A Novel Robust Direct Extraction EI Source for GC-TOFMS and GCxGC-TOFMS

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Introduction

Direct extraction EI sources used in GC-TOFMS and GCxGC-TOFMS create ions from neutral analytes, as well as from the ion packets that are pulsed down the TOF drift region. In most implementations, the direct extraction EI source electrodes have grids over the apertures that ensure the equipotential lines remain flat in the ionization region, as well as areas where the ion packets travel, thus ensuring desired resolution, mass accuracy, and signal intensity of the GC-TOFMS system is achieved. A novel, gridless, direct extraction EI source with high sensitivity and a duty cycle near 100% has been developed to improve detection limit and robustness of GC-TOFMS and GCxGC-TOFMS.

The data presented in this poster were obtained on a Pegasus® BT 4D (Figure 1) prototype with the novel gridless ion source. The system is capable of achieving sub-10 femtogram instrument detection limits (IDL) for Octafluoronaphthalene (OFN), while acquiring data in full mass range, sub-nominal mass accuracy, 5 orders of linear dynamic range, and powerful real time two-dimensional deconvolution along the retention time and time-of-flight axes.

Methods

The OFN standards were purchased from Ultra Scientific (RI, USA). For both GC and GCxGC experiments, data was acquired over an m/z range of 50-550, and an ion source extraction frequency of 32 kHz. The transfer line and ion source temperatures were both set to 250 °C. Data was acquired at 10 spectra/second in GC experiments, and 200 spectra/second in GCxGC experiments.

For GC experiments, 100:1 split injections were performed onto a 30 m x 0.25 mm x 0.25 µm RXI-5MS column. The GC oven was ramped from 50 °C to 170 °C at a rate of 20 °C/minute. For GCxGC experiments, 100:1 split injections were performed onto a 30 m x 0.25 mm x 0.25 µm RXI-5MS first dimension column, and a 2 m x 0.25 mm x 0.25 µm RXI-17SILMS second dimension column, with 0.10 m in the LECO Thermal Modulator and 0.30 m in the secondary oven. The main GC oven was ramped with the following program: 60 °C (0.5 min hold) to 130 °C (2.10 min hold) at 60 °C/min and then to 160 °C at 60 °C/min. The secondary oven used a 5 °C offset relative to the GC oven temperature, and the modulator used a 15 °C offset relative to the secondary oven temperature.

A multi-analyte standard was spiked into a QuEChERS extract of spinach without cleanup at a concentration of 1.25 pg/µl or 2.5 pg/µl. GCxGC injections were acquired at 200 spectra/second over an m/z range of 35-635, and an ion source extraction frequency of 30 kHz. The transfer line and ion source temperatures were 320 °C and 300 °C respectively. The GCxGC experiments utilized 100:1 split injections onto 30 m x 0.25 mm x 0.25 µm RXI-5MS first dimension column, and a 2 m x 0.25 mm x 0.25 µm RXI-17SILMS second dimension column, with 0.10 m in the LECO Thermal Modulator and 0.30 m in the secondary oven. The main GC oven was ramped with the following program: 40 °C (0.5 min hold) to 320 °C (5 min hold) at 20 °C/min. The secondary oven used a 5 °C offset relative to the GC oven temperature, and the modulator used a 15 °C offset relative to the secondary oven temperature.

For the gridless ion source robustness study, the dirty matrix sample used to stress the ion source was a QuEChERS extract of black tea without cleanup. Splitless injections (20 ml/min purge flow at 60 seconds) were performed onto a 15 m x 0.15 mm guard column. The GC oven was ramped from 50 °C to 250 °C at 40 °C/min.

Figure 1. Pegasus BT 4D GCxGC-TOFMS.

StayClean® Ion Source

The novel gridless EI source uses an Open Style design that keeps metal surfaces relatively far away from the ionization region, and thus reduces the effects of contamination on the analyte signal intensity. The exit apertures of the ion source and entrance aperture to the drift region do not have mesh attached. The geometry of the ion source and drift electrodes were optimized to maximize signal intensity and maintain mass resolving power. Figure 2 shows a cross-section view of the gridless source.

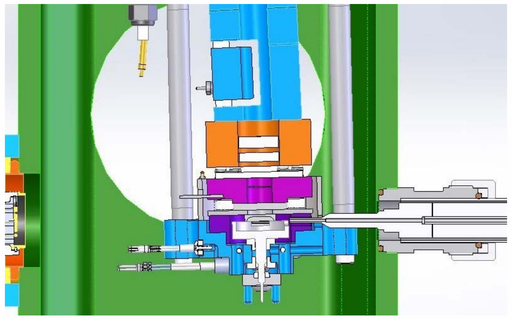

Figure 2. A top cross-section view of the gridless ion source and drift entrance optics. Analyte molecules are ionized, and TOF ion packets are generated in the same volume. Ions can be extracted from the source at frequencies of 15-35 kHz.

Results: Detection Limits

The detection limit of the Pegasus BT is demonstrated by calculating the instrument detection limit (IDL) for OFN in both GC-TOFMS and GCxGC-TOFMS. Eight replicate injections of OFN were acquired in each mode, and the IDLs were calculated by the following formula:

IDL = (%RSD/100) x $t_{student}$(99% confidence) x amount on column

Table 1. IDLs for OFN in GC-TOFMS and GCxGC-TOFMS calculated from eight replicate injections of 20 fg for GC-TOFMS and 10 fg for GCxGC-TOFMS.

Mode	Amount On Column	Average Quant S/N	%RSD	IDL
GC-TOFMS	20 fg	20.6	10.8%	6.5 fg
GCxGC-TOFMS	10 fg	36.5	7.0%	2.1 fg

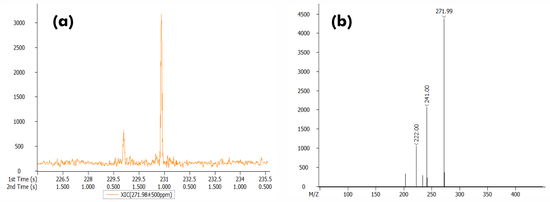

Figure 3. (a) Chromatogram of a GCxGC-TOFMS injection of 10 fg OFN. (b) Deconvoluted Peak True mass spectrum of the 10 fg OFN peak.

Molecular Ion Generation

The following data shows the gridless source's performance in generating molecular ion for dodecanoic acid methyl ester, which has a low m/z fragment as the base peak. The molecular ion intensity is consistent with the NIST library spectrum with an excellent NIST Similarity Score.

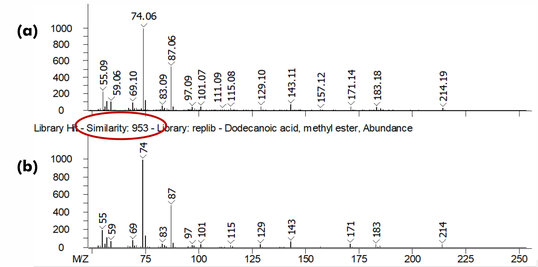

Figure 4. (a) Deconvoluted Peak True spectrum for dodecanoic acid methyl ester, and (b) the NIST library Spectrum for the compound. The NIST Similarity Score for this Peak True Spectrum is 953.

Detection Limits in QuEChERS Extract of Spinach

Table 2. IDLs for 8 analytes calculated from eight replicate injections of 12.5 fg or 25 fg per component on column from a standard solution spiked into a QuEChERS extract of spinach.

Analyte	Amount On Column	Average Quant S/N	%RSD	IDL
OFN	12.5 fg	11.2	11.1%	4.2 fg
Dibromobenzene	25 fg	15.5	10.9%	8.2 fg
Tribromobenzene	25 fg	11.9	10.5%	7.9 fg
Hexachlorobenzene	25 fg	15.8	9.3%	7.0 fg
Phenanthrene	12.5 fg	27.8	9.7%	3.6 fg
Fluoranthene	12.5 fg	14.3	14.6%	5.5 fg
Pyrene	12.5 fg	12.8	15.8%	5.9 fg
Chrysene	25 fg	12.6	28.7%	21.6 fg

Gridless Source Robustness

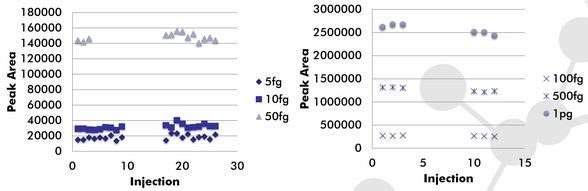

Figure 5. Peak area for replicate injections of OFN on column acquired before (left grouping of data points) and after (right grouping of data points) 1,000 injections of a QuEChERS extract of black tea. The ion optics and detector bias were re-tuned after the black tea injections.

Table 3. %RSDs for the various concentrations of OFN injected. The %RSD calculation included all OFN injections from *before and after* the 1,000 black tea extract injections.

Amount on Column	%RSD Peak Area
5 fg	16.76%
10 fg	9.99%
50 fg	3.29%
100 fg	2.47%
500 fg	3.75%
1 pg	2.89%

Conclusions

The novel gridless source on a Pegasus BT 4D prototype has demonstrated the following performance characteristics.

- Sub-10 fg IDL for GC-TOFMS and sub-5 fg IDL for GCxGC-TOFMS
- Excellent molecular ion generation and NIST similarity scores
- Robust operation: the StayClean ion source preserves signal intensity for multiple concentrations of OFN after 1,000 injections of a black tea extract

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