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Investigation of the Impurities in Erythritol Tetranitrate (ETN) Using Ultrahigh Pressure Liquid Chromatography with Quadrupole Time of Flight Mass Spectrometry

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Abstract: In order to further gain a comprehensive chemical understanding of erythritol tetranitrate (ETN), the synthesis impurities of ETN were investigated using ultrahigh performance liquid chromatography with tandem high resolution mass spectrometry (UHPLC-MS/MS). A total of 12 impurities were identified relating to the synthesis of ETN. We have synthesized pure analytical standards of erythritol-1,4-dinitrate (1,4-EDiN) and erythritol-1,2,4-trinitrate (1,2,4-ETriN). These isomerically pure standards have allowed for confirmation of the identity of some of the discovered impurities. Additionally, partially nitrated with sulfate substituted erythritol was identified which is theorized to have formed from the incomplete displacement of the formed sulfate group on the alcohol position during nitration.

Keywords: Erythritol Tetranitrate, ETN, Homemade explosives, UHPLC

1 Introduction

Erythritol tetranitrate (ETN) is a powerful melt-castable explosive which can be easily synthesized using widely available chemical precursors, making it a potential threat as a homemade explosive. While ETN has been known for well over a century (discovered by Stenhouse in 1849 [1]), it was not until recently that significant attention was given to ETN (compared to other HMEs) due to the lack in availability of the erythritol starting material. The increase in attention ETN has received can be attributed to the now ubiquitous nature of erythritol as an artificial sweetener, owing to the modern inexpensive production methods via microbial conversion of starch from corn to glucose which can be fermented to form erythritol [2]. As a close cousin to the very common explosive pentaerythritol tetranitrate (PETN), ETN has high explosive performance properties like that of PETN, but is melt-castable and has a slightly positive oxygen balance [3–6]. Numerous web pages and videos exist on the internet that give detailed information on the synthesis of ETN. The synthesis of ETN is straightforward requiring only erythritol, concentrated sulfuric acid and nitric acid or a nitrate salt. Belonging to the nitrate ester family, ETN also has applications as a vasodilator, similar to nitroglycerin [7,8].

There are several recent reports on the analytical characterization of ETN via HPLC-MS, GC-MS, DART-MS, and Raman spectroscopy [9–11]. However, all of these reports focused on the detection and identification of ETN. Work by Oxley *et al.* using direct injection MS and HPLC-MS identified ETN as well as the presence of two impurities, erythritol trinitrate (ETriN) and erythritol dinitrate (EDiN), which are partially nitrated

products formed during the synthesis of ETN [12]. Recent work by our group investigated the impurities present from the synthesis of ETN using HPLC-UV/Vis in an attempt to correlate the synthesis impurities to the precursors used in the synthesis [13]. Similar work was performed by Bezemer *et al.* using HPLC-MS to investigate the relationship of partially nitrated erythritol impurities to precursors used in the synthesis of ETN [14]. An outcome of our work and Bezemer *et al.* was the realization that there exists no comprehensive chemical evaluation of ETN. Herein we investigate the synthesis impurities of ETN using UHPLC coupled to high resolution tandem mass spectrometry (MS/MS) as a means to gain a further understanding of the chemical composition of ETN. Furthermore, we have synthesized isomerically pure standards of erythritol dinitrate (EDiN) and erythritol trinitrate (ETriN) allowing for confirmation of these detected impurities.

2 Experimental Section

General

CAUTION: Erythritol tetranitrate (ETN) is a very sensitive and dangerous explosive that has been involved in several recent explosives accidents [15]. It should only be prepared and handled in an explosives

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facility by trained personnel. Although we have not experienced any problems in handling the other materials described in this paper, they are sensitive to various stimuli and should be handled with care, implementing standard safety procedures for handling energetic and explosive materials.

NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at ambient temperature. Chemical shifts were referenced to the residual solvent signal. Melting point and thermal decomposition temperatures were measured by DSC (TA Instruments Q2000 DSC) in hermetically sealed aluminum pans that contain a pinhole lid. A typical analysis utilizes approximately 1 mg of sample with 50 mL/min ultrahigh purity nitrogen purge gas at a thermal ramp rate of 10 °C/min. Unless otherwise noted, all starting materials were obtained from commercial sources and used as received. Sulfuric acid (98%, Certified ACS Plus), nitric acid (70%, Certified ACS Plus), and ammonium nitrate (Certified ACS) were obtained from Fischer Scientific for synthesis of ETN. Acetonitrile (HPLC Plus) and methanol (HPLC Plus) from Sigma-Aldrich were used for UHPLC. Ammonium acetate from VWR was diluted to 10 mM using deionized water obtained from Fischer Scientific prior to use in UHPLC.

Synthesis of erythritol tetranitrate (ETN). ETN was synthesized according to the literature procedure previously reported by Freye *et al* [13]. Ammonium nitrate (1.39 g, 17.4 mmol) was dissolved in 98% H₂SO₄ (5 mL) and the solution was cooled in an ice bath. Erythritol (2.1 g, 17.2 mmol) was slowly added to the solution. The solution was kept at ~15 °C during the addition. After stirring for ~1 h, the solution was poured into ice water (50 mL). The resulting white precipitate was filtered and washed with an aqueous saturated sodium bicarbonate solution (3 x 20 mL) and with DI water (3 x 20 mL). The resulting white powder was then stored in a desiccator until analyzed via UHPLC-MS/MS.

Synthesis of erythritol-1,2,4-trinitrate (1,2,4-ETriN). 1,4-dioxane (32 mL) and ethanol (32 mL) were added to a flask charged with erythritol tetranitrate (ETN, 3.99 g, 13.2 mmol). This mixture was heated with stirring to fully dissolve the ETN. A solution of hydrazine monohydrate (670.5 mg, 13.39 mmol) in DI water (16 mL) was then added and the reaction was refluxed for 4 h and allowed to cool to room temperature. Deionized water (50 mL) was added and the reaction was extracted with dichloromethane (3 x 50 mL). The organic fraction was dried with magnesium sulfate, filtered and the solvent was removed to yield a yellow oil (crude ETriN). This yellow oil was purified by column chromatography on silica gel using 30% EtOAc in hexane as eluent. The resulting pale yellow oil was recrystallized by storage of a dichloromethane (25 mL) solution layered with hexane (25 mL) in a freezer for 18 h. The white solid was isolated by decanting off the supernatant and drying *in vacuo* (2.16 g, 64% yield). Anal. Calc'd for C₄H₇N₃O₁₀ (257.11 g/mol); C 18.44 (calc. 18.69); H 2.69 (2.74); N 16.38 (16.34)%. ¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ 6.24 (d, *J* = 6.1 Hz, 1H,

OH), 5.46 – 5.39 (m, 1H, CH), 5.04 (dd, *J* = 13.0, 2.5 Hz, 1H, CHH), 4.79 (dd, *J* = 13.0, 6.6 Hz, 1H, , CHH), 4.70 (dd, *J* = 11.7, 4.0 Hz, 1H, , CHH), 4.58 (dd, *J* = 11.8, 6.5 Hz, 1H, , CHH), 4.17 (qd, *J* = 6.1, 3.9 Hz, 1H, CH). ¹³C NMR (101 MHz, DMSO-d₆, 25 °C): δ 79.38 (s, 1C), 73.23 (s, 1C), 69.62 (s, 1C), 64.94 (s, 1C). TLC (30% EtOAc in hexane): R_f = 0.54. DSC (°C): M.P. = 47.66, T_{dec} = 160.09, T_{peak} = 203.89.

Synthesis of erythritol-1,4-dinitrate (1,4-EDiN). 1,4-dioxane (32 mL) and ethanol (32 mL) were added to a flask charged with erythritol tetranitrate (ETN, 4.0105 g, 13.27 mmol). This mixture was heated with stirring to fully dissolve the ETN. A solution of hydrazine monohydrate (2.6715 g, 53.37 mmol) in DI water (16 mL) was then added and the reaction was refluxed for 4 h and allowed to cool to room temperature. Deionized water (100 mL) was added and the reaction was extracted with ethyl acetate (3 x 75 mL). The organic fraction was dried with magnesium sulfate, filtered and the solvent was removed to yield a yellow stained solid (2.8 g, crude EDiN). This solid was recrystallized by dissolving in EtOH (20 mL), filtration of the EtOH solution, addition of deionized water (60 mL) and subsequent concentration of the solution by gently blowing air over the surface to precipitate white blocks over the course of 2 d. The white solid was isolated by decanting off the supernatant and drying *in vacuo* (496 mg, 18% yield). Additional product of less purity can be collected from the supernatant upon further concentration. Anal. Calc'd for C₄H₈N₂O₈ (212.11 g/mol); C 22.27 (calc. 22.65); H 3.86 (3.80); N 13.17 (13.21)%. ¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ 5.64 (d, *J* = 5.8 Hz, 2H, OH), 4.73 (dd, *J* = 11.2, 2.1 Hz, 2H, CHH), 4.49 (dd, *J* = 11.4, 6.3 Hz, 2H, CHH), 3.76 – 3.66 (m, 2H, CH). ¹³C NMR (101 MHz, DMSO-d₆, 25 °C): δ 75.15 (s, 2C), 67.97 (s, 2C). TLC (30% EtOAc in hexane): R_f = 0.28. DSC (°C): M.P. = 88.55, T_{dec} = 167.54, T_{peak} = 210.65.

UHPLC-MS/MS Analysis

ETN samples were prepared by dissolving ~25 mg of ETN in 2.5 mL of methanol and the samples were run in duplicate. The analytical standards of ETN, ETriN and EDiN samples were prepared in an identical method with ~25 mg of sample in 2.5 mL of methanol. The samples were prepared at relatively high concentrations to ensure acquired tandem MS/MS spectra were obtained with minimal noise. All samples were evaluated using a Shimadzu UHPLC system (Shimadzu, Japan) coupled to a SCIEX X500R QTOF (SCIEX, Framingham, MA, USA). The UHPLC system consisted of two binary pumps (LC30-AD), degasser (DGU-30A), column oven (CTO-30A), autosampler (SIL-30A), and UV-Vis detector (SPD-30A). The UV-Vis detector collected from 200-700 nm with a slit width of 8 nm at a rate of 6.25 Hz. The QTOF system was equipped with an electrospray ionization source (ESI) that operated in the negative mode. The ESI conditions were as following: ionspray voltage -4.5 kV, temperature 300 °C, ion source gas #1 80 psi, ion source gas #2 80 psi. The CAD gas was set to 9 a.u.

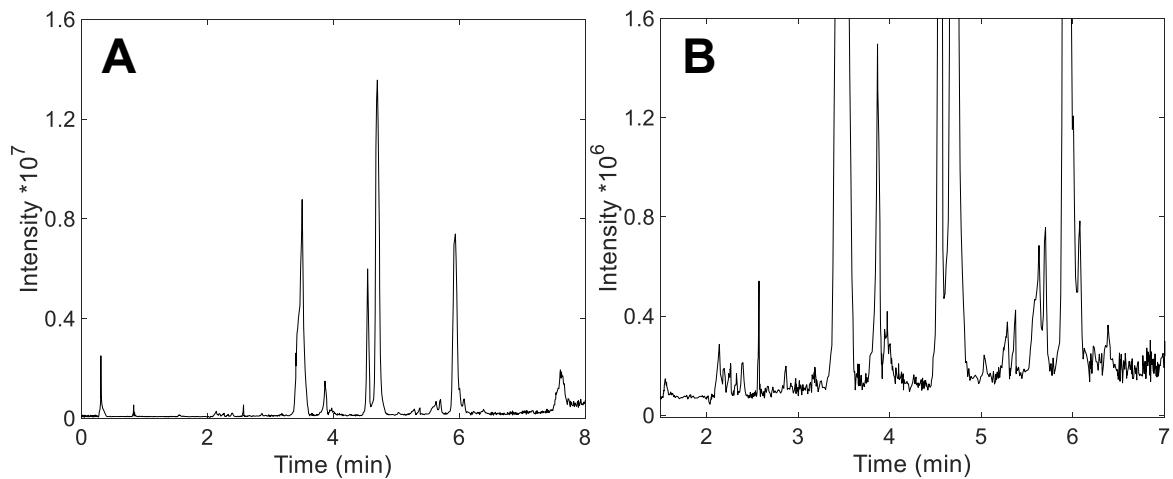


Figure 1: (A) Analytical ion chromatogram shown for the analysis of ETN. (B) Zoom-in of A showing the numerous small impurities present in ETN.

and the declustering potential was -80 V. The instrument was operated in IDA mode, which first collects TOFMS data before selecting specific parent ions to subsequently undergo fragmentation (i.e. MS/MS). In TOFMS mode, mass channels were collected from 100-1000 at an accumulation time of 0.1 seconds. The top 5 ions from each TOFMS scan were selected to undergo fragmentation with the requirement that the intensity threshold exceed 10 counts/second. The quadrupole was set to filter the selected parent ions at unit resolution. For MS/MS mode, mass channels 40-1000 were collected at an accumulation time of 0.1 seconds. The collision energy was set to -15 V with a spread of 10 V. Separations were carried out on a Phenomenex (Torrence, CA, USA) Kinetex C₁₈ column (100 mm × 3.0 mm, 1.7 μ m). The injection volume was 1 μ L, and the column oven was set to 40 °C with a flow rate of 1.0 mL/min. The mobile phase composition consisted of 10 mM ammonium acetate (A) and acetonitrile (B). The gradient program was: 0 min, isocratic at 0% B; 0-10 min, linear gradient to 100% B; 10-15 min isocratic at 100% B. The LC-UV/Vis-QTOF system was controlled by SCIEX OS 1.6.1 software, the data and subsequent data processing was performed using this same software.

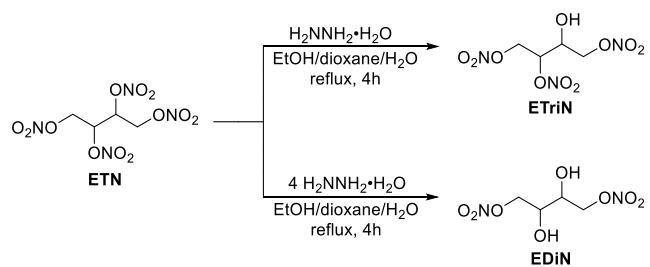
3 Results and Discussion

The analytical ion current (AIC) (e.g. selected mass channels, m/z, to highlight certain compounds) LC-MS chromatogram is shown in Fig. 1A with a zoom-in provided in Fig. 1B. Visual evaluation of Fig. 1 indicates there are numerous impurities present in the synthesized ETN with a wide range of concentrations. ETN elutes at 5.93 minutes. The three isomers of dinitrated species, EDiN, elute at 2.14, 2.38, and 2.74 minutes while the two isomers of trinitrated species, ETriN, elute at 4.51 and 4.68 minutes. Using the peak finding algorithm native to SCIEX OS, a total of 70 different chemical species were proposed. However, as shown below, some of these identified peaks are of isomers that co-elute resulting in a lower number of discovered peaks than are truly in the sample. Moreover, many of the chemical formulas for the

discovered peaks were not identified and thus were subsequently excluded. Table 1 lists all of the discovered impurities listed in order of retention time, t_R . The detected m/z, adduct, true m/z, chemical formula, and chemical nomenclature are included. The chemical formula and subsequent structure were determined by comparing the isotopic ratio of the parent ion and the MS/MS fragmentation, which is automatically performed by the SCIEX OS software. Because the QTOF was operated in negative mode, adducts of [M-H]⁻ and [M+CH₃COO]⁻ were observed but the most common adduct was NO₃⁻. It is believed that this adduct is generated by removal of a nitrate group from a molecule of the chemical species (ETN or ETN impurities) which is subsequently donated to another molecule providing a [M+NO₃]⁻ adduct. In order to confirm the identity of the impurities detected in ETN, ETriN and EDiN standards were independently synthesized by the denitration of ETN with hydrazine, inspired by a previously published procedure for the reduction of pentaerythritol tetranitrate to pentaerythritol trinitrate and pentaerythritol dinitrate [16].

Thus, 1 equiv. of hydrazine monohydrate in H₂O was added to a solution of ETN in a mixture of 1,4-dioxane and ethanol. After 4h of reflux, ETriN was isolated from the reaction and purified to yield a white solid in 64% yield. Similarly, 4 equiv. of hydrazine monohydrate in H₂O was added to a solution of ETN in a mixture of 1,4-dioxane and ethanol (Scheme 1).

Scheme 1. Syntheses of ETriN and EDiN from ETN.



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Retention Time (min)	Detected Mass	Proposed Adduct	Actual Mass	Tentative Formula	Nomenclature
1.28	290.9778	[M-H]-	291.9856	$C_4H_8N_2SO_{11}$	EDiNSulf
1.72	290.9778	[M-H]-	291.9856	$C_4H_8N_2SO_{11}$	EDiNSulf
1.78	290.9778	[M-H]-	291.9856	$C_4H_8N_2SO_{11}$	EDiNSulf
1.96	290.9778	[M-H]-	291.9856	$C_4H_8N_2SO_{11}$	EDiNSulf
2.04	290.9778	[M-H]-	291.9856	$C_4H_8N_2SO_{11}$	EDiNSulf
2.14	211.0208	[M-H]-			
	246.998	[M+Cl]-			
	271.0422	[M+AcO-H]-	212.0208	$C_4H_8N_2O_8$	1,4-EDiN
	274.0166	[M+NO ₃]-			
	423.049	[2M-H]-			
2.38	211.0208	[M-H]-			
	246.998	[M+Cl]-			
	271.0422	[M+AcO-H]-	212.0208	$C_4H_8N_2O_8$	EDiN
	274.0166	[M+NO ₃]-			
	423.049	[2M-H]-			
2.74	211.0208	[M-H]-			
	246.998	[M+Cl]-			
	271.0422	[M+AcO-H]-	212.0208	$C_4H_8N_2O_8$	EDiN
	274.0166	[M+NO ₃]-			
	423.049	[2M-H]-			
3.03	335.9627	[M-H]-	336.9705	$C_4H_7N_3SO_{13}$	ETriNSulf
3.07	335.9627	[M-H]-	336.9705	$C_4H_7N_3SO_{13}$	ETriNSulf
4.51	256.0062	[M-H]-			
	291.9836	[M+Cl]-	257.01311	$C_4H_7N_3O_{10}$	1,2,3-ETriN
	316.0276	[M+AcO-H]-			
4.68	256.0062	[M-H]-			
	291.9836	[M+Cl]-	257.01311	$C_4H_7N_3O_{10}$	1,2,4-ETriN
	316.0276	[M+AcO-H]-			
5.93	363.9867	[M+NO ₃]-	301.9982	$C_4N_4O_{12}H_6$	ETN

Table 1: List of the discovered impurities listed in order of retention time, t_R . The detected mass, proposed adduct, actual m/z, chemical formula, and chemical nomenclature are included.

After 4 h of reflux, EDiN was isolated from the reaction and purified to yield a white solid in 18% yield. The ETriN and EDiN were evaluated via NMR to determine their isomeric confirmations and were subsequently analyzed via UHPLC-MS/MS to determine their retention times and MS/MS fragmentation patterns.

In order to highlight some of the more interesting chemical compounds identified, Figures 2A-D have been prepared. Figure 2A shows the isomeric series for EDiN at m/z 274.0116. Due to our standards, we were able to confirm that the peak at 2.14 minutes is the erythritol-1,4-dinitrate isomer. Figure 2B shows the isomeric series for ETriN at m/z 319.0016. Again due to our standards, we were able to confirm that the peak at 4.51 minutes is the erythritol-1,2,3-trinitrate isomer and the peak at 4.68 minutes is the erythritol-1,2,4-trinitrate isomer. Figure 2C shows the isomeric series for EDiNSulfate (erythritol-dinitrate-sulfate) detected at m/z 290.9778 and Figure 2D shows the isomeric series for ETriNSulfate (erythritol-trinitrate-sulfate) at m/z 335.9627. The formation of nitrate esters is generally thought to occur via electrophilic substitution of the nitronium ion NO_2^+ (nitryl cation), with the presence of sulfuric acid favoring esterification and increasing the concentration of the NO_2^+ ion. We believe the reason these sulfate ETN derivatives are present is due to the

incomplete displacement of the formed sulfate group on the alcohol position during nitration [17]. However, the EMonSulf (erythritol-nitrate-sulfate) as well as the EMoN (erythritol-nitrate) species were never discovered in our investigations.

The MS/MS spectra for four ETN synthesis impurities are presented in Fig. 3A-D with the MS/MS spectra of the standards included for two of the impurities. For the EDiN MS/MS spectrum, Fig 3A respectively, the MS/MS spectrum is very simple showing the presence of the parent ion and hydrocarbon backbone (C_4H_6). For reference, the MS/MS spectrum of the isomerically pure erythritol-1,4-dinitrate (1,4-EDiN) is displayed (bottom). The MS/MS spectrum for erythritol-1,2,4-trinitrate from the synthesized and the isomerically pure erythritol-1,2,4-trinitrate (bottom) is shown in Fig. 3B. The ETriN MS/MS spectra is quite similar to the EDiN MS/MS spectra with only other minor fragments. Figure 3C and 3D shows the MS/MS spectra for the ETN synthesis impurities containing a sulfate group (EDiNSulf and ETriNSulf). It is strongly believed that these compounds are sulfated due to the presence of the 95.9528 mass channel.

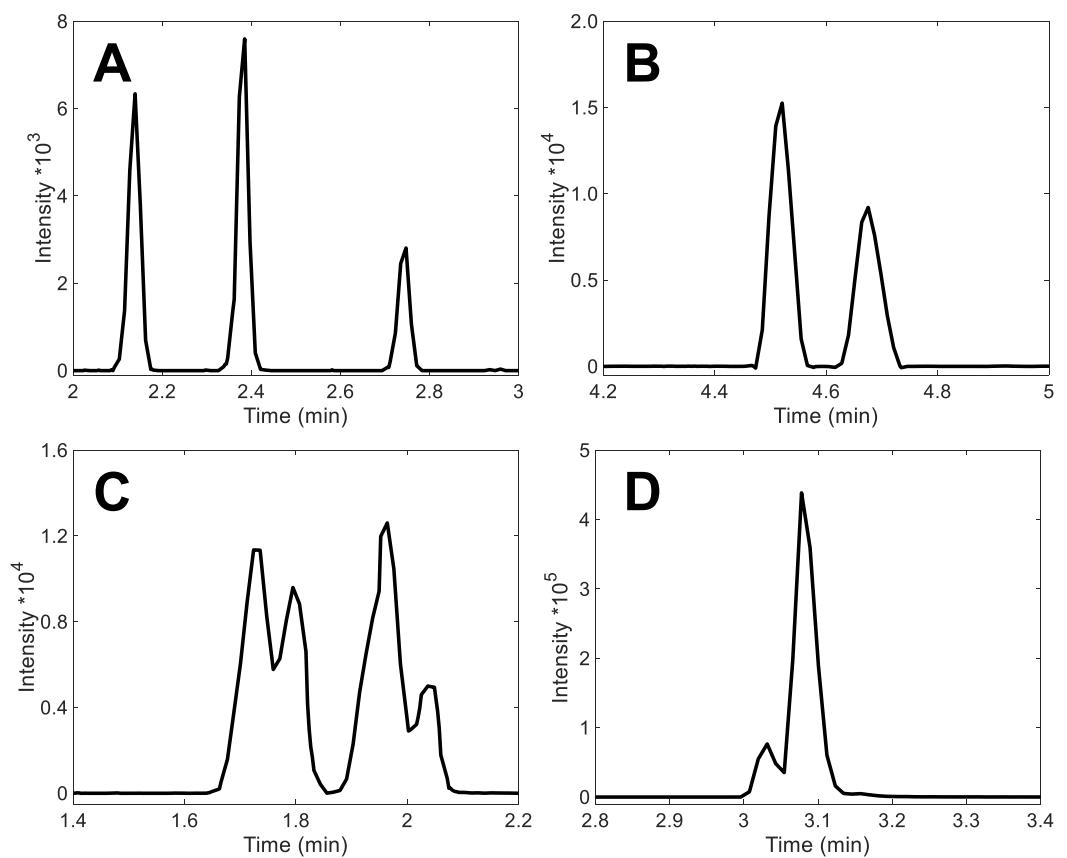


Figure 2: Selected mass channels, m/z , which highlight the presence of EDiN (A), ETrIN (B), EDiNSulfate (C), and ETrIN Sulfate (D).

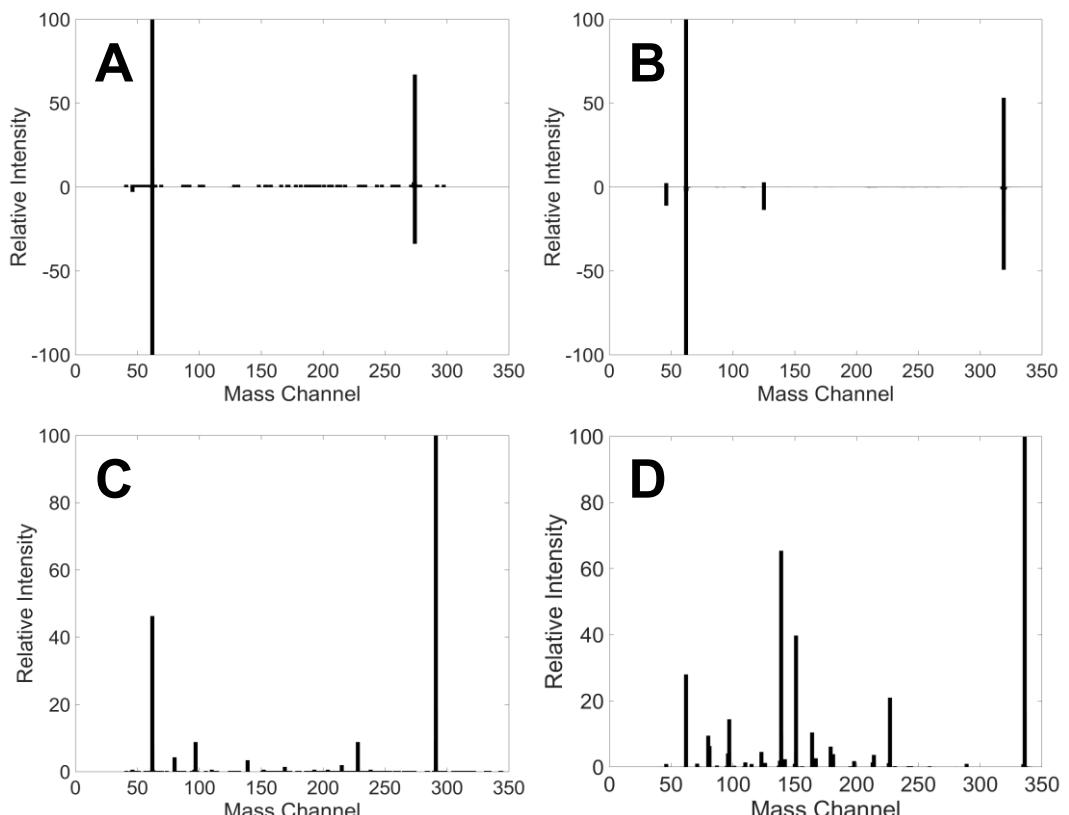


Figure 3: MS/MS spectra for erythritol-1,4-dinitrate (1,4-EDiN) and the isomerically pure standard (A), erythritol-1,2,4-trinitrate (1,2,4-ETrIN) and isomerically pure standard (B), EDiNSulfate (C), and ETrIN Sulfate (D).

4 Conclusion

Using ultra high performance liquid chromatography coupled to high resolution tandem mass spectrometry (UHPLC-MS/MS), we sought to identify impurities present in ETN. A total of 21 different compounds were identified with several compounds such as partially nitrated ETN with a sulfate group having never been identified before. Isomerically pure standards of erythritol-1,4-dinitrate (1,4-EDiN) and erythritol-1,2,4-trinitrate (1,2,4-ETriN) were also independently synthesized. Using these standards, it was possible to identify some of the impurities present in synthesized ETN.

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