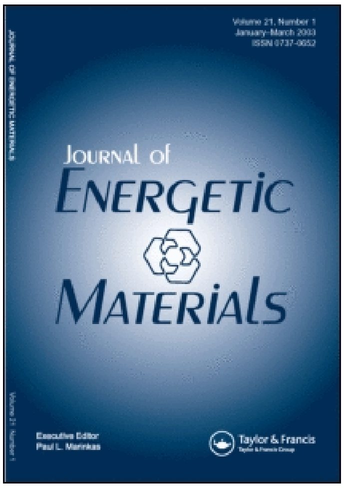

Journal of Energetic Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Analysis of Explosives Using Ultra Performance Liquid Chromatography (UPLC®) with UV and/or Mass Spectrometry Detection

Stuart A. Oehrle[a]

[a] Waters Corporation, Northern Kentucky Field Lab, Northern Kentucky University, Chemistry Department, Highland Heights, Kentucky, USA

To cite this Article Oehrle, Stuart A.(2008) 'Analysis of Explosives Using Ultra Performance Liquid Chromatography (UPLC®) with UV and/or Mass Spectrometry Detection', Journal of Energetic Materials, 26: 4, 197 — 206

To link to this Article: DOI: 10.1080/07370650802182435

URL: http://dx.doi.org/10.1080/07370650802182435

Journal of Energetic Materials, 26: 197–206, 2008

ISSN: 0737-0652 print/1545-8822 online
DOI: 10.1080/07370650802182435

Analysis of Explosives Using Ultra Performance Liquid Chromatography (UPLC®) with UV and/or Mass Spectrometry Detection

STUART A. OEHRLE

Waters Corporation, Northern Kentucky Field Lab,
Northern Kentucky University, Chemistry
Department, Highland Heights, Kentucky, USA

Explosives analysis has gained a great deal of attention due to various needs for both environmental monitoring as well as in the world of forensics. High-performance liquid chromatography (HPLC) is one analytical technique of choice used for this analysis. In this article we investigate the use of newer technologies in detection (mass spectrometry) and smaller column packing (sub 2 µm particles) to improve the selectivity, speed, and resolution of the analysis. Several examples showing the versatility of this technology will be shown.

Keywords: explosives, LC/MS, mass spectrometry, UPLC

Presented at the 7th International Symposium on the Analysis and Detections of Explosives (ISADE), July 2007, Paris, France.

Address correspondence to Stuart A. Oehrle, Waters Corporation, Northern Kentucky Field Lab, Northern Kentucky University, Chemistry Department, Nunn Drive, SC313, Highland Heights, KY 41099. E-mail: stuart_oehrle@waters.com

Introduction

With the closing of military bases throughout the world, a need for identifying polluted sites for remediation has increased. Prolonged manufacturing, storage, and testing at these sites have all been contributing factors to this problem. While many field techniques for identifying major explosive pollutants, such as TNT, exist and have been incorporated into standard methods, HPLC continues to be the main analytical technique for identification and verification of the presence of explosives. Many of these techniques use a dual column verification process whereby two separate analyses are done [1]. Added into this array for the analysis of explosives is the need of the forensic chemist to detect and confirm the identity of explosives. One novel way to analyze and verify many of the explosives and degradation products is to use mass spectrometry (MS) detection. This hyphenated technique allows one to obtain both chromatographic data (such as retention time) and mass spectral information. In addition the incorporation of photodiode array (PDA) detection allows for UV spectra to be obtained and used for identification as well.

Atmospheric pressure ionization (API) techniques were investigated with good results obtained for many of the target compounds. This technique has been used previously to detect some of the same compounds [2–4]. In this work a new multimodal ionization technique [5], known as EScI™, which incorporates both simultaneous electrospray ionization (ESI) and atmospheric pressure chemical ionization (APcI) detection in a single run, was used for detection of various explosives and degradation products. This technique, which has been discussed previously [6,7], uses the electrospray probe and APcI corona pin together, along with fast electronic switching, to provide two simultaneous and separate mass chromatograms in each ionization mode (ESI and APcI). Ultra performance liquid chromatography (UPLC®) was used to both speed up and improve the chromatographic resolution of many of the compounds and, when combined with PDA and MS detection, allow for optimal peak identification and verification.

Experimental

Materials

Explosives standards were obtained from AccuStandard (New Haven, CT). Extracts of various explosives were obtained as gifts from different law enforcement agencies. All solvents used were of HPLC grade or higher. Kimwipes® (Kimberly-Clark, Neenah, WI) were used for hand swiping and were the small sheet size (part number KIM34155, purchased from Fisher Scientific, Pittsburgh, PA).

Ultra-Performance Liquid Chromatography-Mass Spectrometry (UPLC-MS)

UPLC® analyses were performed with a Waters Acquity Ultra Performance LC-MS system (Waters Corporation, Milford, MA). The mass spectrometer (MS) used was an SQ detector (Waters) which is a single quad MS capable of scanning up to 2000 Da or analyzing in selected ion recording where several single masses are monitored. Depending upon the assay, either mode was used. Ionization by MS was done using EScI™, which is a simultaneous ionization mode allowing for electrospray (ESI) and atmospheric pressure chemical ionization (APcI) to occur in the same run with separate mass chromatograms for each ionization generated. UPLC separation was achieved on an Acquity UPLC BEH C_{18} column ($100\,\text{mm} \times 2.1\,\text{mm}$ i.d., 1.7 µm particle size, 130 Å pore size; Waters) maintained at 55°C and the mobile phase consisted of an ammonium acetate and methanol mobile phase (isocratic 28% methanol). Additional detection was done using photodiode array detection in series with mass spectrometry detection. In the case of the newer work, evaporative light scattering (ELS) detection was employed as well as an ammonium acetate and methanol gradient.

Hand Swipes for Residue Analysis

To examine the applicability for explosives exposure, a hand swipe (authors) prior to and after handling a small piece (approx. 1 cm^2) of the explosive composition C-4 was done. The hand was swabbed with a single dry sheet of Kim-Wipe® lab wipes and the wipe was then placed in a small scintillation vial and extracted with a minimal amount of a 50/50 mix of DI

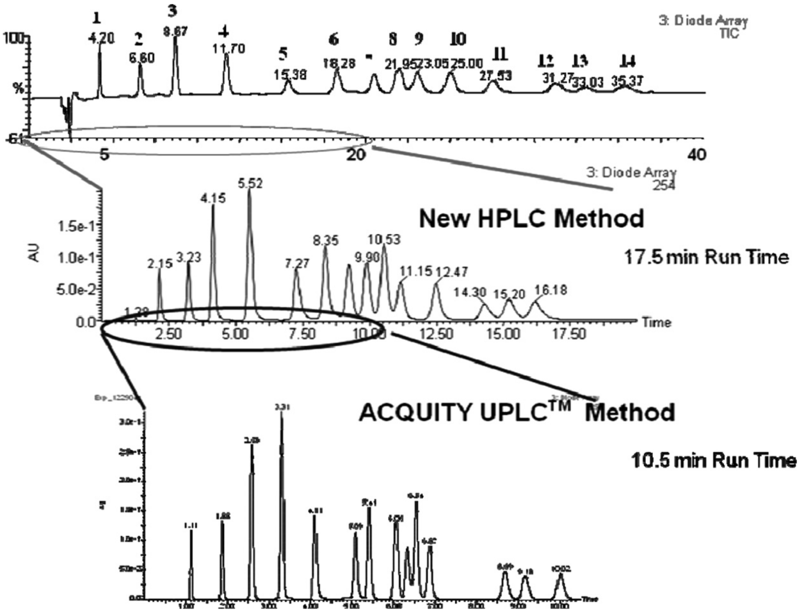

Figure 1. Separation showing the previous HPLC methodology (old method), an improved HPLC method using smaller particle size packing (new method), and the current UPLC® method using small (1.7 µm) particle packing. Photodiode array (PDA) detection is shown in this example. Peak ID (in increasing retention time) 1 = HMX, 2 = RDX, 3 = TNB, 4 = DNB, 5 = NB, 6 = Tetryl, 7 = TNT, 8 = 2Am-DNT, 9 = 4Am-DNT, 10 = 2,4-DNT, 11 = 2,6-DNT, 12 = 2-NT, 13 = 4-NT, and 14 = 3-NT.

water and acetonitrile and vortexed for 10 s. The extract was transferred to an autosampler vial and analyzed.

Results and Discussion

Although UPLC relies on the same selectivity and retention methods as HPLC, the smaller particle sizes in UPLC enable improved limits in the chromatographic separation. Furthermore, UPLC allows for increased efficiency and sensitivity in analysis. This phenomenon may be explained in accordance with the van Deemter equation [8], wherein smaller particles

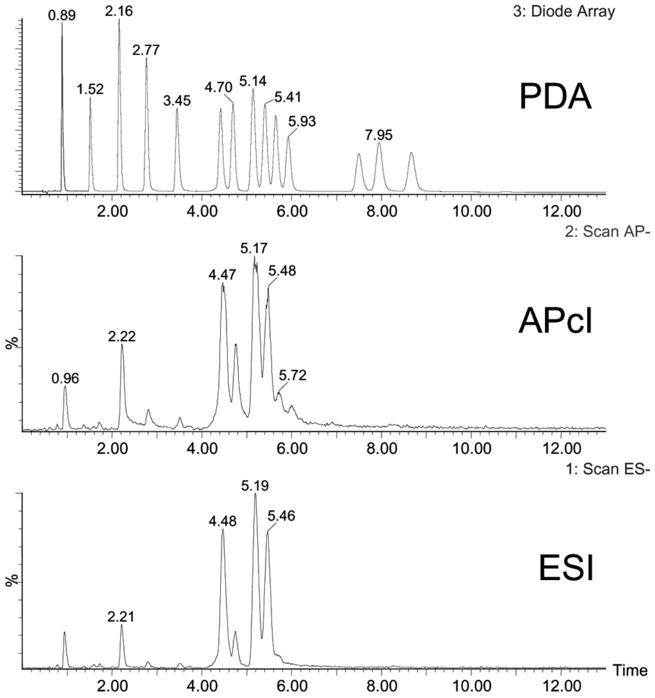

Figure 2. Simultaneous ESI and APcI data for the various explosives using an optimized UPLC®/MS method. Top chromatogram is PDA detection and next are MS detection in each mode in a single injection. Same elution order as Fig. 1.

provide not only increased efficiency but also the ability to work at increased linear velocity without a loss of efficiency, thus providing both resolution and speed. This is demonstrated in Fig. 1, which shows the evolution of HPLC to UPLC separation of the common explosives. In this case, the original HPLC separation of 40 min was moved to less than 10 min using the smaller (sub 2 µm) particle technology with improved resolution. UPLC®/MS detection using the EScI™ ionization is shown in Fig. 2 for a mixture of explosive standards. An example of MS detection for a military dynamite extract is shown in Fig. 3 with the

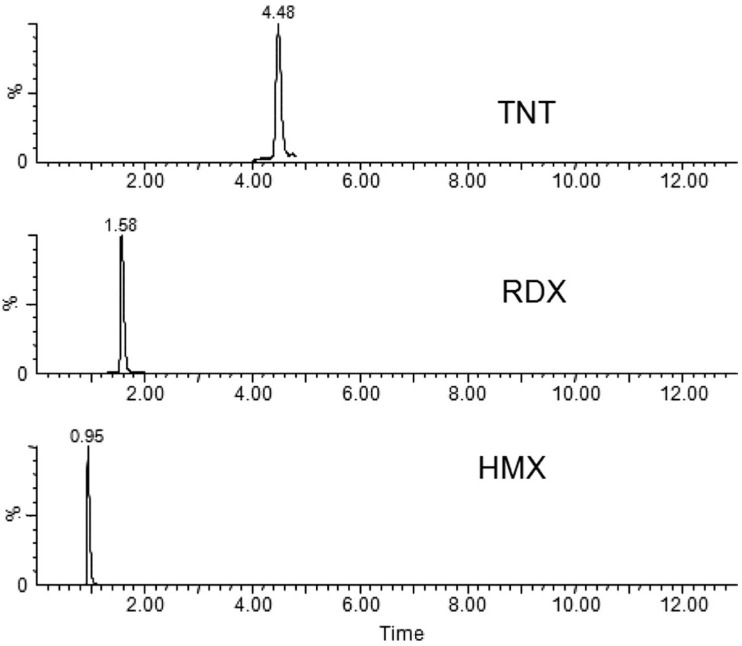

Figure 3. EScI™ MS of military dynamite extract showing the separation of the three main components extracted at each appropriate mass (TNT = mass 226, RDX = mass 281, and HMX = mass 355) and ionization mode. Notice the analysis time is under 5 min.

selectivity of the MS detector apparent in the individual mass monitoring.

A practical example of this is shown in Fig. 4, which is a Kim-Wipe® extract of a hand that had been exposed to C-4 and the hand prior to exposure. Clearly evident in the analysis is the presence of the two main components (HMX and RDX) of C-4. In this case, the total analysis is accomplished in under 2 min.

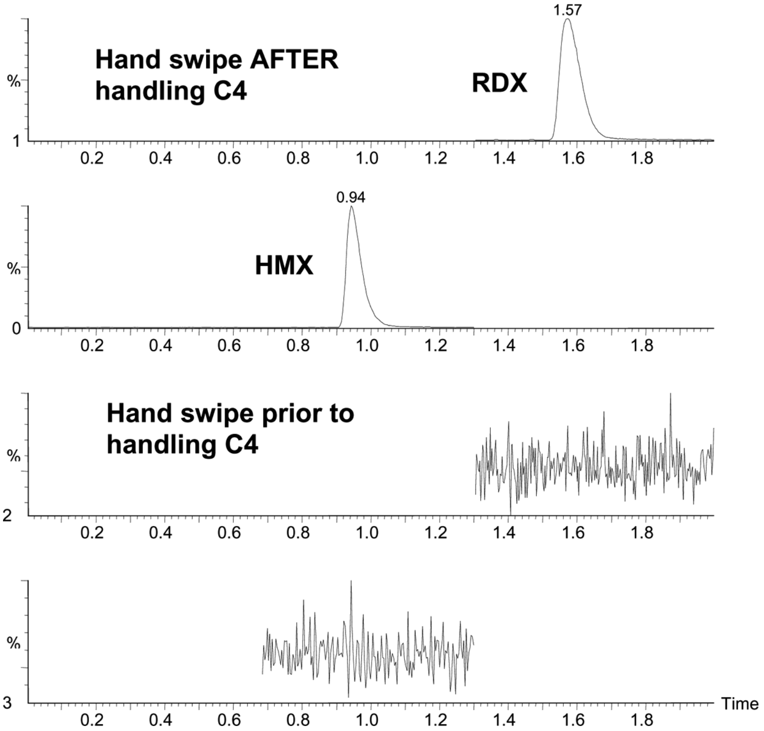

Figure 4. UPLC®-MS analysis showing the detection of the presence of the main components of composition C-4 (plastic explosive) from a hand swipe of a person who handled the explosive as well as a hand swipe prior to handling showing no C-4 present.

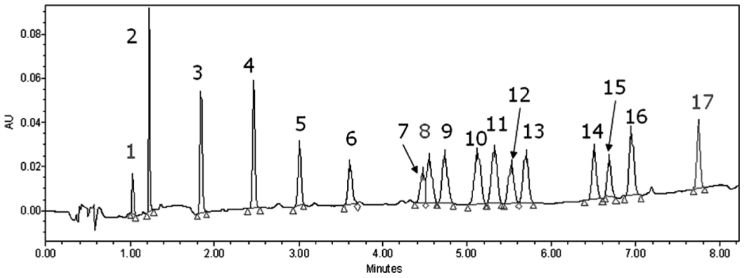

Figure 5. Updated UPLC® method for additional explosives. Ammonium acetate and methanol gradient. Same column as in experimental. PDA detection at 214 nm peaks: **1** = HMTD, **2** = HMX, **3** = RDX, **4** = TNB, **5** = 1,3-DNB, **6** = NB, **7** = Tetryl, **8** = NG, **9** = TNT, **10** = 2 Amino-4,6-DNT, **11** = 4 Amino-2,6-DNT, **12** = 2,4-DNT, **13** = 2,6-DNT, **14** = 2-NT, **15** = 4-NT, **16** = 3-NT, and **17** = PETN.

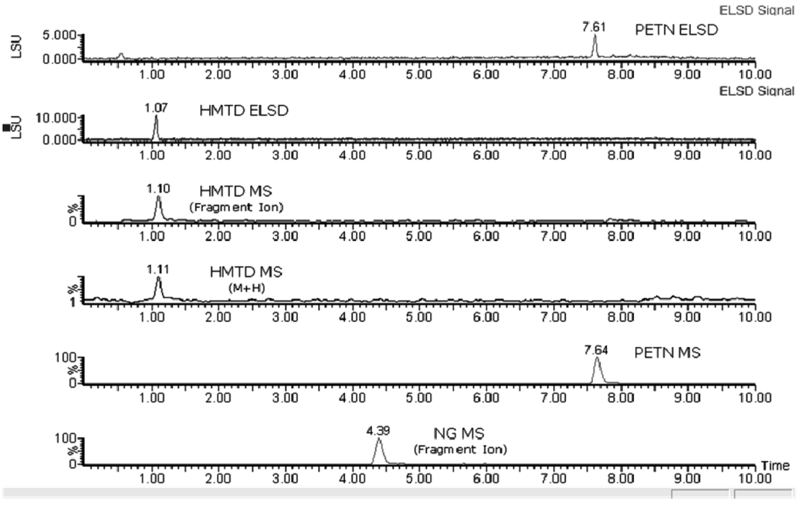

Figure 6. ESci^{TM} MS and ELSD (evaporative light scattering) detection of hexamethylene triperoxidediamine (HMTD), nitroglycerin (NG), and pentaerythritol tetranitrate (PETN).

New Results

work using the same mobile phase and a gradient was used. Using the same mobile phase and gradient described earlier, additional separation of several explosives of interest (PETN, NG and HMTD) was accomplished. Figure 5 shows the PDA detection of all of the additional and other components. MS detection looking at the three new components, as well as evaporative light scattering (ELS) detection, showed detection of all three as shown in Fig. 6. In this case, positive ionization is needed to detect the HMTD, whereas negative ionization is used for the PETN and NG components. In all cases only a single injection and analysis is needed to detect all components.

Conclusions

An improved methodology to analyze for various explosives can be accomplished with increased speed of analysis an improved resolution. In addition, analysis of explosive residues from hand swipes was possible with minimal sample preparation needed. An improved gradient UPLC® method was developed that allowed for additional explosives to be detected using MS, ELS, and UV detection all in less than 9 min. Detection of low picograms on column for the majority of explosives using MS detection was accomplished (data not included). Further enhancements using solid-phase extraction (SPE) can potentially lower these values even more. UPLC® separation of the explosives allows for fast turnaround times for analysis, thus increasing lab output as well as freeing up valuable MS time for additional analysis.

References

[1] *EPA Method 8330 and 8330B, SW-846 Manual*. 2006. U.S. EPA Web site. Available at: http://www.epa.gov/sw-846/ (accessed).

[2] Verweij, A., P. C. De Bruyn, C. Choufoer, and P. Lipman. 1993. Thermospray/negative ion, tandem mass spectrometric (LC/TSP/MS) analysis of some explosives. *Forensic Science International*, 60: 7.

[3] Cassada, D., S. J. Monson, D. D. Snow, and R. F. Spalding. 1999. *Journal of Chromatography A*, 844: 87.

[4] Borch, T. and R. Gerlach. 2004. *Journal of Chromatography A*, 1022: 83.

[5] U.S. Patent Application #10514098, November 11, 2004.

[6] Gallagher, R. T., M. P. Balough, P. Davey, M. R. Jackson, I. Sinclair, and L. J. Southern. 2003. *Analytical Chemistry*, 75(4): 973.

[7] Balough, M. P. 2007. Advances in LC-MS Instrumentation, Achille Cappiello (ed.), *Journal of Chromatogr*, vol 72, New York, Elsevier Publishers.

[8] van Deemter, J. J., F. J. Zuiderweg, and A. Klinkenberg. 1956. *Chemical Engineering Science*, 5: 271.