Analysis of Nitroaromatic and Nitramine Explosives by Atmospheric Pressure Chemical Ionization / High Performance Liquid Chromatography / Mass Spectrometry / Mass Spectrometry– 9025

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ABSTRACT

This procedure is capable of separating and quantifying twenty-nine high explosives and internal surrogates with a single injection. After the initial preparation step, the sample is introduced to the high performance liquid chromatograph for target separation, ionized by atmospheric pressure chemical ionization and the explosives of interest are isolated / quantified by mass spectrometry / mass spectrometry. Concentrations of the target explosives are measured relative to the response of both internal and external standard concentrations. A C-18 reverse phase high performance liquid chromatograph column is used for separation. Ionization is performed using both positive and negative atmospheric pressure chemical ionization resulting in a molecular ion with little fragmentation. These ions are isolated at the first quadrupole of the mass spectrometer, dissociated by collision with argon in the collision cell and the resulting daughter ions are isolated at the second quadrupole. These daughter ions then reach the detector where they are quantified. To date this procedure represents the most thorough high performance liquid chromatography / mass spectrometry / mass spectrometry explosives analysis available in the environmental chemistry market.

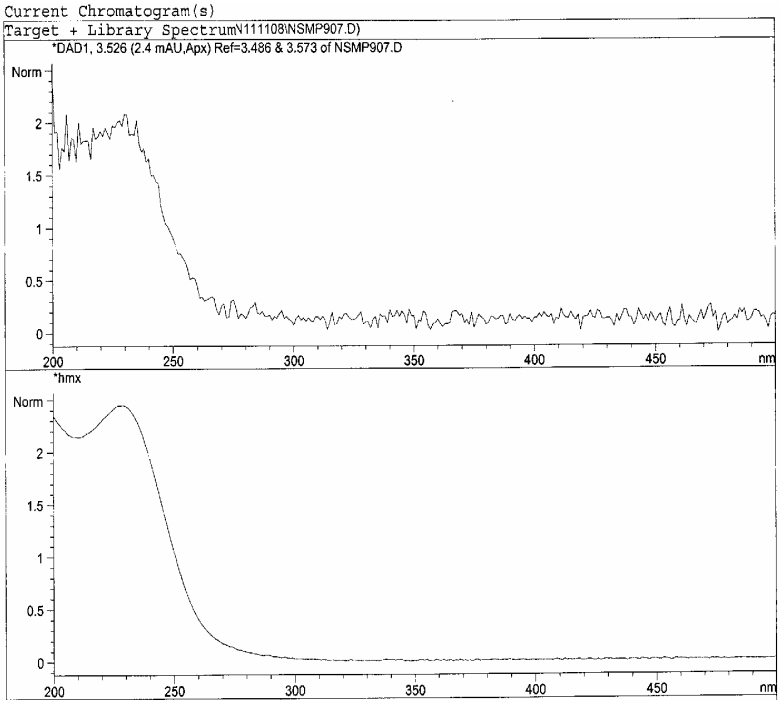
INTRODUCTION

Upon review of the recent history of environmental explosive analysis a dominant theme emerges. High performance liquid chromatography has been coupled with increasingly exotic and more specific detection systems. SW-846 Method 8330 first released in November of 1990 calls for a dual wavelength ultraviolet detector [1]. The ultraviolet detector designed for explosive analysis typically measures absorbance at 254 nm and 210 nm. Ultraviolet absorbance at these wavelengths can be indicative of an aromatic carbon structure, but more generally can be applied to all organic carbon structures. Each of the compounds listed in method 8330 absorb ultraviolet radiation at one or both of these wavelengths. Unfortunately, the problem with this approach is one of specificity.
In addition to explosive compounds hundreds if not thousands of other non-target compounds would also absorb ultraviolet radiation at the monitored wavelengths. When any of these interfering compounds are present in samples and possess similar retention times to the compounds of interest, the possibility of reporting a false positive becomes
unacceptably large. Method 8330 attempts to compensate for this limitation by requiring confirmation of any potential positive detection on a separate, secondary column packed with a resin dissimilar from the primary column. The resin in the confirmation column alters the retention time and the elution order of the compounds of interest. A dual column approach significantly decreases the chance of reporting false positives but does not eliminate it entirely as retention windows are relatively large, about 0.2 minutes,

for high performance liquid chromatography analyses. The large retention time windows allow room for non-target compounds to be misidentified as explosives.

Many modern high performance liquid chromatography systems are equipped with a diode array detector. These detectors have the ability to monitor absorbance over a wide range of wavelengths simultaneously. Laboratories employing this type of detector often use it as a final confirmation for all dual column explosive detections. To properly utilize this technology the laboratory must first build a spectral library of explosives by injecting and analyzing known standards. The unique compound spectra are graphs of absorbance versus wavelength as recorded by the diode array detector.

FIGURE 1: Typical absorbance versus wavelength spectrum for HMX shows reference spectrum (bottom) and possible positive detection (top)



A spectrum is generated for each compound in the list. Once constructed this library provides additional protection against the false positive. A positive detection on both columns can be compared to the reference spectra and assigned a value between 0 -1000 with 1000 representing a perfect match. Under this scenario a positive detection on both columns initiates the reporting of a value, but this value may be flagged with various
qualifiers depending on the quality of the spectral match. In some matrices the laboratory still fails to definitively determine whether or not an explosive is present. Qualified or flagged data may be unsatisfactory to the end user, but under the current architecture of method 8330 the laboratories utilizing the dual column approach in tandem with a diode array spectral library are providing the best product possible.

As high performance liquid chromatography mass spectrometry became more prevalent during the 1990s, a new explosive analytical technique soon emerged. Mass spectrometry greatly enhanced selectivity in the instance of co-eluting compounds. A standardized method dealing specifically with explosives analysis was never promulgated. However, method 8321 does provide regulatory framework for the high performance liquid chromatography mass spectrometry technology which can be applied to the analysis of explosives[2]. In fact most laboratories that wish to achieve National Environmental Laboratory Accreditation Conference accreditation for the analysis of explosives by either high performance liquid chromatography mass

spectrometry or high performance liquid chromatography / mass spectrometry / mass spectrometry are actually being certified for method 8321. Method 8321 provides guidance on tuning and data reporting for high performance liquid chromatography mass spectrometry methodologies. However, references to mass spectrometry / mass spectrometry methodologies appear to have been included in 8321 as if high performance liquid chromatography mass spectrometry and high performance liquid chromatography / mass spectrometry / mass spectrometry were similar, interchangeable technologies. They are not. It remains unclear whether the suggested guidelines found in 8321 for tuning and data analysis are relevant to all mass spectrometry / mass spectrometry methods.

In spite of the lack of clear guidance, the Department of Defense and certain segments of the Department of Energy, most notably Los Alamos National Laboratory, has either mandated the use of high performance liquid chromatography / mass spectrometry / mass spectrometry methods for the analysis of explosives or strongly prefers the use of this technology. In response to this mandate the organic department at TestAmerica St. Louis developed a full list high performance liquid chromatography / mass spectrometry / mass spectrometry method for the analysis of energetic compounds.

METHODS

Function	Compound Name	Abbreviation	RT (mins)	Transition	Internal STD
1	2,6-diamino-4-nitrotoluene +	2,6-DAm-4-NT	4.11	168.1>122.2	None
1	2,4-diamino-6-nitrotoluene +	2,4-DAm-6-NT	4.58	168.1>122.2	None
2	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine 13C4	HMX 13C4	4.45	363.0>151.0	None
3	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	4.45	355.0>147.0	HMX 13C4
4	hexahydro-1,3,5-trinitroso-1,3,5-triazine	TNX	4.69	144.0>86.10	RDX 13C3
5	hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine	DNX	5.49	159.90>86.0	RDX 13C3
5	hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine	MNX	6.23	159.90>86.0	RDX 13C3
6	hexahydro-1,3,5-trinitroso-1,3,5-triazine 13C3	RDX 13C3	6.89	284.0>46.5	None
7	hexahydro-1,3,5-trinitroso-1,3,5-triazine	RDX	6.89	281.0>46.5	RDX 13C3
8	triaminotrinitrobenzene	TATB	6.9	257.0>205.0	RDX 13C3
9	1,2-dinitrobenzene	1,2-DNB	8.8	168.0>138.0	1,3-DNB D4
10	1,3,5-trinitrobenzene	1,3,5-TNB	9.06	213.0>183.0	1,3-DNB D4
13	methyl-2,4,6-trinitrophenylnitramine	Tetryl	11.31	241.1>212.9	1,3-DNB D4
11	1,3-dinitrobenzene D4	1,3-DNB D4	10.52	172.0>142.1	None
12	3,5-dinitroaniline	3,5-DNA	11.18	183.0>153.	1,3-DNB

				0	D4
9	1,3-dinitrobenzene	1,3-DNB	10.65	168.0>138.0	1,3-DNB D4
14	nitrobenzene	NB	12.18	123.0>46.5	1,3-DNB D4
15	nitroglycerin	NG	12.94	241.0>62.4	1,3-DNB D4
16	2,4,6-trinitrotoluene	2,4,6-TNT	13.55	227.0>210.0	1,3-DNB D4
18	2,4-dinitrotoluene D3	2,4-DNT D4	15.55	185.1>168.1	None
19	2,4-dinitrotoluene	2,4-DNT	15.8	182.1>152.1	2,4-DNT D4
19	2,6-dinitrotoluene	2,6-DNT	15.3	182.1>152.1	2,4-DNT D4
17	2-amino-4,6-dinitrotoluene	2-Am-4,6-DNT	13.87	197.1>46.5	2,4-DNT D4
17	4-amino-2,6-dinitrotoluene	4-Am-2,6-DNT	13.31	197.1>46.5	2,4-DNT D4
20	2-nitrotoluene	2-NT	18.61	137.2>46.5	2,4-DNT D4
20	4-nitrotoluene	4-NT	19.85	137.2>46.5	2,4-DNT D4
20	3-nitrotoluene	3-NT	21.26	137.2>46.5	2,4-DNT D4
21	pentaerythritol tetranitrate	PETN	22.22	285.1>62.4	2,4-DNT D4
22	tri-o-cresyl phosphate +	TCP	33.74	369.1>91.3	2,4-DNT D4

+ Signifies use of APCI positive mode – all other compounds utilize negative ionization

Sample preparation of both solids and liquids follows well established protocols. Aqueous samples are extracted onto a solid phase C-18 resin packaged into Restek RTX cartridges. A detailed description of extraction conditions are outlined in EPA Method 3535 [3]. Recoveries are excellent with the exception of Tri–o–cresyl phosphate which possesses a high affinity for the C-18 resin. Under normal conditions, recovery of Tri–o–cresyl phosphate, the lone organophosphate in the list, falls below fifty percent. Tri–o–cresyl phosphate recovery is improved by eluting with methanol immediately after acetonitrile. However, this modification necessitates a time consuming concentration step before analysis can be performed. Solid sample matrices are extracted using the ultrasonic technique outlined in method 8330. Recoveries are excellent for all compounds if care is taken to prevent the thermal degradation of tetryl. Thermostatic controls designed to maintain ultrasonic bath temperatures between two and six degrees Celsius are highly recommended.

Sample extracts are readied for the ionization chamber by the Waters Aquity UPLC system (high performance liquid chromatograph). The high performance liquid chromatograph provides more than an inlet for the mass spectrometer / mass spectrometer and great care must be taken to configure it properly. Sample injection volume into the instrument equals fifty microliters. Under method conditions a co-elution of the isomeric pair 2,6-diamino-4-nitrotoluene and 2,4-diamino-6-nitrotoluene limits the injection volume. A thirty centimeter Restek Allure C-18 column with a particle size of 5 microns provides

chromatographic separation for all isomers. An after market column compartment maintains column temperature at thirty degrees Celsius. The column compartment appears to be a necessity as the Aquity cannot accommodate 30 cm columns in its own smaller compartment. The more compact columns for which the Aquity was designed fail to provide the separation necessary to satisfy all the demands of the method.

The mobile phase consists of 60 parts water doped with 0.01 M ammonium acetate and 40 parts methanol. Free acetate ions in the mobile phase prove essential for adduct formation of RDX and HMX. These adducts, when formed, greatly enhance the response of these two explosives at the detector of the mass spectrometer / mass spectrometer. However, introduction of the acetate into the high performance liquid chromatography system can cause unwanted pressure spikes and instability if proper precautions are not taken. The ammonium acetate solution and methanol should be premixed at the desired ratio and filtered prior to use. This practice virtually eliminates tubing blockage and column degradation which can occur when pure methanol is mixed with the ammonium acetate solution during run conditions inside the high performance liquid chromatograph. The run condition flow rate equals one milliliter per minute and pressure is stable at 2800 psi. When Tri–o–cresyl phosphate is a target of interest a gradient designed to increase methanol to 95% is necessary to elute Tri–o–cresyl phosphate from the column. This greatly increases run time and also increases equilibration time between injections. If Tri–o–cresyl phosphate is not requested then an isocratic run with the aforementioned mobile phase can easily achieve run times below twenty five minutes.

Situated at the interface between the high performance liquid chromatograph and the mass spectrometer / mass spectrometer detection system are the probe assembly and ionization chamber. The probe, termed an APCI probe, utilizes atmospheric pressure chemical ionization for the production of ions. Atmospheric pressure chemical ionization represents a *soft* ionization technique [4] and as such provides the relatively mild ionization conditions required by explosive compounds. Under run conditions probe temperature is lowered to 250 degrees Celsius from a maximum operating temperature of 500 degrees Celsius. The lower temperature protects compounds susceptible to thermal degradation prior to ionization. However, lowering probe temperature decreases ion production for other compounds and overall works to inhibit desolvation. This deficiency is offset by increasing desolvation gas flow entering the probe to near maximum levels. To achieve ionization the probe assembly operates in tandem with a corona pin which applies localized high voltage into the nebulous stream exiting the probe. Similar to the desolvation gas the corona pin also operates near maximum to compensate for lower probe temperatures and to maximize ionization. Ions enter the mass spectrometer through a small opening referred to as the cone. The voltage applied to this cone dramatically affects response of all the compounds. The Quattro Premier XE, the detection system upon which this method was developed, allows for the cone voltage to be variable on a per compound basis. The absence of such control would negatively impact sensitivity to such an extent as to render the analysis useless. Although cone voltage has perhaps the most significant impact on response, many variables of the system are tailored to maximize the response of each compound aside from the obvious mass settings of the quadropoles of the mass spectrometers. During development a syringe pump continuously injects one target compound at a time allowing not merely the identification of a precursor ion to daughter ion transition but for the tuning of the entire detection system to maximize the response of the compound transition. The most notable variables aside from the cone voltage relate to the collision cell. The collision cell, a hexapole, is responsible for the fragmentation of the precursor ion and is situated spatially between the two quadropoles of the mass spectrometer / mass spectrometer system. Argon gas occupies the collision cell and acts as a barrier to the precursor ions exiting the first quadropole. Inside the collision cell precursor ions impact argon atoms and fragment. The operator controls the energy of these impacts by adjusting the entrance gate voltage of the collision cell. At the time of development the second quadropole scans a wide range of masses searching for measurable fragments. When a suitable fragment emerges, the second quadropole is locked onto this mass and minute adjustments are made to the collision energy to realize maximum abundance of the most

responsive daughter fragment. Once the settings for maximum response are elucidated they are saved for that transition. The entire method is simply a series of these saved instrument parameters which are programmed to temporally coincide with the elution of the target from the column. Target compound quantification and identification relies solely on the response of the daughter fragment.

RESULTS

The method performs well in blind testing in both soil and aqueous matrices. In addition the mass spectrometry / mass spectrometry derived concentration results compare well with values produced by the dual column/ diode array / ultraviolet detection system with the added benefit of extremely high specificity.

All data shown was acquired on the dual mass spectrometer system using the parameters previously discussed in the Methods section.

TABLE 1: ERA report 051608D1

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
WP Nitroaromatics & Nitramines							
9306	4-Amino-2,6-dinitrotoluene	µg/L	15.19	11.1	6.10 - 16.1	Acceptable	EPA 8321
9303	2-Amino-4,6-dinitrotoluene	µg/L	17.69	14.3	7.86 - 20.7	Acceptable	EPA 8321
6160	1,3-Dinitrobenzene	µg/L	6.75	5.45	3.00 - 7.90	Acceptable	EPA 8321
6185	2,4-Dinitrotoluene	µg/L	8.11	6.60	3.63 - 9.57	Acceptable	EPA 8321
6190	2,6-Dinitrotoluene	µg/L	9.66	7.58	4.17 - 11.0	Acceptable	EPA 8321
9522	HMX	µg/L	17.65	18.9	10.4 - 27.4	Acceptable	EPA 8321
5015	Nitrobenzene	µg/L	4.79	4.06	2.23 - 5.89	Acceptable	EPA 8321
9507	2-Nitrotoluene	µg/L	16.84	16.4	9.02 - 23.8	Acceptable	EPA 8321
9510	3-Nitrotoluene	µg/L	15.41	14.3	7.86 - 20.7	Acceptable	EPA 8321
9513	4-Nitrotoluene	µg/L	18.02	17.3	9.52 - 25.1	Acceptable	EPA 8321
9432	RDX	µg/L	18.26	15.9	8.74 - 23.0	Acceptable	EPA 8321
6415	Tetryl	µg/L	< 0.28	0.00		Acceptable	EPA 8321
6885	1,3,5-Trinitrobenzene	µg/L	14.27	13.0	7.15 - 18.8	Acceptable	EPA 8321
9651	2,4,6-Trinitrotoluene	µg/L	22.09	17.5	9.62 - 25.4	Acceptable	EPA 8321

TABLE 2: ERA report 051608D2

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
SOIL Nitroaromatics & Nitramines in Soil							
9306	4-Amino-2,6-dinitrotoluene	µg/kg	2670	3660	1640 - 4230	Acceptable	EPA 8321
9303	2-Amino-4,6-dinitrotoluene	µg/kg	1563	1900	1260 - 2320	Acceptable	EPA 8321
6160	1,3-Dinitrobenzene	µg/kg	4103	4310	2460 - 5600	Acceptable	EPA 8321
6185	2,4-Dinitrotoluene	µg/kg	4697	5360	1230 - 8890	Acceptable	EPA 8321
6190	2,6-Dinitrotoluene	µg/kg	5531	5560	2110 - 8360	Acceptable	EPA 8321
9522	HMX	µg/kg	2124	2540	1130 - 3690	Acceptable	EPA 8321
5015	Nitrobenzene	µg/kg	3368	3660	682 - 5900	Acceptable	EPA 8321
9507	2-Nitrotoluene	µg/kg	11008	11700	6550 - 15000	Acceptable	EPA 8321
9510	3-Nitrotoluene	µg/kg	2054	2500	1540 - 3220	Acceptable	EPA 8321
9513	4-Nitrotoluene	µg/kg	7179	7120	4090 - 9450	Acceptable	EPA 8321
9432	RDX	µg/kg	1736	2120	1060 - 2860	Acceptable	EPA 8321
6415	Tetryl	µg/kg	< 10.4	0.00		Acceptable	EPA 8321
6885	1,3,5-Trinitrobenzene	µg/kg	11732	13100	7420 - 15400	Acceptable	EPA 8321
9651	2,4,6-Trinitrotoluene	µg/kg	7501	12300	5840 - 13500	Acceptable	EPA 8321

TABLE 3: ERA report Soil-64

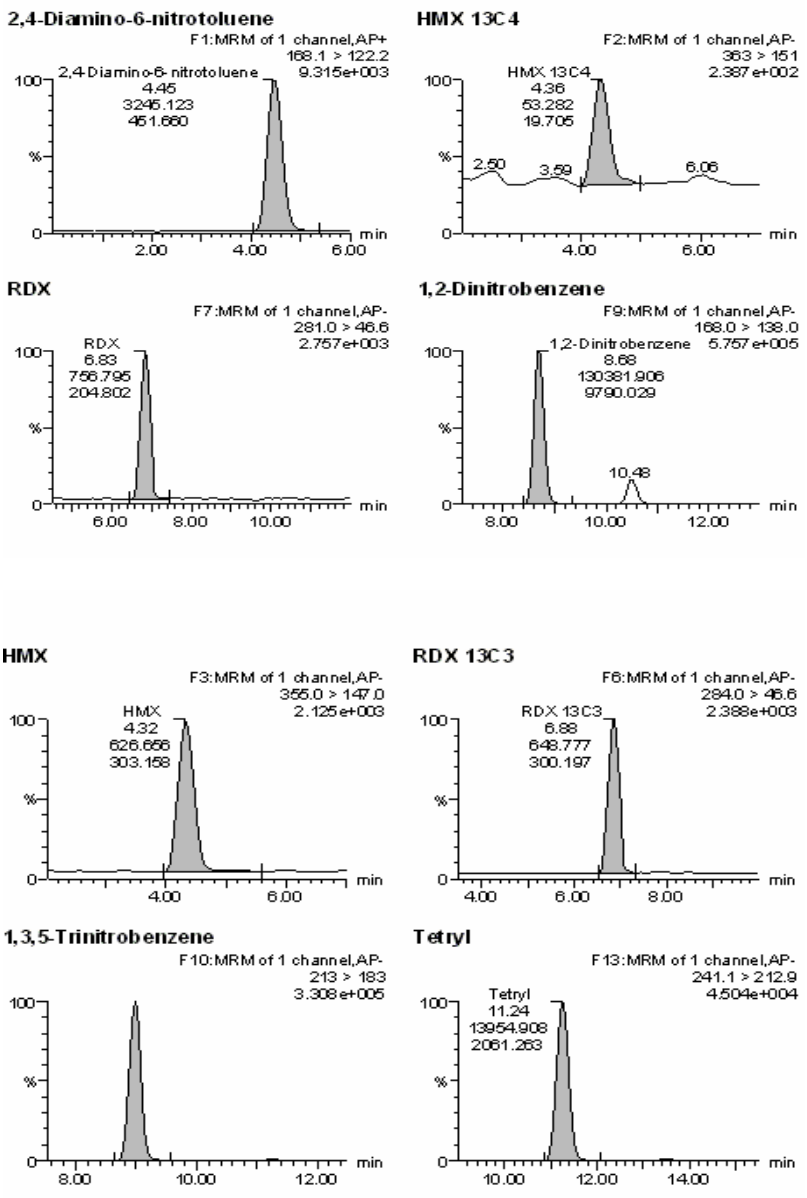
Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
SOIL Nitroaromatics & Nitramines in Soil							
9306	4-Amino-2,6-dinitrotoluene	µg/kg	1270	2060	914 - 2270	Acceptable	EPA 8321
9303	2-Amino-4,6-dinitrotoluene	µg/kg	1300	1670	901 - 1850	Acceptable	EPA 8321
6160	1,3-Dinitrobenzene	µg/kg	1470	1700	985 - 1870	Acceptable	EPA 8321
6185	2,4-Dinitrotoluene	µg/kg	1740	2100	300 - 3450	Acceptable	EPA 8321
6190	2,6-Dinitrotoluene	µg/kg	1810	2280	561 - 3270	Acceptable	EPA 8321
9522	HMX	µg/kg	1740	2210	1080 - 2430	Acceptable	EPA 8321
5015	Nitrobenzene	µg/kg	2050	2240	246 - 3660	Acceptable	EPA 8321
9507	2-Nitrotoluene	µg/kg	4160	4530	2160 - 5560	Acceptable	EPA 8321
9510	3-Nitrotoluene	µg/kg	4990	5430	3180 - 5970	Acceptable	EPA 8321
9513	4-Nitrotoluene	µg/kg	4390	4810	2370 - 5830	Acceptable	EPA 8321
9432	RDX	µg/kg	2190	2950	1540 - 3240	Acceptable	EPA 8321
6415	Tetryl	µg/kg		0.00		Not Reported	
6885	1,3,5-Trinitrobenzene	µg/kg	1290	1710	458 - 2140	Acceptable	EPA 8321
9651	2,4,6-Trinitrotoluene	µg/kg	2050	2800	1290 - 3080	Acceptable	EPA 8321

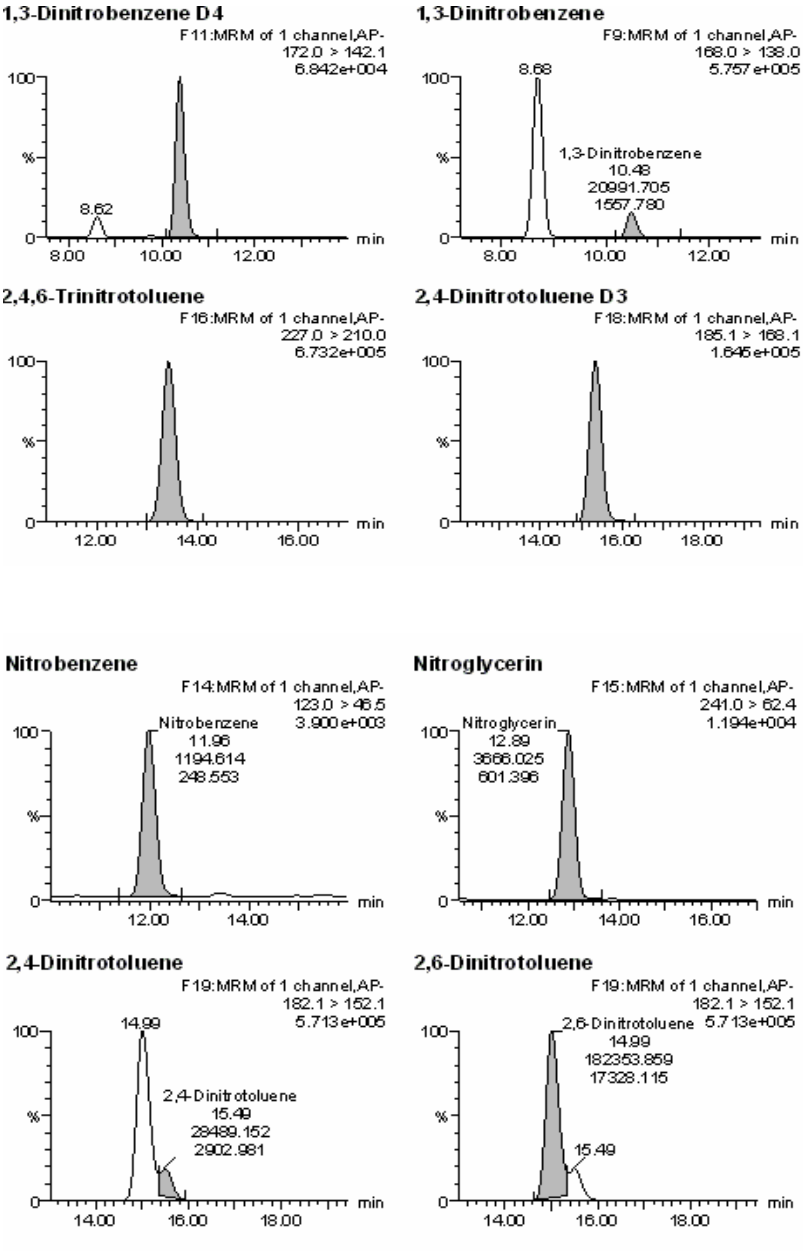
TABLE 4: ERA report WP-162

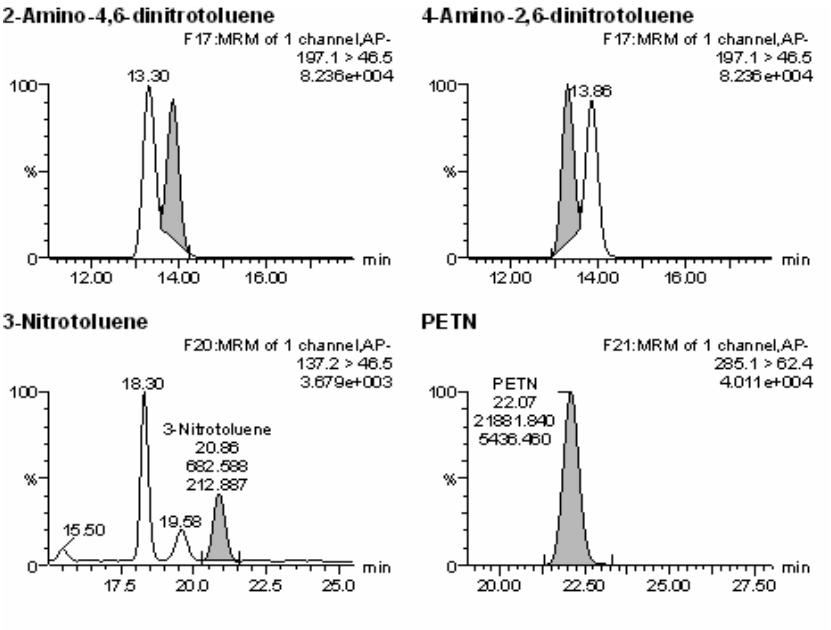
Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
WP Nitroaromatics & Nitramines							
9306	4-Amino-2,6-dinitrotoluene	µg/L	6.85	6.62	3.64 - 9.60	Acceptable	8321
9303	2-Amino-4,6-dinitrotoluene	µg/L	12.8	12.0	6.60 - 17.4	Acceptable	8321
6160	1,3-Dinitrobenzene	µg/L	14.2	15.5	8.52 - 22.5	Acceptable	8321
6185	2,4-Dinitrotoluene	µg/L	14.9	15.6	8.58 - 22.6	Acceptable	8321
6190	2,6-Dinitrotoluene	µg/L	13.4	14.6	8.03 - 21.2	Acceptable	8321
9522	HMX	µg/L	8.32	8.80	4.84 - 12.8	Acceptable	8321
5015	Nitrobenzene	µg/L	14.7	15.9	8.74 - 23.0	Acceptable	8321
9507	2-Nitrotoluene	µg/L	16.6	19.5	10.7 - 28.3	Acceptable	8321
9510	3-Nitrotoluene	µg/L	2.06	2.04	1.12 - 2.96	Acceptable	8321
9513	4-Nitrotoluene	µg/L	8.13	7.98	4.39 - 11.6	Acceptable	8321
9432	RDX	µg/L	14.5	15.5	8.52 - 22.5	Acceptable	8321
6415	Tetryl	µg/L	< 0.200	0.00		Acceptable	8321
6885	1,3,5-Trinitrobenzene	µg/L	11.5	12.1	6.66 - 17.5	Acceptable	8321
9651	2,4,6-Trinitrotoluene	µg/L	6.60	6.46	3.55 - 9.37	Acceptable	8321

Continuing calibration verification provides valuable insight into overall method stability. The goal during development was to consistently achieve CCV recoveries within 20% of expected for all compounds. Unfortunately, not all compounds respond in a consistent manner. TATB and PETN in particular respond erratically and have forced the opening of the acceptable continuing calibration verification window to 30%. In addition RDX and HMX are susceptible to loss of response and need to be tightly controlled. Four internal surrogates normalize responses across the entire list and these two critical compounds each have their own Carbon -13 doped internal standard to ensure reliable reporting. As target lists grow longer issues with a few compounds are not atypical. Method stability overall remains adequate for several weeks in between initial calibrations.

FIGURE 2: Continuing calibration verification chromatograms


2,4-Diamino-6-nitrotoluene
F1:MRM of 1 channel,AP+
168.1 > 122.2
9.315e+003
2,4-Diamino-6-nitrotoluene
4.45
3245.123
451.660
HMX 13C4
F2:MRM of 1 channel,AP-
363 > 151
2.387e+002
HMX 13C4
4.36
53.282
19.705
2.50
3.59
6.06
RDX
F7:MRM of 1 channel,AP-
281.0 > 46.6
2.757e+003
RDX
6.83
756.795
204.802
1,2-Dinitrobenzene
F9:MRM of 1 channel,AP-
168.0 > 138.0
1,2-Dinitrobenzene 5.757e+005
8.68
130381.906
9790.029
10.48
HMX
F3:MRM of 1 channel,AP-
355.0 > 147.0
2.125e+003
HMX
4.32
626.656
303.158
RDX 13C3
F6:MRM of 1 channel,AP-
284.0 > 46.6
2.388e+003
RDX 13C3
6.88
648.777
300.197
1,3,5-Trinitrobenzene
F10:MRM of 1 channel,AP-
213 > 183
3.308e+005
Tetryl
F13:MRM of 1 channel,AP-
241.1 > 212.9
4.504e+004
Tetryl
11.24
13954.908
2061.263
min


1,3-Dinitrobenzene D4
F11:MRM of 1 channel,AP-
172.0 > 142.1
6.842e+004
8.62
1,3-Dinitrobenzene
F9:MRM of 1 channel,AP-
168.0 > 138.0
5.757e+005
8.68
1,3-Dinitrobenzene
10.48
20991.705
1557.780
2,4,6-Trinitrotoluene
F16:MRM of 1 channel,AP-
227.0 > 210.0
6.732e+005
2,4-Dinitrotoluene D3
F18:MRM of 1 channel,AP-
185.1 > 168.1
1.645e+005
Nitrobenzene
F14:MRM of 1 channel,AP-
123.0 > 46.5
3.900e+003
Nitrobenzene
11.96
1194.614
248.553
Nitroglycerin
F15:MRM of 1 channel,AP-
241.0 > 62.4
1.194e+004
Nitroglycerin
12.89
3666.025
601.396
2,4-Dinitrotoluene
F19:MRM of 1 channel,AP-
182.1 > 152.1
5.713e+005
14.99
2,4-Dinitrotoluene
15.49
28489.152
2902.981
2,6-Dinitrotoluene
F19:MRM of 1 channel,AP-
182.1 > 152.1
5.713e+005
2,6-Dinitrotoluene
14.99
182353.859
17328.115
15.49
%
min



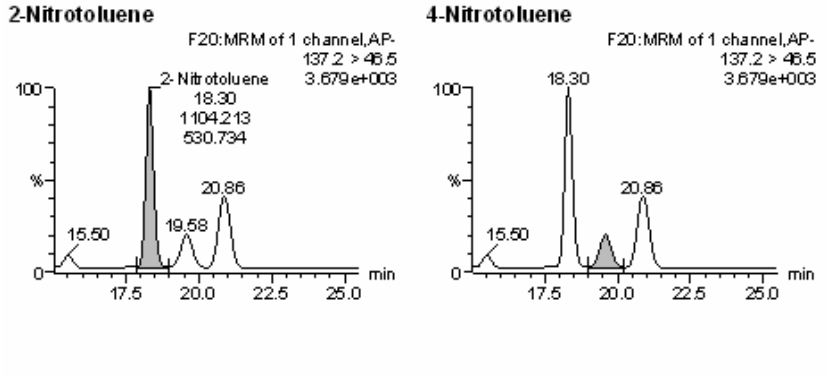


TABLE 5: CCV Results

	#	Name	Sample Text	ID	Std. Conc	RT	Area	IS Area	Response	Det Flags	ug/L	%Rec	Trace
1	2...	2,4-Diamino-6-nitrotoluene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	4.445	3245.123	648.777	3245.123	bb	242.286	96.914	168.1 > 122.2
2	3...	HMX 13C4	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	4.357	53.282		53.282	bb	147.807	59.123	363 > 151
3	4...	HMX	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	4.320	626.656	53.282	2940.280	bb	261.649	104.660	355.0 > 147.0
4	5...	RDX 13C3	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	6.877	648.777		648.777	bb	213.347	85.339	284.0 > 46.6
5	6...	RDX	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	6.832	756.795	648.777	291.624	bb	273.011	109.204	281.0 > 46.6
6	8...	1,2-Dinitrobenzene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	8.677	130381...	15577.343	2092.493	bb	248.503	97.401	168.0 > 138.0
7	9...	1,3,5-Trinitrobenzene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	8.982	74250....	15577.343	1191.635	bb	231.529	92.612	213 > 183
8	1...	Tetryl	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	11.241	13954....	15577.343	223.962	bb	189.757	75.903	241.1 > 212.9
9	1...	1,3-Dinitrobenzene D4	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	10.387	15577....		15577.343	bb	212.720	85.088	172.0 > 142.1
10	1...	1,3-Dinitrobenzene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	10.482	20991....	15577.343	336.895	bb	258.292	103.317	168.0 > 138.0
11	1...	Nitrobenzene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	11.962	1194.614	15577.343	19.172	dd	278.337	111.335	123.0 > 46.5
12	1...	Nitroglycerin	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	12.893	3666.025	15577.343	58.836	bb	666.254	106.601	241.0 > 62.4
13	1...	2,4,6-Trinitrotoluene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	13.416	208812...	15577.343	3351.215	bb	248.522	99.409	227.0 > 210.0
14	1...	2,4-Dinitrotoluene D3	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	15.346	57848....		57848.188	bb	220.933	88.373	185.1 > 168.1
15	1...	2,4-Dinitrotoluene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	15.488	28489....	57848.188	123.120	db	242.590	97.036	182.1 > 152.1
16	1...	2,6-Dinitrotoluene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	14.989	182353...	57848.188	788.071	bd	239.316	95.727	182.1 > 152.1
17	2...	2-Amino-4,6-dinitrotoluene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	13.858	20087....	57848.188	86.812	db	211.330	84.532	197.1 > 46.5
18	2...	4-Amino-2,6-dinitrotoluene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	13.298	22607....	57848.188	97.702	bd	224.603	89.841	197.1 > 46.5
19	2...	2-Nitrotoluene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	18.301	1104.213	57848.188	4.772	bd	255.111	102.044	137.2 > 46.5
20	2...	4-Nitrotoluene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	19.581	307.434	57848.188	1.329	bb	237.683	95.073	137.2 > 46.5
21	2...	3-Nitrotoluene	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	20.864	682.588	57848.188	2.950	bb	267.257	106.903	137.2 > 46.5
22	2...	PETN	8321LANL2 CCV 250p...	LCMS49/67-08	250.000	22.072	21881....	57848.188	94.566	bb	750.809	120.129	285.1 > 62.4

DISCUSSION

Over the last decade liquid chromatography coupled with tandem mass spectrometry has become a widespread technique crossing many disciplines of science. Traditionally this technique has been employed in the areas of pharmacokinetics, proteomics, biomarker quantification, pharmacology screening and medicinal chemistry [5]. Its usefulness across these applications can largely be credited to the technique's power of selectivity which allows it to perform trace analysis of individual compounds in complex biological matrices[6]. The relatively slow penetration rate of tandem mass spectrometry into other branches of chemistry including environmental chemistry can primarily be contributed to the high level of initial capital investment required to obtain and operate the equipment and the lack of a clear regulatory mandate for this technology. Explosives analysis by tandem mass spectrometry will eventually become the standard for all federal
remediation work. The analysis provides highly superior specificity and sensitivity when compared to the ultraviolet detection methodology. Solid chromatography in combination with the remarkably flexible ionization and detection scheme provided by the atmospheric pressure chemical ionization probe / tandem mass spectrometer system allows for a highly simplified and vastly improved mechanism for the reporting of explosives. However, before dual column confirmation and spectral analysis of ultraviolet detector data becomes a matter of history much regulatory work remains to be done. At present dual mass spectrometer methodologies applicable to the analysis of explosives use a variety of mobile phases, ionization techniques, detection, calculation and reporting methods. In many cases mass transitions for the same compound are not equivalent between two methods created at different laboratories. Nor is it obvious that they could be the same given the differences in equipment and mobile phases employed at each laboratory. Certainly the environmental analytical industry has developed a superior method for explosive analysis, but the lack of regulatory guidance and the inherent difficulty in creating consistent guidance for this technology relegates it to performance based specialty work when it is in fact the preferred method.

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