Overcoming Matrix Effects: Quantitation of Explosives via Ambient Ionization with Direct Sample Analysis (DSA)

Joshua A Wilhide; Gregory T. Winter; Laura Nevin, William R. LaCourse
Molecular Characterization and Analysis Complex, University of Maryland Baltimore County

1 Introduction

There is an ever changing need to develop methods which can quickly, unambiguously, and consistently replicate quantitative experiments from various sample matrices. Ambient ionization is the best method because it has no requirement for separation or off-line sample preparation prior to ionization and analysis. Since 2004, ambient ionization has expanded into more than thirty different ionization sources and techniques, which now include the relatively new and commercially available Direct Sample Analysis (DSA) source available from PerkinElmer. The scope of this project is to provide evidence that the DSA source can overcome the stigma ascribed to ambient ionization, its inability to quantitate.

2 HPLC Instrumentation

The HPLC analysis was run on an PerkinElmer HPLC-MS system. The HPLC was equipped with an autosampler (10µL Loop size), a column oven (no switch valve), and a FX-15 UHPLC binary pump. The ambient ionization was used with the DSA ion source, which was attached to a PerkinElmer AxION TOF. The entire source was enclosed to protect the operator from the sample as well as the sample from contamination. The source was mounted to a two axis translator to allow ionization optimization. Source conditions as well as sample position were adjusted to achieve maximum signal.

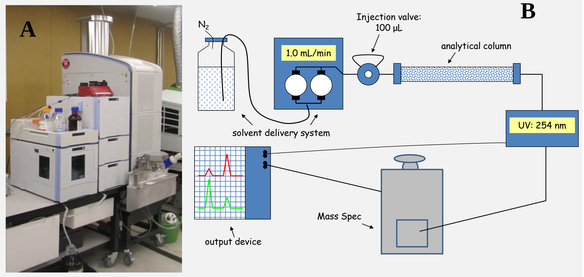


Figure 1. A) Overall view of the HPLC attached to the AxION TOF. **B)** Schematic view of the HPLC-MS configuration used in the initial set of experiments involving HPLC-APCI-MS

HPLC/MS Parameters

Step	Type	Step Time	Flow (ml/min)	%A*	%B**	Curve
0	Equilibration	2.5 min	1.0	100.0	0.0	Linear
1	Run	0.0 min	1.0	100.0	0.0	Linear
2	Run	5.0 min	1.0	0.0	100.0	Linear

Parameter	HPLC-MS	DSA-MS
Capillary Exit (Volts)	100.00	150
Low m/z	100	100
High m/z	3000	500
Ion Polarity	Negative	Negative
Ion Source Type	APCI	DSA
Cylinder Lens (Volts)	400	200
Endplate (Volts)	800	800
APCI voltage (Volts)	-2500	-2200
APCI Vaporizer Temperature (°C)	300	300
Drying Gas Flow Rate (L/m)	8	0
Nebulizer Gas Pressure (PSI)	80	80

* Solvent A: 100mM Ammonium Chloride. **Solvent B: Methanol
Column: PerkinElmer SPP C18, 75 mm by 2.1 mm with 3µm particles

3 HPLC-MS Results

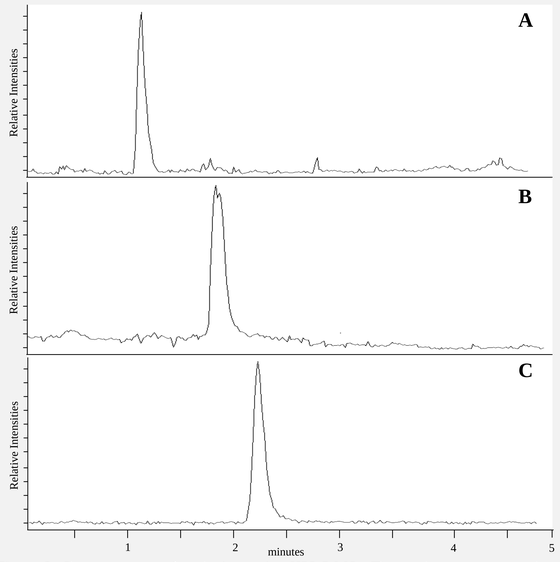


Figure 2. Chromatagrams of explosives using HPLC-MS. The results are represented as TICs. The total amount injected onto the column was 0.01 mg/mL. **A)** HMX explosive **B)** RDX explosive **C)** TNT explosive

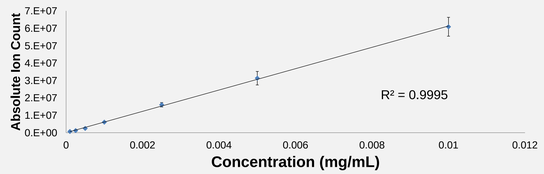


Figure 3. Calibration curve for TNT using HPLC-MS. The linearity was over three orders of magnitude with a limit of detection at 0.0001 mg/mL and a limit of quantification at 0.0005 mg/mL.

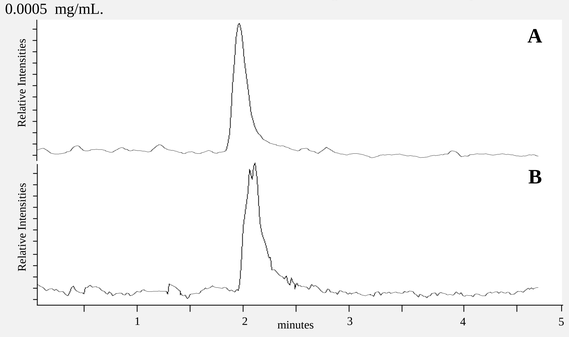
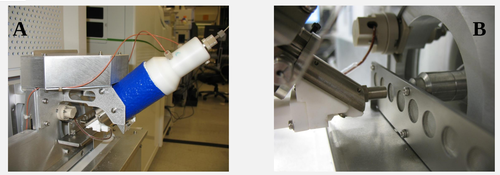


Figure 4. Chromatagrams of multiple injections of RDX. **A)** First injection **B)** fifteenth injection

4 DSA Instrument



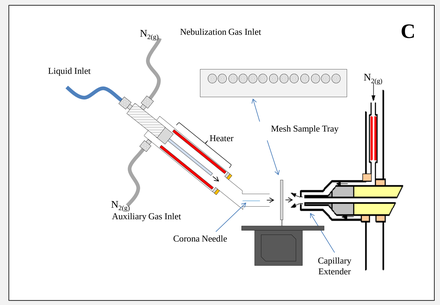


Figure 5. A) Close up view of the DSA. **B)** Close up view of the DSA sample tray inlet to the AxION TOF. **C)** Schematic of the DSA ionization source.

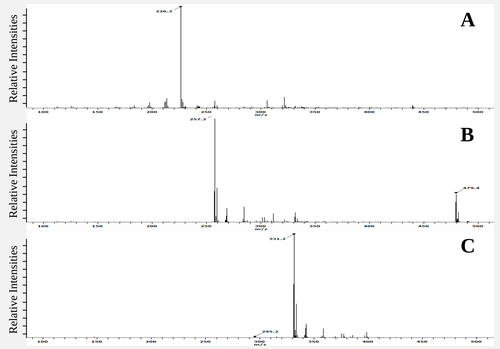


Figure 6. Spectra of the standard explosives using DSA. Some of the species showed [M+Cl]- adducts as base peak, and others showed the [M-H]- as the base peak **A)** TNT **B)** RDX **C)** HMX

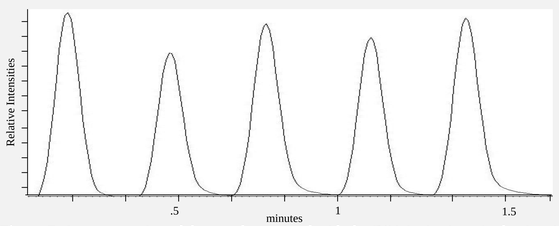


Figure 7. A representation of the speed associated with the DSA ionization. In the time it takes the HPLC-MS to elute RDX off the column, 5 replicate measurements can be made with the DSA.

5 DSA Results

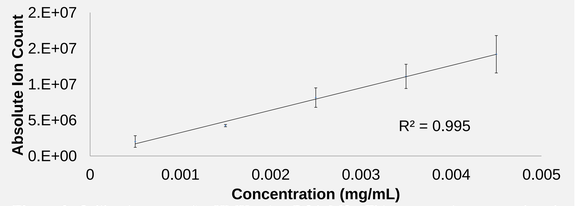


Figure 8. Calibration curve for HMX using DSA-MS. This was run in pure methanol to show proof of concept that the DSA can be quantitative. The linear range was limited to two orders of magnitude, with the LOQ at 0.005 mg/ml. The recovery was 109%. The recovery shows that when limited sample matrix is present, the DSA can determine concentration from a standard curve.

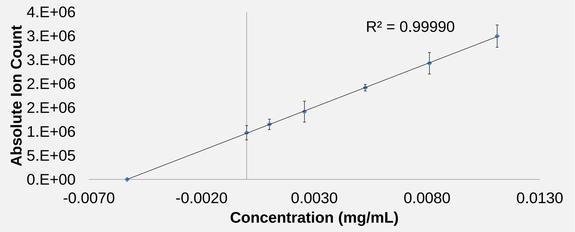


Figure 9. Calibration curve for HMX using DSA-MS extract from a soil sample. The run shows proof of concept that the DSA can be quantitative when high matrix background is present. The recovery was 106%. The recovery shows that although the sample has a high matrix background, the DSA can still determine concentration from standard addition curves.

6 Conclusion

The HPLC-MS was first optimized to show chromatographic separation as well as quantification over at least three orders of magnitude, but undesired reproducibility issues arose due to high ionic strength. Method development with the ambient ionization source was required because the HPLC results were not reproducible. The DSA allows for quick and effective identification of explosives and the ability to quantitate via two pathways: standard curve when the sample is present with a limited matrix, and standard addition curves when the sample is present in a high matrix background. Overall, the DSA ionization source has been shown to provide rapid analysis of samples directly with no pretreatment for both screening and quantification. This method can eliminate the need for HPLC-MS separation, thus cutting time involved as well as cost associated with explosive analysis.

From left to right: Dr. W. LaCourse, J. Yoon, J. Wilhide, A Jiang, G. Winter, S. Tan, D. McCauley, L. Krajewski, and K. Erickson
Not Pictured: S. Rozario, R. Neubauer, L. Nevin, M . LaCourse

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