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Overview

- Certain complex molecules and inorganic salts are difficult to ionize by traditional DART.
- Those compounds may ionize better by ESI, but samples are required to be in liquid form.
- Thermal desorption enabled ionization of solids in their native form by ESI and low vapor pressure inorganic salts by DART.

Introduction

Direct Analysis in Real Time (DART) provides a means for rapid thermal desorption and ambient ionization of small molecules. More complex molecules such as certain antibiotics and metal complexes, as well as inorganic salts from black powder substitutes (BPS), however, are difficult to ionize by DART. Some may ionize better by ESI, but samples are required to be in liquid form. Thermal desorption was investigated for ESI ionization, permitting solids to be ionized without the need for dissolution. This thermal desorption technique also permits vaporization of extremely nonvolatile samples, such as inorganic salts, for DART ionization.

Methods

A DART-SVP ionization source is interfaced to a Thermo QExactive orbitrap MS, LTQ and JEOL AccuTOF MS.

- Tablets were crushed into a fine powder and deposited onto the OpenSpot card mesh.
- BPS was deposited onto the mesh by rubbing the mesh against the powder.
- The mesh is positioned in a device where a variable electrical current is applied to heat and vaporize the sample.
- The ESI sources were modified with a connection to an external low vacuum pump to draw the vapors into the electrospray region and DART ionization region via a ceramic tube.
- ESI was completed using methanol:water (1:1) as the spray solvent with a flow rate of 3 μ L/min and voltage of 3 kV.

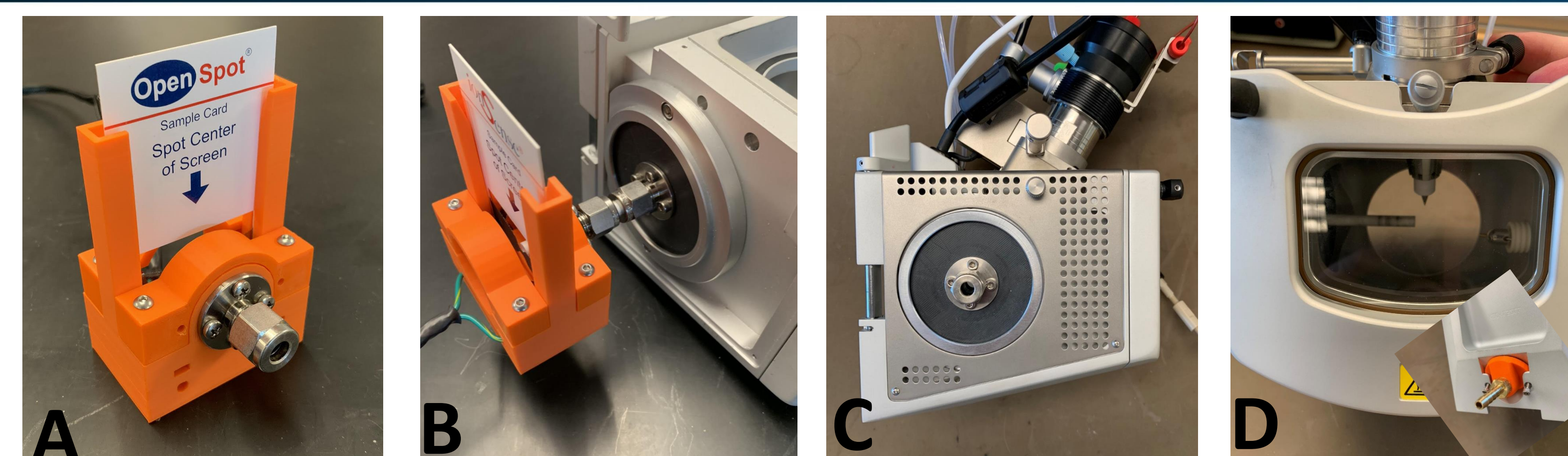


Figure 1: Source components include: (A) desorption module with OpenSpot card, (B) module attached to source, (C) exposed port for gas transfer tube and (D) TD ESI transfer tube adjacent ESI needle and connection port for external vacuum.

Results

Inorganic Salts in Black Powder Substitutes by TD-ESI

- Triple Seven and Jim Shockey's Gold black powder substitutes were rubbed on the OpenSpot card mesh.
- OpenSpot card inserted into thermal desorption module and BPS vaporized using the highest current setting on the power supply (~500-700°C).

Compound	Ion Observed	m/z
Potassium Nitrate	[KNO ₃ +NO ₃] ⁻	163
Potassium Perchlorate	ClO ₄ ⁻	99
	[KClO ₄ +NO ₃] ⁻	200
	[KClO ₄ +ClO ₄] ⁻	237
	[(KNO ₃)(KClO ₄)+NO ₃] ⁻	301
	[(KNO ₃)(KClO ₄)+ClO ₄] ⁻	338
	[(KNO ₃) ₂ (KClO ₄)+NO ₃] ⁻	402
Sodium Benzoate	C ₆ H ₅ COO ⁻	121
	[DCD-H] ⁻	83
Dicyandiamide (DCD)	[DCD+NO ₃] ⁻	146
	[DCD+C ₆ H ₅ COO] ⁻	205
	[NBA-H] ⁻	166
3-nitrobenzoic acid (NBA)	[NBA+NO ₃] ⁻	229
	[DCD+NBA-H] ⁻	250
	Nitrates	NO ₃ ⁻
	[HNO ₃ +NO ₃] ⁻	125

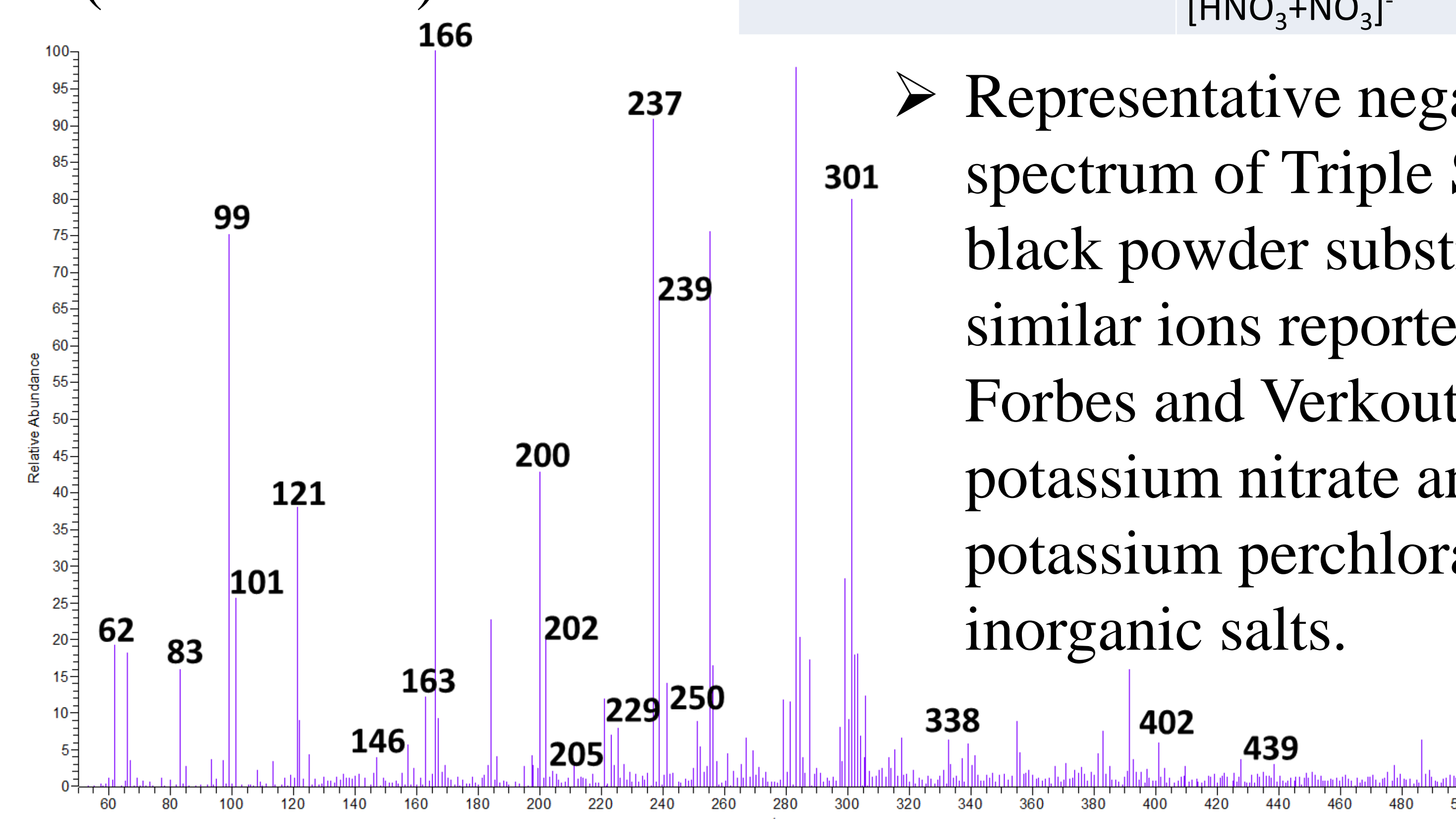


Figure 2: Thermal desorption ESI mass spectrum of Triple BPS showing ions consistent with those reported by Forbes and Verkouteren.

- Representative negative ion spectrum of Triple Seven black powder substitute show similar ions reported by Forbes and Verkouteren¹ for potassium nitrate and potassium perchlorate inorganic salts.

Inorganic Salts in Black Powder Substitutes by TD-DART

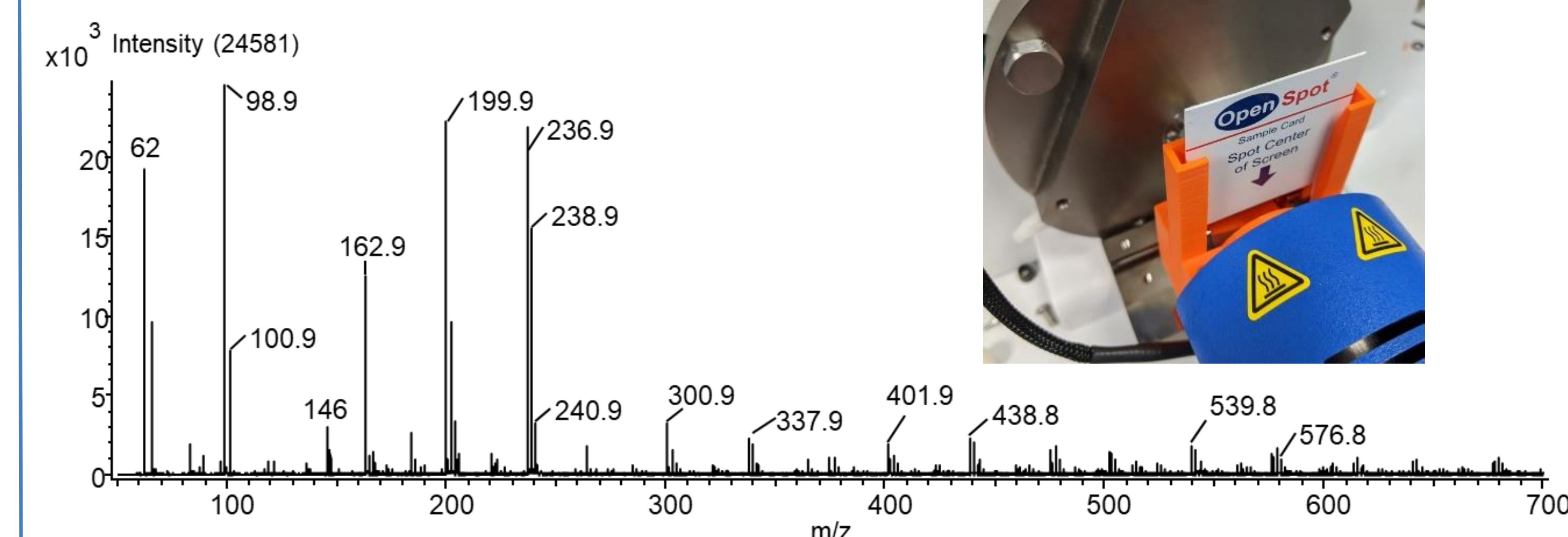


Figure 3: Thermal desorption DART mass spectrum of Pyrex P BPS showing ions consistent with those reported by Forbes and Verkouteren.

Complex Molecules by TD-ESI

- Complex molecules such as antibiotics often contain glycol-conjugates which may be cleaved by ambient ionization methods. Below is the TD-ESI mass spectrum of Azithromycin.

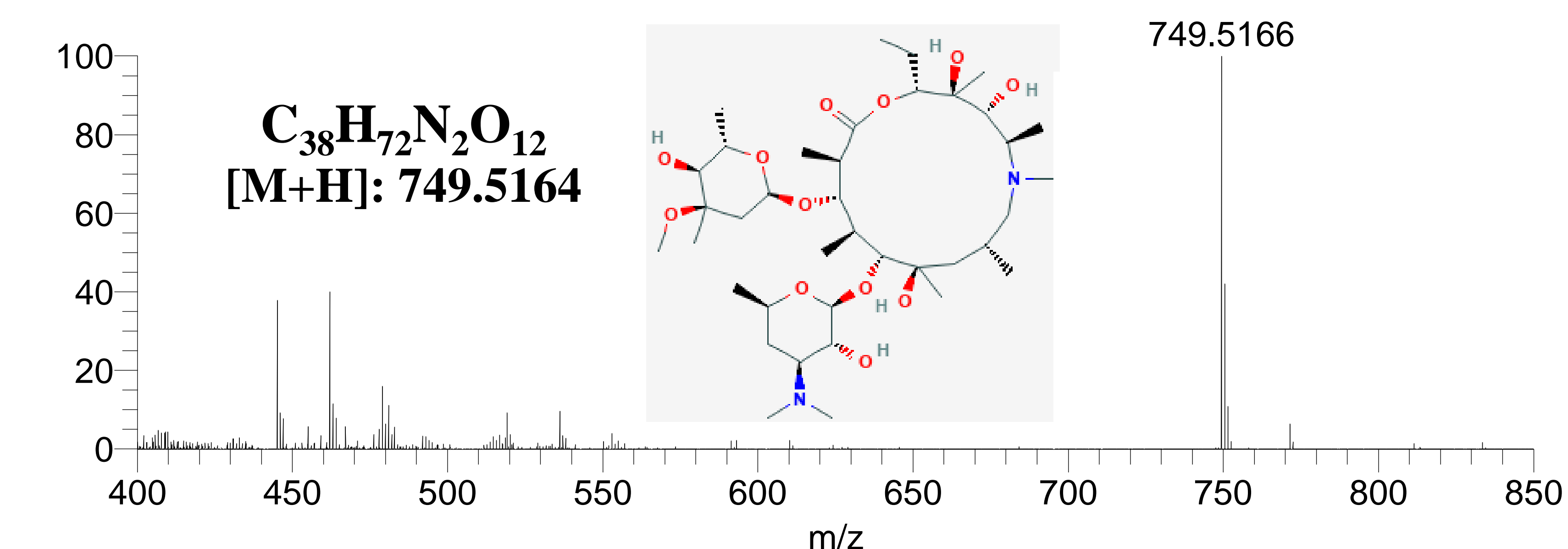


Figure 4: TD-ESI MS of Azithromycin (structure inset) acquired with low current setting and methanol/water ESI solvent.

Conclusion

- Thermal desorption enabled analysis of solids by ESI-MS and inorganic salts by DART.
- Both intact organic compounds and inorganic salts from BPS were detected by TD-ESI and TD-DART without dissolution.

References

1. T.P. Forbes and J.R. Verkouteren. *Anal. Chem.* 2019, 91, (1), 1089-1097. DOI: 10.1021/acs.analchem.8b04624