Sub-Picogram Detection and Identification of Analytes in Complex Matrices Using a Novel GC-TOFMS

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Introduction

Improved detection limits in GC-MS analyses allow for the following advantages: detection of lower concentration analytes that were previously undetectable, reduction in the amount of sample required to be prepared for analysis, and operation of the GC in split injection mode to reduce matrix loading on the GC column and ion source.

The data presented in this poster were obtained on a novel GC-TOFMS system, the Pegasus® BT (Figure 1). This system includes a novel open style ion source, robust mass analyzer ion optics, a state-of-the-art Data Acquisition System, and powerful signal processing and data processing software algorithms. These design elements are combined to provide sub-picogram detection limits while acquiring data in full mass range, sub-nominal mass accuracy, 5 orders of linear dynamic range, and powerful two-dimensional deconvolution along the retention time and time-of-flight axes.

Methods

The multi-analyte standards were prepared in concentrations ranging from 1.25 pg/µl to 25 ng/µl in methylene chloride, and spiked into a QuEChERS extract of black tea. GC methods utilized 20:1 split injections onto a 30 m x 0.25 mm x 0.25 µm RXI-5MS column. The GC oven was ramped from 35°C (1 minute hold) to 330°C (5 minute hold) at a rate of 20°C/minute. Injections were acquired for the standards with and without matrix. The transfer line and ion source temperatures were set to 320°C and 300°C, respectively. Data was acquired over an m/z range of 35-640, an ion source extraction frequency of 30 kHz, and spectra acquisition rate of 10 spectra/second.

The Octafluoronaphthalene (OFN) standards were purchased from Ultra Scientific (RI, USA). The GC method utilized 100:1 split injections 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. The transfer line and ion source temperatures were both set to 250°C. Data was acquired over an m/z range of 50-640, an ion source extraction frequency of 30 kHz, and an acquisition rate of 10 spectra/second.

Figure 1. Pegasus BT GC-TOFMS

Ion Source

The EI source uses an open style design that keeps metal surfaces relatively far away from the ionization region and thus reduce the effects of contamination on the analyte signal intensity. For example, the test data show that even after 2500 injections of samples with matrix (10 % crude oil and diesel), the instrument was still meeting all analytical specifications without any source cleaning or other maintenance steps.

Data Acquisition System

The Pegasus BT data acquisition system was internally developed by LECO Corporation specifically for this system. Two 500 MHz, 12 bit ADCs generate two data streams (low gain and high gain), which are overlapped to create 15 bits of vertical resolution. The data is summed on the data acquisition board, and mass spectra are transferred to the PC in profile form, which allows sub-nominal mass accuracy, as well as two-dimensional deconvolution along both the retention and TOF axes.

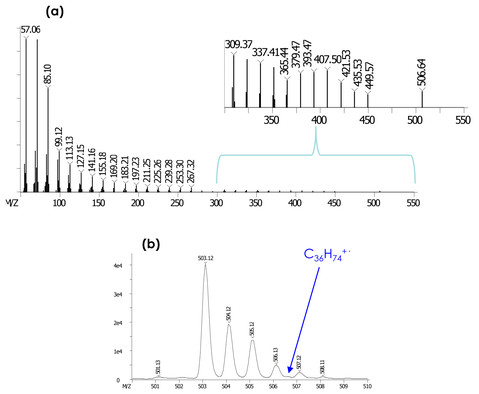

Figure 2. (a) Deconvoluted Peak True mass spectrum for 50 pg of C_{36} n-alkane. The inset shows a zoomed view of the higher m/z range. (b) The Profile Caliper mass spectrum of the molecular ion of C_{36} n-alkane. The resolving power of the mass spectrometer combined with the power of two-dimensional deconvolution pulls the molecular ion apart from the column bleed ion's interference.

Results: Detection Limits

The detection limit of the Pegasus BT is demonstrated by calculating the instrument detection limit (IDL) for 14 analytes in the multi-analyte standard mix. Eight replicate injections of 62.5 fg per component on column are acquired, and the IDL is calculated by the following formula:

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

Table 1. IDLs for 14 analytes calculated from eight replicate injections of 62.5 fg per component on column from a standard solution in methylene chloride.

Analyte	% RSD	IDL (fg)
OFN	5.19%	9.7
Naphthalene	10.26%	19.2
Dibromobenzene	9.95%	18.6
Tribromobenzene	7.39%	13.8
Acenaphthene	4.78%	9.0
Benzophenone	16.21%	30.4
Tetrabromothiophene	8.44%	15.8
Hexachlorobenzene	5.9%	11.1
Phenanthrene	10.06%	18.8
Anthracene	8.2%	15.4
Fluoranthene	5.75%	10.8
Pyrene	9.59%	18.0
Chrysene	8.57%	16.1
Benzo(a)anthracene	8.43%	15.8

Detection Limits in Black Tea Matrix

Table 2. IDLs for 14 analytes calculated from eight replicate injections of 62.5 fg per component on column from a standard solution spiked into a QuEChERS extract from black tea. The analytes without IDLs listed were not detected at these low levels due to interfering ions from the black tea matrix.

Analyte	Amount Injected	IDL (fg)
OFN	62.5	18.0
Naphthalene	62.5	20.8
Dibromobenzene	62.5	14.6
Tribromobenzene	125	18.3
Acenaphthene	-	-
Benzophenone	-	-
Tetrabromothiophene	125	22.2
Hexachlorobenzene	62.5	18.4
Phenanthrene	-	-
Anthracene	-	-
Fluoranthene	62.5	14.5
Pyrene	62.5	17.1
Chrysene	-	-
Benzo(a)anthracene	62.5	18.1

Dynamic Range

Dynamic range performance is demonstrated for the same 14 analytes over amounts on column from 25 fg to 2.5 ng (5 orders of magnitude).

Table 3. Reported correlation coefficients (r) for 14 analytes calculated from calibration curves built from triplicate injections over the range of 25 fg to 2.5ng (5 orders of magnitude) per component on column.

Analyte	Concentration Range	Correlation Coefficientb (r)
OFN	25 fg-2.5 ng (5 orders)	0.996
Naphthalene	25 fg-1.25 ng (4.5 orders)	0.998
Dibromobenzene	25 fg-2.5 ng (5 orders)	0.996
Tribromobenzene	25 fg-2.5 ng (5 orders)	0.997
Acenaphthene	25 fg-2.5 ng (5 orders)	0.995
Benzophenone	25fg-2.5 ng (5 orders)	0.995
Tetrabromothiophene	62.5 fg-2.5 ng (4+ orders)	0.996
Hexachlorobenzene	25 fg-2.5 ng (5 orders)	0.998
Phenanthrene	25 fg-2.5 ng (5 orders)	0.996
Anthracene	25 fg-2.5 ng (5 orders)	0.995
Fluoranthene	25 fg-2.5 ng (5 orders)	0.995
Pyrene	25 fg-2.5 ng (5 orders)	0.994
Chrysene	25fg-2.5 ng (5 orders)	0.991
Benzo(a)anthracene	25 fg-2.5 ng (5 orders)	0.993

Reproducibility and Mass Stability

The reproducibility and mass stability of the Pegasus BT was recorded over several days with injections of 500 fg OFN on column.

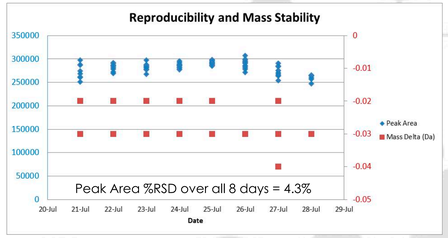

Figure 3. Peak area for replicate injections of 500fg OFN on column acquired on eight consecutive days without re-tuning the ion optics or mass calibrating.

Conclusions

The new Pegasus BT has demonstrated the following performance characteristics:

- Sub-20 fg IDL for several analytes in a multi-analyte standard mix
- Up to 5 orders of linear dynamic range
- Excellent reproducibility and mass stability
- Powerful two-dimensional deconvolution
- Small footprint (benchtop)

Delivering the Right Results