American Soc. Mass Spectrometrists
Palm Springs, CA. June 2-5, 1997

438

Increased Sensitivity and Detection Limits for Nitro Containing Explosives by On-Column HPLC Reductions and ESI/APCI MS

Kevyn Smith, David Schrum, and David C. White
Microbial Insights Rockford, Tennessee

Abstract

On-line reduction of nitro groups contained on explosive compounds increases the ionization affinity for the reduced species. APCI and electrospray MS are excellent analytical techniques primarily due to the increases in ionization affinity. The explosives investigated were mononitrotoluene, monoamino-dinitrotoluene, and diamino-mononitrotoluene. An on-line acid catalyzed reduction in the presence of Palladium granules was ulitized to reduce nitro aromatic explosives. In APCI mode, the resulting detection limit increased an order of magnitude for the mononitrotoluenes. In electrospray mode, the reduced mononitrotoluenes had an three orders of magnitude increase in detection limit with an average reaction efficiency of 90%; wheras, the reduction of the monoamino and diamino-nitrotoluenes resulted in a three orders of magnitude increase in detection limits with an average reaction efficiency of 35%.

Introduction

Bioremediation of sites that contain undetonated oridinances has become a serious concern of environmentalists. Ecosystems that contain these explosive contaminates may experience damage for years to come. Detection by conventional GC methods are often hindered by analyte degredation. Upon the advent of LC/MS systems, thermally labile compounds are fully detected without sample loss due to thermal decomposition. Explosive compounds do not ionize due to the charge destabilization from the nitro groups contained in their structures. By reducing these nitro groups, the ionization affinity of these particular compounds greatly increases from that of the unreduced species. Upon the nitro group replacement with an amino group, a charge is placed on the explosive compound without being delocalized.

Methods

Sample introduction into the mobile phase flow was achieved via a Thermo Separation's AS3000 autosampler equipped with a 5uL loop. A dual pump system (Microtech) was utilized for the chromatographic system. In positive ionization mode, the aqueous mobile phase was acidified with 0.1M Formic acid (Aldrich). The organic portion of the mobile phase contained HPLC grade methanol (Burdick & Jackson). In negative ionization mode, nanopure water was used as the aqueous constituent. A Timberline TL-50 column heater (Alltech) coupled with a Timberline TL-30 thermostat (Alltech) maintained the mobile phase temperature at 80°C. Samples were analyzed using a VG Platform II mass spectrometer. The APCI and electrospray probes were provided by VG.

APCI

A 2.1 x 150mm analytical column (Alltech) was coupled downstream from a 2.1 x 150mm column (Alltech) packed with 1:1 mixture of 75um glass beads (Aldrich)/Palladium granules (Aldrich). 10%/min methanol gradient was used to elute the explosives at a flowrate of 150uL/min.

Electrospray

A 1 x 150mm C_{18} analytical column (Alltech) was coupled downstream from a 1x 20mm column (Upchurch) packed with 1:1 mixture of 75um glass beads/Palladium granules. A 70/30 methanol/0.1M Formic acid isocratic method was run at 25uL/min to elute the explosives.

Results

In APCI mode, the detection limits were increased by an average of an order of magnitude when the nitro groups were reduced to amines. In electrospray mode, the detection limits were increased an average of three orders of magnitude when the nitro functionalities were reduced to amines.

	Negative Ion Mode Detection Limits		Positive Ion Mode Detection Limits (Reduced)	
Compound	APCI (fmole)	ESI (fmole)	APCI (fmole)	ESI (fmole)
o-Nitrotoluene	4.67E+05	2.80E+07	4.67E+02	7.00E-03
m-Nitrotoluene	4.67E+05	2.80E+07	4.67E+02	7.00E-03
p-Nitrotoluene	4.67E+05	2.80E+07	4.67E+02	7.00E-03
2-Amino-dinitrotoluene	Not Analyzed	1.52E+07	Not Analyzed	5.00E-03
4-Amino-dinitrotoluene	Not Analyzed	1.52E+07	Not Analyzed	5.00E-03
2,4-Diamino-6-nitrotoluene	Not Analyzed	1.80E+07	Not Analyzed	7.60E-02

Figure I. Detection Limits for Explosives with APCI and electrospray.

As the number of amino groups increased on the Toluene ring, the reaction efficiency deceased linearly. The most efficient reduction occured with o-nitrotoluene (107%) and the least effecient reduction occured with 2,4-Diamino-6-nitrotoluene (30%). The other nitro aromatic explosives had the following reduction efficiencies: m-nitrotoluene-90%, p-nitrotoluene-90%, 2-Amino-dinitrotoluene-41%, and 4-Amino-dinitrotoluene-39%.

Conclusion

The nearly complete reductive efficiencies of the mononitrotoluenes provide a realistic model for other explosive compounds. The amino containing explosives serve as an effective model for studying the competing factors in catalytic reduction reactions. Amino groups inhibited the deoxidation of the amino containing explosives by a yet undetermined mechanism. An increased detection limit for the amino containing explosives may be obtained by further experimentation of their reductive efficiencies. The detection limits of the investigated compounds could be theoretically lowered by an order of magnitude by using nanospray ionization. Other explosive compounds to be investigated will include: TNT, RDX, and various AzoDimers of TNT. The data generated from these analytical techniques will be applied to real world samples.