

Pushing Environmental Analysis to the Next Dimension

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What is ion mobility?

Ion mobility offers an extra dimension of separation that aids in a number of areas including spectral clean-up, elucidation of unknowns, and confirmation of target compounds. In this article we will discuss how Waters uses ion mobility in environmental analysis and how it can provide increased confidence in the results. Ion mobility is available on the Waters SYNAPT G2-Si and the Vion IMS QTof.

So what do we mean when we talk about ion mobility? Ion mobility is the separation of ionic species as they travel through a gas under the influence of an electric field. The rate of an ions drift through the mobility cell is known as drift time. The drift time is dependent on factors including the mass, charge and shape of an ion. The ion mobility separation (IMS), occurs in the gas phase within the instrument. It is not influenced by chromatographic separation or matrix interference.

At Waters we combine IMS with data independent analysis known as MSE. This involves alternating scans between low and high energy fragmentation conditions, which results in two separate data functions being produced. The first function contains all the precursor ion information and the second function contains fragment ion information. A proprietary peak detection algorithms to align the data by retention time. Combining this with IMS allows

alignment by retention time and drift time. Figure 1 shows schematic of the Vion IMS QTof and a theoretical example of how IMS can be used for spectral clean-up.

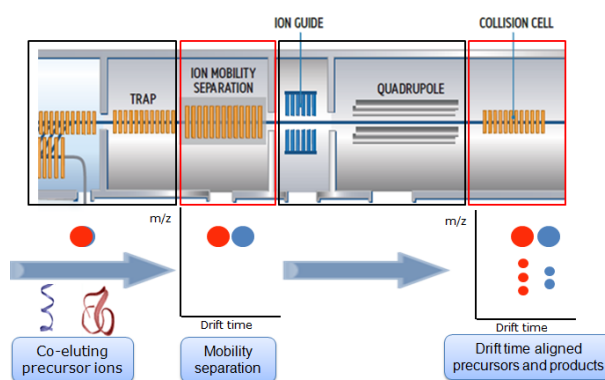


Figure 1. Drift alignment of precursor and product ions on Waters Vion IMS QTof

An example of how this spectral clean up can be used is drawn from a presentation delivered at INEF 2015 by one of our scientists Lauren Mullin. This work was performed in collaboration with Frank Dorman at Penn State. This investigation looked at controlled burn studies for mixed halogenated dioxins and furans. The samples produced were very complex mixtures. Using retention time and drift time alignment of the atmospheric pressure gas chromatography (APGC) analysis the precursor and product ion spectra were cleaned up making it easier to identify other mixed halogenated dioxins and furans. Figure 2 shows the unaligned and aligned drift spectral data for one of the identified compounds.

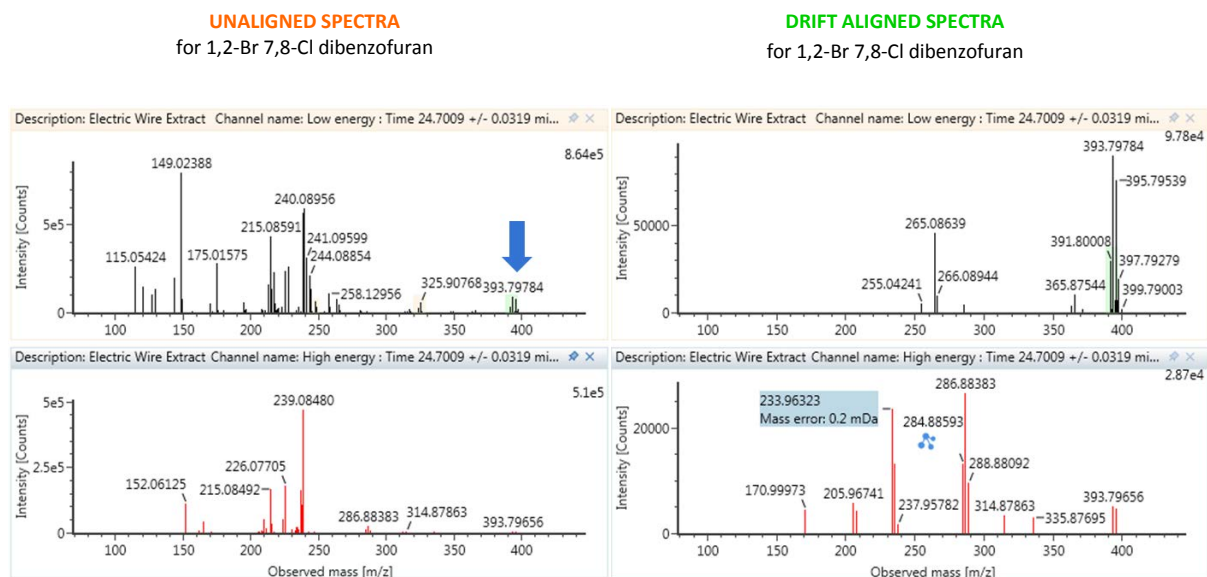


Figure 2. High definition mass spectrometry (HDMSE) spectral clean up of a mixed halogenated dibenzo furan

Spectral clean up is very valuable in elucidation of known and unknown compounds in complex mixtures. In addition to spectral clean-up the collisional cross section (CCS) of an ion can be measured. CCS describes the three-dimensional orientation of a molecule as it tumbles in the gas phase. The drift cell is calibrated with a compound of known CCS and all ions are measured against this calibration. As these measurements are performed in the gas phase they are independent of sample introduction and matrix interferences.

In order to demonstrate that CCS is independent of ionization and chromatographic technique a comparison of a solvent mix of 73 GC and LC amenable pesticides was injected five times each for both the LC and GC analyses. When retention times under the two techniques were compared, as would be expected no correlation was observed (Figure 3). The CCS values were found to be strongly correlated to one another (Figure 4). A regression analysis of these two techniques' results for CCS produced an R² value of 0.998,

indicating a very high degree of correlation. Moreover, the CCS values across the five injections in each technique showed minimal deviation. From these results, it could be seen that CCS values of the ions generated were conserved, regardless of how the analytes were introduced into the ion mobility MS system. These results support the use of CCS values, in addition to mass and characteristic product ions, for compound identification.

So what can ion mobility do for you? It can clean up your spectra to aid identification of known and unknown compounds. At the same time it provides a robust and reproducible CCS measurement for each component, which gives added confidence in results and can be a powerful tool in screening experiments. Ion mobility could play a vital role in the future of environmental analysis.

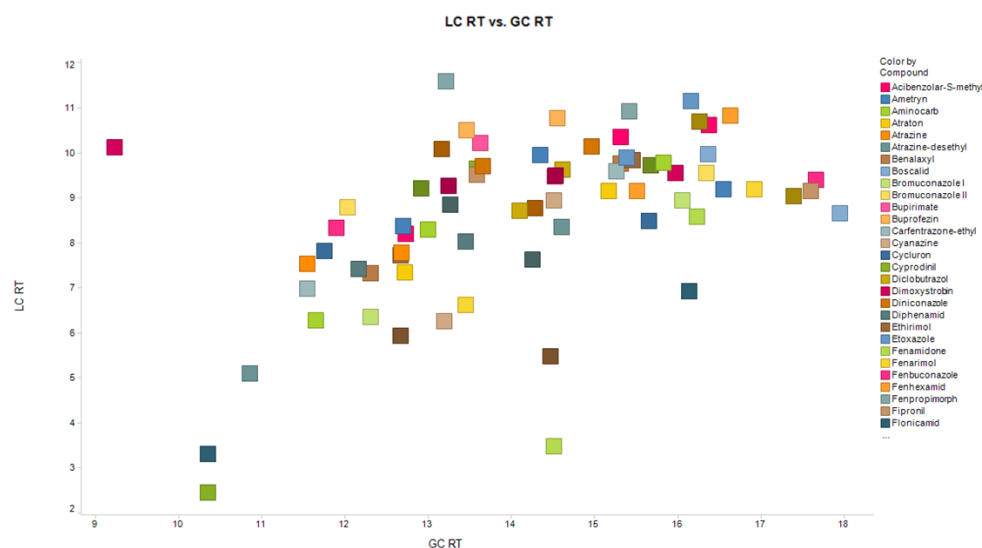


Figure 3. Retention time regression analysis of GC and LC analyses, indicating no correlation between the two approaches for 73 pesticides analyzed

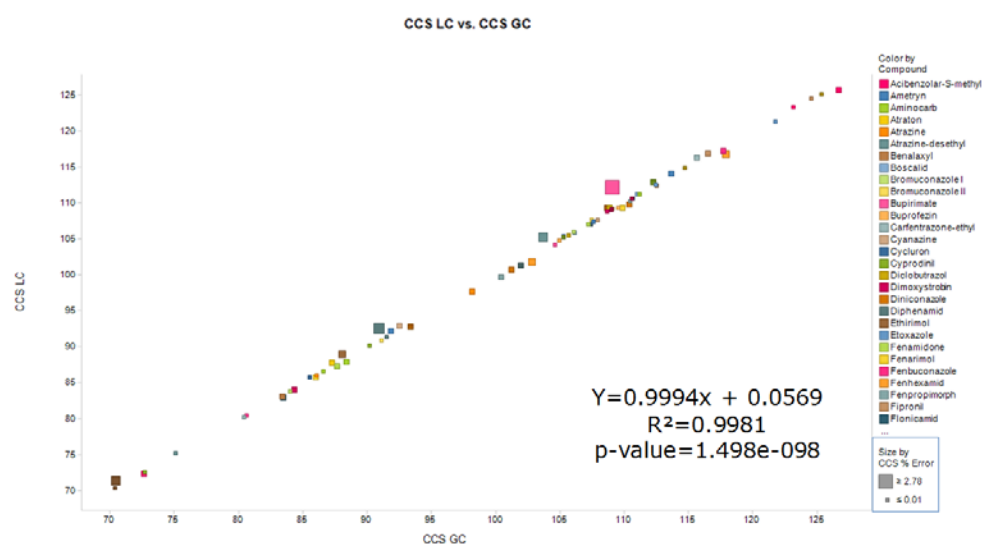


Figure 4. CCS value regression analysis of GC and LC analyses, indicating conversely to the RT comparisons, a strong correlation between CCS measurements obtained under GC and LC analyses for the 73 pesticides

What is Atmospheric Pressure Gas Chromatography (APGC)?

APGC was mentioned in the article and was featured at INEF 2015. APGC is one of the many ionization techniques offered by Waters as part of the universal source architecture. By designing versatility into instruments, a single instrument

can be utilized for both LC and GC amenable compounds. The time to switch between LC and GC is less than 10 minutes and does not require any instrument venting.

APGC utilizes a corona discharge in order to induce ionization for compounds eluting from a GC column. The source is completely enclosed

and ionization can occur by two mechanisms: charge transfer or proton transfer (Figure 5). APGC ionization is much softer than traditional EI GC. This results in molecular ions being the base peak in most cases giving extra selectivity for MRM transitions and more information for structural elucidation (Figure 6). APGC is not limited by flow rate unlike traditional vacuum GC systems. Flow rates can be increased beyond the regular GCMS flow rates, allowing faster GC separations to be performed and analysis time to be reduced. Advanced techniques like IMS separations are available with APGC. The ability to perform APGC on Waters allows the latest MS techniques including Ion mobility separation to be applied to GC amenable compounds.

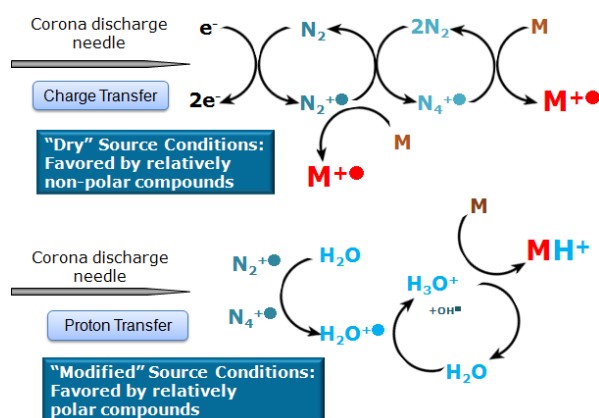


Figure 5. APGC mechanisms of ionization

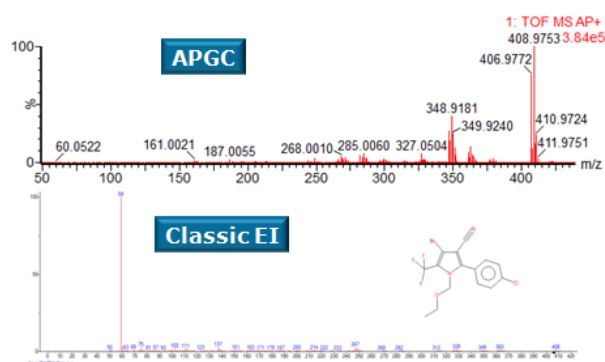


Figure 6. Chlorfenapyr showing enhanced ionization under proton transfer conditions with APGC compared with EI

Acknowledgements

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References

To learn more about IMS visit;

http://www.waters.com/waters/en_US/Ion-Mobility-Mass-Spectrometry/nav.htm?cid=134656158

To learn more about APGC visit;

http://www.waters.com/waters/en_US/Waters-Atmospheric-Pressure-Gas-Chromatography-%28APGC%29/nav.htm?cid=10100362

Demonstration of Collisional Cross Section Value Conservation across LC and GC Analyses;

<http://www.waters.com/waters/library.htm?cid=511436&lid=134854844>

Ion Mobility Enhanced Separation of Poly-Halogenated Dioxins and Furans in Controlled Burn Samples;

<http://www.waters.com/waters/library.htm?cid=511436&lid=134848054>

The Implementation of Ion Mobility Quadrupole Time-Of-Flight Mass Spectrometric Analysis of PFOS Isomers;

<http://www.waters.com/waters/library.htm?cid=511436&lid=134854852>