A Novel Solution to the Analysis of Highly Complex Environmental Samples

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Overview

Gas chromatography coupled with time-of-flight mass spectrometry provides some of the best analytical tools for both targeted and non-targeted methods of environmental analysis with increased selectivity, sensitivity, reliability, and information capacity. The GC-MS identification of known compounds of interest and the structural elucidation of unknown compounds becomes considerably more reliable if accompanied by accurate mass measurements generated by High Resolution Mass Spectrometry (HRMS). When analyzing real-life samples in a complex matrix, a large number of analytes of interest, with a wide range of concentrations, are likely present. Consequently, a significant increase in chromatographic peak capacity is required which can be realized by the use of comprehensive GCxGC. An ultra-high resolution time-of-flight mass spectrometer with enhanced sensitivity from LECO Corporation was used to analyze various residue and environmental samples. Select examples of pesticide residue matrix spiked samples along with some arctic ice samples were analyzed to show a variety of complex environmental sample types. Examples will be shown of how the use of this instrument provides highly reliable data suitable for automatic, accurate spectral deconvolution of coeluting analytes present in samples with a wide concentration range. The addition of the GCxGC technique increases the separation power by allowing for chromatographic separation of closely eluting constituents, thus making analyte identification more reliable and the comprehensive analysis of environmental samples more realistic.

Introduction

The Pegasus® GC-HRT+ is a High Resolution Multi-Reflecting TOFMS. This technology achieves a full mass range resolving power > 25,000, with sub-ppm mass accuracies, acquisition rates up to 200 spectra/sec, and excellent isotope ratio fidelity. This is made possible because of a long flight path (20 m), and a long flight time (1 ms), but still packed into just a 760 mm long analyzer vacuum chamber by using a Folded Flight Path® (FFP®). This design also uses a non-trapping orthogonal pulser, which means that there will be ions that are lost during the interval between push pulses which may affect its sensitivity. To resolve this problem, LECO has developed Encoded Frequent Pushing™ (EFP™).

EFP is a novel multiplexing approach which allows for an increase in sensitivity by increasing the duty cycle of the instrument, but with reduced/minimal overlapping m/z peaks in the resulted mass spectra. The feature that separates this approach to multiplexing from other approaches is the use of unequal pulse intervals. It's this unequal pulse interval that prevents the possible loss in sensitivity due to overlapping m/z peaks in the analyzer[1,2]. In brief, it does not use a Hadamard transform.

Experiments

A set of eight injections of 1 ppb (pg/µL) of OFN were collected using EFP to demonstrate the sensitivity of the instrument. This resulted in an IDL calculation of 0.04 ppb. Figure 1 Plot A shows overlapped chromatographic plots of m/z 271.987 ± 4 mDa for the 0.1 ppb OFN runs. Plot B shows the benefit of EFP by comparing a 1 ppb OFN standard collected with and without EFP. Plot C shows the added benefit of EFP with regard to dynamic range by an increase in the order of magnitude due to an increase in sensitivity without affecting the high end of the dynamic range.

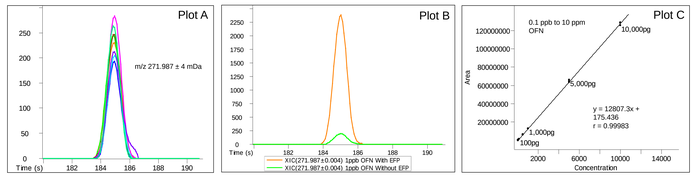

Figure 1. Plot A shows 8 replicate injections of 0.1 ppb OFN injection overlaid. Plot B is an overlaid plot of a 1ppb OFN standard with and without EFP. And Plot C is a dynamic range plot of OFN showing 5 orders of magnitude.

Sensitivity can be demonstrated with a typical performance standard, but the next step is to see how well EFP behaves with a set of environmental standards in matrix. A set of six calibration standards containing 107 pesticides in an eggplant matrix were prepared at concentrations ranging from 0.5 ppb to 20 ppb. Figure 2 shows a chromatographic plot displaying the TIC of the 10 ppb standard along with a chromatographic plot displaying the quant masses (AIC) for each of the analytes in the sample.

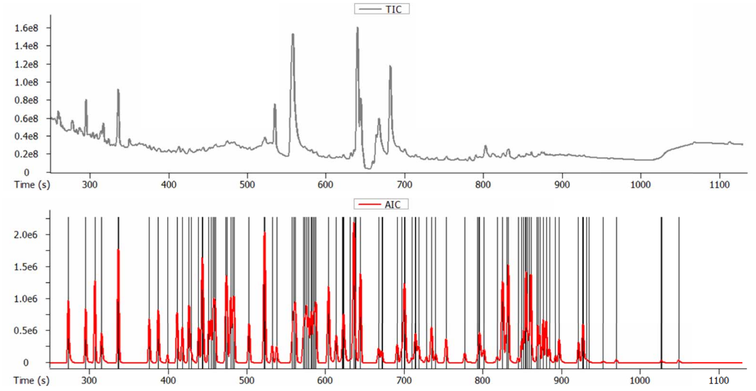

Figure 2. Chromatographic plot of a 10 ppb standard in an eggplant matrix displaying the TIC above and the AIC below.

The instrument needs to be able to produce very good spectral quality at the required low concentrations. Figure 3 shows two examples of the excellent spectral quality of a-BHC and Tefluthrine at 10 ppb in an eggplant matrix displaying their caliper spectrum, deconvoluted (Peak True) spectrum, and library match spectrum generated from this instrument. The a-BHC has a similarity match of 894 and the Tefluthrine has a similarity match of 929.

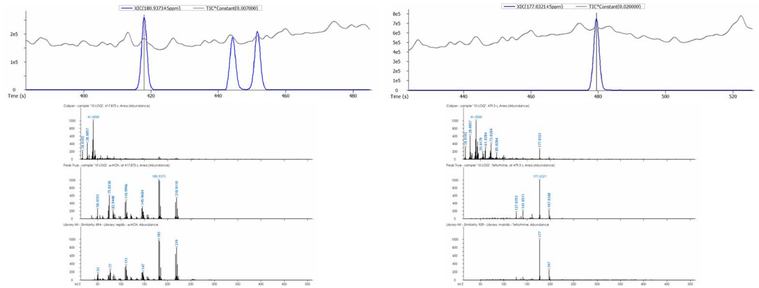

Figure 3. Zoomed in chromatographic plots of a-BHC and Tefluthrine with their respective spectral plots below.

To address the situation where a sample has a large number of analytes at various concentrations in a complex sample matrix, high chromatographic peak capacity is essential. Comprehensive two-dimensional gas chromatography was therefore applied to the same sample set with slightly different methodology to demonstrate the ability to separate the sample matrix from the analytes of interest due to the increased peak capacity. Figure 4 shows a contour plot of a 2.5 ppb standard in an eggplant matrix. Figure 5 is a zoomed in portion of the same plot displaying the sample complexity.

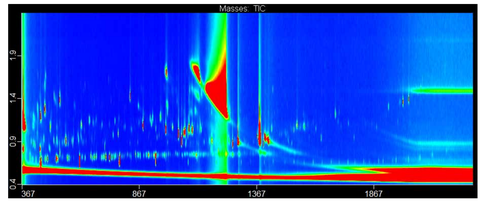

Figure 4. GCxGC Contour plot of a 2.5 ppb eggplant matrix standard.

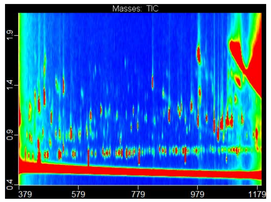

Figure 5. Zoomed in plot of the 2.5 ppb eggplant matrix standard.

The addition of EFP to GCxGC has not only helped to improve peak detectability, but it has also shown to improve library similarity scores. To demonstrate the benefits of EFP with GCxGC, an arctic ice sample provided by Prof. A. Lebedev (Moscow State University) was analyzed in the conventional 1D approach using EFP and by GCxGC with and without EFP enabled. Figure 6 shows a GCxGC surface plot of the two GCxGC runs collected along with the 1D chromatogram of the ice sample. Figure 7 shows an example of the benefits of GCxGC to resolve peaks that were unidentifiable when run one-dimensionally. Figure 8 displays two bar graphs demonstrating the benefits of EFP to find more peaks when combined with GCxGC.

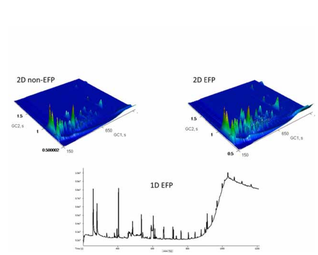

Figure 6. GCxGC surface plots with and without EFP enabled and a one-dimensional plot of the same arctic ice sample.

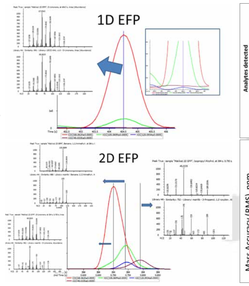

Figure 7. Two plots demonstrating the enhancement of GCxGC.

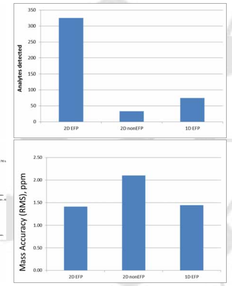

Figure 8. Peak finding and identification improvements with GCxGC and EFP.

Conclusion

The use of a novel multiplexing approach called Encoded Frequent Pushing has demonstrated the ability to increase the sensitivity of a High Resolution Multi-Reflecting TOFMS without compromising other aspects of its performance. This new approach has the potential to bring the benefits of a HR-TOFMS coupled with GC or GCxGC to applications that need extra sensitivity along with sub-ppm mass accuracies and a full mass range resolving power greater than 25,000 for better confidence in peak identification at present and in future retrospective analysis of complex samples.

Acknowledgements

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References

[1] ASMS 2015 Proceedings, TOA am, P. Willis et al. "High Resolution Multi-Reflecting TOFMS with Multiplexing by Encoded Frequent Pulsing for increasing the duty cycle 10-100 times"

[2] Technical Brief: Encoded Frequent Pushing 209-066-018 at www.leco.com

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