representing a 65.9% recovery by the Teflon wipe. A 100% transfer of RDX from the suspension to the surface would have resulted in a maximum of 474 ng of RDX on the surface. The total recovery of 313.5 ng of RDX from the combined surface wipe and surface wash represents a transfer of 66.1% of the theoretical maximum amount in the suspension to the surface. As described earlier, a small amount of RDX remained on the surface of the water when the stirring of the suspension was stopped, thus accounting for a transfer of less than the theoretical amount.

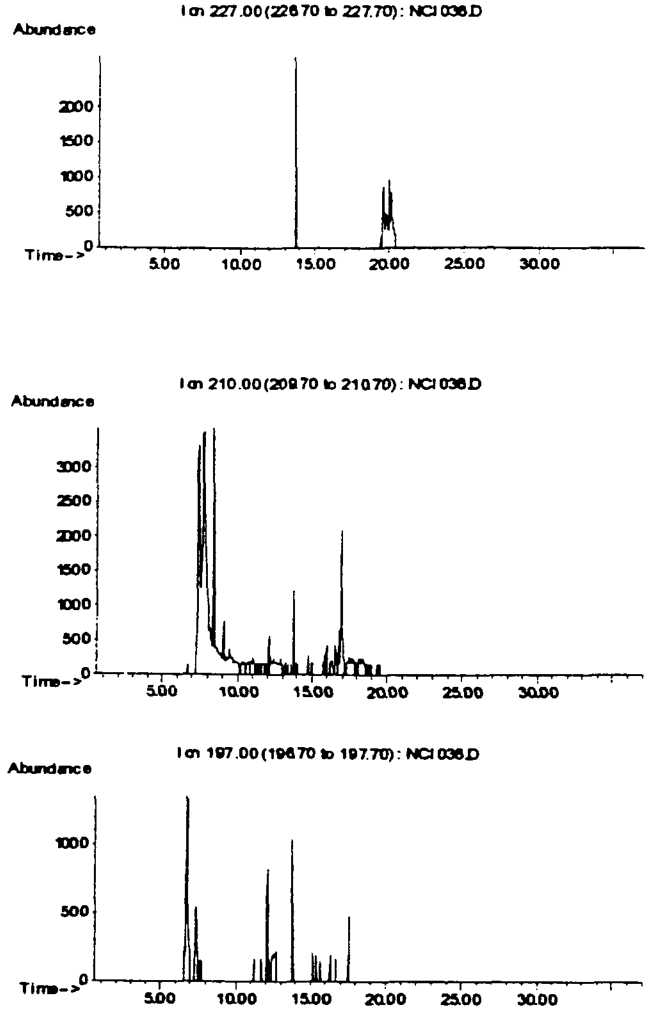


Figure 5. Extracted ion chromatographs for *m/z* of 227, 210, and 197 for the GC/NICI chromatogam shown in Figure 4.

The amount of RDX used in this test is representative of the levels expected to be found in postblast debris. Kolla has presented results from a study of the absolute amounts of explosives residue found on a 1 m^2 steel plate at distances varying from 1 to 10 m from a dynamite blast.[8] The values from two dynamites were found to range from a low of 20 ng at 10 m for the highly volatile nitroglycerine (NG) to a high of 184.57 μg at 2 m for TNT. The total recoveries of EGDN (ethyleneglycol dinitrate), NG, DNT (mix of dinitrotoluenes), and TNT from Geosite 3 dynamite at distances of 1, 2.5, 5, 7.5, and 10 m were 81.83, 211.3, 11.03, 8.67 and 7.42 μg, respectively. The total recovery at each distance is significantly larger than the amount of RDX used to test the Teflon surface-wipe recovery. The total amounts of explosive reported by Kolla at each distance are also significantly larger than the LODs determined by ECD and NICI using the method described in this paper.

Analysis of Postblast Debris. A sample of postblast debris, Figure 3, from a TNT-containing device was obtained for analysis.

The sample was in excess of two months old by the time it was received in our laboratory. A 1 cm^2 area of the debris surface was sampled by wiping with an abraded Teflon tube followed by in-injection port thermal desorption GC/NICI analysis. The resulting chromatograph is shown in Figure 4. This chromatograph demonstrates the complexity of a real sample and the necessity of mass-spectral-assisted peak identification. The extracted-ion chromatograms corresponding to m/z of 227, 210, and 197 are shown in Figure 5. These are the three most abundant ions in the NICI spectrum of TNT. The presence of TNT at a retention time of approximately 14 min is clear in the m/z 227, 210, and 197 ion chromatograms. The full-scan mass spectrum for the peak at 14 min also matches that of a standard TNT sample.

CONCLUSION

We have demonstrated a new dry surface wipe method of rapidly sampling postblast debris for the presence of trace chemical evidence of explosives. This method involves a dry surface wipe that is thermally desorbed for GC analysis. By this methodology, solvent workup is circumvented, and the entire sample is analyzed upon desorption. The method has been rigorously validated for GC/ECD and GC/NICI. The method has been tested on real debris. In an alternative implementation, the in-injection port thermal desorption method could be utilized to analyze explosives-containing organic solvent extracts following preconcentration by repeated spiking and solvent evaporation. Particles found in postblast debris by microscopic investigation could be analyzed by thermal desorption after transfer to a conditioned Teflon tube. The method described in this report provides another resource for forensic investigators faced with the daily challenge of crime scene investigation.

ACKNOWLEDGMENT

Research sponsored by the National Institute of Justice (NIJ) DOE No. 2089-K023-A1, U.S. Department of Energy under contract DE-AC05-96OR2464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

Received for review February 1, 1999. Accepted June 28, 1999.

AC9901079

Appendix II: Operational Procedure, published as *ORNL-Technical Manuscript*, **1999**.

ornl

OAK RIDGE
NATIONAL
LABORATORY

LOCKHEED MARTIN

ORNL/TM-1999/315

OPERATIONAL GUIDELINE: TEFLON DRY SURFACE WIPE COLLECTION AND IN-INJECTION PORT THERMAL DESORPTION ANALYSIS OF TRACE LEVELS OF ORGANIC EXPLOSIVES

DECEMBER 1999

Michael E. Sigman and Cheng-Yu Ma

Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
P.O. Box 2008, MS-6100
Oak Ridge, Tennessee 37831-6100

Research sponsored by the National Institute of Justice, DOE No. 2089-K023-A1, U.S. Department of Energy under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy ResearchCorp.

MANAGED AND OPERATED BY
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

ORNL-27 (3-96)

OPERATIONAL GUIDELINE: TEFLON DRY SURFACE WIPE COLLECTION AND IN-INJECTION PORT THERMAL DESORPTION ANALYSIS OF TRACE LEVELS OF ORGANIC EXPLOSIVES

DECEMBER, 1999

Michael E. Sigman and Cheng-Yu Ma

Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
P.O. Box 2008, MS 6100
Oak Ridge, TN 37831-6100

Research sponsored by the National Institute of Justice, DOE No. 2089-k023-A1, U.S. Department of Energy under contract DE-AC0596OR2464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

TABLE OF CONTENTS

List of Tables

List of Figures

Opening Remarks: This document contains operational guidelines for an organic explosives sampling and analysis method developed in the Chemical and Analytical Sciences Division at Oak Ridge National Laboratory under funding provided by the National Institute of Justice. This document is written in a format resembling that of a standard operating procedure (SOP); however, it is intended only as an operational guideline for those wishing to implement the method. We have chosen to prepare the document as an operational guideline rather than a rigorous SOP in keeping with current practices of explosives analysis in the forensics community.

1. *Scope and Application*

1.1. This procedure describes a method of preparing dry Teflon surface wipes for sampling, from solid surfaces, trace levels of organic explosives and organics related to the production and decomposition of organic explosives.

1.2. This procedure also describes a gas chromatographic method utilizing thermal desorption (TD) of dry Teflon surface wipes for explosives analysis. Thermal desorption is performed within a split/splitless injection port, followed by gas chromatographic analysis using either electron capture (GC/ECD) and/or negative ion chemical ionization (GC/NICI) mass spectrometric detection.

1.3. The method has been applied to post explosion debris and is suitable for sampling explosive residues from other surfaces including, luggage, clothing, hands, etc.

1.4. This method has been validated for the organic explosives and organics related to the manufacture or decomposition of organic explosives listed in Table 1.

1.5. Refer to Reference Section 13.1 for sources of supply for explosive and related standards.

2. *Summary of Method*

2.1. Trace explosive residues are collected by wiping post-explosion debris with a surface-abraded Teflon tubing.

2.2. The explosive residues are thermally desorbed from the Teflon tubing within a split/splitless injection port of a GC and focused onto the head of a capillary column.

2.3. Quantification of desorbed explosives are carried out by gas chromatographic analysis with either electron capture detection or negative ion chemical ionization mass spectrometry.

3. *Accuracy, precision, linearity and limit of detection*

3.1. The accuracy of the method ranges from 85 to 113% for nine analytes and 87% for internal standard (see list in Table 1).

3.2. The precision (defined as percent relative standard deviation, %RSD) of the method ranges from 3 to 71% for nine analytes determined by GC/ECD with loading range of 0.1-51.9 ng. The precision ranges from 1 to 38% for nine explosives analyzed by GC/NICI with loading range of 0.7-138.2 ng.

3.3. The method limit of detection (LOD, defined in Section 12.2) ranges from 29 to 340 pg for nine analytes determined by GC/ECD, and 0.1-5.6 ng by GC/NICI.

3.4. The method limit of quantitation (LOQ, defined in Section 12.3) ranges from 88 to 1030 pg for nine explosives analyzed by GC/ECD, and 300 to 17000 pg analyzed by GC/NICI.

4. *Hazards*

4.1. Benzene is a carcinogen. Wear nitrile gloves when handling it.

4.2. Methanol and acetonitrile are flammable. Wear nitrile gloves when handling them and aviod ignition sources.

4.3. Properly dispose of spent solvents according to appropriate waste handling procedures.

4.4. Insulated (thermal) gloves should be worn when handling liquid nitrogen.

4.5. Desorptions are performed at high temperatures (ca. 170 °C). Avoid contact with the thermal desorption injector while a desorption is in progress.

4.6. The gases used in the analytical operation are contained in cylinders under high pressure. Be sure all cylinders are securely strapped. Safety glasses should always be worn when changing cylinders.

4.7. Guidelines for handling explosives in the specific site should be followed (see Section 13.5, or explosives handling guidelines at your specific site).

5. *Interferences*

5.1. Since a short column with a thin film thickness is used in this method, excessive quantities of sample will eventually diminish the column performance.

5.2. Non-target components (such as phthalates and halogenated compounds), that respond to ECD and/or NICI detection, may interfere with the analysis of explosives.

6. *Personnel Qualifications*

6.1. Personnel with adequate instrumentation analysis background can be trained to perform this method.

6.2. It is recommended that personnel demonstrate proficiency before attempting to perform this method without supervision.

6.3. It is mandatory to have explosive handling guidelines implemented before using this method.

7. *Material and Instrumentation*

7.1. Procedure for Manufacturing and Conditioning Teflon Tubes.

7.1.1. Teflon tubing, 1/8" OD and 1/16" ID (Upchurch Scientific, Oak Harbor, WA), is used as the surface wipe/thermal desorption material.

7.1.2. The tubing is cut to 55 mm in length and held in a standard drill chuck attached to a laboratory stirrer motor.

7.1.3. The tubing is lightly sanded with a 240-grit emory cloth at a rate of several hundred revolutions per minute. The abraded tubing provides a better surface contact when wiping debris (Figure 1).

7.1.4. The abraded tubes are heated at 220 ^{0}C under a flow of argon at 360 ml/min for at least 5 hours (Figure 2).

7.1.5. The resulting tubes should have little or no detectable background signal on the ECD or NICI when thermally desorbed by the procedure described below.

7.1.6. When analyzing explosive residue, a freshly conditioned Teflon tube should be used for wiping debris surface. It is recommended that the Teflon tube should make a good contact with the debris surface (Figure 3) during wiping. A known quantity of internal standard should be spiked onto the Teflon tube after sampling the debris and before analysis.

7.2. Preparation of calibration standards.

7.2.1. The stock solutions for each of the ten compounds (as listed in Table 1) can be prepared in either methanol or acetonitrile at a nominal concentration of 1 mg/ml. The stock solutions can be stored in a flamable-storage approved refrigerator for at least two months.

7.2.2. The individual calibration standard or mixture of standards with known concentrations is prepared in benzene from the individual stock solutions at levels given in Table 3.

7.3. GC column sppecifications.

7.3.1. A HT-5 column (5% phenyl polycarborane siloxane, Scientific Glass Engineering, Inc., Austin, TX) or an equivalent column (such as DB-5 or Rtx-5) can be used in this method.

7.3.2. A short (12 m), narrow bore (0.22 mm ID) column, coated with thin film (0.1 µm) is recommended for the optimal analytical separation and recovery of explosives.

7.3.3. A helium (or nitrogen for ECD) carrier flow rate of greater than 2 ml/min is recommended for GC/ECD analysis. With vacuum compensation, a flow rate of greater than 1 ml/min is recommended for GC/NICI analysis. Slower flow rates or longer column length can lead to degradation of PETN on the column.

7.4. Instrumental conditions for GC/ECD analysis.

7.4.1. A Hewlett-Packard 5890 Series II Gas Chromatograph, equipped with an electron capture detector or an equivalent gas chromatograph can be used for this method.

7.4.2. An on/off valve should be attached to the split-vent on the front of the gas chromatograph (Figure 4a), and a single gooseneck splitless liner (4.0 mm ID, 6.5 mm OD x 78.5 mm) should be installed in the injection port (Figure 4b).

7.4.3. The auxiliary flow should be set at an optimal flow rate (ca 100 ml/min) to minimize ECD background signal and maximize ECD sensitivity.

7.4.4. The ECD detector temperature should be set between 250 to 300 °C for optimal detection.

7.5. Instrumentatal conditions for GC/NICI analysis.

7.5.1. Hewlett-Packard 5989B Gas Chromatograph/Mass Spectrometer with dual ion source or an equivalent instrument can be used for this method.

7.5.2. The analysis should be performed in electron capture negative ion chemical ionization mode.

7.5.3. With methane as reagent gas, the source pressure (0.8 to 1.2 Torr) should be optimized for maximum sensitivity and mass accuracy (see Quality Control section for details).

7.5.4. Source temperature should be set at 150 ^{0}C, source temperature at 100 ^{0}C.

7.5.5. With the electron energy set at 230 eV, and emission current at 300µA, full scan (50-550 amu) spectral data should be acquired at a rate as predetermined by the manufacture's software.

7.6. Calibration and internal standard spiking.

7.6.1. Over a pre-determined concentration range, a five-point calibration curve with replicate measurements at each point should be constructed for each target analyte.

7.6.2. In a typical calibration (or sample) analysis, a 2 µl sample of calibration solution (or internal standard solution) should be deposited on a Teflon tube by a micro-syringe (Figure 5) and the solvent should be allowed to dry (approximately 5 minutes).

7.7. Procedure for thermal desorption and gas chromatographic analysis.

7.7.1. The injection port temperature should be reduced to less than 50 ^{0}C to allow the Teflon tube to be inserted into the injection port. This step can be facilitated by blowing with a stream of house air or cold nitrogen drawn from a liquid nitrogen dewar (see Hazard section for proper handling of liquid nitrogen).

7.7.2. When analyzing explosive residue, a freshly conditioned Teflon tube should be used for wiping debris surface. It is recommended that the Teflon tube should make a good contact with the debris surface (Figure 3) during wiping. A known quantity of internal standard should be spiked onto the Teflon tube after sampling the debris and before analysis.

7.7.3. Prior to inserting the Teflon tube inside the injection port, the split purge valve should be turned off and the split vent should be blocked by closing the on/off valve.

7.7.4. After inserting the Teflon tube inside the injection port (Figure 6), the port should be closed securely and heated to 170 °C. The carrier flow during desorption process should be increased to at least 6.5 ml/min for GC/ECD, and 10 ml/min (with vacuum compensation) for GC/NICI analysis. Failure of the carrier flow to reach the pre-determined rate may indicate a leak in the system.

7.7.5. Thermal desorption should be allowed to proceed for 7 minutes, including 3.5 - 4 minutes injector heating time.

7.7.6. The GC oven should be held at ambient temperature during theraml desorption to allow the desorbed target analytes to be condensed and focused at the head of the column.

7.7.7. A two-tiered oven program is recommended for optimal separation of the analytes. The initial oven temperature should be held for 3 min at 70 °C, and then heated to 185 °C at a rate of 8 °C/min in the first tier of the program. The oven temperature should then be heated to 280 °C at a rate of 30 °C/min and held at 280 °C for 10 minutes.

7.8. Data reduction.

7.8.1. Calibration curves can be constructed by plotting the concentration ratios of target analytes relative to the internal standard versus their corresponding area ratios.

7.8.2. The integrated area for each analyte should be obtained either from the integrated area of a peak as anlyzed by TD/GC/ECD or from an integrated area of the most abundant ion as analyzed by TD/GC/NICI.

7.8.3. The concentration and area ratios can be used to perform linear regression with, or without, intercept to obtain the Response Factor (slope) and correlation coefficient (r) for each target analyte. The Response Factor is defined as the slope of a plot of Area Ratio (ordinate) versus the Concentration Ratio (abscissa). A standard t-test should be used to determine whether the intercept from each calibration curve is significantly different from zero at the 95% confidence level.

7.8.4. The quantity of explosives collected on the Teflon tube can be calculated using one of the following equations:

Quantity (ng) = (Area ratio /Response factor) * (ng of IS spiked)

Quantity (ng) = [(Area ratio – Intercept)/Response factor]*(ng of IS spiked)

8. *Quality Control and Quality Assurance*

8.1. Reproducibility of Teflon tube preparation.

8.1.1. If more than one batch of abraded tubes are prepared, reproducibility of tube preparation should be ensured so that the method accuracy and precision are independent of the surface-wipe preparation.

8.1.2. One tube randomly selected from each batch of prepared tubes should be spiked with known quantities of explosive standards and analyzed for their recovery either by TD/GC/ECD or by TD/GC/NICI.

8.1.3. The spiking and analysis should be repeated in triplicate for each tube, and the average analyte recovery based on an established calibration should be determined. The resulting average recovery should be used to calculate the percent relative standard deviation (%RSD) for each tube.

8.1.4. In general, the %RSD should be less than 10% for every analyte as listed in Section 2.5 except for PETN. The thermal instability of PETN will result in a higher %RSD (ca. 15%) for this analyte.

8.2. Column Performance.

8.2.1. By using a short capillary column coated with thin film thickness of moderately polar liquid phase (as recommended in Section 7.3.1), baseline separation should be achieved for all the explosives and related compounds including internal standards.

8.2.2. The order of gas chromatographic elution should be as the following (Figure 7): beyond 7 min, DEGN; 2,6-DNT; 2,5-DNT; 2,4-DNT; 2,3-DNT; 3,4-DNT; TNT; PETN; RDX; and DNN (IS).

8.2.3. If the gas chromatograph is equipped with an electronic pressure control for maintaining a constant column flow throughout the entire GC program, then a baseline resolution should be achieved with the pair of 2,3- and 2,4-dinitrotoluene isomers. Otherwise, partial resolution of this pair of isomers is acceptable.

8.2.4. As part of QA/QC procedure, GC column performance (peak resolution, elution order, etc.) check should be carried out prior to calibration and/or sample analysis.

9. *Method Performance*

9.1. If the analysis is to be performed on a mass spectrometer, the following procedure is recommended for checking the NICI tune:

9.1.1. 300 pg of decachlorobiphenyl and 100 pg of hexachlorobenzene should be injected onto the column and analyzed with the following temperature program: 100 °C hold for 3 min, ramp to 280 °C at 20 °C/min.

9.1.2. The resulting spectra should be compared with reference spectra (Reference 13.6): for decachlorobiphenyl *m/z* 498 (100%), 464 (>27%), and 430 (>5%); for hexachlorobenzene *m/z* 284 (100%), 286 (>70%), 250 (>10%).

9.1.3. If the relative abundance is out of range, the instrument must be re-tuned. The GC peak height for both compounds acquired over the full scan (100-550 amu) must be at least three times greater than the noise.

9.1.4. The eight most abundant ions (m/z) and their relative intensities (% abundance) for the nine target analytes are listed in Table 2.

10. *Thermal Desorption Efficiency of the Methodology*

10.1. The thermal desorption (TD) efficiency (method accuracy) should be determined by comparing the ratios of instrumental response due to spiked analyte thermally desorbed from Teflon tube relative to the response from a liquid injection of the same quantity of analyte.

10.2. The analysis can be carried out either by TD/GC/ECD, or by TD/GC/NICI. It is recommended to obtain average recovery rate value from at least three successive sets of thermal desorption and liquid injections.

10.3. The resulting desorption efficiencies (%) for the analytes should be comparable to those listed in Table 3 (ranged from 85% for 2,5-DNT to 113% for RDX) with comparable loading quantities for each analyte.

11. Precision and Linearity of the Methodology

11.1. Teflon tubes should be spiked in triplicate with calibration standard mixtures that include nine target analytes and an internal standard at minimal of five concentrations ranging 0.5 to 80 ng/tube.

11.2. The spiked Teflon tubes should be analyzed either by TD/GC/ECD or by TD/GC/NICI. The spiking and analysis should take place in a random order over a period of a week.

11.3. The relative response and relative concentration for each analyte at each concentration should be calculated:

Relative response = Area of analyte/Area of IS

Relative concentration = Concentration of analyte/Concentration of IS

11.4. The relative responses obtained from triplicate analysis for each analyte at each concentration should be used to calculate the average response, which in turns should be used to calculated the percent relative standard deviation (%RSD).

11.5. The ranges for %RSD should be comparable to those listed in Table 3 for the specified loading range.

11.6. A linear regression curve should be fitted between the arrays of relative responses and relative concentrations to construct a five-point calibration.

11.7. The linearity (r^2) resulting from linear regression should be comparable to those listed in Table 4 for the specified loading range.

12 *Limit of Detection and Limit of Quantitation*

12.1 The data used for the precision and linearity should also be employed to determined the method limit of detection (LOD) and limit of quantitation (LOQ) for each analyte using both methods of detection.

12.2 The LOD should be determined as:

LOD (ng) = 3.3 (SD/S) * (ng of IS spiked)

Where SD is the standard deviation of the relative response near the detection limit and S is the slope of the calibration curve

12.3 The LOQ should be determined as :

LOQ = 10 (SD/S) * (ng of IS spiked)

12.4 The resulting LOD and LOQ for each analyte determined for TD/GC/ECD and TD/GC/NICI should be comparable to those listed in Table 4.

13 *References*

13.1 Michael E. Sigman, and Cheng Yu Ma, "In-Injection Port Thermal Desorption for Explosives Trace Evidence Analysis" Analytical Chemistry, *71*, pp 4119-4124, 1999.

13.2 Hewlett Packard Gas Chromatograph and Mass Spectrometer 5989B system Operating Manuals, including HP 5989B Hardware Manual (Copyright 1993, Part

05989-90071), MS Chemstation User's Guide (Copyright 1993, HP G 1034C, Part # HP G 1034-90043).

13.3 Hewlett-Packard 5890 Series II Gas Chromatograph Operating Manual (Copyright 1989, Part # 05890-90260).

13.4 Microsoft Excel 97 Spreadsheet Program (Microsoft, 1997, Part # 98722).

13.5 Lockheed Martin Energy Research Corporation ORNL Explosives Program, number ORNL-SH-P05, Rev. 1, dated 10/5/98.

13.6 E. A. Stemmler; R. A. Hites, *Electron Capture Negative Ion Mass Spectra of Environmental Contaminants and Related Compounds*, PP 39, and 253, VCH Publisher, New York, 1988.

Table 1. List of analytes (explosives and explosives related compounds), abbreviations and CAS numbers.

Analyte	Abbreviation	CAS
Diethyleneglycol dinitrate	(DEGN)	[693-21-0]
2,6-Dinitrotoluene	(2,6-DNT)	[606-20-2]
2,5-Dinitrotoluene	(2,5-DNT)	[619-15-8]
2,4-Dinitrotoluene	(2,4-DNT)	[121-14-2]
2,3-Dinitrotoluene	(2,3-DNT)	[602-01-7]
3,4-Dinitrotoluene	(3,4-DNT)	[610-39-9]
2,4,6-Trinitrotoluene	(TNT)	[118-96-7]
Pentaerythritol tetranitrate	(PETN)	[78-11-5]
Hexahydro-1,3,5-trinitro-1,3,5-triazine	(RDX)	[121-82-4]
1,3-Dinitronaphthalene (*internal standard, IS*)	(DNN)	[606-37-1]

Table 2 The eight most abundant NICI ions (m/z) and their relative intensities (% abundance) for the nine target analytes.

Analyte	m/z	% Abundance	Analyte	m/z	% Abundance
DEGN	62	100	**2,6-DNT**	182	100
	46	91		183	9
	242	71		152	8
	258	20		184	1
	90	10		166	1
	93	10		153	1
	103	9		150	1
	109	5		164	1
2,5-DNT	182	100	**2,4-DNT**	182	100
	183	9		152	12
	152	3		183	8
	166	2		166	2
	184	1		165	1
	153	1		150	1
				184	1
				164	1
2,3-DNT	182	100	**3,4-DNT**	182	100
	152	9		183	9
	166	1		152	6
	184	1		184	1
	153	1		166	1
				153	1
				134	1
TNT	227	100	**PETN**	62	100
	197	22		46	19
	210	16		101	16
	228	10		99	9
	198	3		84	8
	167	3		240	6
	195	2		256	5
	229	2		378	5
RDX	102	100			
	129	80			
	176	30			
	268	25			
	46	17			
	324	15			
	130	4			
	103	4			

Table 3 Thermal desorption efficiency and reproducibility determined by TD/GC/ECD and TD/GC/NICI.

		GC/ECD		GC/NICI	
Analyte	Accuracy (Desorption Efficiency)	Reproducibility (%RSD)	Loading Range (ng)	Reproducibility (%RSD)	Loading Range (ng)
DEGN	95	8-45	0.15-24.51	13-34	2.60-37.76
2,6-DNT	93	5-26	0.11-18.17	15-27	0.68-10.04
2,5-DNT	85	5-30	0.14-22.88	9-30	0.86-12.64
2,4-DNT	97	5-19	0.29-46.72	7-31	1.18-17.22
2,3-DNT	96	3-29	0.11-17.30	7-29	0.66-9.56
3,4-DNT	96	4-23	0.14-22.49	5-19	0.86-12.44
TNT	89	4-24	0.20-31.72	2-32	1.20-17.54
PETN	95	6-71	0.33-51.91	4-38	8.25-119.96
RDX	113	5-33	0.31-49.98	1-11	4.74-138.18

Table 4 Limit of detection and limit of quantitation determined by TD/GC/ECD and TD/GC/NICI.

	GC/ECD			GC/NICI		
Analyte	Calibration Linearity (r^2)	Method LOD (pg)	Method LOQ (pg)	Calibration Linearity (r^2)	Method LOD (ng)	Method LOQ (ng)
DEGN	0.991	229	694	0.995	1.8	5.4
2,6-DNT	0.998	29	88	0.988	0.5	1.5
2,5-DNT	0.967	78	236	0.990	0.5	1.5
2,4-DNT	0.997	174	527	0.993	0.7	2.1
2,3-DNT	0.979	39	118	0.994	0.5	1.5
3,4-DNT	0.999	59	179	0.995	0.1	0.3
TNT	0.998	340	1030	0.995	0.4	1.2
PETN	0.988	133	403	0.997	5.6	17.0
RDX	0.997	332	1006	0.983	1.8	5.6

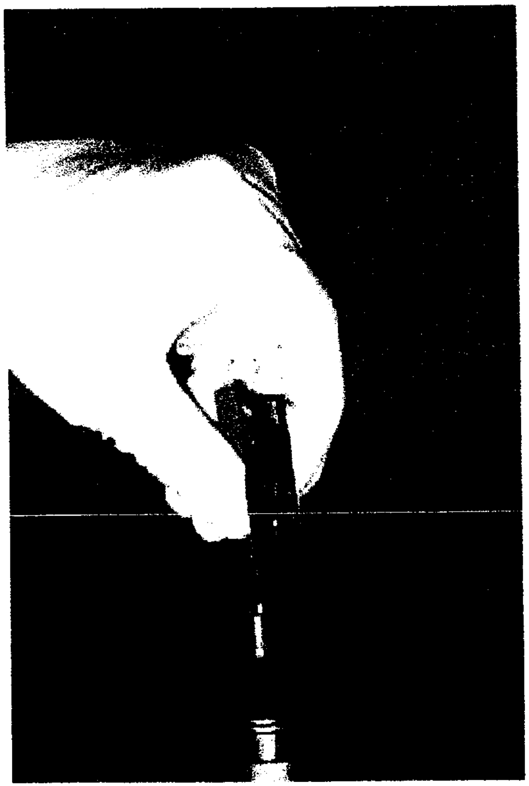


Figure 1: Abrasion of Teflon tube with 240-grit emory cloth.

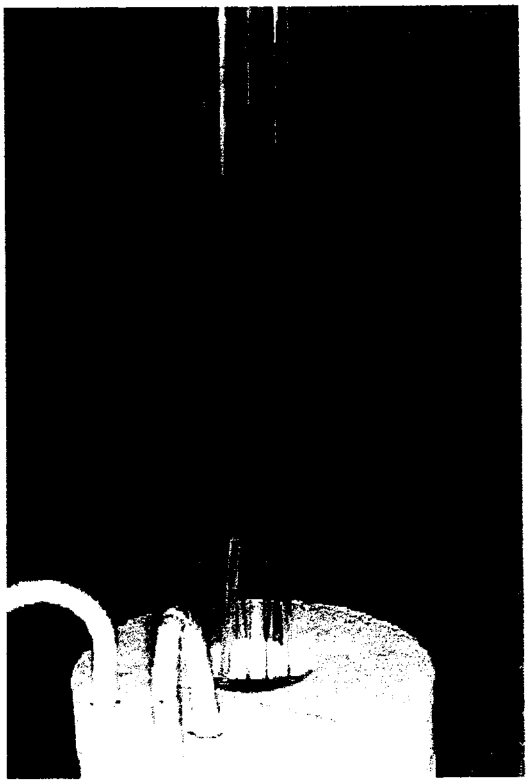


Figure 2: Heating of abraded Teflon tube in a tube furnace.

Figure 3: Example of debris sampling by surface wipe.

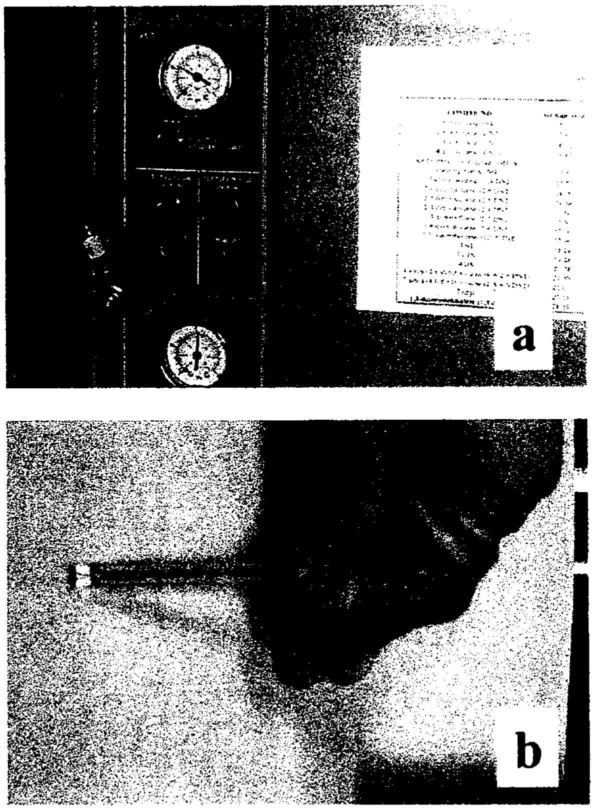


Figure 4: (a.) On/off valve attached to split-vent on the front of the gas chromatograph. (b.) Single gooseneck splitless liner.

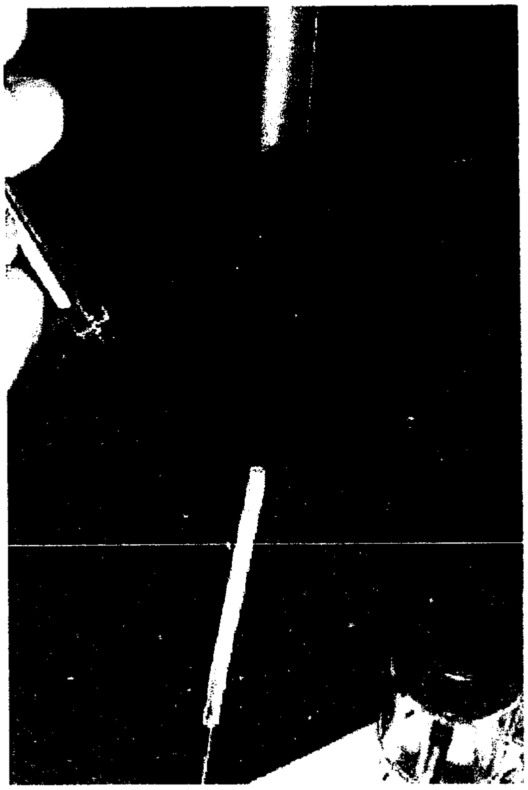


Figure 5: Deposition of calibration solution (or IS) on a Teflon tube by a microsyringe.

Figure 6: Inserting Teflon tube inside GC injection port.

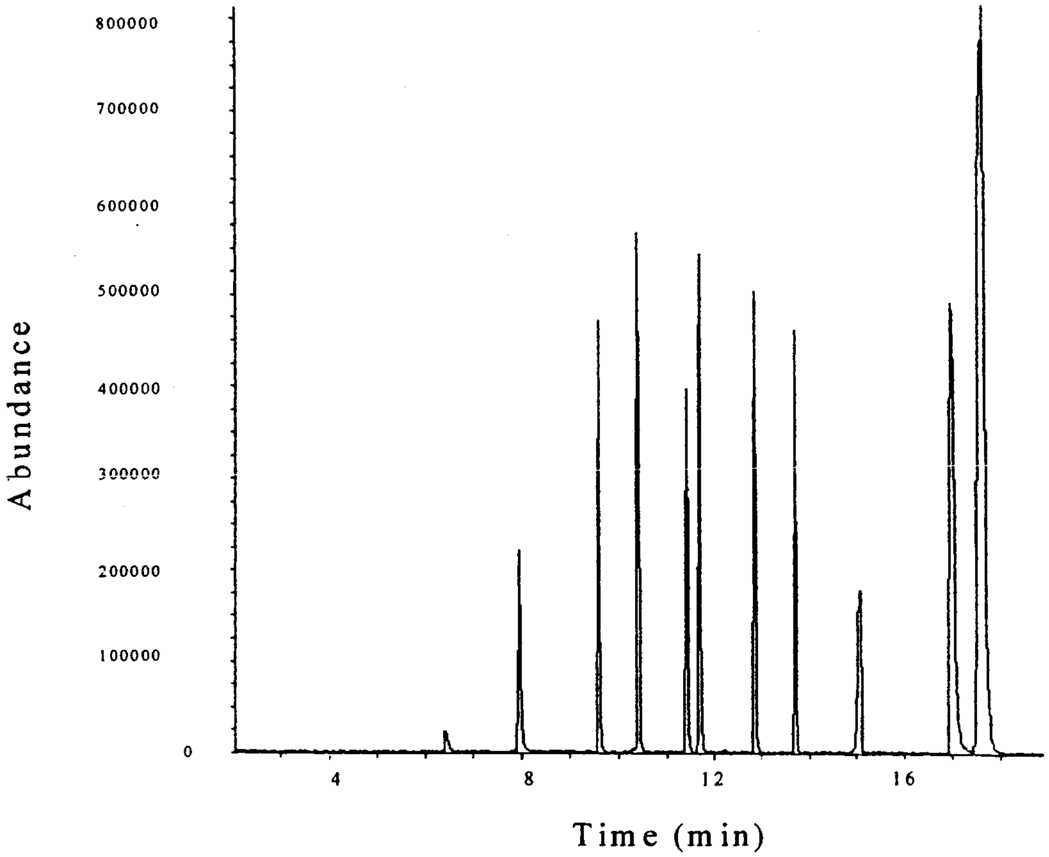


Figure 7: In-injection port thermal desorption GC/NICI chromatogram of a standard mix of explosives. The peak identities (starting at 8 min) are listed in Table 1.

Appendix III: Manuscript for publication in *Journal of Forensic Science*, **2000**.

Detection Limits for GC/MS Analysis of Organic Explosives

Michael E. Sigman Ph.D.* and Cheng-Yu Ma Ph.D.

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory,

PO Box 2008, MS 6100, Oak Ridge, TN 37831-6100

* To whom correspondence should be addressed
Phone: (423) 576-2173
Fax: (423) 574-4902
e-mail: sigmanme@ornl.gov

For publication in *Journal of Forensic Sciences*

Research sponsored by the National Institute of Justice (NIJ) DOE No. 2089-K023-A1, U.S. Department of Energy under contract DE-AC05-96OR2464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

Explosives Detection Limits by GC/MS

Abstract: Method detection limits are determined and compared for analysis of liquid injections of organic explosives and related compounds by gas chromatography-mass spectroscopy utilizing electron impact (EI), negative ion chemical ionization (NICI) and positive ion chemical ionization (PICI) detection methods. Detection limits were rigorously determined for a series of dinitrotoluenes, trinitrotoluene, two nitroester explosives and one nitramine explosive. The detection limits are lower by NICI than by EI or PICI for all explosives examined, with the exception of RDX. The lowest detection limit for RDX was achieved in the PICI ionization mode. Judicious choice of the appropriate ionization mode can enhance selectivity and significantly lower detection limits. Major ions are reported for each analyte in EI, PICI and NICI detection modes.

Key Words: gas chromatography-mass spectrometry, detection limits, organic explosives

Analysis of explosives trace chemical evidence in post-blast material is typically achieved through the application of multiple physical and chemical techniques (1-4). One technique of analysis involves extracting a debris sample with organic solvent to remove organic explosive trace evidence. Following appropriate cleanup procedures, the organic solvent is analyzed by gas chromatography using of any one of a number of detection methods. The detection limits vary from method to method as do the analyte specificity and analysis information content. Gas chromatographic methods of analysis for trace explosive and incendiary chemicals have recently been reviewed (2,5,6). The three most sensitive detection methods for gas chromatographic analysis of explosives are thought to be electron capture detection (ECD) (7), thermal energy analyzer (TEA) (7) and negative ion chemical ionization mass spectrometry (NICI) (8-11).

Trace analysis of picogram quantities of explosives, by injection of standard mixtures, has previously been demonstrated by Douse and coworkers using a gas chromatography/electron capture detection (GC/ECD) method (12). The method utilized a 165°C injection port temperature to prevent degradative losses of the analytes. Kolla later reported an injection port temperature of 170°C to be the optimal for giving the minimum analyte degradation and maximum analytical sensitivity for GC analysis of a series of explosives (13). Kolla also reported that thin film (<0.25 μm) moderate-polarity stationary phases and high carrier gas flow rates (up to tens of ml min^{-1}) were required for optimum analyte separation and recovery.

Martz has shown that gas chromatography with negative ion chemical ionization mass spectrometric detection (GC/NICI) exhibits nanogram sensitivity levels for explosives when scanning a range of ions (14). Picogram detection levels were demonstrated for GC/NICI using selected ion monitoring. Levensen and coworkers have reported picogram detection limits for a series of five nitroaromatics by EI, NICI and PICI detection following gas chromatographic separation (15). The detection limits were defined by a signal-to-noise ratio of three.

Mass spectrometry offers a higher information content than ECD or TEA and the use of extracted ion chromatograms and selected ion monitoring offer added descrimination in data analysis. Many forensic laboratories today have access to mass spectrophotometric detection, although NICI is probably less common than EI and PICI ionization modes due to the added expense of instruments possessing this capability. In this paper we present a study of the rigorously determined method detection limits for the analysis of a set of organic explosives by mass spectrometric detection. Limits of detection are determined on a single instrument operating in the EI, PICI and NICI ionization modes. This work allows for a direct comparison between explosives detection limits for these commonly available mass spectral ionization modes. The method detection limits reported here were determined in a full scan mode. The full scan mode of detection was used because this method allows for the identification of a suite of explosives without *a-priori* knowledge of the sample composition. Lower detection limits can certainly be achieved for each ionization mode through the use of selected ion monitoring. Major spectral features are also given for each analyte detected by the three ionization modes and mass spectral characteristics are discussed and compared to previous reports (15).

Experimental

Apparatus: GC/MS analysis was performed on a Hewlett-Packard 5989 Gas Chromatograph/Mass Spectrometer (quadrupole) operating in three ionization modes: eletron impact (EI), positive ion chemical ionization (PICI) and electron capture negative ion chemical ionization (NICI). Methane gas was used as reagent gas in both PICI and NICI. The instrument was tuned using the manufature's procedure and the electron multiplier voltage was set 200 V above the tune value for analysis in each ionization mode. The pertinent instrument operating parameters are listed in Table 1.

The gas chromatograph was fitted with a 12 m HT5 column (5% phenyl polycarborane siloxane, Scientific Gas Engineering, Inc., Austin, TX) with a 0.22 mm I.D. and a 0.1 μm film thickness. An initial temperature of 70°C was held for 3 min, followed by a temperature increase to 185°C at a rate of 8°C min^{-1} and a subsequent increase to 250°C at a rate of 25°C min^{-1}. The final temperature was held for 5 min. A He carrier flow rate of 1.2 ml min^{-1} was determined to allow for analysis of the less stable analytes (i.e. PETN) without degradaton on the column. The injection port and transfer line temperatures were 170°C and 260°C respectively. In a typical analysis, a 2 μl sample of a standard solution was injected (splitless for 2 min).

Reagents: Diethyleneglycol dinitrate (DEGN [693-21-0]) was obtained from Trojan Corporation (Spanish Fork, UT). Dinitrotoluenes (DNT) and 1,3-dinitronaphthalene (DNN [606-37-1]) were purchased from Aldrich Chemical Co. (Milwaukee, WI). This study included 2,6-DNT [606-20-2], 2,4-DNT [121-14-2], 2,3-DNT [602-01-7] and 3,4-DNT [610-39-9]. Benzene and 2,5-DNT [619-15-8] were purchased from Fisher Scientific Co. (Pittsburgh, PA). Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX [121-82-4]) and 2,4,6-trinitrotoluene (TNT [118-96-7]) were supplied by the Naval Explosive Ordnance Disposal Technical Division at the Naval Surface Warfare Center (Indian Head, MD). Pentaerythritol tetranitrate (PETN [00078-11-5]) was from the US Army Standard Analytical Reference Material respository, US Army Environmental Center (Aberdeen Proving Ground, MD). All explosives were used as received without further purification.

Acetonitrile was obtained from EM Science (Gibbstown, NJ) and used to prepare stock solutions containing DEGN (0.85 mg ml^{-1}), 2,6-DNT (6.30 mg ml^{-1}), 2,5-DNT (11.90 mg ml^{-1}), 2,4-DNT (16.20 mg ml^{-1}), 2,3-DNT (6.00 mg ml^{-1}), 3,4-DNT (7.80 mg ml^{-1}), TNT (6.60 mg ml^{-1}), PETN (2.70 mg ml^{-1}), RDX (5.20 mg ml^{-1}) and DNN (3.70 mg ml^{-1}). Stock solutions were stored at 0°C and used to prepare mixtures of known concentrations in benzene for method detection limit determinations.

Results and Discussion

To determine the precision of the liquid injection method, six solutions were prepared, each containing all of the explosives analytes and DNN as an internal standard. Two microliters of a given solution were injected to give the range of column loadings for each analyte reported in Tables 2 - 4. The loading of the internal standard was 37 ng for each sample. At least three replicate analyses were performed for each of the six solutions. The average response for the total ion abundance and the percent relative standard deviation (%RSD) was determined for each analyte at each loading for EI, PICI and NICI detection. The observed ranges in %RSD are listed in Tables 2 - 4 as a measure of the precision of the method. The larger %RSD values listed in the tables resulted from analyte loadings that approached the limit of detection (discussed below). The largest overall %RSD was determined for DEGN detection by EI (Table 1).

The linearity of the liquid injection method was determined from the averaged ratios of the instrument response for each analyte relative to the response for the internal standard. The average response ratios were plotted against the analyte to internal standard concentration ratios and linear regression was used to obtain calibration curves. The resulting linearities (r^2) and slopes are given in Tables 2 - 4 for EI, PICI and NICI detection respectively. Greater than 96.8 percent of the variance was accounted for by the linear model in all cases and greater than 99 percent of the variance was accounted for in most cases.

The method limit of detection (LOD) values, given in Tables 2 - 4, represent the lowest analyte concentration in a sample that can be detected, but not quantified (16). In this work the LOD is calculated as 3.3(SD/S), where SD is the standard deviation of the response near the detection limit and S is the slope of the calibration curve (16). The LOD values in Tables 2 - 4 are liquid injection method limits of detection (16,17). A standard t-test was used to insure that the fitted intercept from each calibration curve was not different from zero at the 95% confidence level. The slope of each calibration with the intercept forced to zero was used to calculate the LOD. A graphical comparison of the LOD for each explosive detected by each ionization method is given in Figure 1. The lowest LOD values for the analytes included in this study are generally achieved by NICI. The one exception is the detection of RDX, where PICI gives the lowest LOD. EI generally gives the highest LOD, although the values are less than a factor of 20 higher than the NICI values. The LOD values determined for 2,6-DNT in this work are considerably higher than those previously reported based on an estimated signal-to-noise ratio of 3 (15)

The method limit of quantitation (LOQ) is the lowest analyte concentration that can be qantified in a sample with acceptable precision and accuracy (22). The LOQ values given in Tables 2 - 4 are defined as; LOQ=10(SD/S). The largest LOQ was determined by EI for RDX as 10.17 ng. Although these values appear to be large relative to the instrument limit of detection, they are 70-700 times smaller than the amounts of TNT reported post-blast on a 1 m^2 steel plate located 10 m from dynamite blasts (18). The lowest LOQ was determined by NICI for 3,4-DNT as 0.32 ng.

In order to make an equitable comparison between the three modes of analysis (EI, PICI, and NICI), the LOD and LOQ values for each analyte were determined based on the ion abundance obtained with the electron multiplier voltage set at 200 V above the tuned value (as listed in Table 1). However, the background associated with NICI is virtually zero at the electron multiplier voltage of 1834 V. We expect that when the electron multiplier is set as high as 1000V above the NICI tuned value, the background would still be low enough to increase the sensitivity by at least one order of magnitude. Thus the LOD and LOQ would be much lower than those listed in Table 4 for NICI.

A list of the major ions (m/z) and their relative abundance for each analyte determined by EI, PICI and NICI are given in Table 5. The general fragmentation pattern observed for the nitroaromatics in each ionization mode agree with those previously reported by Levensen (15). EI spectra for all the analytes are consistent with those listed in the NIST/EPA/NIH Mass Spectral Data Base (19). Ions corresponding to $[M-NO_2]^+$ are the most prominent ions for all the nitroaromatics except for 3,4-DNT. The molecular ion is the most prominent ion for 3,4-DNT, a unique characteristic for this isomer. However, the nitroesters (DEGN, PETN) and the nitramine (RDX) produced very few diagnostic ions in the EI spectra. The most abundant ions for those compounds are m/z 46, and m/z 30 (for ions NO_2, and NO).

In the PICI spectra, with the exceptions of PETN and RDX, all analytes exhibit protonated ions $[M+1]^+$ and adduct ions $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$, which are characteristic ions observed when methane is used as a reagent gas (20). The protonated fragment ion (m/z 149) corresponding to $[MH-CH_2N(NO_2)]^+$ is the most abundant ion for RDX (21). The most prominent ion for PETN is m/z 85; the fragment identity is unknown. In addition, ions for $[MH-NO]^+$ were also observed for all the nitroaromatics, which is consistent with the observation reported elsewhere (20).

In the NICI spectra, molecular ions were detected for all the nitroaromatics. Fragment ions corresponding to $[M-NO]^-$ and $[M-OH]^-$ were also observed for those compounds, as also reported elsewhere for dinitrotoluenes (11, 22). Molecular ions were not detected for the nitroesters (DEGN, PETN), or for the nitramine (RDX). Instead, highly fragmented ions $[NO_3]^-$ (m/z 62) were detected as the most abundant ion for DEGN and PETN, in addition to adduct ions $[M+NO_2]^-$ and $[M+NO_3]^-$. The most abundant ion for RDX is m/z 102, which has previously been reported to be due to $[CH_2N(NO_2)CH_2N]^-$ (23). The adduct ion m/z 268 corresponding to $(M+NO2)^-$ is also observed for RDX, in accord with earlier reports (24).

Conclusion: NICI gives the lowest detection limits for each of the explosives examined in this paper, with the exception of RDX. Detection limits in the MS scanning mode are highly dependant on the chemical structure of the explosive and vary from the low picogram range to a few nanograms. The use of NICI generally gives a factor of less than 10 decrease in LOD relative to EI and PICI, although larger decreases in LOD were observed for 3,4-DNT.

Acknowledgement: Research sponsored by the National Institute of Justice (NIJ) DOE No. 2089-K023-A1, U.S. Department of Energy under contract DE-AC05-96OR2464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

References:

1. Bender, E.; Hogan, A.; Leggett, D; Miskolczy, G.; MacDonald S. Surface contamination by TNT. J. Forensic Sci. 1992;37:1673-8.
2. Steinfeld, JI Explosives detection: A challenge for physical chemistry. Annual Review of Physical Chemistry 1998;49:203-32.
3. Beveridge, A. D. Development of the detection and identification of explosive residues Forensic Sci. Rev. 1992;4:17-49.
4. Garner, DD, Fultz, ML The ATF approach to post-blast explosives detection and identification. J. Energetic Mat. 1986;4:133-148.
5. Fultz MA, DeHaan JD. Gas Chromatography in Arson and Explosives Analysis. In: Tebbett, I, editor. Gas Chromatography In Forensic Science, New York: E. Horwood, 1992;109-63.

6. Walsh ME, Ranney T 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. J. Chromatogr. Sci. 1996;36:406-16.
7. Douse JMF Trace analysis of explosives at the low nanogram level in handswab extracts suing columns of amberlite XAD-7 porous polymer beads and silica capillary column gas chromatography with thermal energy analysis and electron-capture detection. J. Chromatog. 1985;328:155-65.
8. Barshick SA, Griest WH Trace analysis of explosives in seawater using solid-phase microextraction and gas chromatography/ion trap mass spectrometry. Anal. Chem. 1998;70:3015-20.
9. Yinon, J. Analysis of explosives by negative ion chemical ionization mass spectrometry. J. Forensic. Sci. 1980;25:401-7.
10. Echenrode, BA; Glish, GL; McLuckey, SA; Negative-ion chemical ionization in a quadrupole ion trap using reatent anions injected from an external ion-source. Int. J. Mass Spectrom. Ion Proesses 1990;99:151-67.
11. Yinon, J. Mass Spectrometry of Explosives. In: Forensic Mass Spectrometry, Yinon, J. editor. Boca Raton, CRC Press 1987; 105-30.
12. Douse JMF Trace analysis of explosives at the low picogram level by silica capillary column gas-liquid chromatography with electron-capture detection. J. Chromatog. 1981; 208:83-88.
13. Kolla P. Gas chromatography, liquid chromatography and ion chromatography adapted to the trace analysis of explosives. J. Chromatog. A 1994;674:309-318.

14. Martz RM, Munson TO, Lassel LD. Identification of smokeless powders and their residues by capillary column gas chromatography/mass spectrometry. In: Proceedings of the International Symposium on Analysis and Detection of Explosives; 1983 Mar 29-31; U. S. Department of Justice, Federal Bureau of Investigation, 245-54.

15. Feltes J, Levensen K, Volmer D, Spiekermann M. Gas chromatographic and mass spectrometric determination of nitroaromatics in water. J. Chromatography 1990;518;21-40.

16. Krull I, Swartz M. Analytical methods: National and international guidelines. LC-GC 1997;15:535-9.

17. ACS Committee on Environmental Improvement and Subcommittee on Environmental Analytical Chemstry,Guidelines for data acquisition and data quality evaluation in environmental chemistry. Anal. Chem. 1980;52:2242-9.

18. Kolla P. Detecting hidden explosives. Anal. Chem. 1995;67:184 A.

19. McLafferty FW, Stauffer DB editors. The Wiley Registry of Mass Spectral Data, 6th Edition. NewYork, John Wiley & Sons, Inc., 1995.

20. Harrison AG Chemical Ionization Mass Spectrometry, 2nd Edition. Boca Raton: CRC Press, Inc., 1992;71-72.

21. Zitrin S, Yinnon J. Advances in mass spectrometry in biochemistry and medicine. New York: Spectrum, 1976, 369.

22. Stemmler EA, Hites RA. Electron Capture Negative Ion Mass Spectra of Environmental Contaminants and Related compounds. New York: VCH, 1988:39,253.

23. McLuckey SA, Goeringer DE, Asan KE. High explosive vapor dteection by atmospheric sampling glow discharge ionization/tandem mass spectrometry. Oak Ridge (TN) Oak Ridge National Laboratory; 1993 Technical Manuscript No.: ORNL/TM-13166.
24. Yinnon J, Harvan DJ, Hass JR. Mass spectral fragmentation pahtways in RDX and HMX. A mass analyzed ion kinetic energy spectrometric/collisional induced dissociation study. Org. Mass Spectrom. 1982;17:321-326.

Table 1: Mass spectrometer parameters used for detection limit determinations in EI, PICI and NICI ionization modes.

	Ionization Mode		
Mass Spectrometer Parameter	EI	PICI	NICI
Source temperature (^{0}C)	200	150	150
Quadruple temperature (^{0}C)	100	100	100
Electron energy (eV)	70	230	230
Electron multiplier (V)	2302	2562	1834
Emission current (mA)	300	300	300
Full scan mass range scanned (AMU)	29-400	60-500	40-400
mass scan rate (scan/sec)	1.2	1.6	1.6
Reagent gas pressure (Torr)	na*	1.2	1.2

* not applicable

TABLE 2: Validation data for the analysis of explosives by GC/EI

Analyte	Reproducibility (%RSD)	Calibration Slope	Calibration Linearity (r^2)	Method Limit of Detection (ng)	Method Limit of Quantitation (ng)	Conc Range (ng/μL)
DEGN	10-42	0.855	0.998	2.31	7.01	1.30-66.09
2,6-DNT	4-12	0.689	0.998	0.78	2.36	1.60-17.58
2,5-DNT	3-21	0.623	0.997	1.80	5.47	2.01-22.14
2,4-DNT	3-11	0.659	0.998	1.37	4.16	2.74-30.13
2,3-DNT	5-15	0.741	0.998	1.45	4.39	1.52-16.74
3,4-DNT	3-13	0.748	0.999	1.47	4.45	1.98-1.76
TNT	5-9	0.657	0.997	0.71	2.14	2.79-30.69
PETN	6-15	0.249	0.999	2.75	8.33	4.12-209.93
RDX	3-14	0.422	0.999	3.36	10.17	4.74-241.82

TABLE 3: Validation data for the analysis of explosives by GC/PICI

Analyte	Reproducibility (%RSD)	Calibration Slope	Calibration Linearity (r^2)	Method Limit of Detection (ng)	Method Limit of Quantitation (ng)	Conc Range (ng/µL)
DEGN	12-25	1.348	0.999	1.20	3.62	1.30-66.09
2,6-DNT	7-18	1.150	0.983	1.40.	4.25	0.84-17.58
2,5-DNT	8-28	0.997	0.998	1.89	5.72	1.05-22.14
2,4-DNT	7-20	0.979	0.993	1.77	5.37	1.43-30.13
2,3-DNT	6-18	1.441	0.979	1.20	3.63	0.80-16.74
3,4-DNT	5-29	1.296	0.993	1.70	5.14	1.04-21.76
TNT	4-22	0.645	0.994	1.32	4.01	1.46-30.69
PETN	2-18	0.144	0.996	2.38	7.21	4.12-209.93
RDX	3-16	0.846	0.999	0.64	1.92	4.74-241.82

TABLE 4: Validation data for the analysis of explosives by GC/NICI

Analyte	Reproducibility (%RSD)	Calibration Slope	Calibration Linearity (r^2)	Method Limit of Detection (ng)	Method Limit of Quantitation (ng)	Conc Range (ng/µL)
DEGN	10-35	0.519	0.969	0.75	2.28	0.65-11.02
2,6-DNT	5-38	2.927	0.982	0.21	0.63	0.17-2.93
2,5-DNT	5-43	2.788	0.979	0.17	0.50	0.22-3.69
2,4-DNT	4-23	1.348	0.982	0.18	0.55	0.30-5.02
2,3-DNT	5-36	3.649	0.979	0.16	0.49	0.16-2.79
3,4-DNT	1-221	2.357	0.984	0.10	0.32	0.21-3.63
TNT	3-27	1.668	0.976	0.19	0.58	0.30-5.12
PETN	3-21	0.188	0.994	0.78	2.36	2.06-34.99
RDX	2-14	0.637	0.964	1.11	3.37	2.37-40.30

Table 5: Observed ions (m/z) and relative intensities observed.

	EI		PICI		NICI	
Analyte	m/z	% Abundance	m/z	% Abundance	m/z	% Abundance
DEGN	46	100	197	100	62	100
	73	50	90	99	46	91
	30	20	87	99	242	71
	45	19	103	96	258	20
	44	10	73	96	90	10
	43	9	134	50	93	10
	76	4	75	43	103	9
	90	3	76	22	109	5
2,6-DNT	165	100	183	100	182	100
	63	86	184	17	183	9
	89	70	211	14	152	8
	90	50	153	10	184	1
	51	45	223	4	166	1
	77	45	166	3	153	1
	64	42	150	3	150	1
	78	42	185	3	164	1
2,5-DNT	165	100	183	100	182	100
	89	80	153	17	183	9
	63	73	184	13	152	3
	119	45	211	10	166	2
	39	39	165	5	184	1
	64	36	223	4	153	1
	78	35	166	3		
	90	33	167	2		
2,4-DNT	165	100	183	100	182	100
	89	97	184	23	152	12
	63	79	211	17	183	8
	39	36	153	13	166	2
	119	33	223	6	165	1
	51	33	165	6	150	1
	90	32	166	4	184	1
	78	26	185	4	164	1

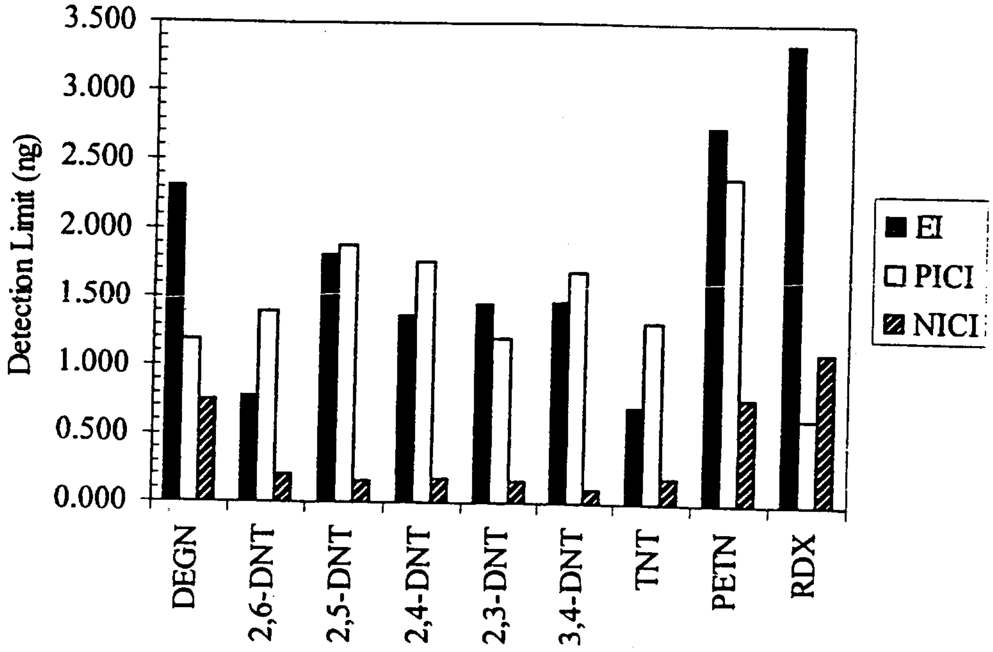
Table 5 cont.

	EI		PICI		NICI	
Analyte	m/z	% Abundance	m/z	% Abundance	m/z	% Abundance
2,3-DNT	165	100	183	100	182	100
	135	67	184	27	152	9
	52	58	223	8	166	1
	39	52	166	6	184	1
	89	45	165	5	153	1
	51	38	151	4		
	77	34	150	4		
3,4-DNT	182	100	183	100	182	100
	39	112	184	18	183	9
	63	80	153	13	152	6
	78	76	223	5	184	1
	52	72	166	4	166	1
	65	57	135	4	153	1
	94	48	167	3	134	1
	66	48	137	3		
TNT	210	100	228	100	227	100.
	63	85	198	17	197	22
	89	81	229	11	210	16
	62	39	256	8	228	10
	39	38	69	3	198	3
	76	32	71	3	167	3
	51	27	168	2	195	2
	50	26	85	2	229	2
PETN	46	100	85	100	62	100
	30	37	132	55	46	19
	76	10	116	49	101	16
	42	7	69	36	99	9
	31	6	76	34	84	8
	56	3	71	26	240	6
	55	2	64	26	256	5
	57	2	73	23	378	5
RDX	46	100	149	100	102	100
	42	98	75	64	129	80
	30	91	103	55	176	30
	75	42	85	23	268	25
	56	31	69	13	46	17
	128	24	133	11	324	15
	71	23	104	9	130	4
			150	9	103	4

Figure Captions:

Figure 1: LOD in ng for each explosive detected by ionization method EI, NICI and PICI.

Figure 1



Explosives Detection Limits by GC/MS