

Overview

- Helium is primarily utilized as the DART ionization gas and the current global helium shortage has increased its price and reduced its availability.
- Nitrogen is mainly used for DART in standby mode to improve operational cost efficiency; however, it is also a viable ionization gas.
- Nitrogen was used as the ionization gas for DART and a variety of compounds were analyzed and compared to helium.
- Results were comparable to helium with nitrogen as the ionization gas. In some instances, spectra were simpler and cleaner with nitrogen.

Introduction

- Helium has been predominantly used as the ionization gas for DART.
- Nitrogen, which can be produced by generators, is more readily available and cost-effective compared to helium. Yet nitrogen has mainly been utilized for DART in standby mode.
- There have been a few recent nitrogen DART studies, but at present nitrogen has not been extensively utilized or studied
- In consideration of the helium shortage, nitrogen was evaluated to determine viability as an ionization gas for DART for a variety of compounds. DART grid voltage and flow rate, as well as, nitrogen purity was also examined.

Methods

- A DART-SVP ionization source was interfaced to a Waters QDa single quadrupole MS and a Thermo Q Exactive orbitrap high resolution MS.
- A PEAK Scientific NG3000A nitrogen generator was used to produce the nitrogen for DART.
- Transmission mode DART and gas temperatures of 250°C and 300°C were utilized for pesticides and drugs/explosives, respectively.
- A 2² full factorial design of experiment (DOE) was employed to study and identify DART parameter and nitrogen purity considerations.

Tables 1 & 2: DOE factors and their high and low levels.

		Level	
Factors		+	-
A	DART Grid Voltage	350 V	150 V
B	Nitrogen Source	Cylinder	NG3000A

		Level	
Factors		+	-
A	DART Grid Voltage	350 V	150 V
B	Nitrogen Flow Rate	2.14 L/min	1.84 L/min



Figure 1: PEAK Scientific NG3000A N₂ generator and its specifications.

Specifications	
Purity	99.9995%
Pressure	80 PSI
Flow Rate	3 L/min
Hydrocarbon	<1ppm
Oxygen	<5ppm

Results

Comparison between N₂ Cylinder and Generator

- N₂ DART spectrum of cocaine is comparable between using the generator and cylinder tank.
- Main effect plot shows higher peak area with the cylinder; however, it is not statistically significant as the effect value is within the 95% confidence level.

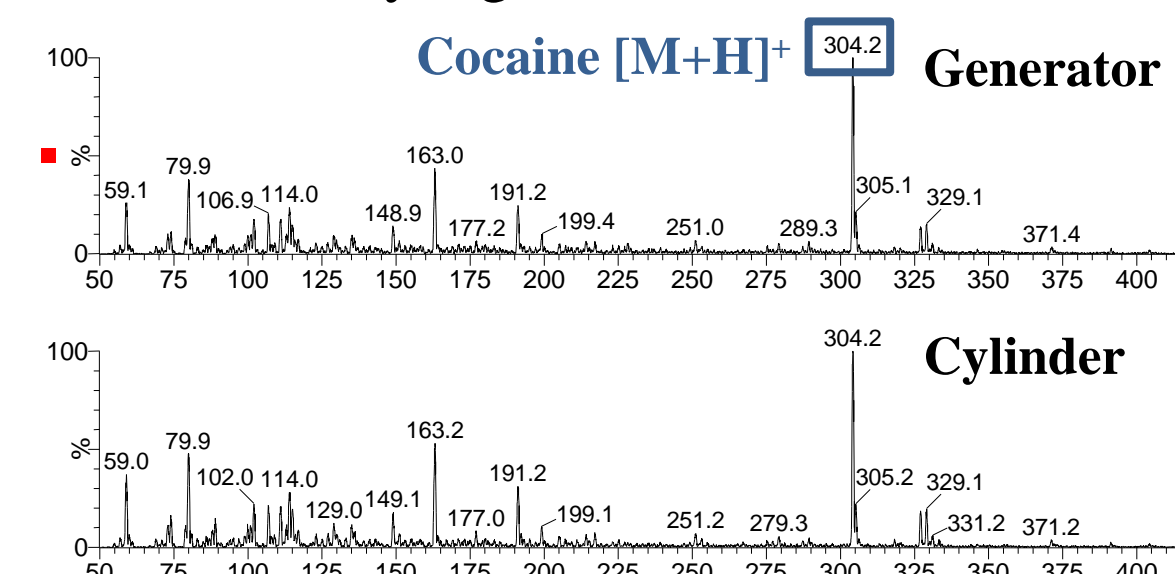


Figure 2: Positive ion nitrogen DART spectra of cocaine comparing the generator and cylinder tank.

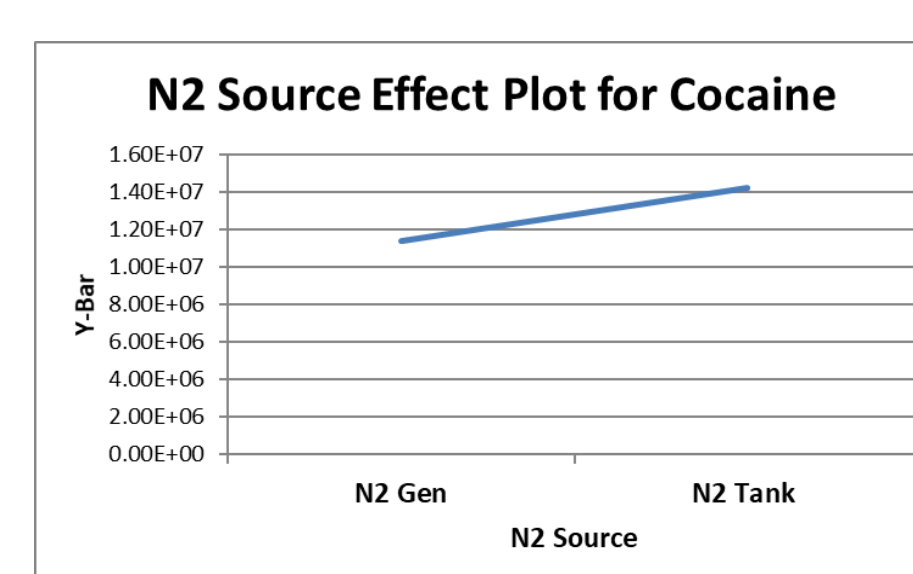


Figure 3: Main effect plot comparing the generator and cylinder tank.

Table 3: DOE run sequence and parameters as well as results for cocaine when comparing cylinder and generator.

Run	A	B	AB	Y ₁	Y ₂	y-bar	R
1	-	-	+	4.40E+06	7.01E+06	5.70E+06	2.61E+06
2	+	-	-	5.06E+06	6.39E+06	5.72E+06	1.33E+06
3	-	+	-	7.42E+06	7.66E+06	7.54E+06	2.41E+05
4	+	+	+	6.22E+06	7.19E+06	6.71E+06	9.67E+05
Effect	-4.08E+05	6.41E+05	-1.52E+05				
Confidence Level	2.23E+06						

Effect of DART Grid Voltage and Flow Rate

- Low grid voltage increases peak area and is significant only for RDX.
- Higher flow rate increases peak area and is significant for both cocaine and RDX.

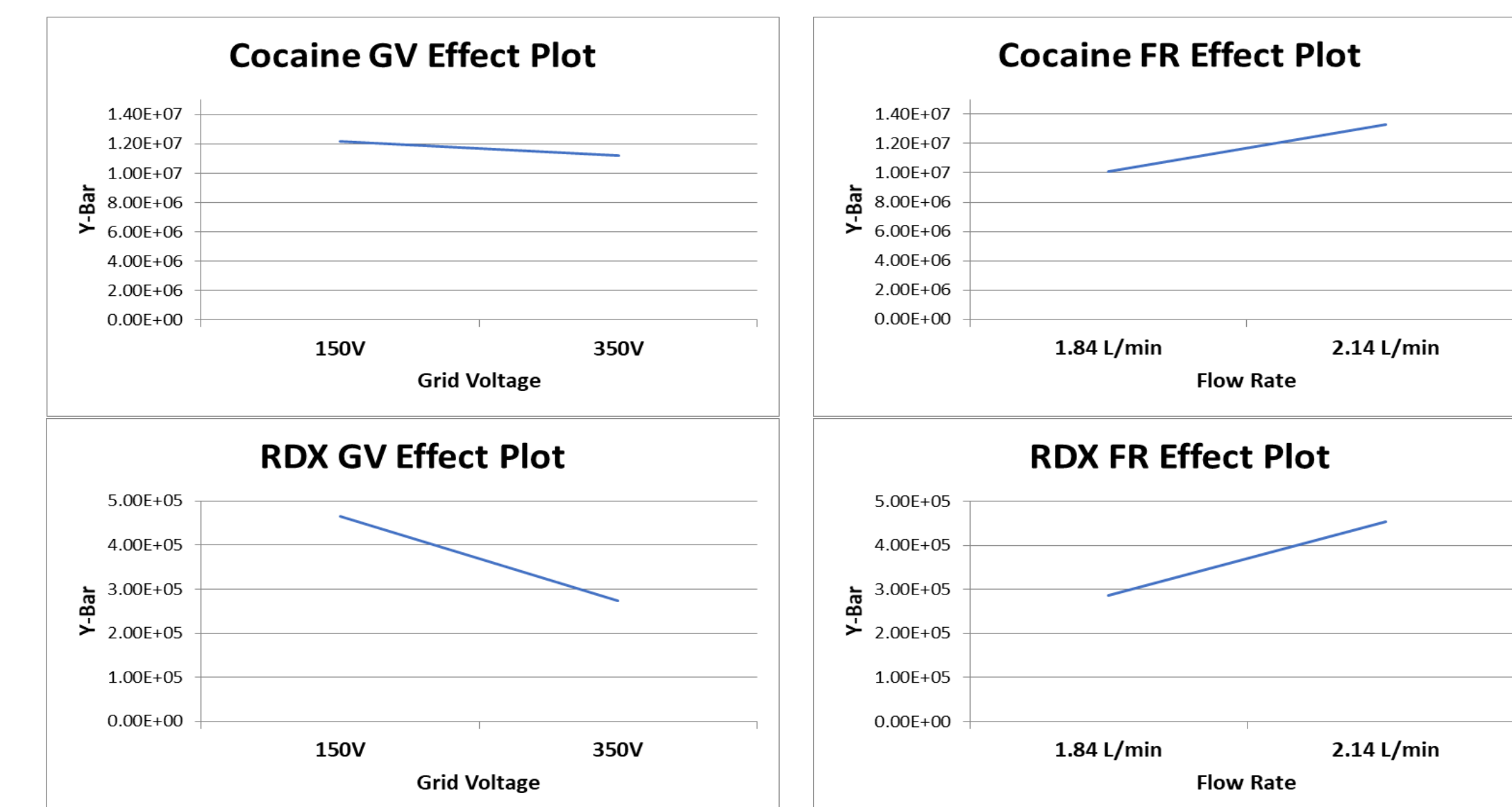


Figure 4: Main effect plots for cocaine and RDX showing the effect of varying grid voltage and flow rate.

Comparison between Helium and Nitrogen

- Spectra are comparable between helium DART and nitrogen DART for all tested compounds.
- In certain instances, such as with RDX, the spectrum is simpler and cleaner with nitrogen DART.
- Replacement and oxidation occurs more frequently with nitrogen DART and is dependent on chemical structure.

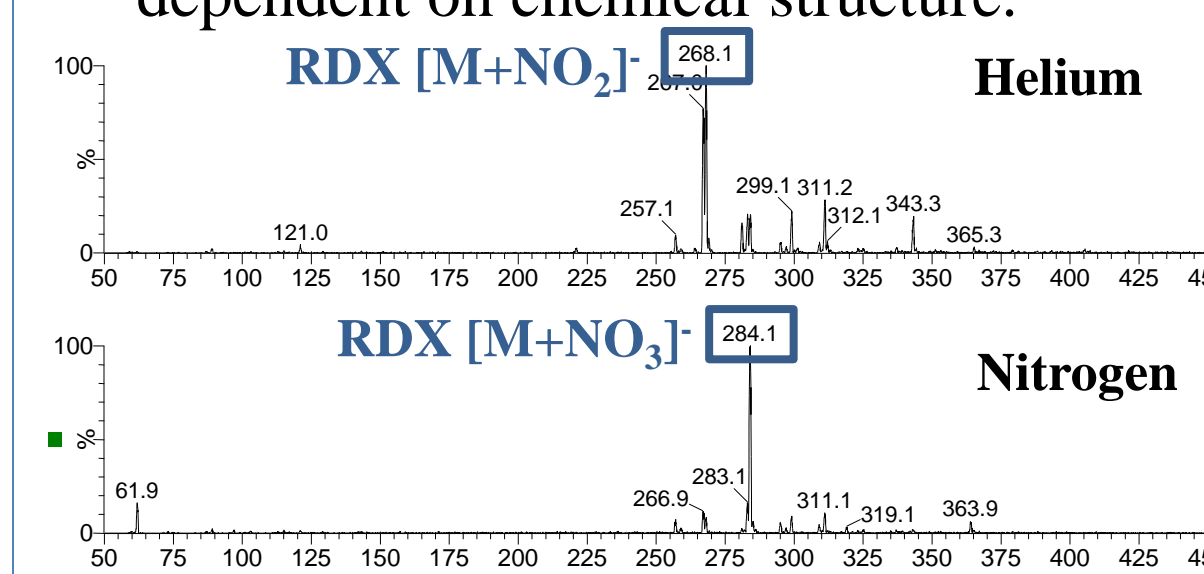


Figure 5: Negative ion spectrum of RDX obtained using helium and nitrogen as the DART ionizing gas.

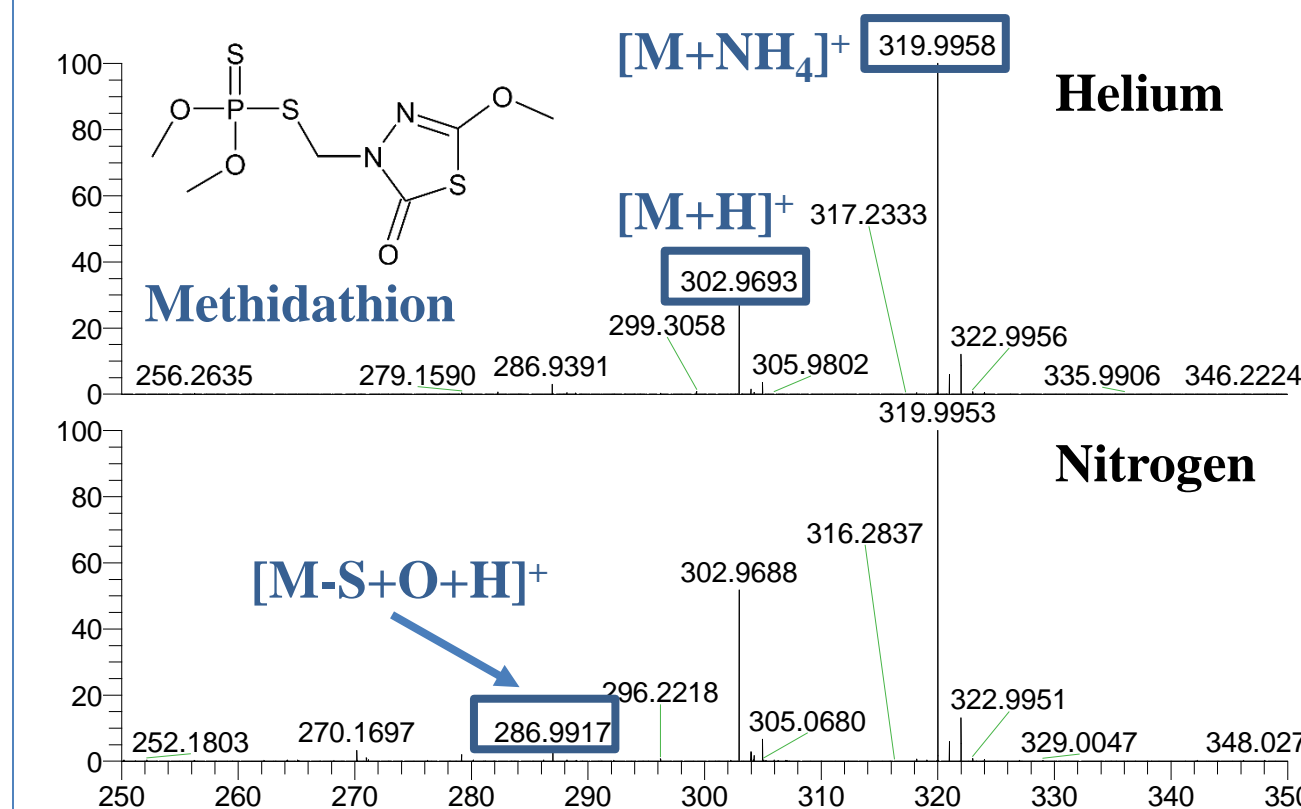


Figure 7: Helium and N₂ DART spectrum of methidathion showing S replacement occurring with only N₂ DART.

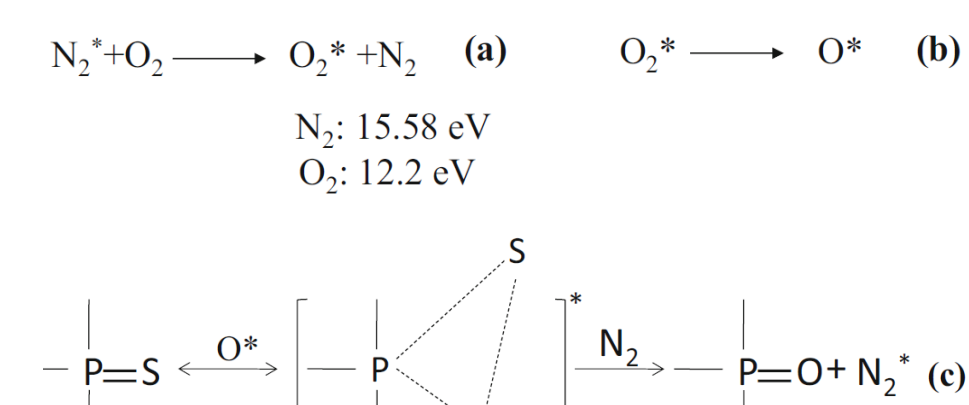


Figure 6: Proposed replacement reaction mechanism for P=S double bond.¹

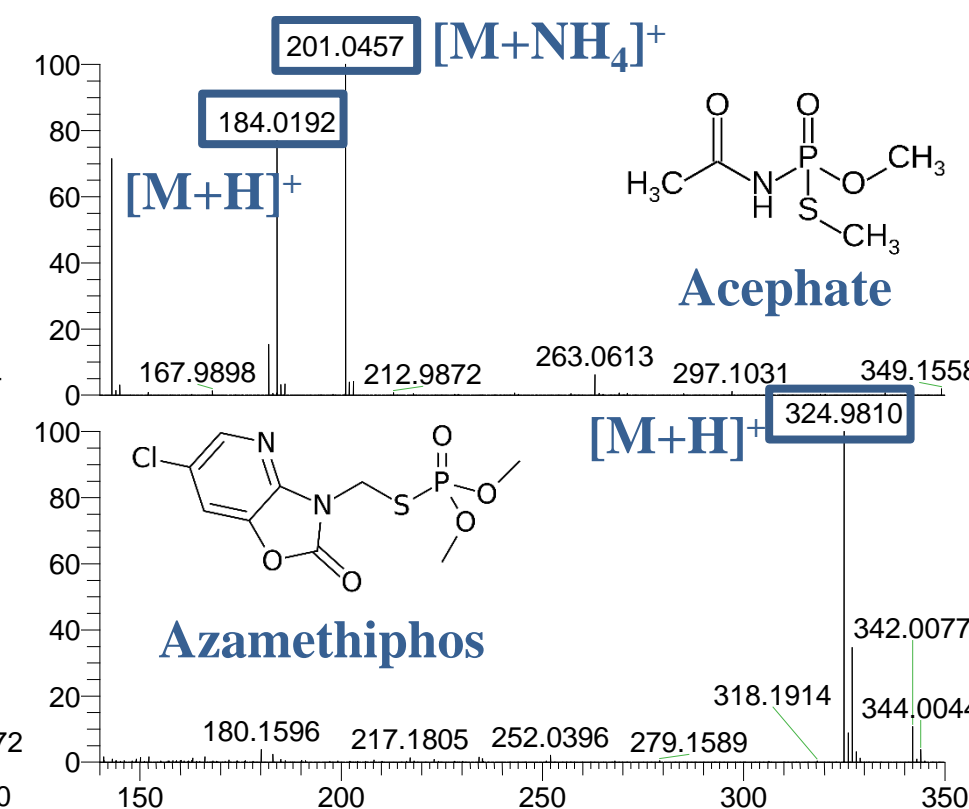


Figure 8: N₂ DART spectrum of acephate and azamethiphos showing no S replacement.

Conclusions

- PEAK Scientific NG3000A is the only generator found suitable for DART and the results are comparable to those obtained using Grade 4.8-cylinder tanks.
- DART gas flow rate has a significant effect on signal response for all tested drugs whereas grid voltage has a significant effect only for explosives.
- Replacement and oxidation ion reactions occur more with nitrogen DART.

References

1. Su, R., et al.: The ion source of nitrogen direct analysis in real-time mass spectrometry as a highly efficient reactor: generation of reactive oxygen species. *J. Am. Soc. Mass Spectrom.* **30**, 581-587 (2019)
2. Song, L., Chuah, W.C., Lu, X., Remsen, E., Bartmess, J.E.: Ionization mechanism of positive-ion nitrogen direct analysis in real time. *J. Am. Soc. Mass Spectrom.* **29**, 640-650 (2018)