The Application of High Resolution SWATH® MS/MS^{ALL} for the High Throughput Screening of Explosive Residues

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INTRODUCTION

The increasing threat from [1]improvised explosive devices (IEDs) requires an enhancement in our detection and screening capabilities. Current analytical security screening methods in public places traditionally rely on the combination of thermal desorption (TD) with ion mobility for the detection of illicit and explosive residues. The combination of TD with atmospheric pressure chemical ionization (APCI) aligns well with current security screening requirements as a rapid sample introduction approach. However confident identification cannot be achieved by the measurement of collisional cross section alone.

The use of the data independent acquisition (DIA) methods could be of a significant benefit when employed for security screening. The SWATH® MS/MS^{ALL} acquisition process generates accurate mass precursor TOF MS data which is automatically processed using the SCIEX OS software to predict elemental compositions and match isotopic pattern data to any extracted peaks. In addition to the precursor data the entire TOF MS mass range is segmented into SWATH windows which are transmitted into Q2 for fragmentation generating high resolution MS/MS product ion data for all ions in a sample which can then be matched against a library spectra for confident identification. This provides the complete view of all intact molecular ions and their associated MS/MS fragments.

Here we present the prototype proof of principle combination of the SCIEX X500R QTOF system with the Mass Spec Analytical Ltd (MSA) manufactured Thermal Extraction Ion Source (TEIS) for the rapid and accurate identification of explosive residues using SWATH MS/MS^{ALL} methodology.

METHODS AND MATERIALS

The prototype hyphenation of TEIS with the SCIEX X500R QTOF system is shown in Figure 1. The TEIS source allows the introduction of liquid and solid samples into the heated block region for desorption.

Figure 1. Image of SCIEX X500R QTOF™ and the MSA TEIS ambient ionization source

A series of explosive standards at 100 ng/mL were analysed under a Information Dependent Acquisition (IDA) method to generate high resolution MS and MS/MS data which can be added to the database for screening. Following library generation, the SWATH MS/MS^{ALL} DIA was used to monitor a TOF MS mass range of 100-500 Da in 50 ms. SWATH MS/MS data was collected using 15 SWATH windows each spanning 25 Da to cover the precursor mass range, accumulation time of 30 ms per window resulted in a total scan time of 0.5 seconds

The generation of explosive $[Cl]^-$ adducts were found to produce a greater analytical response than $[M-H]^-$ ions, therefore a DCM vapour was introduced into the TEIS source using a flow of air at 25 L/h

RESULTS

Generation of High Resolution Library for Screening

The analysis of explosive residues using the DIA SWATH MS/MS^{ALL} acquisition process requires a database/library entry that can be used to match screened samples based upon the full scan product ion data. This is performed by directly injecting a 10 µL volume of a 100 ng/mL mixture of the explosive standards using a IDA acquisition where the top 10 ions observed in TOF MS are automatically selected for fragmentation.

The example data below (Figure 2) shows the IDA of $[RDX+Cl]^-$ which was used in the creation of the library entry.

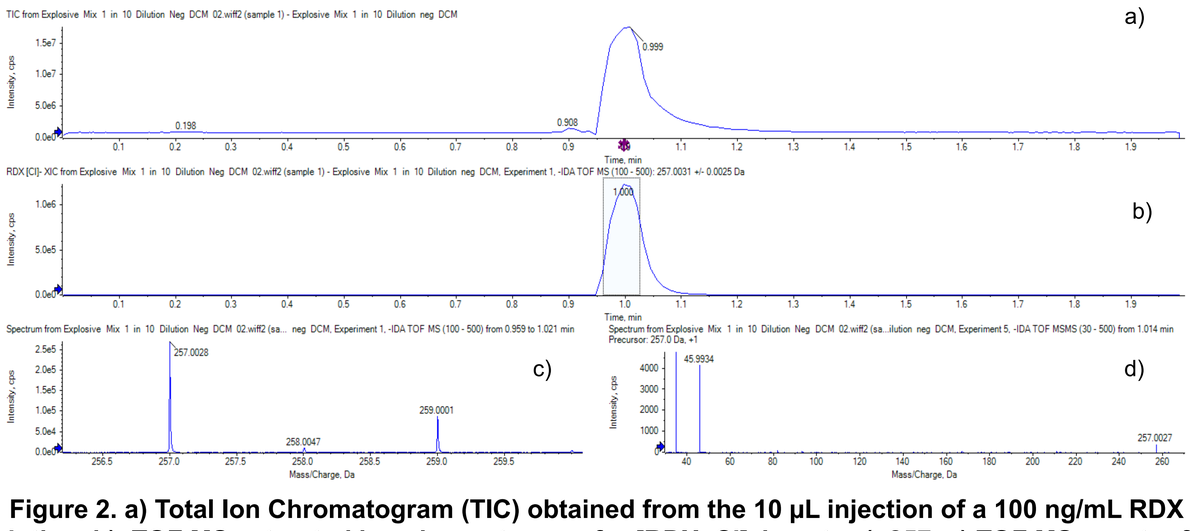

Figure 2. a) Total Ion Chromatogram (TIC) obtained from the 10 µL injection of a 100 ng/mL RDX solution, b) TOF MS extracted ion chromatogram for $[RDX+Cl]^-$ ion at *m/z* 257, c) TOF MS spectra for $[RDX+Cl]^-$ showing isotopic pattern and d) associated full scan TOF MS/MS data for $[RDX+Cl]^-$

The analysis of the RDX standard generates a typical TD response where a baseline blank is observed in the TIC before a sharp response upon sample introduction followed by a tailing in response back to the baseline. The use of the Cl adduct of RDX results in the expected isotope distribution in the TOF MS spectra which fragments to generate the product ions at *m/z* 45.9 and *m/z* 34.9

SWATH MS/MSALL Screening of Explosive Residues Using TEIS

To assess the capabilities of the prototype hyphenation of the TEIS source and the SCIEX X500R QTOF, 30 µL of the 100 ng/mL explosive residue mix was placed on a clean surface. The solution was allowed to completely evaporate before a passport sized piece of plain white paper was 'rubbed' in the area where the sample was placed in order to transfer the explosive residues. The paper was then passed through the TESI source block. The entire process is shown in the images in Figure 3.

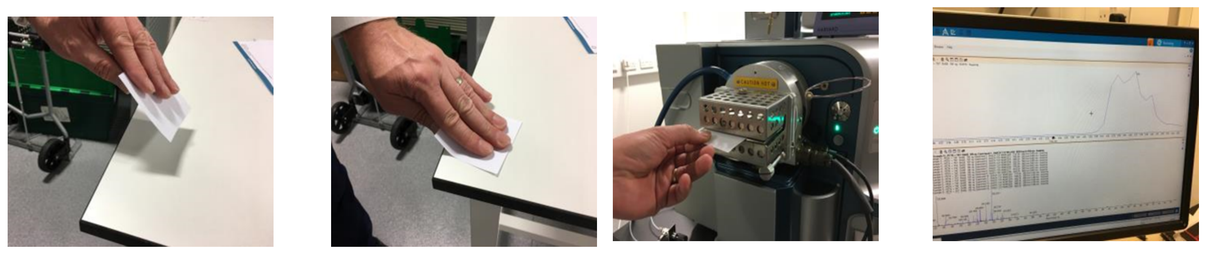

Figure 3. Images showing the deposition, evaporation, extraction and presentation of the sample to the heated blocks of the TEIS source

The SWATH MS/MS^{ALL} detection of the transferred explosive residue is nearly instantaneous with a TD profile observed in real-time using the Explorer portion built into SCIEX OS acquisition software. The qualitative result for PETN is provided in Figure 4.

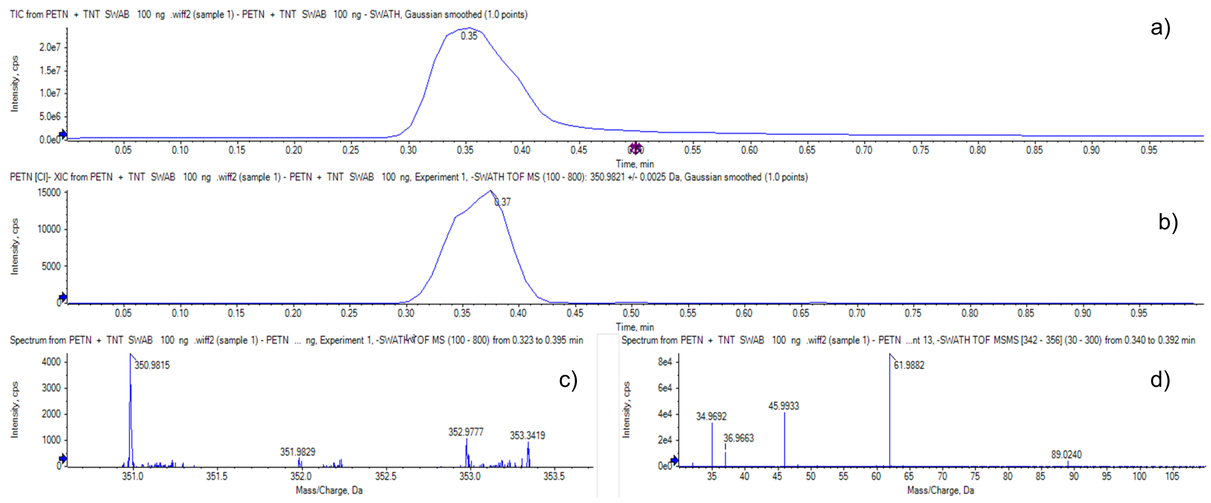

Figure 4. Analysis of PETN residue from a 300 ng surface swab a) TIC from the TESI-SWATH analysis b) XIC for [PETN+Cl]- m/z 350.9 c) TOF MS spectra for [PETN+Cl]- and d) associated SWATH MS/MS spectra showing full product ion data

The positive identification of PETN residue is confirmed through the used of the Analytics portion of the SCIEX OS software. Using Analytics we can rapidly screen any given sample against a target library (known-unknowns) and true unknowns using the ChemSpider plug-in. The result of the targeted screen from the residue swab is shown in Figure 5.

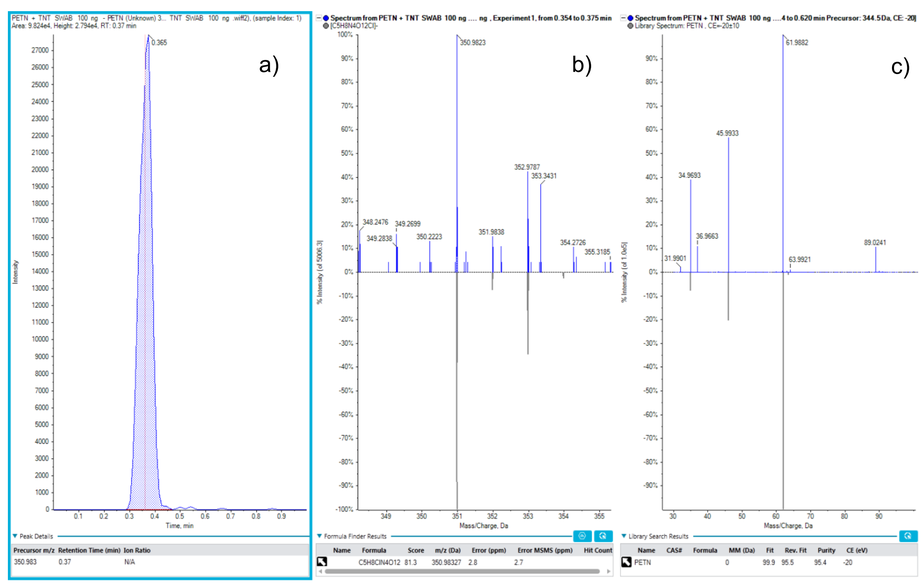

Figure 5. Example out-put from the Analytics screening process using the SCIEX OS operating software a) XIC for [PETN+Cl]-, b) TOF MS data corresponding to [PETN+Cl]- at m/z 350.9, c) SWATH MS/MS product ion matching against the database

SCIEX OS Analytics software automatically detects and extracts any potential peaks as XICs, the software then investigates the high resolution precursor ion data, predicts elemental compositions, calculates mass error and matches isotope pattern. Furthermore the analytics then screens the associated SWATH MS/MS data against the user customisable databases to identify the unknown based upon the product ion information

CONCLUSIONS

The prototype hyphenation of the MSA TEIS source and the SCIEX X500R QTOF system is shown to produce high resolution data for confident compound identification in a rapid manner suitable for high throughput screening. The accurate identification of explosive residues based upon the combination of precursor and product ion information using the SWATH MS/MSALL acquisition process and is shown to be a significant enhancement over the current analytical screening methods.

The application of TEIS combined with the data independent SWATH MS/MSALL acquisition shows potential application to the direct analysis of a variety of screening applications in particular the detection of elicit drug residues from parcels and packages.

REFERENCES

1https://blogs.state.gov/stories/2017/07/17/en/us-policies-and-actions-aim-counter-improvised-explosive-device-threats

TRADEMARKS/LICENSING

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