THE DETECTION AND IDENTIFICATION OF POLYMERS USING ION-MOBILITY MASS SPECTROMETRY AND PATTERN TARGETING SOFTWARE

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INTRODUCTION

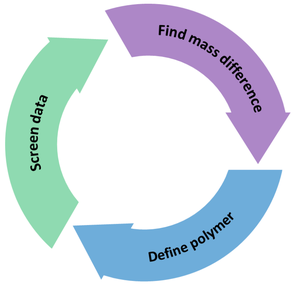
A software application that targets patterns within complex data is presented. The application is aimed at samples containing compounds such as polymers and hydrocarbons which are described by repeating mass units, multiple charges states and multiple adducts. Such samples contain hundreds of individual ions related to a single compound which can make both the assignment of, and the differentiation between, individual species difficult.

For this study polymeric samples were infused into an ion-mobility enabled mass spectrometer and the acquired data analysed. The Pattern Targeting Application (PTA) yields information on individual oligomeric contributions together with a measure of the overall abundance of each polymer in a sample.

EXPERIMENTAL

Polymeric standards were infused into a Waters™ Synapt™ XS mass spectrometer at a flow rate of 5 µL/min. The instrument was mass and ion-mobility calibrated using sodium formate and Major Mix, respectively, and HDMS™ data were acquired.

Figure 1. Waters™ Synapt™ XS mass spectrometer.



Find A Common Mass Difference

The acquired data were peak detected and the resulting ions were imported into the PTA. The application performs isotope clustering to yield a collection of components which can be displayed alongside the imported data (Figure 2).

Several ion series are clearly visible in the Component Spectrum. Focussing on one of the series reveals a repeating mass difference of 11 Da. Examining the isotope cluster of one of the ions in the series indicates that the ion has a charge state of 4. Therefore the data contains a polymer with a repeat unit of 44 Da which is indicative of polyethylene glycol (PEG).

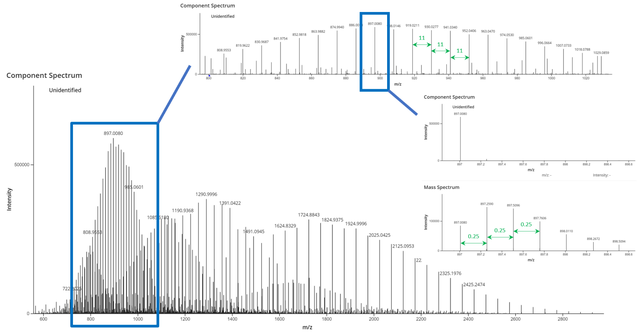


Figure 2. Component and mass spectra from the PTA.

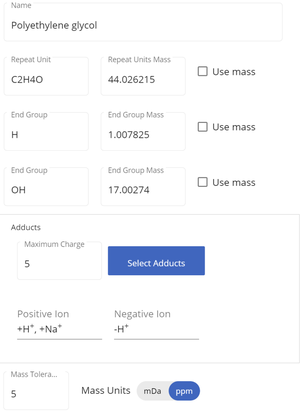


Figure 3. Polymer definition dialog

Define Polymer

Target polymers are specified in the PTA via a dialog in which the repeat unit and two end groups can be entered, either as chemical formulae or as mass values. The definition for PEG is shown in Figure 3. Adducts and the maximum charge expected are also specified on the dialog together with a mass tolerance used to screen the measured data for the generated targets. Once a polymer has been defined, a list of potential target oligomers, are generated as shown in Figure 4. The measured data is then screened against the targets generated for all selected polymers.

	m/z	Charge	Adduct	Neutral Mass	Repeats	Formula
83	170.6082	4	$+4H^+$	678.4038	15	$H(C_2H_4O)_{15}OH$
84	171.9090	5	$+5H^+$	854.5087	19	$H(C_2H_4O)_{19}OH$
85	173.0784	1	$+Na^+$	150.0892	3	$H(C_2H_4O)_3OH$
86	175.7468	3	$+3Na^+$	458.2727	10	$H(C_2H_4O)_{10}OH$
87	176.2805	5	$+5Na^+$	766.4562	17	$H(C_2H_4O)_{17}OH$

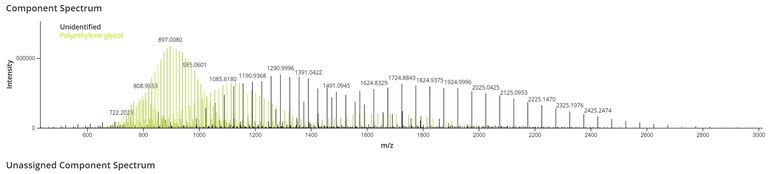
Figure 4. Example polymer targets.

RESULTS

Screen Against The Data

On screening for PEG within the measured data, the components that match a target are highlighted in the component spectrum, and a spectrum showing the unassigned components is generated (Figure 5).

Of the ion series remaining in the unassigned component spectrum, a doubly charged series repeating every 50 Da is evident. Thus the data also contains a polymer with a repeat unit of 100 Da, which is indicative of polymethyl methacrylate (PMMA). Defining PMMA in a similar way to PEG via the polymer definition dialog (Figure 3) and re-running the application yields the component and unassigned component spectra shown in Figure 6. No ion series are now present in the unassigned component spectrum indicating all polymeric content in the sample has been assigned.



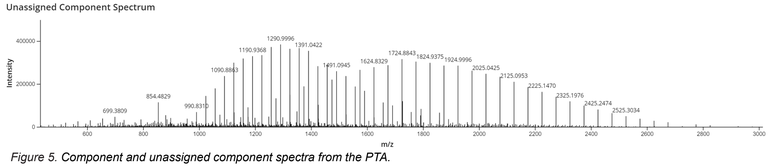
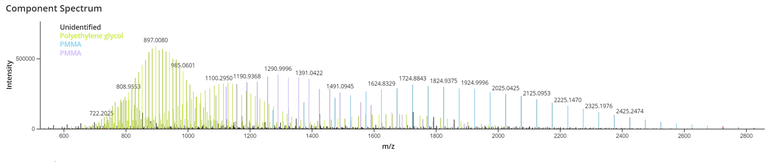


Figure 5. Component and unassigned component spectra from the PTA.



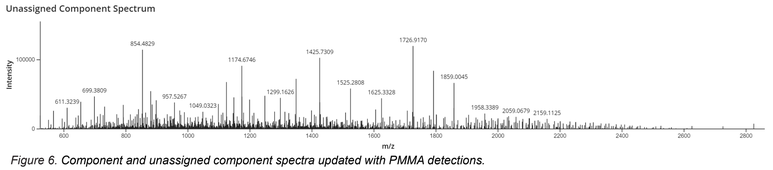


Figure 6. Component and unassigned component spectra updated with PMMA detections.

Target	m/z	Charge	Adduct	Neutral Mass	Repeats	Formula	Component m/z	m/z error (mDa)	m/z error (ppm)	Component Retention Time	Component Drift Time	Component Intensity
Polyethylene glycol	762.7630	3	$+3Na^+$	2219.3213	50	$H(C_2H_4O)_{50}OH$	762.7613	-1.68	-2.20	2.52	5.35	1,752
Polyethylene glycol	762.7630	3	$+3Na^+$	2219.3213	50	$H(C_2H_4O)_{50}OH$	762.7613	-1.68	-2.20	2.52	4.97	37,642

Figure 7. Section from the PTA results table showing the separation of isomeric components through the application of ion mobility

DISCUSSION

One advantage of ion-mobility mass spectrometry is the ability to separate isomeric compounds due to their different conformations. Figure 7 displays a section of the results table from the PTA which highlights the separation of two isomers.

Additionally, since all oligomers from a given polymer are known, standard polymeric quantities including the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) can be determined from each mass, intensity pair (m_i, I_i). The complete list of quantities determined in the PTA are shown in Figure 8.

$$M_n = \frac{\sum_i I_i m_i}{\sum_i I_i}, \quad M_w = \frac{\sum_i I_i m_i^2}{\sum_i I_i m_i}, \quad M_z = \frac{\sum_i I_i m_i^3}{\sum_i I_i m_i^2},$$

$$M_{z+1} = \frac{\sum_i I_i m_i^4}{\sum_i I_i m_i^3}, \qquad PDI = \frac{M_w}{M_n}$$

Figure 8. Polymeric quantities determined by the PTA.

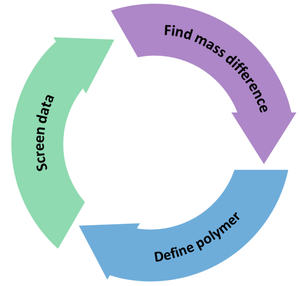
Polymer Calculations:

Name:	Polyethylene glycol
Mn:	3,318
Mw:	3,459
Mz:	3,567
Mz+1:	3,688
Polydispersity:	1.04
Total Response:	24929600

Figure 9. Polymer calculation for the PEG detected in the example.

CONCLUSIONS

- **The PTA targets compounds consisting of repeated mass differences.**
- **Polymers are defined using a simple dialog encompassing repeat units, end groups, adducts and charge states.**
- **Peak list data are isotope clustered into components.**
- **Targets are screened against the list of components.**



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