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INTRODUCTION

The defensive search for explosives and other threats to life and infrastructure is being challenged by the ever-increasing diversity and speed at which new target materials are emerging. Tests today are predominantly conducted using ion mobility instrumentation, however, as the number of explosives and other threats that need to be detected increases, new detector technology is being investigated to potentially produce a broader, more specific, and sensitive system.

The prototype system by Mass Spec Analytical Limited (Bristol, UK) (MSA) demonstrates that a new approach to desktop, easily transported, trace detection instrumentation, can detect threats across a wide range of compound groups using a traditional sampling technique. Detection at low nanogram ranges for a sample via direct injection, and 100-200 ng from a sampling material of a liquid sample dried onto a glass slide and then collected, was demonstrated for ten explosives, seven pesticides and six illicit drugs.

METHODS AND MATERIALS

The approach utilises a prototype Thermal Desorber (TD) ion source designed by MSA coupled to a RADIANTTM Single-Quad Mass Spectrometer (MS) (Waters Instruments, Wilmslow, UK) optimised for trace detection from sampling materials. The TD prototype source is fully integrated and controlled by the instrument and uses novel materials to improve sensitivity and performance. The RADIANT features the ability to use different cone voltages to bring about differing degrees of in-source fragmentation. This innovation significantly increases the performance achieved, enabling the prototype to compete with Ion Mobility Spectrometers in terms of cost, whilst significantly outperforming them in terms of analytical precision. Most of the samples investigated ionised in negative ionisation mode, but several did preferentially ionise in positive ionisation mode.



Figure 1: MSA Prototype Thermal Desorber fitted to Waters RADIANT Instrument

Analysis and method development used Waters MassLynxTM software. Waters LiveIDTM Software was used for real-time identification of samples.

The MSA TD source is interchangeable with the Waters Atmospheric Solids Analysis Probe (ASAP[®]) supplied with the instrument. Both sources rely on Atmospheric Pressure Chemical Ionisation (APCI) as an ionisation method. Methods developed for either source are, for the most part, interchangeable. A beneficial characteristic of the TD source over the ASAP is the ability to utilise different sampling media. As a rule of thumb, the ASAP approach is more suited to bulk samples, whereas using sampling materials is more suited to trace detection analysis.

RESULTS

Screening of Explosive Residues

The MSA thermal desorber is optimised for use with sampling materials. Analysis of TNT, using 7 different sampling materials, demonstrated that the sample desorbs in approximately 1-2 seconds. Our initial conclusion is that the order of best performance based on these results is: 1. WhatmanTM No. 2 filter Cat. No: 1002-110, 2. Nomex paper. 0.13 mm thick. Sourced from R.S. Pt. No: 349-9728, 3. DSA DetectionTM sample trap for E Mode paper Pt. No: ST1140P, 4. Stainless steel cloth 0.20 mm. Twill weave, 5. Teflon coated fiberglass sheet (unknown), 6. PTFE in a cardboard holder (unknown), 7. Aluminium Foil (Sainsburys). The TD source was set at 200° C and the corona voltage was -2-3 kV.

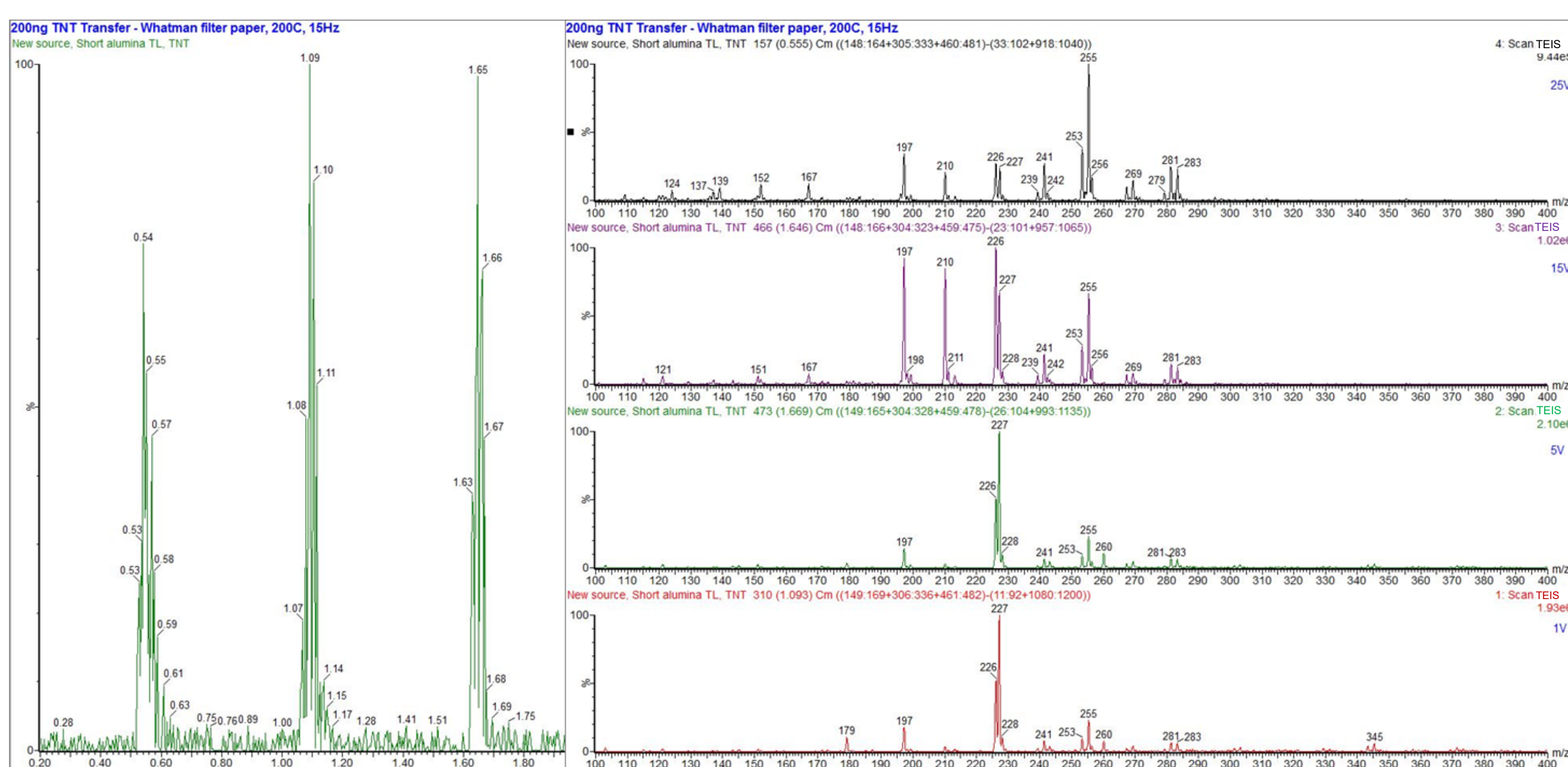


Figure 2: TNT Chromatograph Created Using MassLynx for Whatman No. 2 Sampling Material. Note Desorption Duration and Separate Results for Each Cone Voltage (1 V, 5 V, 15 V and 25 V)

Working from explosive standards (Merck Group), 10 different explosives were detected, for which 8 individual methods were optimised (Figure 3). A general method was developed to identify explosives analysed in negative ionisation mode. The cone voltages chosen cover a large enough range to see distinctive fragmentation patterns for each compound, whilst including two smaller cone voltages that are helpful in the identification of the easily fragmented compounds such as nitroglycerine. The TD source supports the integration of Cl dopant providing increased sensitivity for selected compounds.

Explosive	Ionisation Mode	Chloride Adducts	Cone Voltages (V)	Heater Temp (°C)	Main Target m/z Values
TNT	Negative	No	5, 15, 25	220	227, 226, 210, 197, 196
DNT	Negative	No	20, 25, 30	180-200	181, 135, 116
NG	Negative	Yes	1, 5, 7.5	150-170	289, 264 (Cl), 262 (Cl), 62
HMX	Negative	Yes	5, 10, 15, 20	220	373, 342, 333 (Cl), 331 (Cl), 295
RDX	Negative	Yes	5, 7.5, 10, 12.5	200	299, 284, 268, 259 (Cl), 257 (Cl)
PETN	Negative	Yes	1, 5, 7.5, 10	180	378, 353 (Cl), 351 (Cl), 315
Tetryl	Negative	No	5, 15, 25, 35	180-200	241, 228, 227, 196
HMTD	Positive	No	1, 10, 15, 20	200	209, 179, 145, 88

Figure 3: Summary of Explosive Compounds Detected

Detection of Illicit Drugs

Working from drug seizure samples, and illicit drug standards provided by Waters Instruments at their UK Headquarters, the prototype detected a range of illicit drugs including conventional, psychoactive, synthetic cannabinoid, and synthetic opioid types. Rather than developing new methods, MSA worked from the Pandora "illicit drugs" library available from Waters for their ASAP source.

Cone Voltages (V)	Ceramic Heater Temp (°C)	Ionisation Mode	Successful Identification with LiveID TM	Additional Identification Required
15, 25, 35, 50	200-275	Positive	Cocaine, Fentanyl, MDMA, MMB-Fubina, Ketamine	Heroin – successful identification determined through MassLynx

Figure 4: Summary of Illicit Drugs Detected Using LiveID

LiveID is a library matching software used to determine if a sample contains any of the compounds within the defined library. Figure 5 shows the LiveID browser illustrating the presence of fentanyl from a sample. A 2 µL syringe injection of a 20 ng/µL stock solution of fentanyl was analysed. The temperature of the source was set to 200° C. The report below shows the response of the injection in the chromatogram and the 4-function acquisition and library matches.



Figure 5: LiveID Sample Analysis of 2 µL Syringe Injection of 20 ng/µL Solution of Fentanyl

Development of Pesticide/Herbicide methods

A Sigma-Aldrich Triazine (CRM48392) pesticide standard mix was used to determine the ability of the Waters Radian single quadrupole mass spectrometer and the MSA thermal desorber source in detecting pesticides. Triazine contains seven common pesticides: Ametryn, Atrazine, Prometon, Prometryn, Propazine, Simazine, and Terbutryn. A library for use with Waters Live ID was created using the data gathered during analyses and reference material from AB SCIEXTM.

For this analysis, 1 µL of a 5 ng solution was injected into the instrumentation. The ceramic heater temperature was set to 200° C. As expected, all seven compounds were detected with very high match scores, proving the ability of the instrumentation and the validity of the library.

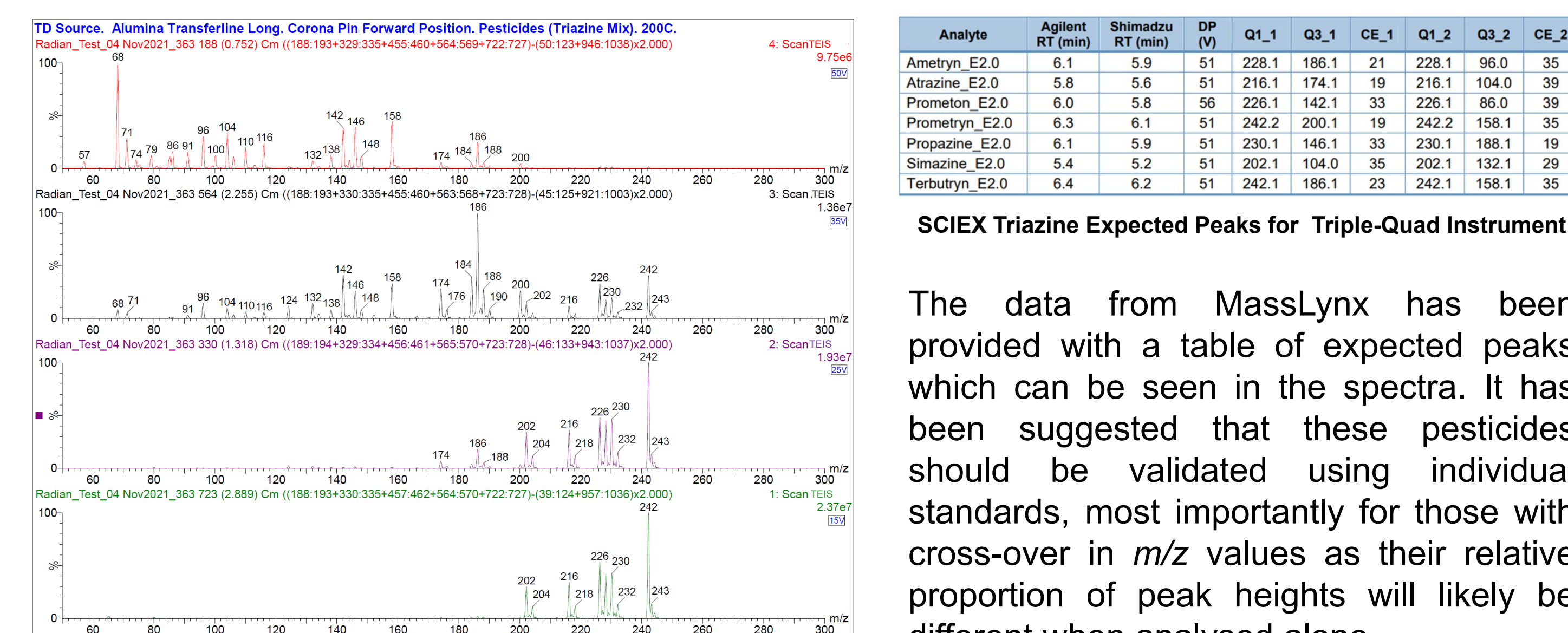


Figure 6: MassLynx Spectra for Triazine

CONCLUSIONS

The RADIANT TD-prototype demonstrated the ability to detect a range of compounds to a comparable level across three different groups using similar parameters (cone voltages, heater temperatures), underscoring its potential as a defensive detection capability. The TD prototype source is fully integrated and controlled by the instrument. The instrument is self-calibrating, self-sustaining, does not use special gases or a radioactive source, and is able to be used by all operator skill levels.

ACKNOWLEDGEMENTS

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TRADEMARKS/LICENSING

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Analyte	Agilent RT (min)	Shimadzu RT (min)	DP (V)	Q1_1	Q3_1	CE_1	Q1_2	Q3_2	CE_2
Ametryn_E2.0	6.1	5.9	51	228.1	186.1	21	228.1	98.0	35
Atrazine_E2.0	5.8	5.6	51	216.1	174.1	19	216.1	104.0	39
Prometon_E2.0	6.0	5.8	56	226.1	142.1	33	226.1	86.0	39
Prometryn_E2.0	6.3	6.1	51	242.2	200.1	19	242.2	158.1	35
Propazine_E2.0	6.1	5.9	51	230.1	146.1	33	230.1	188.1	19
Simazine_E2.0	5.4	5.2	51	202.1	104.0	35	202.1	132.1	29
Terbutryn_E2.0	6.4	6.2	51	242.1	186.1	23	242.1	158.1	35

SCIEX Triazine Expected Peaks for Triple-Quad Instrument

The data from MassLynx has been provided with a table of expected peaks which can be seen in the spectra. It has been suggested that these pesticides should be validated using individual standards, most importantly for those with cross-over in m/z values as their relative proportion of peak heights will likely be different when analysed alone.