Characterization of Nitrated Sugar Alcohols by Atmospheric-Pressure Chemical-Ionization Mass Spectrometry

Alla Ostrinskaya, Jude A. Kelley and Roderick R. Kunz

Chemical, Microsystem, and Nanoscale Technology Group
MIT-Lincoln Laboratory, Lexington, MA 02420
jude.kelley@ll.mit.edu

RATIONALE: The nitrated sugar alcohols mannitol hexanitrate (MHN), sorbitol hexanitrate (SHN) and xylitol pentanitrate (XPN) are in the same class of compounds as the powerful military grade explosive pentaerythritol tetranitrate (PETN) and the homemade explosive erythritol tetranitrate (ETN), but unlike PETN and ETN the ways to detect MHN, SHN and XPN by mass spectrometry (MS) have not been fully investigated.

METHODS: Atmospheric-pressure chemical-ionization mass spectrometry (APCI-MS) was used to detect ions characteristic of nitrated sugar alcohols. Time-of-flight APCI mass spectrometry (TOF APCI-MS) and collisional dissociation mass spectrometry (CID MSMS) were used for confirmation of each ion assignment. In addition, the use of the chemical ionization reagent dichloromethane was investigated to improve sensitivity and selectivity for MHN, SHN and XPN detection.

RESULTS: All of the nitrated sugar alcohols studied followed similar fragmentation pathways in the APCI ionization source. MHN, SHN and XPN were detectable as fragment ions formed by the loss of NO_2, HNO_2, NO_3, and CH_2NO_2 groups, and in the presence of dichloromethane chlorinated adduct ions were observed. It was determined that chlorinated adducts of MHN and SHN had the lowest limits of detection (LOD) while for XPN the lowest LOD was for detection of the $[XPN\text{-}NO_2]^-$ fragment ion. **CONCLUSION**: APCI-MS technique provides a selective and sensitive method for the detection of nitrated sugar alcohols. The methods disclosed here will benefit the area of explosives trace detection for counterterrorism and forensics.

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INTRODUCTION

The military-grade explosive pentaerythritol tetranitrate (PETN) is used as a base charge in blasting caps, in detonation cord, and as a major ingredient in plastic explosives. [1] The homemade explosive erythritol tetranitrate (ETN) is chemically similar to PETN and as reported [2], the detonation velocities are similar between PETN, ETN and MHN. According to Camp et al. [3] MHN, SHN and XPN can be used as energetic plasticizers for double-base propellants with a significant advantage over traditional propellants because the large molecules capable of hydrogen bonding provide for a more stable and dense plasticizer formulation.[4] As a result, methods to detect MHN, SHN, and XPN should be pursued for the same security and forensics applications as methods for detecting PETN and ETN.

MHN, SHN and XPN are white crystalline materials in pure form. The chemical structures and formulas are shown in Figure 1 where it is also shown that MHN and SHN are stereoisomers. They are produced by nitrating the isomeric sugar alcohols (2R,3R,4R,5R)-hexane-1,2,3,4,5,6-hexol (mannitol) and (2S,3R,4R,5R)-hexane-1,2,3,4,5,6-hexol (sorbitol). The R-type chiral carbon is more stable resulting in higher thermal stability for MHN with a melting point of 112 ºC compared to SHN which has a melting point of just 55 ºC. These properties affect thermal decomposition, combustion, and detonation performance [5].

The first report of MHN and SHN detection was by Parihar et al.[6] via thin-layer chromatography where 4 µg of mannitol and sorbitol hexanitrate were separated from a mixture of PETN, ethylene glycol dinitrate, nitroglycerin and diethylene glycol dinitrate. More recently, Crowson et al.[7] reported detection of mannitol hexanitrate in a mixture with other explosives by direct chemiluminescent emission during thermally induced gas-phase decomposition reactions. The limit of detection for this technique was reported at ~1 µg. Detection of compounds by chemiluminescent emission is both sensitive and selective, but does not directly detect the parent compound. Current methods for explosives trace detection, such as electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) mass spectrometry (MS) along with ion mobility mass spectrometry (IMS) provide direct detection of molecular ions,[8] and thus are preferred for most security and forensic applications. In general, mass spectrometry techniques are based on mass-to-charge ratio and cannot separate isomeric molecules. However, the use of APCI ionization, where the compound's ionization and in-source fragmentation depend on the thermal stability and conformational energetics of the molecules, may allow for some level of distinction between MHN and SHN. This work details the results of the APCI-MS (triple quadrupole) analysis in which tandem mass spectrometry collisional induced dissociation (MSMS – CID) is utilized for highly sensitive identification of the molecular ions characteristic of nitrated sugar alcohols and their fragments. A TOF APCI-MS (with accurate mass capability) was used for confirmatory analysis of relevant ions.

EXPERIMENTAL

Chemicals:

Nitrated sugar alcohols: MHN, SHN and XPN as 1-mg/ml solutions in acetonitrile were obtained from Signature Sciences LLC (Austin, TX). These materials were prepared from sources of mannitol and sorbitol for which chiral purity was not confirmed. However, conservation of precursor chirality was expected during the nitration reaction. The 1-mg/ml solutions in acetonitrile of the pentaerythritol tetranitrate and erythrytol tetranitrate were purchased from AccuStandard Inc. (New Haven, CT). Acetonitrile (LCMS grade) and dichloromethane (99.8% purity) were purchased from VWR International (Radnor, PA). All compounds were diluted with acetonitrile to a desired concentration prior to analysis. A 10% solution of dichloromethane in acetonitrile was used as a diluent for nitrated sugar alcohols when detected as chlorinated adducts.

Atmospheric Pressure Chemical Ionization Source and Mass Spectrometer:

All measurements were performed on either an AB SCIEX 4000 QTrap hybrid triple-quadrupole linear ion-trap mass spectrometer (Applied Biosystems, Framingham, MA, USA) in combination with an ABSCIEX TurboV™ ion source with an APCI probe or with an Agilent 6520 QTOF quadrupole time-of-flight (TOF) mass spectrometer (Agilent technologies, Santa Clara, CA, USA) equipped with an APCI source. Samples were introduced by direct syringe infusion into the APCI probe at the rate of 10 µL/min. Ultra-pure nitrogen gas (>99.999%) was used as the source and collision gas.

AB SCIEX 4000 QTrap parameters: The curtain gas pressure setting was 10 psi, the source gas pressure setting was 40 psi, the source temperature was 200 °C, the declustering potential was set at negative 10V; all data were acquired in negative polarity with corona voltage set at negative 5 kV. For MSMS scans the collision gas flow was set to “high”, the collision cell entrance potential was set to negative 10V, and the collision cell exit potential was set at negative 15V. The collision energy (CE) was optimized for each analyte’s fragment in multiple-reaction-monitoring (MRM) mode by adjusting the CE voltage to the maximum instrumental response for each MRM transition. The optimized collision energy varied for each analyte and is specified in the results and discussion section in Table 4. The software used to control the instrument was Analyst (Version 1.5).

Agilent 6520 QTOF parameters: The source gas temperature was 225 °C, the vaporizer temperature was 250 °C, the drying gas flow rate was 5 L/min, the nebulizer pressure was 30 psi, the fragmenter voltage was 50 V and the v-cap voltage was positive 3.5 kV. All spectra were acquired in negative polarity mode.

RESULTS AND DISCUSSION

MHN, SHN and XPN are nitrate esters with high electron affinities[1], therefore all of the compounds' characteristic ions were observed in negative polarity ionization mode.[8] To obtain APCI-MS spectra of the nitrated sugar alcohols, 10 µg/ml MHN, SHN and XPN solutions in acetonitrile were infused into the APCI ionization source at the rate of 10 µL/min. Examples of the negative APCI mass spectra for MHN, SHN, and XPN are shown in Figure 2. Although a triple-quadrupole mass spectrometer such as AB SCIEX 4000 offers good sensitivity and reproducibility of the mass spectra, the unit mass resolution cannot determine the exact mass-to-charge ratio assignment. As a result, the mass assignments of the ions were confirmed using accurate-mass time-of-flight mass spectrometry. To obtain TOF mass spectra we used the same concentration of the nitrated sugar alcohols infused into the APCI probe at the same flow rate used for analysis in the triple-quadrupole APCI-MS. In general, the same ions were observed in the TOF APCI-MS spectra as in the APCI-MS. The TOF APCI-MS spectra for MHN, SHN and XPN are shown in the supplemental information section, Figure S1. A list of the main ions for MHN, SHN and XPN in the APCI-MS and TOF APCI-MS spectra, their mass-to-charge ratio, and proposed ion assignments are listed in Table 1.

The low mass errors in Da and ppm shown in the Table 1 are good confirmation of the proposed ion assignments for the MHN, SHN and XPN fragments. Nitrite and nitrate ions at *m/z* 46, 62 are commonly observed background peaks in the negative APCI mass spectra of the pure acetonitrile used in this study, as shown in the Figure S2, supplemental information section. In addition, the nitric acid cluster at *m/z* of 125 is present in all negative MS APCI spectra due to the high number of nitrate ions produced by in-source fragmentation of the nitrated sugar alcohols. Although we did not observe a typical $M\text{-}H^-$ molecular ion in the negative-ion MS spectra for MHN, SHN and XPN molecules, in-source fragmentation of the nitrated sugar alcohols produced an abundance of fragment ions. The fragmentation pathways for the nitrated sugar molecules studied here are very similar. The main observed loss channel in the mass spectrum involved loss of n (where n = 1, 2, 3) NO_2 groups. We observed an ion representative of the loss of one nitrate group (M-46) in all nitrated sugar alcohol spectra at *m/z* of 406 for both MHN and SHN, and at *m/z* 331 for XPN; loss of three nitro groups (M-138) at *m/z* of 314 for both MHN and SHN, and *m/z* 239 for XPN. In some cases, the fragmentation pathway of the nitrated sugar alcohols combines loss of nitro groups with a loss of alkyl and/or nitrate and nitrous acid groups. For example an ion at *m/z* of 392 was assigned to the loss of $CH_2NO_2^-$ for both MHN and SHN. The same $M\text{-}CH_2NO_2^-$ ion was observed in the XPN spectra at *m/z* of 317 shown in the Figure 3 below. The fragment ion representative of the loss of two nitrite groups, nitrate and nitrous acid groups (M-201) was observed at *m/z* of 251 for both MHN and SHN, and at *m/z* of 176 for the XPN. For the ions at *m/z* of 361 for both MHN and SHN and at *m/z* of 286 for XPN, the fragment ion is a result of NO_2 loss and formation of the OH group, where a proposed chemical structure is shown in Figure S3, supplemental information.

For comparison purposes, we also recorded the APCI MS spectra of the better studied nitroesters ETN and PETN.[1, 7] ETN has a similar molecular structure to the nitrated sugar alcohols with four carbon-

carbon bonds in a linear chain. PETN has four primary carbons and one quaternary carbon-carbon. The chemical structures and formulas for ETN and PETN are shown in Figure 4 below. The negative APCI-MS for PETN in acetonitrile (Figure 5) shows the molecular ion representative of PETN $(M\text{-}H)^-$ at *m/z* of 315. We observed carbonate and nitrate ion adducts of the intact molecules for all compounds at *m/z* of 512 and 514 for both MHN and SHN, at *m/z* 437 and 439 for XPN, at *m/z* 376 and 378 for PETN, and at *m/z* 362 and 364 for ETN. However, in marked contrast with the nitrated sugar alcohols, these adducts are the most abundant ions in the spectrum for PETN due to less in-source fragmentation. Unlike PETN, however, ETN's APCI-MS negative spectrum did not show a $(M\text{-}H)^-$ molecular ion (Figure 6). The fragment ions observed are in agreement with the ions reported by Forbes et al.[7] in the ETN study by direct analysis in real time (DART) TOF MS, where the main ions detected for ETN were the ETN-nitrate adduct (*m/z* 364) and ETN minus nitrite (*m/z* 256).

As expected, the stereoisomers MHN and SHN exhibited similar spectra in negative-mode APCI-MS with one of the most intense peaks at *m/z* of 361 assigned to a loss of two nitrite and formation of one hydroxyl group (chemical formula $C_6H_9N_4O_{14}^-$) as shown in Table 1. Close examination of the spectra showed that the ratio between fragments at the same declustering potential and sample concentration is different. The APCI-MS spectrum of MHN shows more nitrite, nitrate and nitric acid cluster ions than that of SHN. The most intense ion in the MHN spectra is at *m/z* 406 and is assigned to a loss of a nitrite group, although we observed the same peak for SHN, it's only 23% the intensity of the main fragment ion at *m/z* of 361. In addition the peaks at *m/z* of 314 and 316 assigned as a loss of three nitrite groups and formation of two hydroxyl groups respectively are present in both spectra, but the MHN spectrum contains more of the peak at *m/z* of 314 and the SHN spectrum has distinctively more of the *m/z* 316 fragment (see details in Table 1). The peak at *m/z* of 218 assigned to the loss of four nitrous acid groups and one nitrite is not found in the SHN spectra. An overlay of the MHN and SHN spectra is shown in Figure 7. We observed similar behavior of the isomers in the time-of-flight spectra of MHN and SHN shown in Figures S1 and S2 in the supplemental information section. Although in these spectra the ratio between the fragments to the peak of *m/z* 361 does not match exactly the Q-TRAP data, the relations between the MHN and SHN fragments are the same and we observed the same difference between fragments at *m/z* of 314 and 316. The summary of the MHN and SHN fragment peaks is shown in the Table 2. This spectral distinction is useful for determining the starting material used to synthesize a given sample of explosive, thus providing an extra identification for criminal or terrorism related investigations.

To further confirm the nitrated sugar alcohols' ions assignments and identify the most selective MSMS detection pathways we used CID-MSMS product-ion scans to identify the fragments. The typical product-ion scan of the nitrated sugar alcohols primarily consists of nitrite, nitrate ions and their clusters. An example, a MHN product-ion scan of the fragment at *m/z* of 392 is shown in Figure 8. Similar product-ion scans for SHN and XPN are shown in Figures S4 and S5 in the Supplemental Information section.

Previous APCI MS measurements of PETN and ETN using dichloromethane as an APCI reagent have shown evidence of chloride adduct formation.[1] In this report, we have also seen MHN, SHN and XPN all form chlorinated molecular-ion and fragment adducts. To obtain these spectra, 10 µg/ml of MHN, SHN and XPN in a 90%/10% acetonitrile/dichloromethane solution were infused directly into the APCI ionization probe at the rate of 10 µL/min. The APCI MS spectra of MHN, SHN, and XPN in the presence of dichloromethane are shown in Figures 9, 10 and 11, respectively, where the chlorinated adducts $[M\cdot Cl]^-$ for all three compounds are shown (*m/z* 487 for both MHN and SHN and *m/z* 412 for XPN). The chlorinated adduct corresponding to the loss of one nitrate $[(M\text{-}NO_2)\cdot Cl]^-$ was found at *m/z* 442 for both MHN and SHN. However, only for MHN was there a large peak corresponding to the non-chlorinated $[M\text{-}NO_2]^-$ ion at *m/z* 406 when measured in the presence of dichloromethane. An important feature of chloride adduct formation is the ionization of otherwise neutral (and undetectable) fragments, which can provide further information to discriminate between the isomers MHN and SHN. For example, the neutral molecule corresponding to loss of two nitrates $[(M\text{-}2NO_2\text{+}2H)\cdot Cl]^-$ at *m/z* 397 is the chlorinated adduct of a neutral molecule at 362 Da ($C_6H_{10}N_4O_{14}$), and was only observed for SHN. Likewise, the signal at *m/z* 379 is the chlorinated adduct of the neutral molecule at 344 Da ($C_6H_8N_4O_{13}$) and also only was present for the SHN. These differences can provide further means to discriminate differences between MHN and SHN using APCI MSMS.

To identify the most sensitive transitions for MHN, SHN and XPN detection by APCI-MSMS we performed collision induced dissociation (CID) MSMS scans with a collision energy ramp. The results of these experiments allowed us to determine the best precursor-to-product ion transition and optimize the collision energy to achieve the highest instrument response. The optimized collision energies for the main nitrated sugars' fragments are listed in Table 3. In addition we determined limits of detection for the main fragment ions in MSMS modes by analyzing a wide range of concentrations. The solutions were prepared by serial dilution of the MHN, SHN and XPN stock solutions in acetonitrile. Table 3 is a summary of the ions observed in negative-ion APCI-MS and APCI-MSMS along with the relative LOD for each MS transition, where relative LOD is normalized to the LOD of the most sensitive transition. The detection pathway that provides the most sensitive means of trace detection of both MHN and SHN is by using dichloromethane as a chemical ionization reagent for detection of intact molecules as chlorinated adducts. In case of XPN the most sensitive transition was in-source fragmentation resulting in the loss of NO_2 and CH_2NO_2 groups, resulting in ions at *m/z* of 331, 317 and 286.

CONCLUSIONS

This study reports the detection of MHN, SHN and XPN by APCI-MS and APCI-MSMS as both fragment ions and as chlorinated adducts in the presence of dichloromethane. The fragment-ion assignments were confirmed using high resolution TOF APCI-MS. We have observed that MHN, SHN and XPN all follow the same in-source fragmentation pathways when ionized by APCI, including loss of one or more

nitro (M-$n$$NO_2$, n = 1, 2, 3) groups, loss of the nitro (-NO_2) and alkyl groups (-CH_2NO_2) and loss of nitrate (-NO_3) and nitrous acid (-HNO_2) groups. Like PETN and ETN, we observed both carbonated [M+CO_3] and nitrated [M+NO_3] adducts in the spectra of the other nitrated sugar alcohols, but unlike PETN, the nitrated sugar alcohols MHN, SHN and XPN all did not form a molecular ion representative of the intact molecule $[M-H]^-$. Use of dichloromethane as a chemical ionization reagent was beneficial for MHN and SHN detection. In contrast, for XPN the detection of this molecule as ions resulting from the loss of NO_2, CH_2NO_2 and $2NO_2$ fragments is the most sensitive. Finally, we have observed for the first time specific mass fragments that allow for the discrimination between MHN and SHN, both with and without the chloride APCI reagent.

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Table 1.

MHN, SHN and XPN main ions in the APCI-MS and APCI TOF MS spectrum, mass to charge ratio, proposed ion's assignment and calculated *m/z* of the ion's and mass error for the mass to charge ratios acquired on the TOF mass spectrometer

***m/z* Q-TRAP**	**Intensity (counts per second)**	**Loss/gain (M±X)**	**Normalized to the largest peak at *m/z* 361 for MHN, SHN and 331 for XPN (%)**	**Proposed Assignment**	**Formula**	**Observed *m/z* Q-TOF**	**Calculated Mass (Da)**	**Abs Error (Da)**	**Error (ppm)**
MHN									
46	2.5E+06	M-406	70	Nitrite	NO_2^-	45.993	45.993	0.000	6.5
62	1.7E+06	M-390	48	Nitrate	NO_3^-	61.988	61.988	0.000	0.0
125	1.3E+06	M-327	37	Nitric acid nitrate cluster	$HNO_3NO_3^-$	124.982	124.984	0.002	14.4
218	7.3E+05	M-234	20	MHN loss of the 4 nitrous acid groups and 1 nitro group	$C_6H_4NO_8^-$	217.992	217.994	0.001	6.9
251	3.1E+06	M-201	87	MHN loss of 1 nitrous acid,1 nitrate and 2 nitro groups	$C_6H_7N_2O_9^-$	251.014	251.015	0.001	4.4
314	1.9E+06	M-138	54	MHN loss of 3 nitro groups	$C_6H_8N_3O_{12}^-$	314.010	314.011	0.001	2.9
316	2.7E+05	M-136	7	MHN loss of 3 nitro and formation of two hydroxyl groups	$C_6H_{10}N_3O_{12}^-$	316.023	316.024	0.001	2.2
361	3.6E+06	M-91	100	MHN loss of 2 nitro and formation of one hydroxyl groups	$C_6H_9N_4O_{14}^-$	361.011	361.012	0.001	1.9
392	1.9E+06	M-60	54	MHN loss of 1 alkyl and one nitro groups	$C_5H_6N_5O_{16}^-$	391.992	391.991	0.001	3.1
406	2.9E+06	M-46	80	MHN loss of 1 nitro group	$C_6H_8N_5O_{16}^-$	405.996	405.997	0.001	2.7
512	1.6E+06	M+60	46	MHN carbonate adduct	$C_6H_8N_6O_{18}CO_3^{*}$	511.971	511.974	0.003	6.6
514	1.3E+06	M+62	36	MHN nitrate adduct	$C_6H_8N_6O_{18}NO_3^-$	513.974	513.977	0.003	6.0

Table 1 (continued).

MHN, SHN and XPN main ions in the APCI-MS and APCI TOF MS spectrum, mass to charge ratio, proposed ion's assignment and calculated *m/z* of the ion's and mass error for the mass to charge ratios acquired on the TOF mass spectrometer

***m/z* Q-TRAP**	**Intensity (counts per second)**	**Loss/gain (M±X)**	**Normalized to the largest peak at *m/z* 361 for MHN, SHN and 331 for XPN (%)**	**Proposed Assignment**	**Formula**	**Observed *m/z* Q-TOF**	**Calculated Mass (Da)**	**Abs Error (Da)**	**Error (ppm)**
SHN									
46	1.1E+05	M-406	6	Nitrite	NO_2^-	45.993	45.993	0.000	6.5
62	9.5E+05	M-390	56	Nitrate	NO_3^-	61.988	61.988	0.000	0.0
125	2.6E+05	M-327	15	Nitric acid nitrate cluster	$HNO_3NO_3^-$	124.982	124.984	0.002	13.6
251	3.8E+05	M-201	22	SHN loss of 1 nitrous acid,1 nitrate and 2 nitro groups	$C_6H_7N_2O_9^-$	251.014	251.015	0.001	3.2
314	2.2E+05	M-138	13	SHN loss of 3 nitro groups	$C_6H_8N_3O_{12}^-$	314.010	314.011	0.001	1.9
316	9.1E+05	M-136	54	SHN loss of 3 nitro and formation of two hydroxyl groups	$C_6H_{10}N_3O_{12}^-$	316.026	316.024	0.002	7.9
361	1.7E+06	M-91	100	SHN loss of 2 nitro and formation of one hydroxyl groups	$C_6H_9N_4O_{14}^-$	361.011	361.012	0.000	0.6
392	1.6E+05	M-60	10	SHN loss of 1 alkyl and one nitro groups	$C_5H_6N_5O_{16}^-$	391.993	391.991	0.002	6.1
406	3.9E+05	M-46	23	SHN loss of 1 nitro group	$C_6H_8N_5O_{16}^-$	405.996	405.997	0.001	2.0
512	1.5E+05	M+60	9	SHN carbonate adduct	$C_6H_8N_6O_{18}CO_3^{*}$	511.971	511.974	0.003	5.5
514	1.1E+05	M+62	7	SHN nitrate adduct	$C_6H_8N_6O_{18}NO_3^-$	513.974	513.977	0.003	5.6

Table 1 (continued).

MHN, SHN and XPN main ions in the APCI-MS and APCI TOF MS spectrum, mass to charge ratio, proposed ion's assignment and calculated *m/z* of the ion's and mass error for the mass to charge ratios acquired on the TOF mass spectrometer

***m/z* Q-TRAP**	**Intensity (counts per second)**	**Loss/gain (M±X)**	**Normalized to the largest peak at *m/z* 361 for MHN, SHN and 331 for XPN (%)**	**Proposed Assignment**	**Formula**	**Observed *m/z* Q-TOF**	**Calculated Mass (Da)**	**Abs Error (Da)**	**Error (ppm)**
XPN									
46	9.8E+05	M-331	65	Nitrite	NO_2^-	45.993	45.993	0.000	6.5
62	1.9E+06	M-315	128	Nitrate	NO_3^-	61.988	61.988	0.000	0.0
125	1.8E+05	M-252	12	Nitric acid nitrate cluster	$HNO_3NO_3^-$	124.982	124.984	0.002	13.6
176	3.3E+05	M-201	22	XPN loss of 1nitric acid and 3 nitro groups	$C_5H_6NO_6^-$	176.018	176.020	0.002	10.8
190	1.4E+05	M-187	9	XPN loss of 3 nitrous acid and 1nitro groups	$C_5H_4NO_7^-$	189.997	189.999	0.002	12.1
239	6.4E+05	M-138	43	XPN loss of 3 nitro groups	$C_5H_7N_2O_9^-$	239.014	239.015	0.001	5.4
286	2.9E+05	M-91	19	XPN loss of 2 nitro and formation of one hydroxyl groups	$C_5H_8N_3O_{11}^-$	286.015	286.016	0.001	3.5
317	7.6E+05	M-60	51	XPN loss of 1 alkyl and one nitro groups	$C_4H_5N_4O_{13}^-$	316.986	316.985	0.001	3.2
331	1.5E+06	M-46	100	XPN loss of 1 nitro group	$C_5H_7N_4O_{13}^-$	331.000	331.001	0.001	2.7
437	4.9E+05	M+60	33	XPN carbonate adduct	$C_5H_7N_5O_{15}CO_3^{*}$	436.977	436.979	0.002	3.9
439	6.4E+05	M+62	42	XPN nitrate adduct	$C_5H_7N_5O_{15}NO_3^-$	438.980	438.982	0.002	4.1

Table 2.

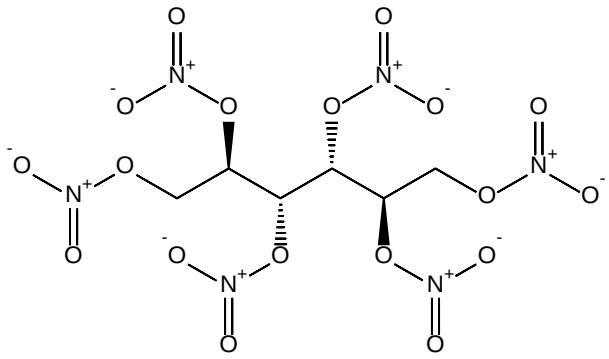
Peak ratios between fragment ions observed in the MHN and SHN APCI-MS spectra measured on both the ABSCIEX Q-TRAP and Agilent Q-TOF. Major differences between MHN and SHN are highlighted in bold italic.

	Q-TRAP (triple quad) data		**Q-TOF (time-of-flight data)**	
m/z	**MHN fragments normalized to the peak at *m/z* 361 (%)**	**SHN fragments normalized to the peak at *m/z* 361 (%)**	**MHN fragments normalized to the peak at *m/z* 361 (%)**	**SHN fragments normalized to the peak at *m/z* 361 (%)**
46	70	6	37	10
62	103	56	166	85
125	37	15	22	12
218	20	N.F.	13	N.F.
251	87	22	34	10
314	***54***	***13***	***22***	***6***
316	***7***	***54***	***2***	***31***
361	100	100	100	100
392	54	10	3	1
406	80	23	60	10
512	46	9	21	6
514	36	7	9	2

Table 3.

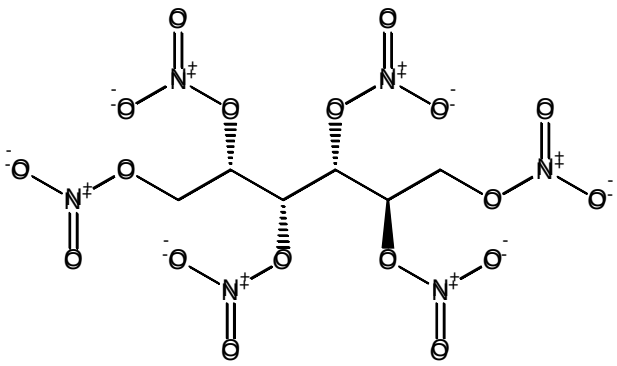
Mass spectral ions and limits of detection for MHN, SHN and XPN.

Analyte	Proposed ion	m/z	Proposed assignment	Relative LOD MS	Collision energy (V)	Product ion assignment	m/z	Relative LOD MSMS
MHN $C_6H_8N_6O_{18}$	$[MHN+Cl]^-$	487	$C_6H_8N_6O_{18}Cl^-$	2	-30	NO_3^-	62	1
	$[MHN-NO_2]^-$	406	$C_6H_8N_5O_{16}^-$	1	-35	NO_3^-	62	8
	$[MHN-HNO_2-HNO_3-2NO_2]^-$	251	$C_6H_7N_2O_9^-$	9	-20	NO_3^-	62	8
	$[MHN-CH_2NO_2]^-$	392	$C_5H_6N_5O_{16}^-$	1	-32	NO_3^-	62	9
	$[MHN-3NO_2]^-$	314	$C_6H_8N_3O_{12}^-$	36	-35	NO_3^-	62	10
	$[MHN-2NO_2+H]^-$	361	$C_6H_9N_4O_{14}^-$	3	-30	NO_3^-	62	20
SHN $C_6H_8N_6O_{18}$	$[SHN+Cl]^-$	487	$C_6H_8N_6O_{18}Cl^-$	12	-30	NO_3^-	62	1
	$[SHN-3NO_2]^-$	314	$C_6H_8N_3O_{12}^-$	7	-35	NO_3^-	62	3
	$[SHN-3NO_2+2H]^-$	316	$C_6H_{10}N_3O_{12}^-$	10	-35	NO_3^-	62	9
	$[SHN-HNO_2-HNO_3-2NO_2]^-$	251	$C_6H_8N_2O_9^-$	8	-20	NO_3^-	62	10
	$[SHN-CH_2NO_2]^-$	392	$C_5H_6N_5O_{16}^-$	1	-32	NO_3^-	62	11
	$[SHN-2NO_2+H]^-$	361	$C_6H_9N_4O_{14}^-$	7	-30	NO_3^-	62	31
	$[SHN-NO_2]^-$	406	$C_6H_8N_5O_{16}^-$	1	-35	NO_3^-	62	72
XPN $C_5H_7N_5O_{15}$	$[XPN-NO_2]^-$	331	$C_5H_7N_4O_{13}^-$	1	-20	NO_3^-	62	1
	$[XPN-CH_2NO_2]^-$	317	$C_4H_5N_4O_{13}^-$	2	-22	NO_3^-	62	1
	$[XPN-2NO_2+H]^-$	286	$C_5H_8N_3O_{11}^-$	5	-20	NO_3^-	62	1
	$[XPN-3NO_2]^-$	239	$C_5H_7N_2O_9^-$	17	-40	NO_3^-	62	5
	$[XPN-HNO_3-3NO_2]^-$	176	$C_5H_6NO_6^-$	43	-20	NO_3^-	62	110
	$[XPN+Cl]^-$	412	$C_5H_7N_5O_{15}Cl^-$	327	-30	NO_3^-	62	520



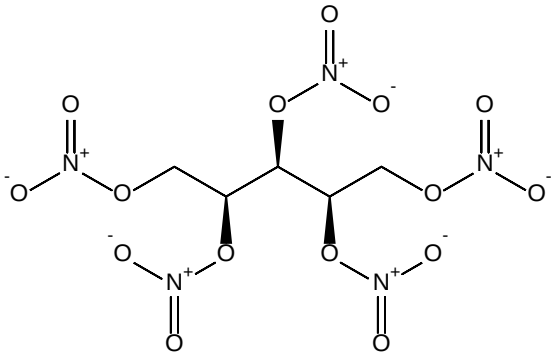
Chemical Formula: $C_6H_8N_6O_{18}$
Exact Mass: 451.990

MHN



Chemical Formula: $C_6H_8N_6O_{18}$
Exact Mass: 451.990

SHN



Chemical Formula: $C_5H_7N_5O_{15}$
Exact Mass: 376.994

XPN

Figure 1. Chemical structures and formulas of the nitrated sugar alcohols.

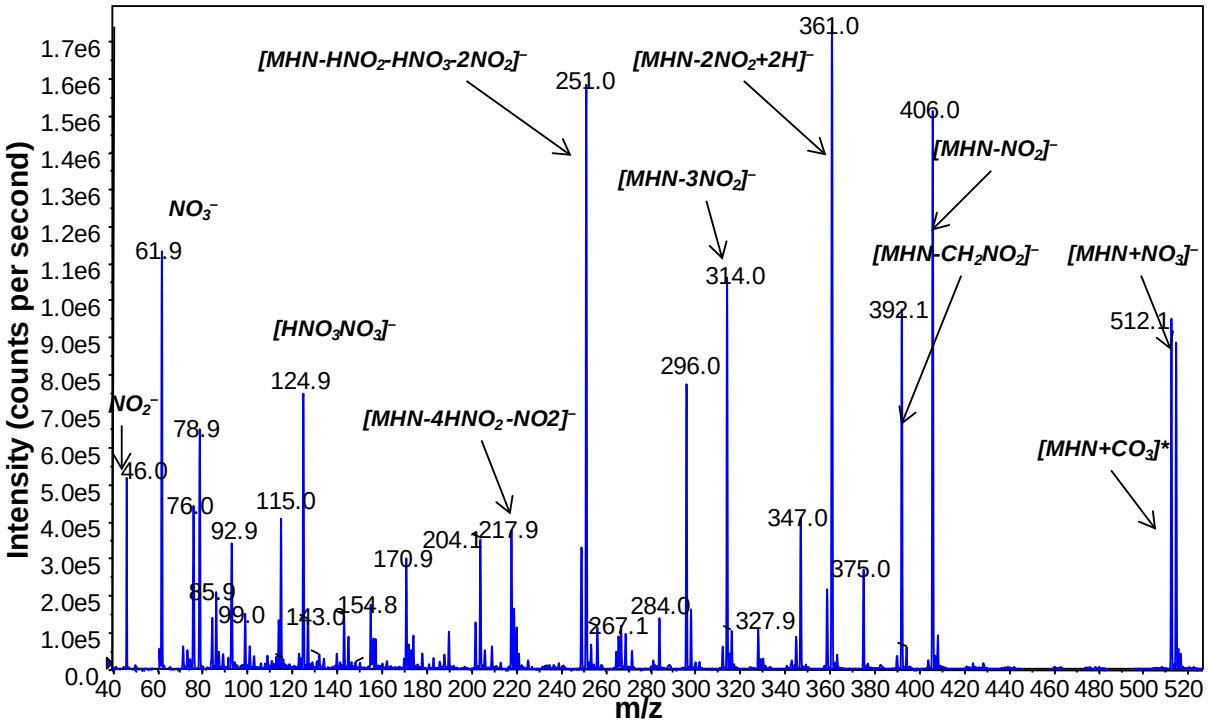


Figure 2(a). Negative-ion APCI mass spectrum of MHN.
* - denotes radical anion.

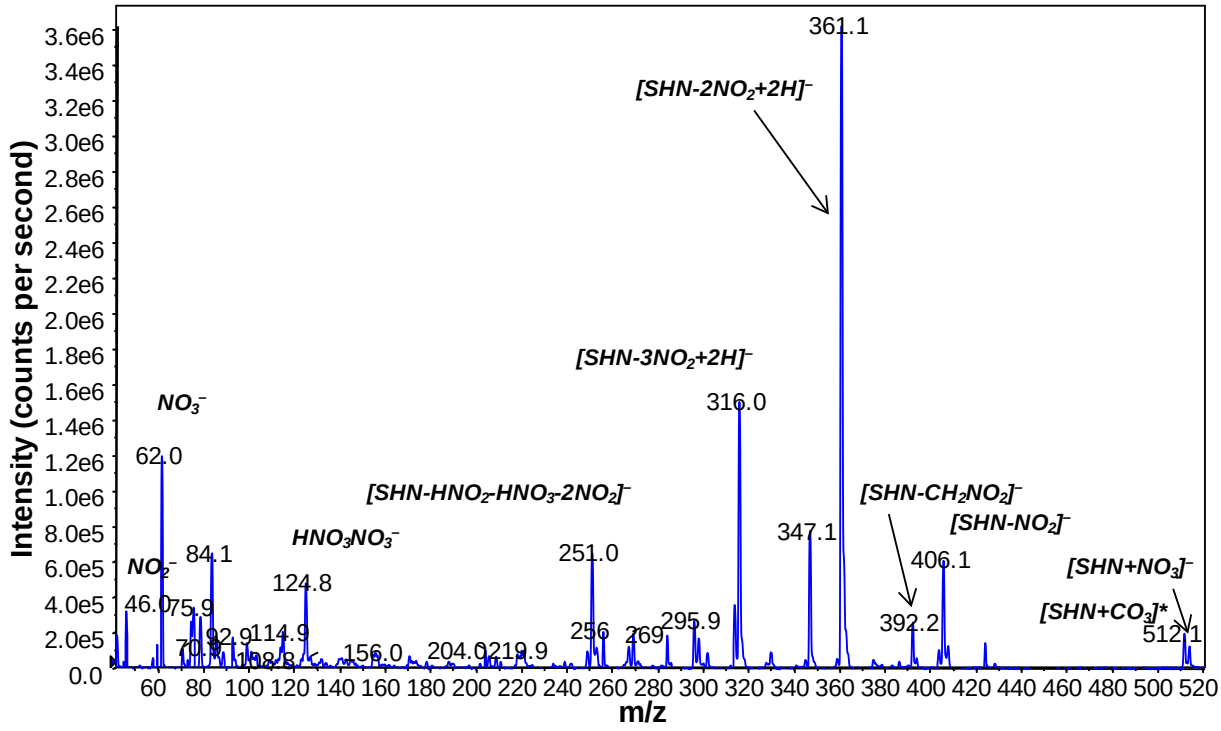


Figure 2(b). Negative-ion APCI mass spectrum of SHN.
* - denotes radical anion.

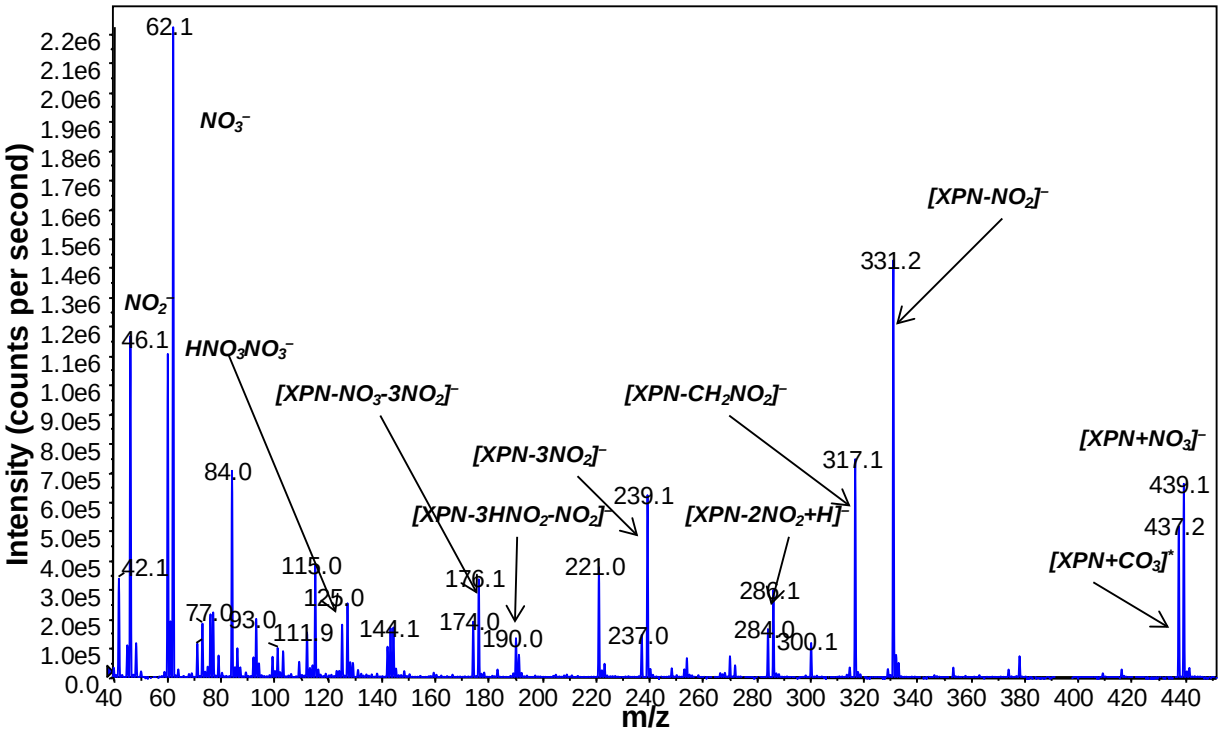
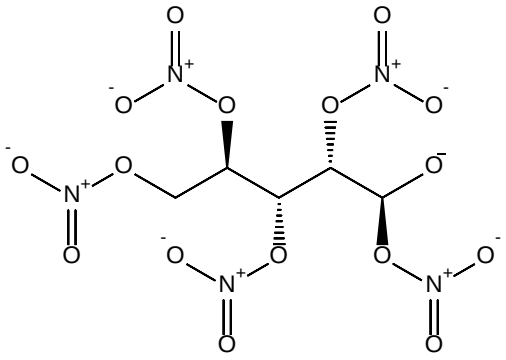
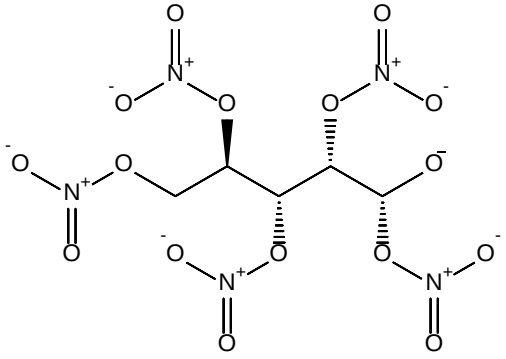


Figure 2(c). Negative-ion APCI mass spectrum of XPN.
* - denotes radical anion.



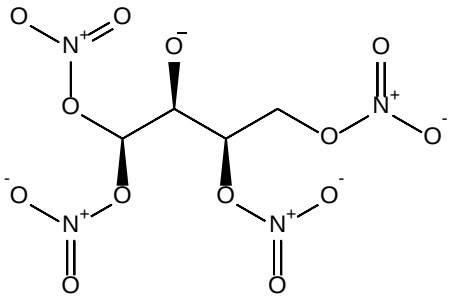
Chemical Formula: $C_5H_6N_5O_{16}^-$
Exact Mass: 391.982

MHN-$CH_2NO_2^-$



Chemical Formula: $C_5H_6N_5O_{16}^-$
Exact Mass: 391.982

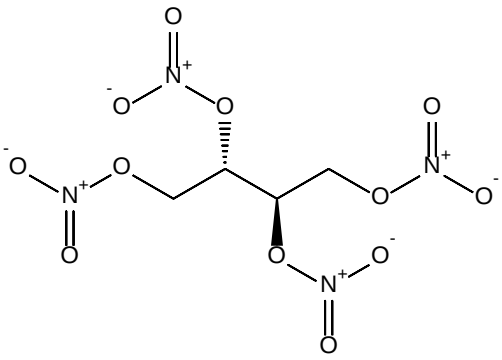
SHN-$CH_2NO_2^-$



Chemical Formula: $C_4H_5N_4O_{13}^-$
Exact Mass: 316.986

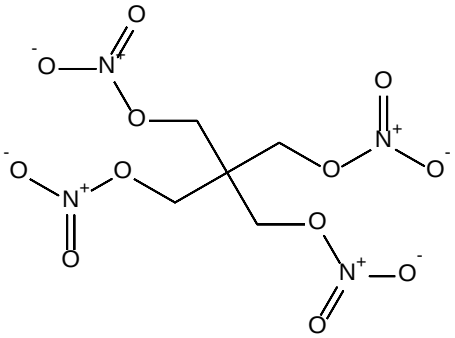
XPN M-$CH_2NO_2^-$

Figure 3. Proposed chemical structures of the M-$CH_2NO_2^-$ ion for MHN, SHN and XPN



Chemical Formula: $C_4H_6N_4O_{12}$
Exact Mass: 301.998

ETN



Chemical Formula: $C_5H_8N_4O_{12}$
Exact Mass: 316.014

PETN

Figure 4. ETN and PETN structures and chemical formulas

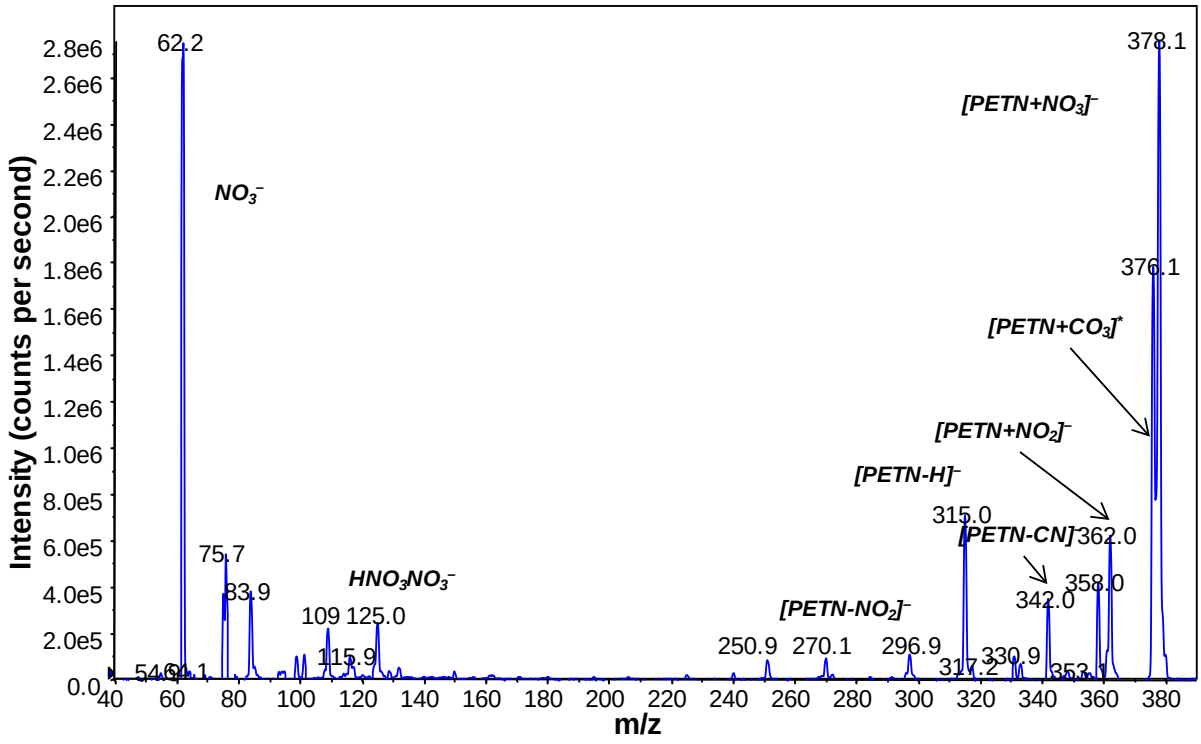


Figure 5. Negative-ion APCI mass spectrum of PETN.
* - denotes radical anion.

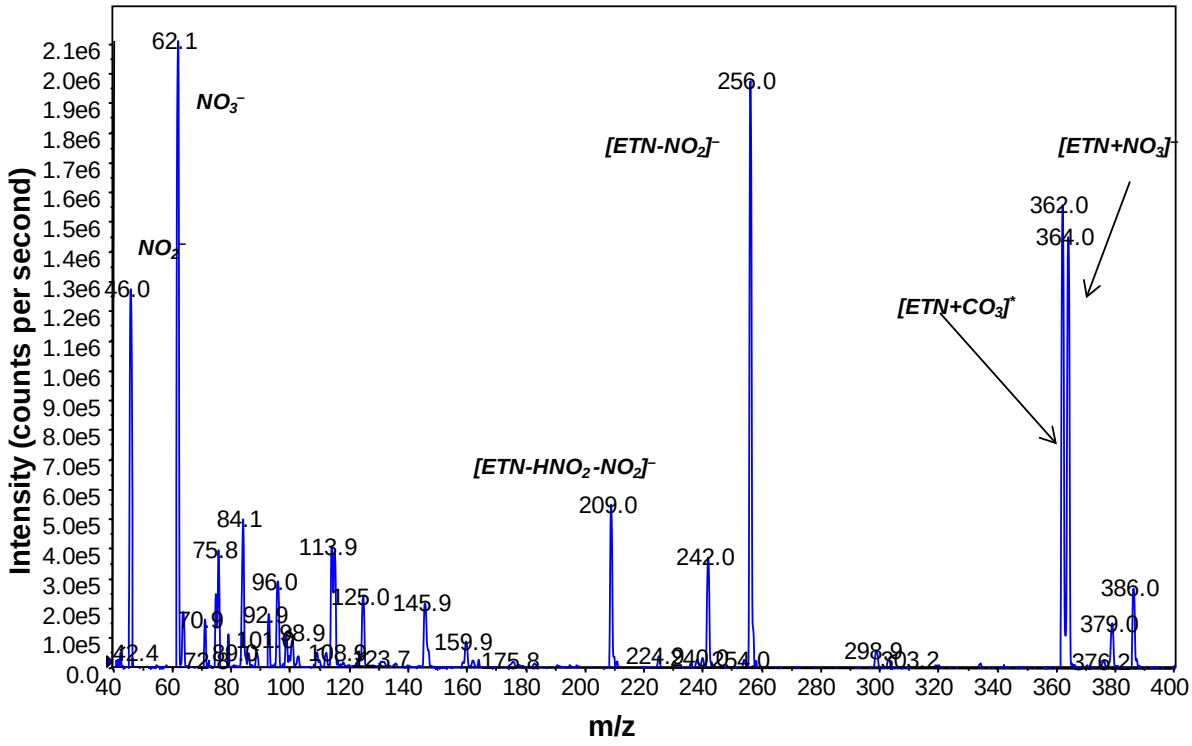


Figure 6. Negative-ion APCI mass spectrum of ETN.
* - denotes radical anion.

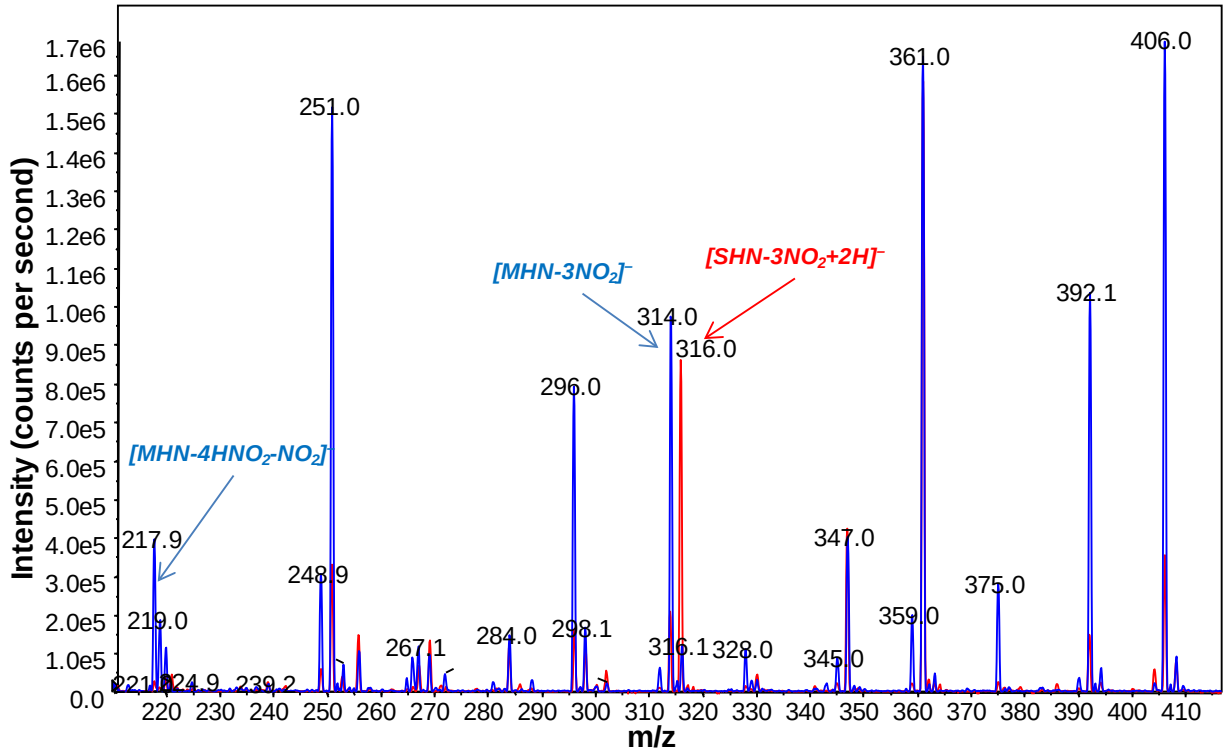


Figure 7. An overlay of the negative-ion APCI spectra of MHN (blue) and SHN (red) showing the main difference between the stereoisomer ions at *m/z* 314, 316 and 218. See Table 2 for a list of the relative abundances.

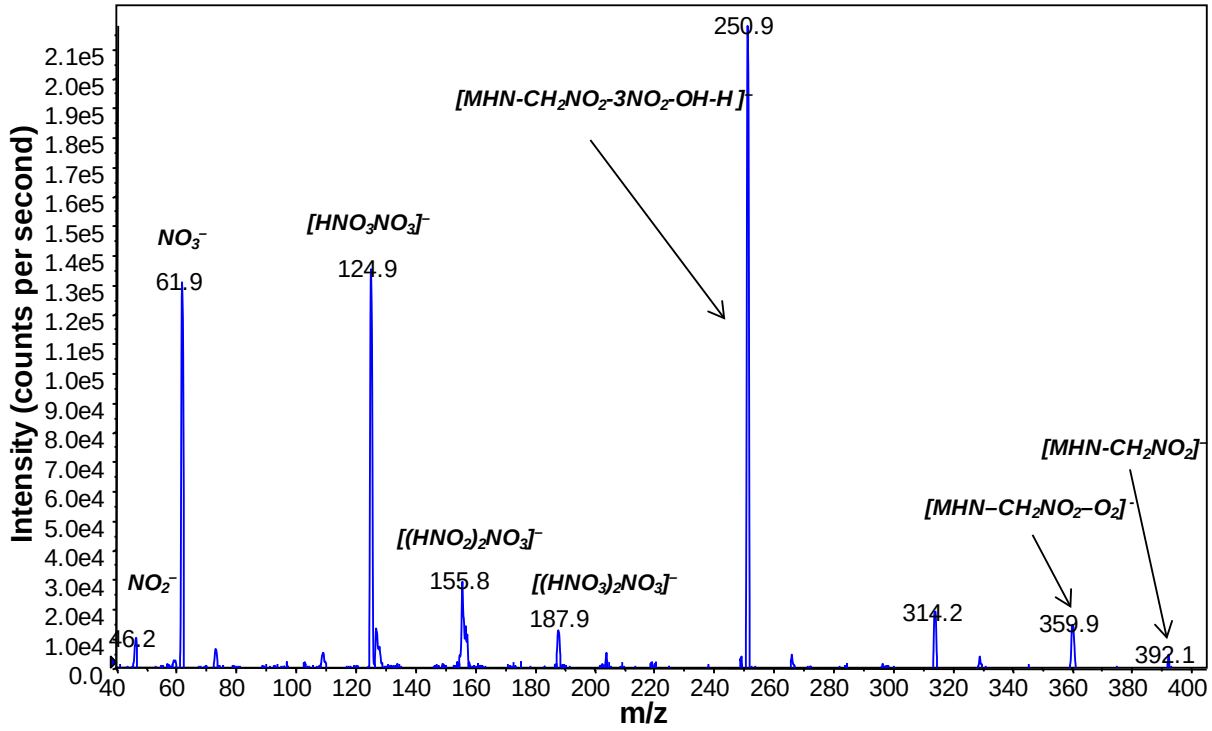


Figure 8. Negative-ion APCI-MSMS product ion scan of $[MHN\text{-}CH_2NO_2]^-$ at *m/z*=392.

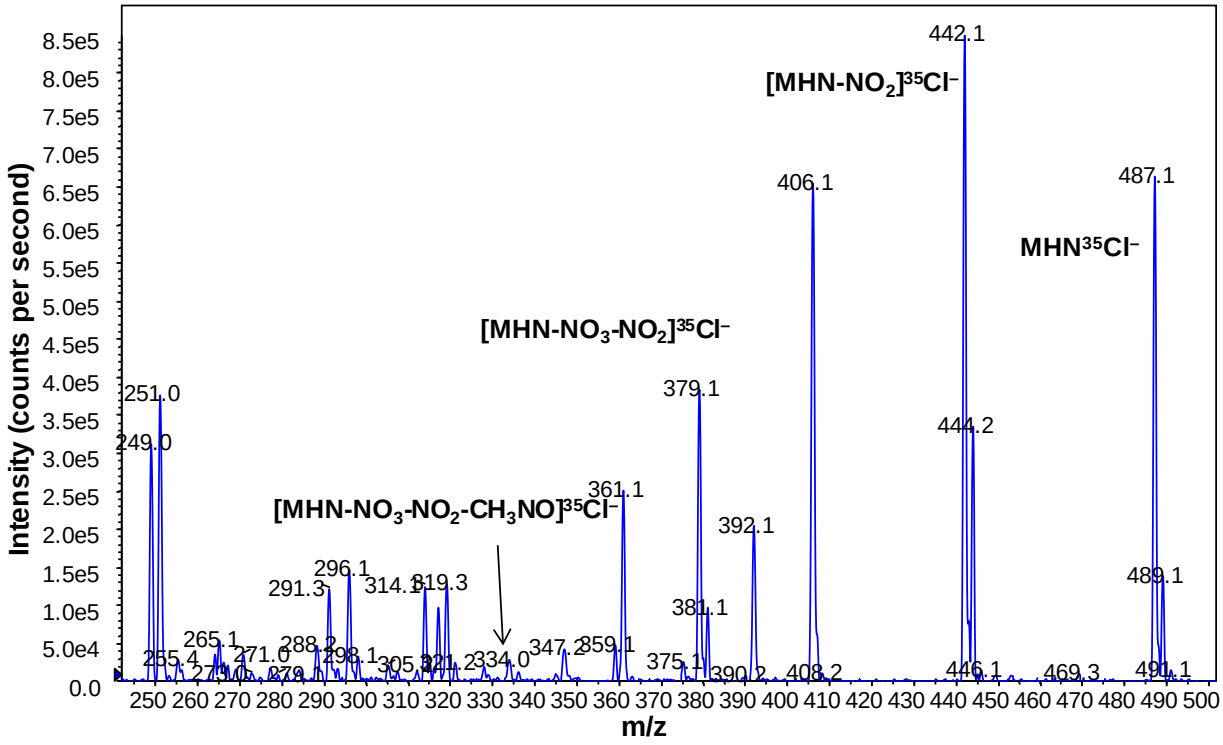


Figure 9. Negative-ion APCI-MS spectrum of MHN in the presence of dichloromethane.

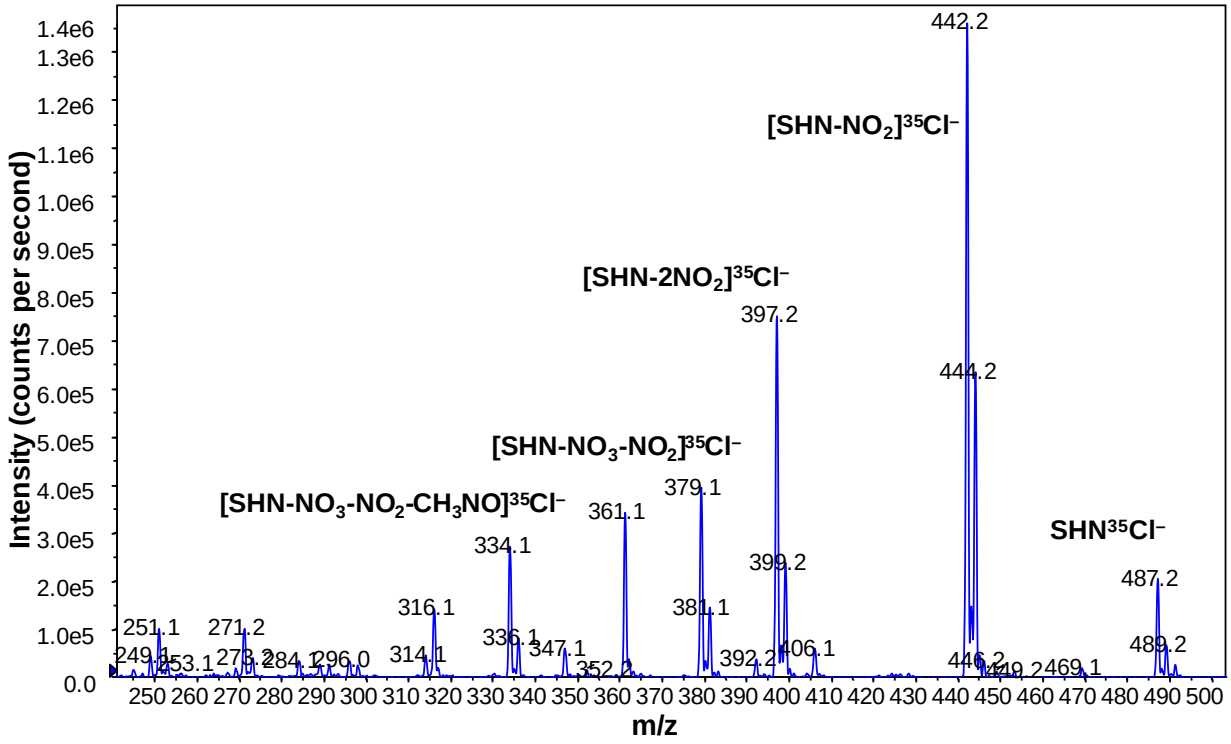


Figure 10. Negative-ion APCI-MS spectrum of SHN in the presence of dichloromethane.

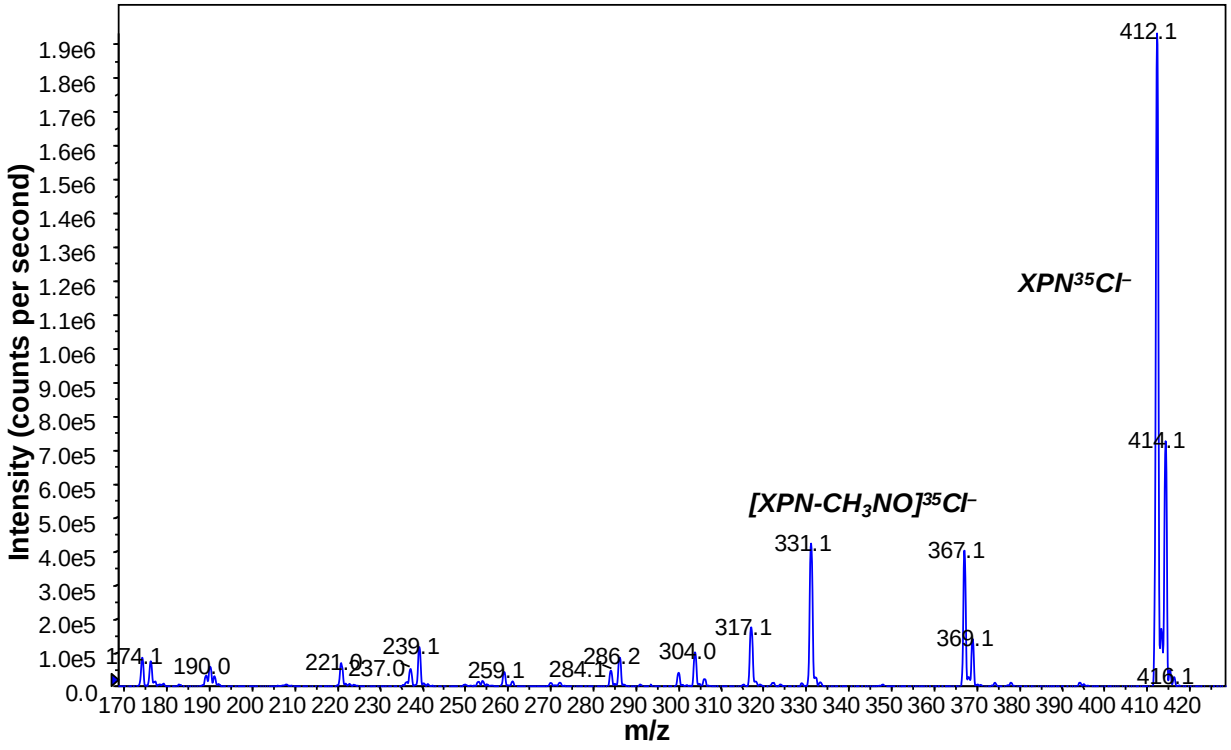


Figure 11. Negative-ion APCI-MS spectrum of XPN in the presence of dichloromethane.

SUPPLEMENTAL INFORMATION

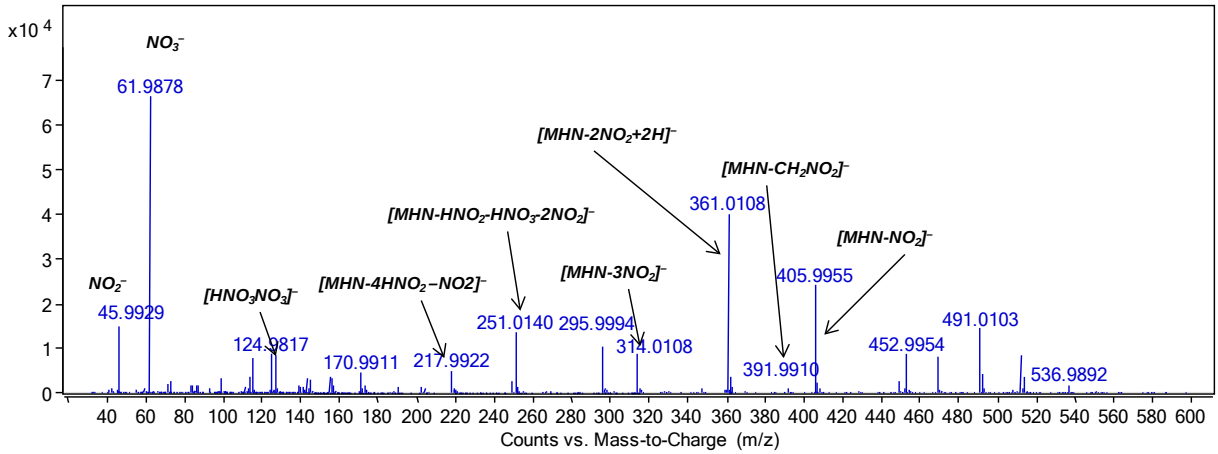


Figure S1(a). Negative-ion APCI TOF MS spectrum of MHN.

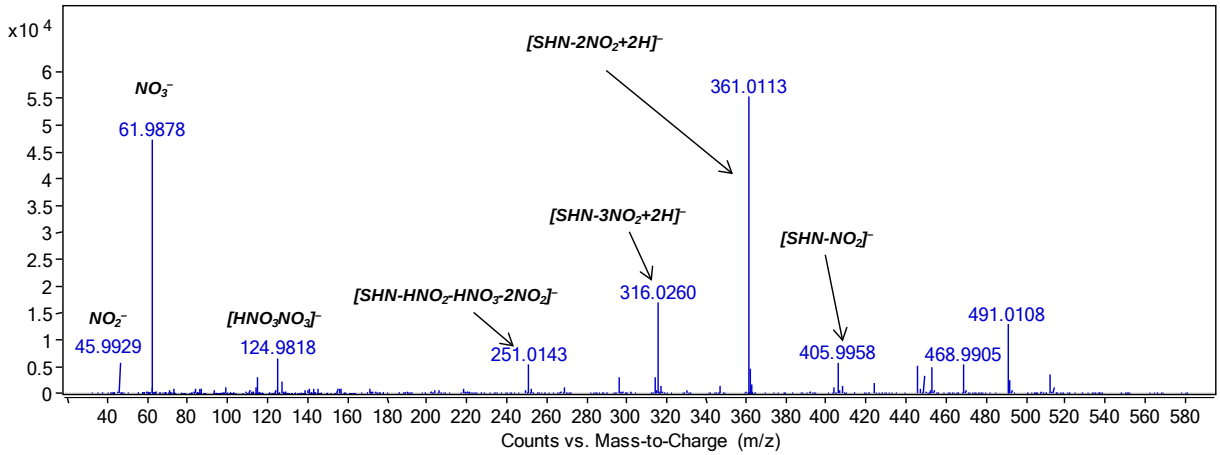


Figure S1(b). Negative-ion APCI TOF MS spectrum of SHN.

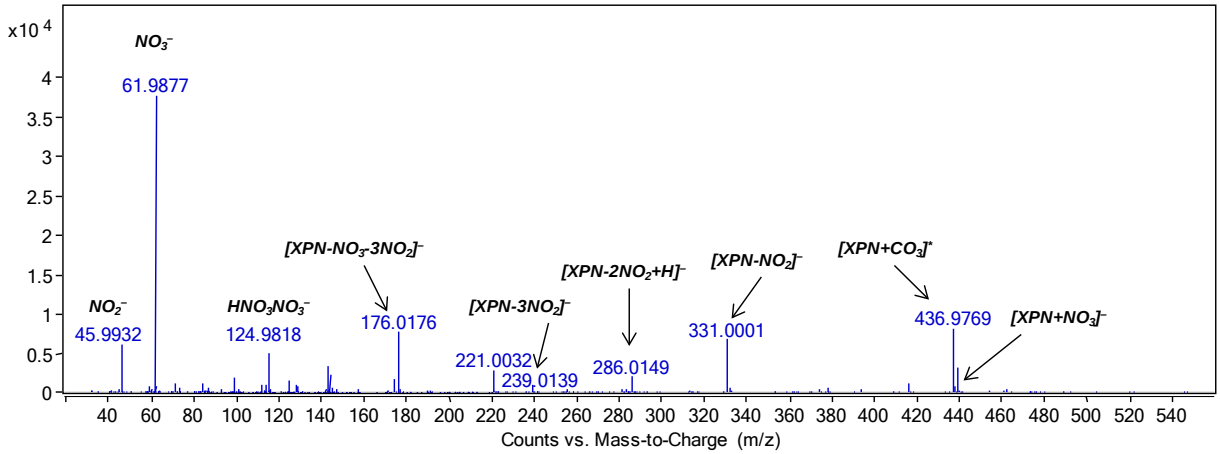


Figure S1(c). Negative-ion APCI TOF MS spectrum of XPN.
* - denotes radical anion.

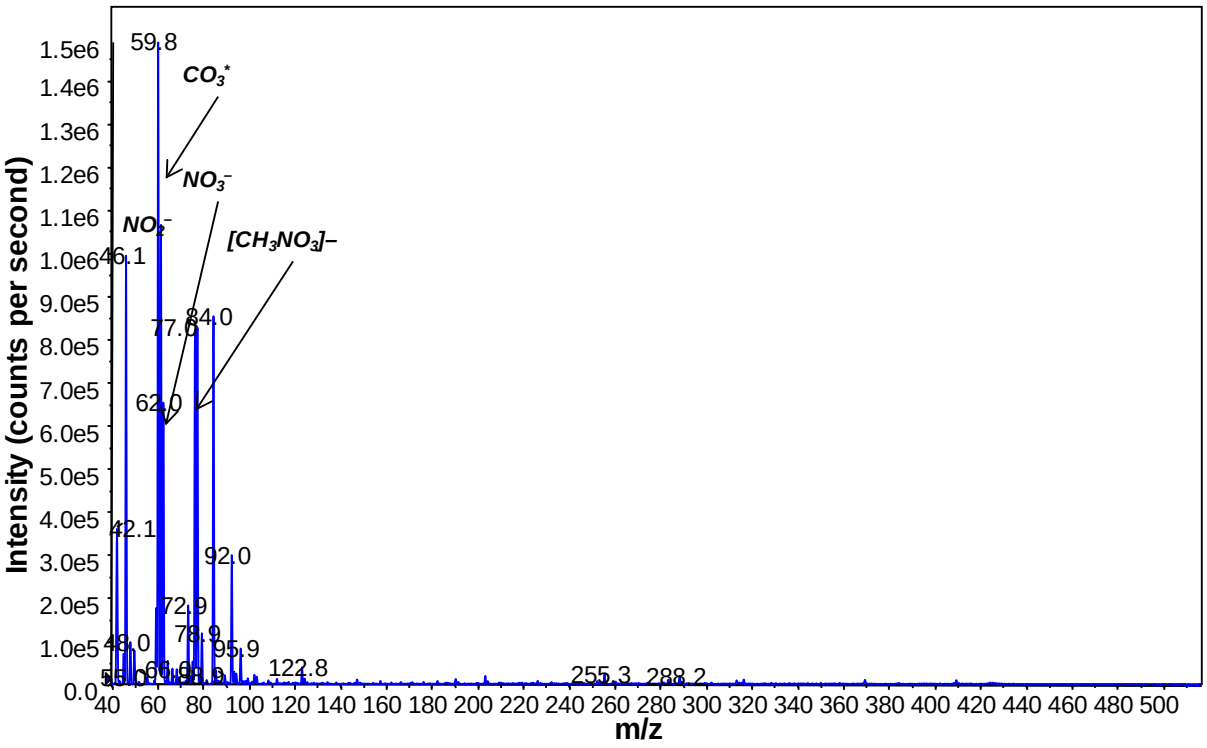
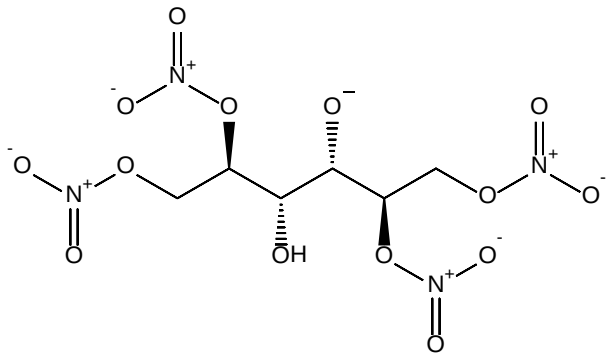
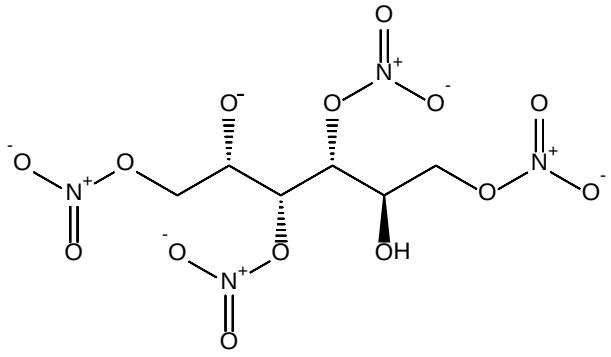


Figure S2. Negative-ion APCI-MS spectrum of acetonitrile.



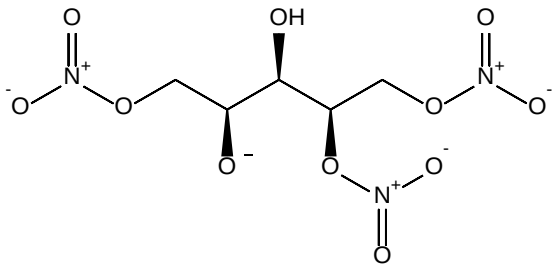
Chemical Formula: $C_6H_9N_4O_{14}^-$
Exact Mass: 361.01

MHN $[M-2NO_2+H]^-$ fragment ion.



Chemical Formula: $C_6H_9N_4O_{14}^-$
Exact Mass: 361.012

SHN $[M-2NO_2+H]^-$ fragment ion.



Chemical Formula: $C_5H_8N_3O_{11}^-$
Exact Mass: 286.016

XPN $[M-2NO_2+H]^-$ fragment ion.

Figure S3. Proposed chemical structures for the $[M-2NO2+H]^-$ ions of MHN, SHN and XPN.

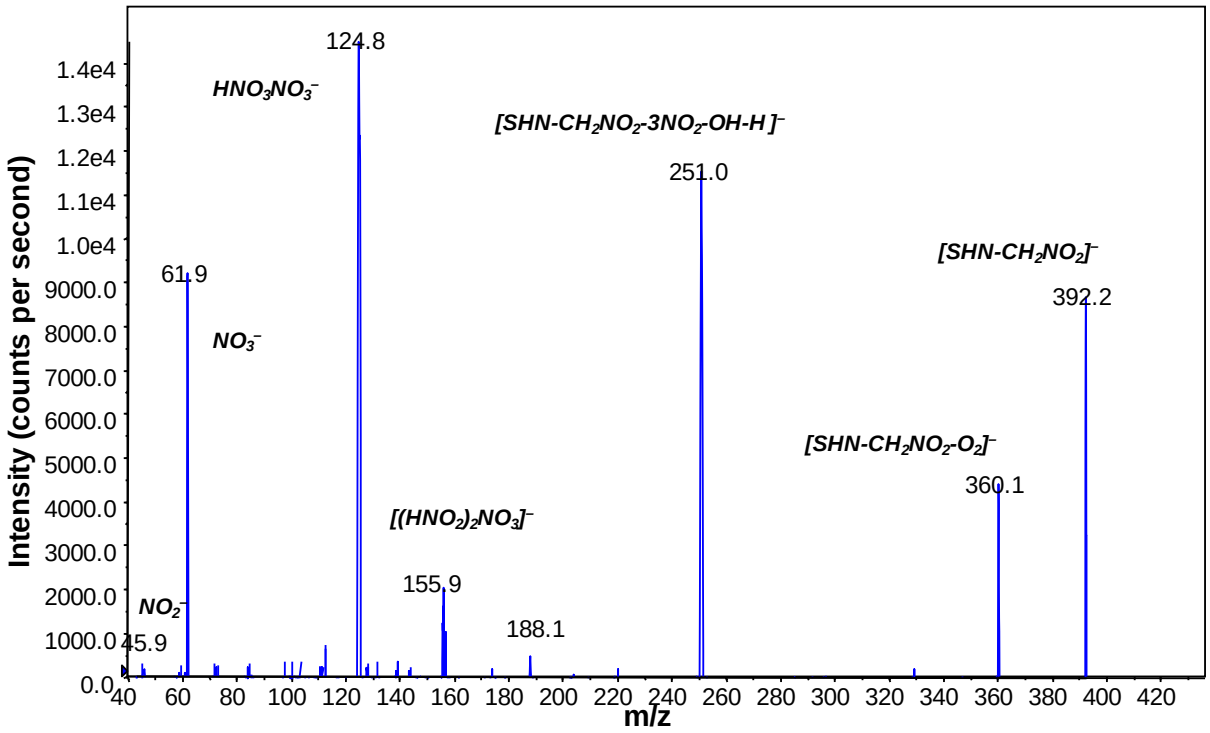


Figure S4. Negative-ion APCI-MSMS product ion scan of $[SHN\text{-}CH_2NO_2]^-$ at *m/z*=392.

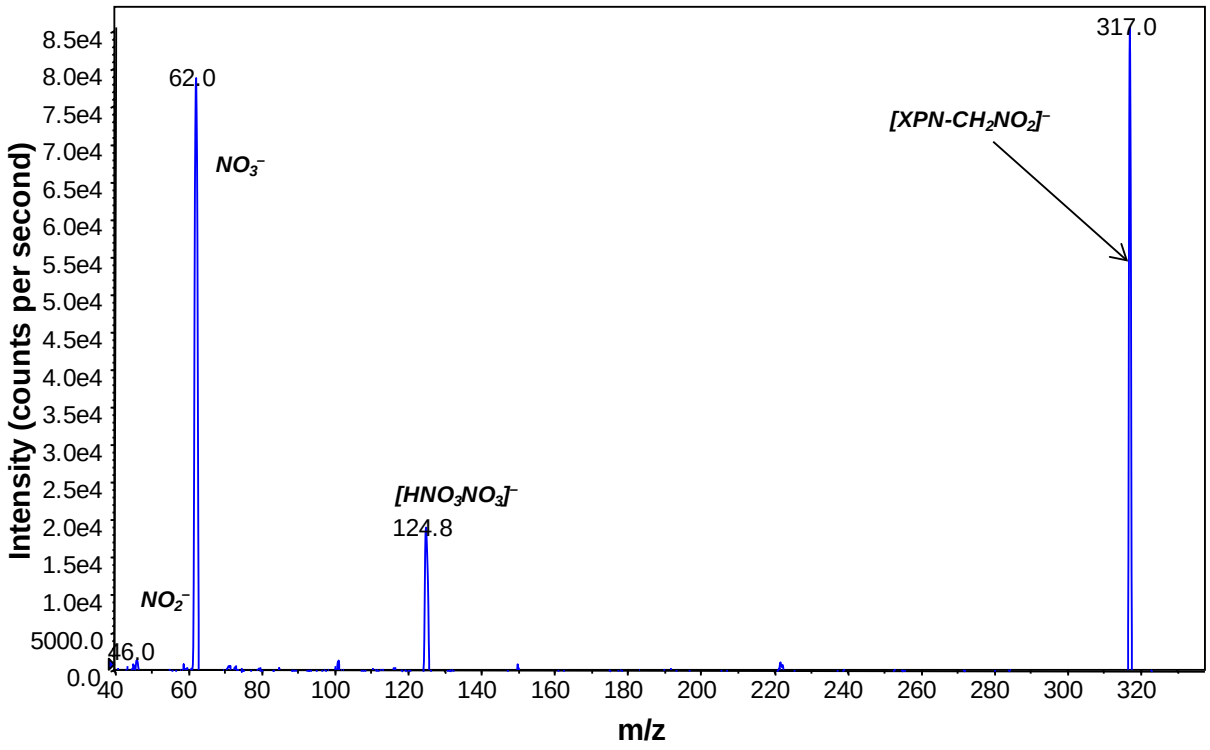


Figure S5. Negative-ion APCI-MSMS product ion scan of $[XPN\text{-}CH_2NO_2]^-$ at *m/z*=317.