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eBook

Thermo Scientific Orbitrap Exploris GC Mass Spectrometer

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Contents

Foreword

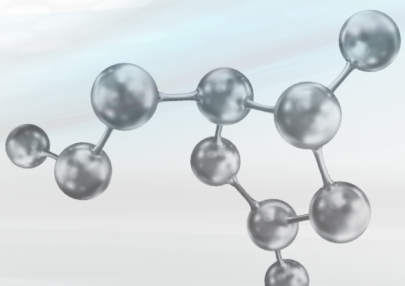
Although the technological principles that underlay its conception date back to 1923, when Kingdon first described orbital trapping using an enclosed metal can and charged wire, the first Orbitrap-based mass spectrometer entered the market more than 80 years later. In 2005, we introduced our first Orbitrap mass spectrometer.

This initial commercial Orbitrap system combined high-resolution, accurate mass (HRAM) detection with the benefits of a linear ion trap. The research community, and especially proteomics as a discipline, enthusiastically welcomed an instrument that met the then-current standard for resolution, mass accuracy, and speed while eliminating the issues that came with FT-ICR machines (maintenance and space concerns) or time-of-flight (TOF) instruments (lower sensitivity, dynamic range and resolution). HRAM capability allowed researchers to detect multiply charged species in complex mixtures and improved database searching with accurate mass detection. For discovery, scientists were able to harness this instrument's full-scan mode to compile a list of precursors suitable for MS/MS by collision-induced dissociation (CID) within a single run. And even though the technology appears to be more complex, the high resolution and accurate mass actually make analyses simpler, reducing the need for tedious method development.

Further accessibility to Orbitrap mass analyzer technology came in the form of the Thermo Scientific™ Orbitrap Exactive™ and Q Exactive™ mass spectrometers. By 2011, the speed of the Orbitrap was further improved by a factor of four, by combining enhanced Fourier transform algorithms that doubled resolving power, and the high-field "compact Orbitrap." The elimination of the ion trap mass analyzer reduced cost and complexity, producing a bench-top instrument that could perform full-scan detection and higher energy collisional dissociation (HCD) without precursor selection. This led to the development of protocols for Orbitrap-only detection, and enabled HRAM screening of known and unknown analytes with very high selectivity (< 5 ppm). It also facilitated retrospective analysis of full scan data. Finally, there was an Orbitrap analyzer that was completely compatible with gas chromatography (GC) separations. In 2015, exactly 10 years after the introduction of the first Orbitrap system, the Q Exactive GC and later Exactive GC were launched.

The Orbitrap Q Exactive GC was an important milestone in GC-MS history but that was just the beginning. The next-generation Thermo Scientific Orbitrap Exploris GC mass spectrometer provides the sensitivity, selectivity, and linear dynamic range to meet the toughest analytical challenges. It allows analytical testing laboratories to simplify operations and deliver consistently accurate results.

This eBook provides an overview of this exciting and powerful system as well as specifications, applications, case studies, and more. Learn how it can take your laboratory to unprecedented levels of performance and productivity.



New opportunities for analytical testing

The Thermo Scientific Orbitrap Exploris GC mass spectrometer with the Thermo Scientific™ TriPlus™ RSH autosampler.

Evolved to exceed the demands of everyday testing, the Thermo Scientific™ Orbitrap Exploris™ GC mass spectrometer simplifies operations and delivers consistently accurate results. Transform analytical workflows to keep pace with changing demands, maximize system uptime, and expand laboratory capability.

Simplify | Confidence | Everyday

- **Power productivity**

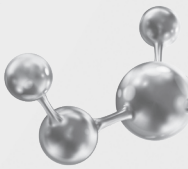
  Simplify analytical workflows with the compact Orbitrap Exploris GC mass spectrometer that brings the versatility of full-scan high-resolution accurate mass data to screening and quantitation. With proven robustness and reliability across all applications, the system delivers accurate results sample after sample.

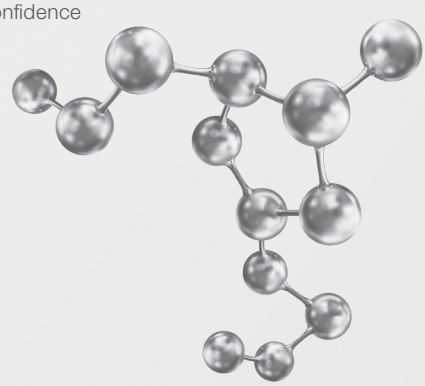
- **Ensure certainty in results**

  Reduce time evaluating data and increase confidence with exceptional levels of selectivity, sensitivity, and linear dynamic range that come together to deliver accurate results, in all sample matrices. Full-scan high-resolution MS data allows multipoint compound identification with spectral matching, isotope patterns, retention indices, and elemental compositions to reduce time to result.

- **Maximize uptime**

  Deliver results on time and with ease. With an intuitive instrument control and method templates, the system is fully accessible to all members of your analytical team and provides complete confidence that the system is always operating at maximum performance.





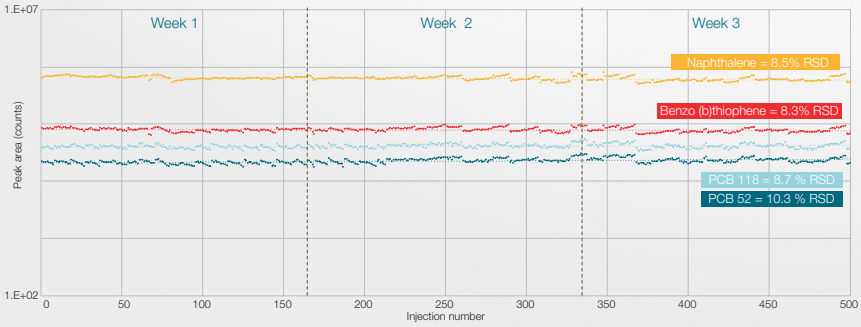
Environmental | Food safety | Anti-doping | Clinical and toxicology | Industrial

Expand analytical capability with simplicity

The Orbitrap Exploris GC mass spectrometer provides high-confidence detection and precise quantitation in complex matrices, with minimal method development for maximum productivity. As one of the next-generation Thermo Scientific™ mass spectrometers, the Orbitrap Exploris GC mass spectrometer brings together exceptional levels of mass resolution, sensitivity, speed, and linear dynamic range without detector saturation to deliver accurate results even for your most challenging samples.

Transform profitability

The efficiency of operations from sample receipt to report drives profitability in analytical testing laboratories. Every step in the process is critical and every instrument needs to provide a return on investment. The Thermo Scientific Orbitrap Exploris GC mass spectrometer delivers new opportunities for analytical services to simplify operations and improve efficiency. With outstanding real-world performance and analytical flexibility, the system can reduce costs and increase the quality of quantitative results.



Repeatability for high-throughput analysis of 500 replicate injections of a QuEChERS soil extract post spiked with PAHs and PCBs at 10 pg/µL (ppb) without internal standard correction.

Benefits that boost productivity

Increase scope

Gain the flexibility to quickly add new compounds without compound optimization and decide post acquisition which analytes to measure.

Fast system setup

Walk up, tune, and calibrate in under five minutes with full confidence that the system is operating at maximum performance for all users.

Efficient review and reporting

Use multiple points of identification to quickly confirm or reject detections, increasing peace of mind. Spectral matching, isotope patterns, retention indices, and elemental compositions provide high confidence in results.

Accurate quantitation

Six orders of linear dynamic range covers the concentrations encountered in even the most complex sample matrices.

Method consolidation

Combine acquisition methods onto a single system, reducing the need for multiple systems and streamlining data processing.

Retrospective analysis

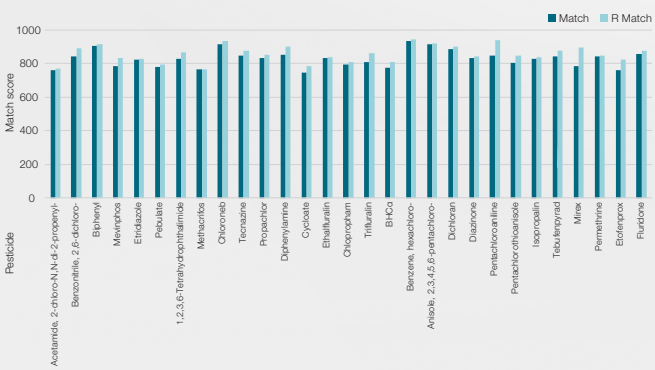
Interrogate previously acquired high-resolution accurate-mass (HRAM) data in multiple ways to answer additional analytical questions without additional sample injections.

Be certain with multipoint compound identification

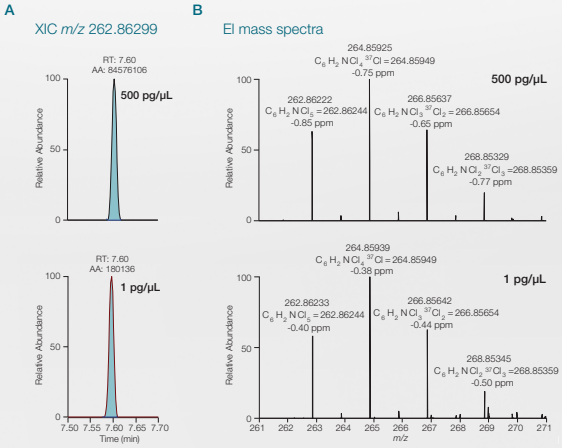
Add comprehensive HRAM spectral library matching to breakthrough performance to access the highest-confidence screening and quantitative workflows available today to speed up time to result. Full-scan HRAM data with spectral matching, isotope patterns, retention indices, and elemental compositions allow multi point compound identification, eliminating false results and accelerating report generation. Accurate masses provide certainty in proposed elemental compositions for both confirmation and unknown identification workflows.

Intelligent screening to increase scope

When used with Chromeleon CDS and TraceFinder software, the Orbitrap Exploris GC mass spectrometer offers a powerful, yet easy to use, screening solution with the durability demanded by laboratories focused on high-throughput analyses. Both software take advantage of multiple library sources (nominal mass and exact mass) to automate compound identification, including commercially-available libraries and Thermo Scientific™ Orbitrap™ HRAM GC-MS libraries. Sensitivity and dynamic range offer deeper insights into every sample.



Library search scores for pesticides from an Orbitrap Exploris GC mass spectrometer analysis of a mixed pesticide standard in a whole flour matrix (a score of 1,000 equals a perfect match). Forward search scores (Match) and reverse search scores (R Match) when searched again the NIST library are given for each pesticide.



Spectral fidelity for pentachloroaniline at two levels (1 and 500 pg/µL) in whole flour matrix using the Orbitrap Exploris GC mass spectrometer. [A] extracted ion chromatograms (XIC) for pentachloroaniline at each level annotated with peak retention time (RT) and peak area (AA); and [B] a zoomed-in view of EI mass spectra of the molecular ion cluster at each concentration level, annotated with the measured mass, elemental composition, theoretical mass, and mass accuracy (ppm).

Power GC-MS with Thermo Scientific software solutions

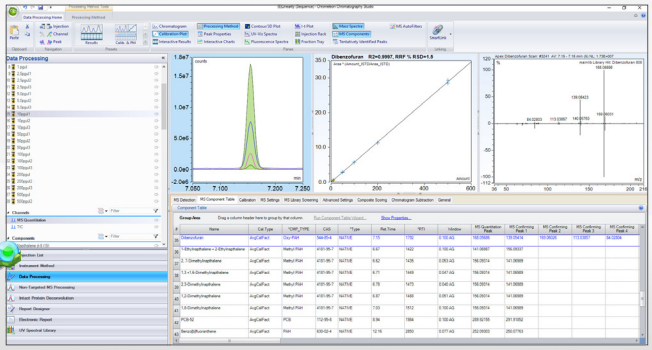
Providing fast and accurate results requires screening, quantitation, and discovery workflows that are accessible and efficient for users with different levels of MS expertise. Both Chromeleon CDS and TraceFinder software are workflow solutions that increase laboratory productivity from method setup to acquiring and processing data, and reporting results. Compound Discoverer software makes sample profiling and unknown analysis fast and easy with intelligent and flexible functionality to really get the most from your data.

Providing reportable results in a timely manner requires access to a truly connected data-processing ecosystem. Regardless of application, Thermo Scientific small-molecule data analysis solutions streamline unknown identification, screening, and quantitation using a powerful suite of software tools.

Chromeleon CDS

Enterprise-ready, regulatory-compliant quantitation

- Streamline chromatography and MS software training using the first CDS with quantitative MS analysis control
- Prepare for audits confidently with support for GLP, GMP, and 21 CFR Part 11 regulations
- Connect multiple sites and locations to a central data center with network failure protection
- Easily connect to third-party software applications and multi-vendor LC and GC chromatography instruments

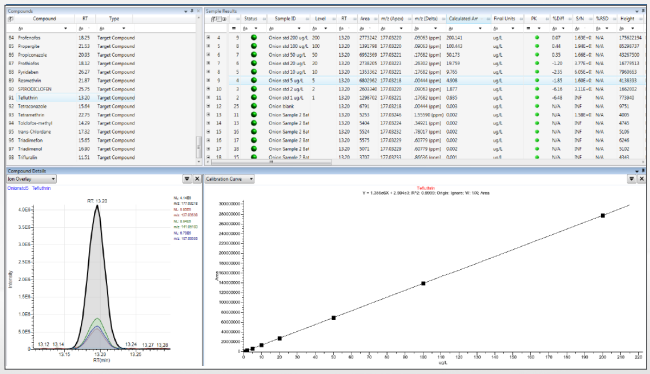


Chromeleon CDS data review for quantitation and confirmation of environmental contaminants.

TraceFinder software

High-throughput screening and quantitation

- TraceFinder software provides a single platform for both screening and quantitation, including peak deconvolution and spectral library matching
- View only desired data parameters with a customizable user interface
- Efficiently analyze and report data with customizable flagging and report templates

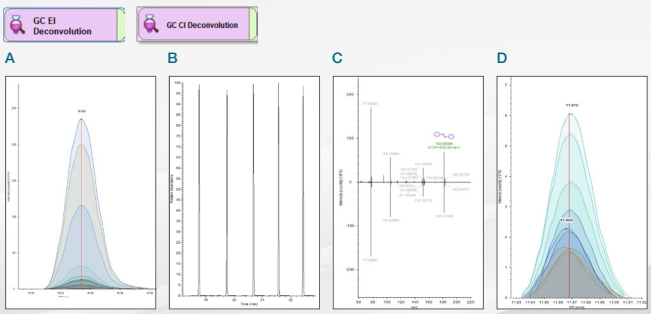


TraceFinder software data review of tefluthrin in onion with extracted ion overlay of the quantifier ion and three confirming ions (±5 ppm window) and matrix matched calibration series.

Compound Discoverer software

Small-molecule unknown identification

- Streamline and customize HRAM data analysis to simplify and gain insights fast. Node based workflows include GC EI and CI deconvolution with statistical analysis tools.
- Confidently profile your samples, compare sample groups, and identify unknowns faster using nominal mass and high-resolution mass spectral libraries
- Specify desired data flows with drag-and-drop workflow nodes
- Review only data you choose with customizable data visualization



Compound Discoverer software EI and CI node functionality. [A] Peak deconvolution. [B] Retention indexing. [C] Library search. [D] Cross sample peak grouping.

Fourth-generation quadrupole-Orbitrap mass spectrometer

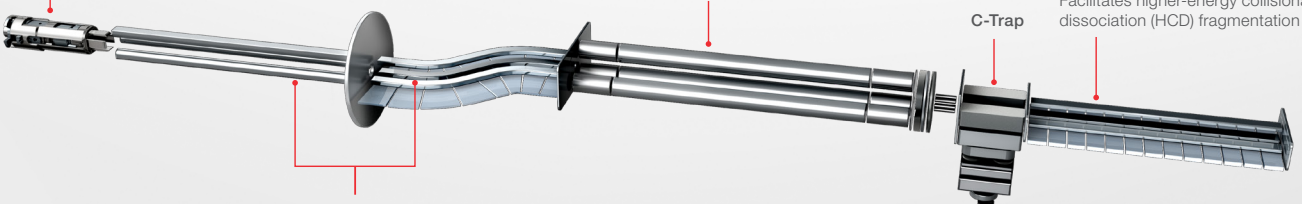
The Orbitrap Exploris GC mass spectrometer combines proven technology refined over more than 20 years with advanced performance and speed capabilities, day-to-day reliability, and a compact footprint. Now both novice and expert high-resolution MS users can efficiently obtain highly reliable and accurate results.

Thermo Scientific ExtractaBrite EI/CI ion source
Robust electron impact (EI) and chemical ionization (CI) performance. Fully removable for maintenance or column changes without breaking vacuum

Advanced Quadrupole Technology (AQT)
Improves sensitivity with 0.4 Da FWHM precursor isolation widths

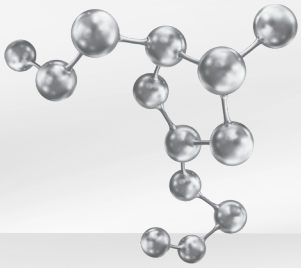
Ion-routing multipole (IRM)
Facilitates higher-energy collisional dissociation (HCD) fragmentation

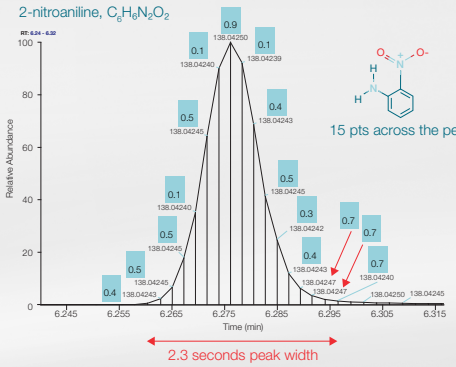
C-Trap



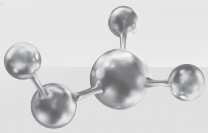
Advanced Active Beam Guide (AABG) with axial gradient
Reduces noise and increases robustness by preventing neutrals from entering the quadrupole mass filter, and by eliminating effects of local charging

High-field Orbitrap mass analyzer
Configure resolution up to either 30,000 or 60,000 (FWHM) at *m/z* 200 and acquisition rates up to 40 Hz

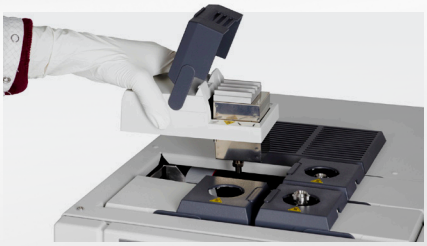




XIC of 2-nitroaniline (*m/z* 138.04238 ± 5 ppm window). Data were acquired in full scan at 60,000 resolution. Excellent ppm mass accuracy is shown for each individual scan across the peak (as ppm values in blue boxes).



Step into modern gas chromatography



Access unprecedented flexibility. Switch instant-connect injectors and detectors in minutes without tools.

Modularity increases uptime

The unique modular design of the Thermo Scientific™ TRACE™ 1300 Series GC empowers users with new time-saving capabilities and unmatched flexibility. Swapping modules is easy by removing and replacing just three screws, accessible from the top of the GC system. The entire process takes less than five minutes without requiring specialized service assistance. This modularity provides maximum uptime with offline cleaning and servicing of the GC inlet when a spare module is purchased.

Also, rapid response to different application needs or sudden workload requirements is possible with a limited investment in spare modules.

Take advantage of a comprehensive range of the The Thermo Scientific™ Instant Connect injectors and detectors interchangeable modules, right available at fingertip at any time for any need:

- Instant Connect Helium Saver split/splitless (SSL) injector
- Instant Connect Cold On-Column (COC) injector
- Instant Connect Flame Ionization Detector (FID)
- Instant Connect micro-volume Thermal Conductivity Detector (TCD)
- Instant Connect Electron Capture Detector (ECD)
- Instant Connect Nitrogen Phosphorous Detector (NPD)
- Instant Connect Flame Photometric Detector (FPD)
- Instant Connect Pulsed Discharge Detector (PDD)

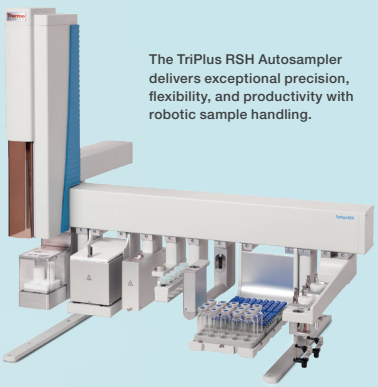
Add productivity with automated sample handling

The Thermo Scientific TriPlus RSH autosampler offers advanced robotic sample handling to extend automation beyond liquid injection, headspace, and solid-phase microextraction (SPME). Your results will benefit from improved precision and reproducibility, while your laboratory will increase productivity with sample handling flexibility. Several tools are available to reliably automate the most common sample preparation procedures, such as dilution, internal standard addition, and complex derivatization methods, including online microSPE cleanup of QuEChERs extracts.

Ready-to-use prep cycles are available or it is possible to easily create custom workflows using the Thermo Scientific™ Sampling Workflow Editor software, with intuitive drag-and-drop visual programming.

Key benefits

- Improved data repeatability
- Increased automation and laboratory efficiency
- Reduced cost per sample



The TriPlus RSH Autosampler delivers exceptional precision, flexibility, and productivity with robotic sample handling.

Efficiency transformed

Orbitrap Exploris GC Mass Spectrometer

Benefits

- Premium quantitative and qualitative performance with the fast-scanning High-Field Thermo Scientific™ Orbitrap™ mass analyzer
- Best-in-class mass accuracy, sensitivity, and dynamic range for quantitative certainty
- Configurable with up to 60,000 resolving power, enabling compound detection in complex matrices
- NeverVent™ technology for Vent-free ion source and column exchange
- Compatible with Thermo Scientific Chromeleon software for streamline analyte screening and quantitation
- EI and CI Thermo Scientific™ ExtractaBrite™ sources included
- VeV low electron energy acquisition for increased molecular ion production
- Optional MS/MS

The Thermo Scientific™ Orbitrap Exploris™ GC hybrid quadrupole Orbitrap mass spectrometer is a Thermo Scientific™ quadrupole-Orbitrap™ mass spectrometer joining the Orbitrap Exploris family built on proven hardware and instrument control software designs of the next-generation Thermo Scientific mass spectrometers.

Evolved to exceed the demands of analytical testing the Thermo Scientific Orbitrap Exploris GC-MS will simplify operations and deliver consistently confident results. Transform everyday quantitation, screening and sample profiling through a unique depth in analysis, with the highest accuracy and precision, where maximum system uptime is essential. Gain the flexibility to keep pace with ever changing regulations and explore new opportunities through increased scope and method consolidation. Simple instrument set up and intelligent informatics enable users of all ability to access data rich information with ease.

Customizable to meet application requirements with optional resolution and scan mode upgrades.

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Hardware features

Ion source

- Thermo Scientific™ ExtractaBrite™ Electron Ionization (EI) source
- Ion source includes ion volume, repeller, source lenses, RF lens and dual filaments in all ionization modes, programmable from 50 ˚C to 350 ˚C
- VeV tuning allows optimized low electron energy acquisition down to 8 eV
- Chemical Ionization (CI) source for acquisition with Positive Ion Chemical Ionization (PCI) and Negative Ion Chemical Ionization (NCI)
- Remove entire ion source or change to CI source in under 2 minutes without venting
- Vent-free column exchange with patented source plug

Combination EI/PCI/NCI ion volume can be used without need for source interchange.

Ion optics

Advanced active beam guide (AABG)

Axial field reduces noise by preventing neutrals and high-velocity clusters from entering the quadrupole mass filter using double bent design geometry.

Advanced quadrupole technology (AQT)

- Segmented quadrupole mass filter for precursor ion selection with variable precursor isolation width from 0.4 to 1,200 Da
- SIM and MS/MS (optional) precursor ion selection with high transmission from *m/z* 30 to 2,000

Ion-routing multipole (IRM)

- Robust ion trapping for higher energy collisional dissociation (HCD) (Optional)
- Nitrogen collision gas

Automatic gain control (AGC)

Reliable AGC measurements for controlled injection of the number of ions.

Thermo Scientific Orbitrap mass analyzer

- High-Field Orbitrap mass analyzer
- Low noise detection pre-amplifier
- 4 kV central electrode voltage

Vacuum system

- A compact single turbo pump design providing the adequate vacuum in five stages for the aluminum high-vacuum analyzer chambers
- Advanced vacuum technology reduces pressure in the ultra-high vacuum regions, enhancing transmission of ions to the Orbitrap mass analyzer

Optional MS upgrades

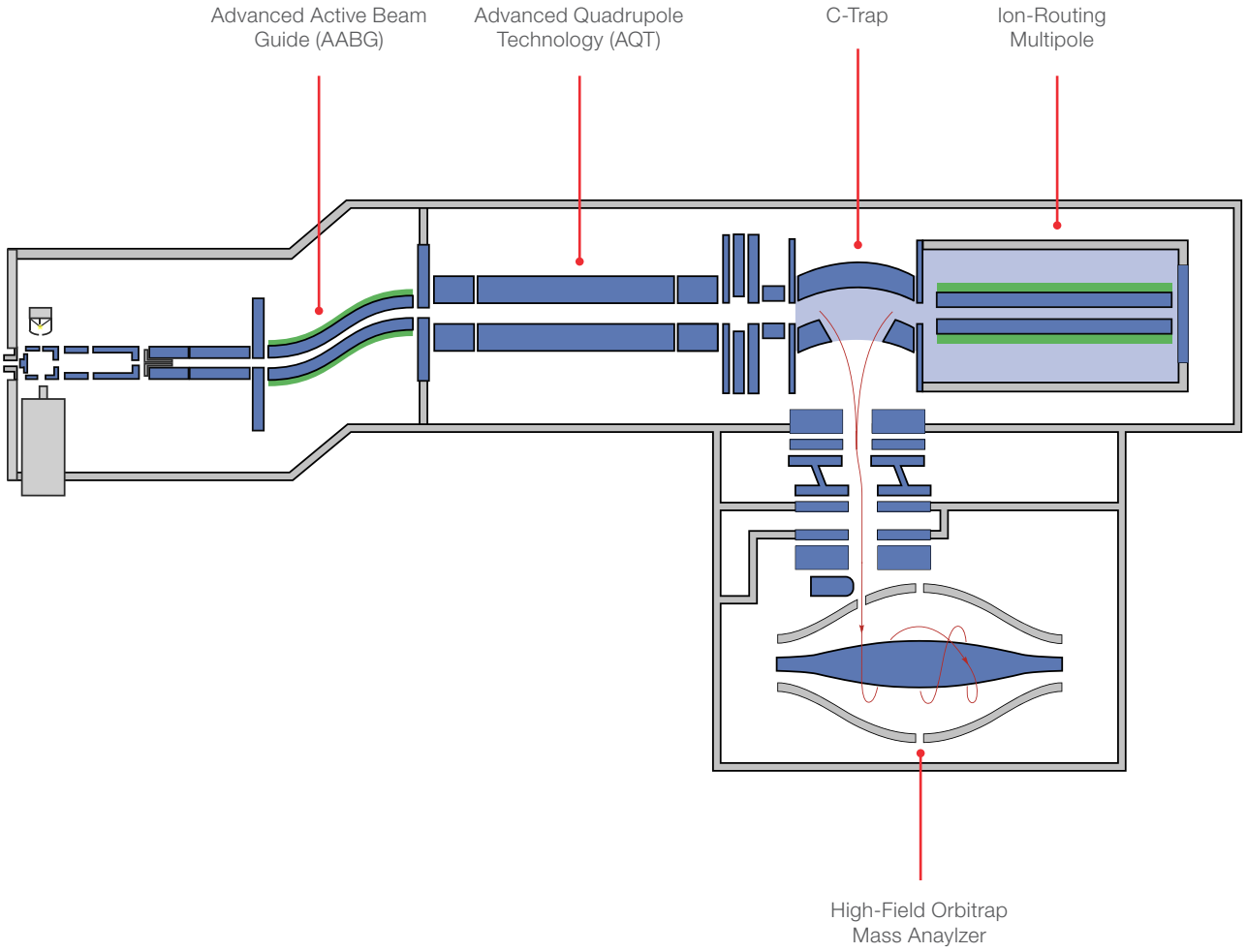
- 60,000 resolution option recommended for applications with complex matrices
- MS/MS upgrade with data dependent scanning recommended for applications focused on unknown compound identification

Optional hardware

Direct sample probe system option

- Switch to probe <3 min with GC undisturbed
- Available in two styles: rapid heating filament Direct-Exposure Probe (DEP, capable of flash vaporization or pyrolysis at up to 1,600 ˚C) or slower volatilization Direct-Insertion Probe (DIP, capable of accommodating powders and solid samples in a quartz or aluminum crucible) up to 450 ˚C.

Orbitrap Exploris GC mass spectrometer ion path



Performance specifications	
Mass range	*m/z* 30–3,000
Orbitrap mass analyzer resolution	Up to 30,000 (Up to 60,000 optional) at *m/z* 200
Scan rate*	Up to 40 Hz at resolution setting 7,500 at *m/z* 200
Mass accuracy*	External calibration achieves <3 ppm RMS drift over 24 hours Internal lock mass calibration achieves <1 ppm RMS drift over 24 hours
Sensitivity	EI: 100 fg octafluoronaphthalene on column, scanning *m/z* 50–300, S/N 10,000:1 EI IDL**: 6 fg octafluoronaphthalene derived at the 99% confidence level PCI: 10 pg benzophenone on column, scanning *m/z* 80–230, S/N 150:1
Dynamic range	$>10^6$ analytical dynamic range* >5,000 within a single Orbitrap mass analyzer spectrum
Polarity switching	One Full Scan cycle*** <700 ms equals >1.4 Hz One tSIM Scan cycle*** <600 ms equals >1.6 Hz
Multiplexing	Up to 20 precursors per scan

* Under defined conditions

** Demonstrated at installation with purchase of Thermo Scientific™ TriPlus™ RSH Autosampler and Exploris GC system IQ/OQ

*** One cycle consists of acquiring one Full scan in positive mode and one Full scan in negative mode at resolution setting 60,000
One tSIM scan in positive mode and one tSIM scan in negative mode at resolution setting 60,000

Data acquisition system

Data system

- High-performance PC with Intel® microprocessor
- High-resolution LED color monitor
- Microsoft® Windows® 10 Enterprise (Long Term Service version) operating system
- High-speed real-time data acquisition and instrument control
- Automatic calibration of all ion transfer and analysis parameters via instrument control software

Thermo Scientific Orbitrap Exploris instrument control software

- Tune application for instrument mass and system calibrations and checks, diagnostics, and manual data acquisition
- Method Editor with a comprehensive application- specific template library, method setup supported by tooltips, and a drag-and-drop user interface to facilitate method development
- Consistent instrument control software whether using Thermo Scientific™ Xcalibur™ or Thermo Scientific™ Chromeleon™ Chromatography Data Systems (CDS) for data acquisition

Included software

Thermo Scientific Xcalibur software

- Xcalibur software is the control software for the next-generation Thermo Scientific mass spectrometer portfolio
- Accelerates familiarization and reduces training needs

Thermo Scientific™ Orbitrap™ GC-MS contaminants library

Allows fast start-up for environmental and food safety screening and quantitation applications. Contains over 800 food and environmental contaminants, including pesticides, PAHs, PCBs, dioxins, and furans. User guide included detailing how to install and make custom enhancements to library.

Optional software

Thermo Scientific Chromeleon Chromatography Data System (CDS)

Streamlined chromatographic and MS screening and quantitative workflows within an enterprise and compliance-ready single software application.

Thermo Scientific™ Compound Discoverer™ software

Streamlines small molecule unknown identification, determination of real differences between samples, and elucidation of biological pathways with an integrated suite of data analysis tools.

Thermo Scientific™ Orbitrap™ GC-MS metabolomics library

Pair with Compound Discoverer to quickly implement metabolite profiling and identification of biomarkers. Contains over 1,000 GC-Orbitrap spectra covering multiple metabolite classes. The majority of metabolite reference spectra have been derivatized with standard MSTFA and methoxyamine protocol.

Thermo Scientific™ TraceFinder™ software

Acquire and process your high-throughput screening and quantitation with built-in intelligence, driving productivity gains from data acquisition and processing to reporting.

Operation modes

Resolution settings

Ranging from 7,500 to 30,000 (60,000 optional) at *m/z* 200

Scan functions

The following scan modes are standard with the Orbitrap Exploris GC:

Full scan

High sensitivity, high selectivity full scan for targeted and untargeted analyses

tSIM

- Targeted SIM with Mass List Table
- With Targeted Mass Filter for ddMS^2
- Isolation Width, Resolution, Polarity, Microscans set values are definable compound- dependent (w/o msx)
- Isolation Width: 0.4 u to 50 u
- Multiplexing for up to 20 compounds
- MSX ID, multiplexing groups definable
- Isolation Width set values are definable compound-dependent (w/ msx)

The following scan modes are included with the MS/MS upgrade:

tMS^2
- Targeted MS^2 with Mass List Table
- Isolation Width, HCD Collision Energy, Polarity, Microscans set values are definable compound-dependent (w/o msx)
- Isolation Width: 0.4 u to 50 u
- Multiplexing for up to 20 compounds
- Isolation Width set values can be defined compound-dependent (w/ msx)

SIM by Data-Dependent Acquisition (DDA) following a master scan
- With up to Top 100 for ddSIM
- With Targeted Mass Filter
- 'Number of Scans' (TopN) and 'Cycle Time' (Top Speed) option
- Isolation Width: 0.4 u to 50 u
- By performing a dependent scan on the most intense ion, if no target mass is found (optional)

MS^2 by Data-Dependent Acquisition (DDA) following a master scan
- With up to Top 100 ddMS^2
- With Targeted Mass Filter
- 'Number of Scans' (TopN) and 'Cycle Time' (Top Speed) option
- Isolation Width: 0.4 u to 50 u
- HCD Collision Energy set value is definable per compound
- By performing a dependent scan on the most intense ion, if no target mass is found (optional)

General
- Multiple experiments can be set up within one method
- One experiment can contain combinations of scans
- With MS/MS option, Collision Energy Mode' can be selected: 'Fixed' and 'Stepped'

Filters (included with MS/MS option)
Filters guide data-dependent (discovery and conformational) decisions on the fly and in real time. To achieve optimum results when applying application- and sample-dependent filter settings, the user is guided with appropriate application-dependent parameter settings and tool tips with tailored recommendations and detailed 'learn more' sections.

Filters can be selected as follows:
- Dynamic Exclusion
- Intensity
- Precursor Fit
- Targeted Inclusion
- Targeted Exclusion
- Apex Detection
- Precursor Selection Range

System templates
System templates provide predefined parameters in each template for users to fast load in Method Editor for data acquisition. To achieve optimum results when applying a template, the user is guided with more detailed information in help files.

System templates categories:
- Food Safety and Environmental
- POPs
- Impurity Testing
- Metabolomics
- Anti-Doping Control
- Flavor and Fragrances
- PCI Data Dependent MSMS

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Installation requirements

Power

- 2 × 208–240 Vac single phase, 15 A, 50/60 Hz, with earth ground for instrument and source vacuum pump
- 208–240 Vac single phase, 15 A, 50/60 Hz, with earth ground for the data system

Gas

Helium

- High-purity helium gas supply (99.999% pure)
- Regulator output pressure adjustable from 300 to 1,000 kPa (3 to 10 bar, 45 to 145 psi)

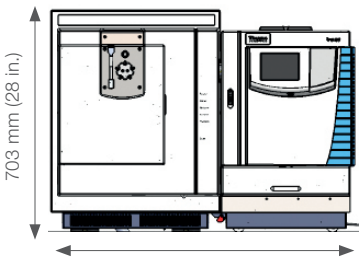
Methane (required for CI installation)

- High-purity methane gas supply (99.999% ultra high purity)
- Regulator output pressure adjustable from 35 to 240 kPa (0.3 to 2.4 bar, 5 to 35 psi)

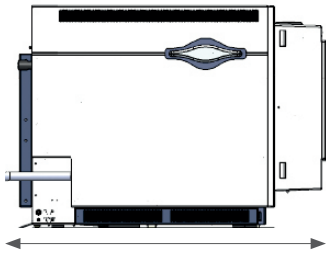
Nitrogen

- High-purity nitrogen gas supply (99.999% ultra-high purity)
- Regulator output pressure at 800 ± 30 kPa (8.0 ± 0.3 bar, 166 ± 4 psi)

Front view



Side view



Dimensions (w, d, h)

- 954 × 1,036 × 703 mm (38 × 41 × 28 in)

Weight

- 156 kg (344 lb) including GC and one injector, without data system, vacuum rough pumps, and optional items

Environment

- System averages 3,440 W (11,730 Btu/h) output when considering air conditioning needs
- Operating environment must be 18–27 ˚C (64–81 ˚F). Relative humidity must be 20–80% with no condensation
- Designed for indoor use at an altitude of up to 3,000 m (10,000 ft) above sea level

Find out more at **thermofisher.com/OrbitrapExplorisGC**

ThermoFisher SCIENTIFIC

APPLICATION NOTE 10724

Breakthrough performance of the Orbitrap Exploris GC for analytical testing and scientific research applications

Authors: Jane Cooper, Dominic Roberts, and Cristian Cojocariu
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Keywords: Orbitrap Exploris GC, Orbitrap technology, high resolution, mass accuracy, sensitivity, gas chromatography, analytical testing, scientific research, unknown identification, structural elucidation

Goal

To demonstrate the Thermo Scientific™ Orbitrap Exploris™ GC mass spectrometers deliver exceptional analytical performance for both analytical science and scientific research applications.

Introduction

The Orbitrap Exploris GC mass spectrometers have been designed for analytical testing and scientific research applications. These highly selective high-resolution Orbitrap-based analytical platforms aim to deliver unprecedented and flexible performance with up to 240,000 mass resolving power.

The objective of this study was to further explore the power of high resolution and accurate mass using Orbitrap-based GC-MS[1] by evaluating key analytical parameters that are essential for analytical testing and scientific research applications. These include linear dynamic range, sensitivity, NIST library search matching, spectral fidelity, scan speed, mass accuracy, robustness, compound confirmation using positive chemical ionization, and resolving power.

Experimental

In all experiments, a Thermo Scientific Orbitrap Exploris GC was used. Some additional experiments were performed on the Thermo Scientific Orbitrap Exploris GC 240, which has a maximum resolving power of 240,000 (at *m/z* 200 FWHM). Sample introduction was performed using a Thermo Scientific™ TriPlus™ RSH autosampler, and chromatographic separation of the gas-phase chemical components was achieved using a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph equipped with various capillary columns. The Orbitrap Exploris GC was tuned and calibrated using PFTBA to achieve mass accuracy of <1.0 ppm.

The routine ionization mode was electron ionization (EI) and the mass spectrometers were operated using full scan with default 60,000 mass resolution (FWHM, measured at *m/z* 200). Data acquired was lock-mass corrected using GC column bleed siloxane masses.

Standard and sample preparation

Standard preparation

To assess key analytical parameters, standards were prepared from stock standards in solvent and in matrix:

A) 8270 MegaMix (Restek, catalogue number 31850) was diluted in hexane to produce 12 calibration level standards (ranging from 0.1 ppb to 10,000 ppb)

B) Mixed pesticide calibration standards were prepared from stock standards (Restek, catalogue number 32562), and diluted in matrix to generate 11 calibrations standards (ranging from 0.1 to 500 ppb)

C) Mixed standard, containing octafluoronaphtalene (OFN) (0.1 pg/µL) and hexachlorobenzene (HCB) (10 pg/µL) in iso-octane.

Sample preparation

Locally purchased organic wheat flour or oats (10 g) were weighed into a 50 mL centrifuge tube. Acetonitrile (10 mL), containing 1% (v/v) of acetic acid, was then added to the sample, which was then vortexed for 1 min. To this, 3 g of magnesium sulfate ($MgSO_4$), 1.7 g of sodium acetate, and 0.5 g of disodium hydrogen citrate were added, and the tube was vortexed for 1 min and centrifuged at 4,000 rpm for 10 min. After centrifugation, 5 mL of the supernatant was transferred into a polypropylene tube with 250 mg C18 sorbent, 750 mg $MgSO_4$, and 750 mg primary/secondary amine (PSA). The tube was vortexed for 1 min and centrifuged for 10 min at 4,000 rpm and supernatant used for GC-MS analyses.

For unknown identification and structural elucidation experiments, commercially available oregano samples were purchased locally. Samples were weighed (150 mg) and transferred into 10 mL crimp top headspace vials (vials P/N 10-CV, caps P/N 20-MCBC-ST3) for analysis.

Results and discussion

Scan speed

Fast data acquisition, to allow sufficient data points across narrow GC peaks, is critical in order to achieve accurate and precise compound identification. An example using the Orbitrap Exploris GC is shown in Figure 1, where 15 data points across the 2.3 s wide peak for 2-nitroaniline (extracted ion chromatogram of *m/z* 138.04238) were obtained.

Compound identification using spectral libraries

The Exploris Orbitrap GC, with full scan range mass accuracy and sensitivity, enables accurate and reliable commercial library (e.g. NIST/Wiley) matching. Figure 2 shows the NIST library search results achieved using the Exploris Orbitrap GC for the analysis of aldrin in a mixed pesticide standard, with both forward and reverse library match scores of >890 achieved.

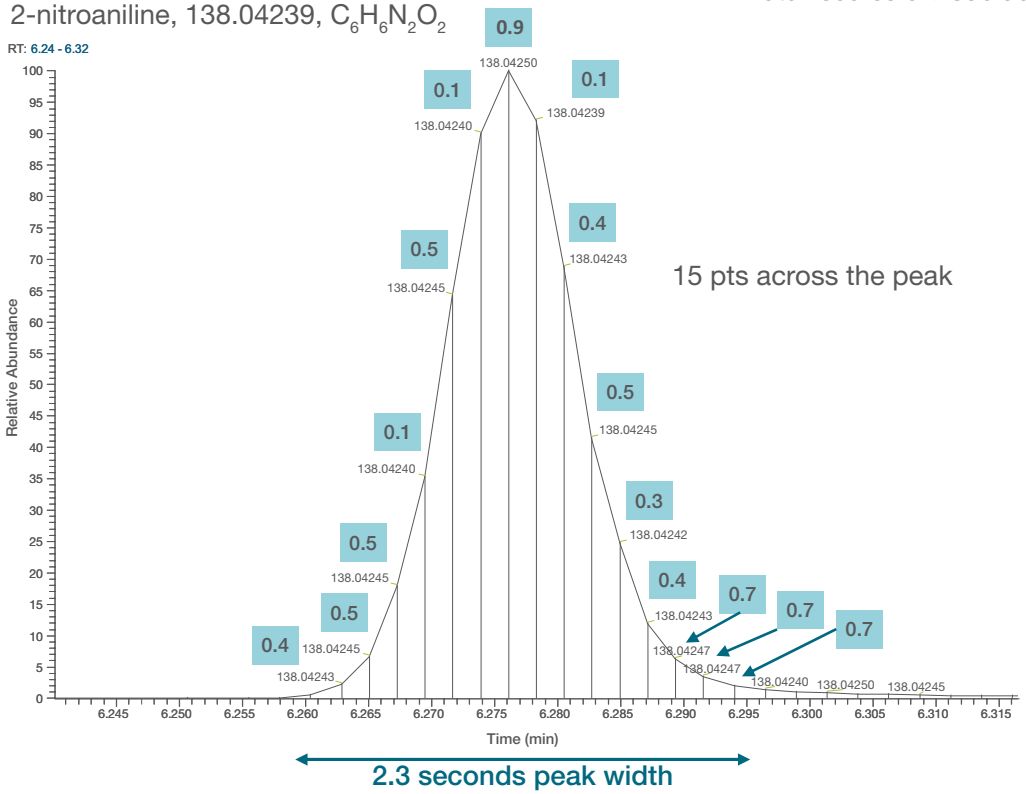


Figure 1. Extracted ion chromatogram (XIC) of 2-nitroaniline (*m/z* 138.04238 ± 5 ppm window) in a 1,000 pg/µL mixed solvent standard. Data acquired in full scan at 60k resolution (FWHM at *m/z* 200). Excellent mass accuracy is shown for each individual scan as well as mass difference (in ppm). An average mass difference of 0.4 ppm was measured across the peak.

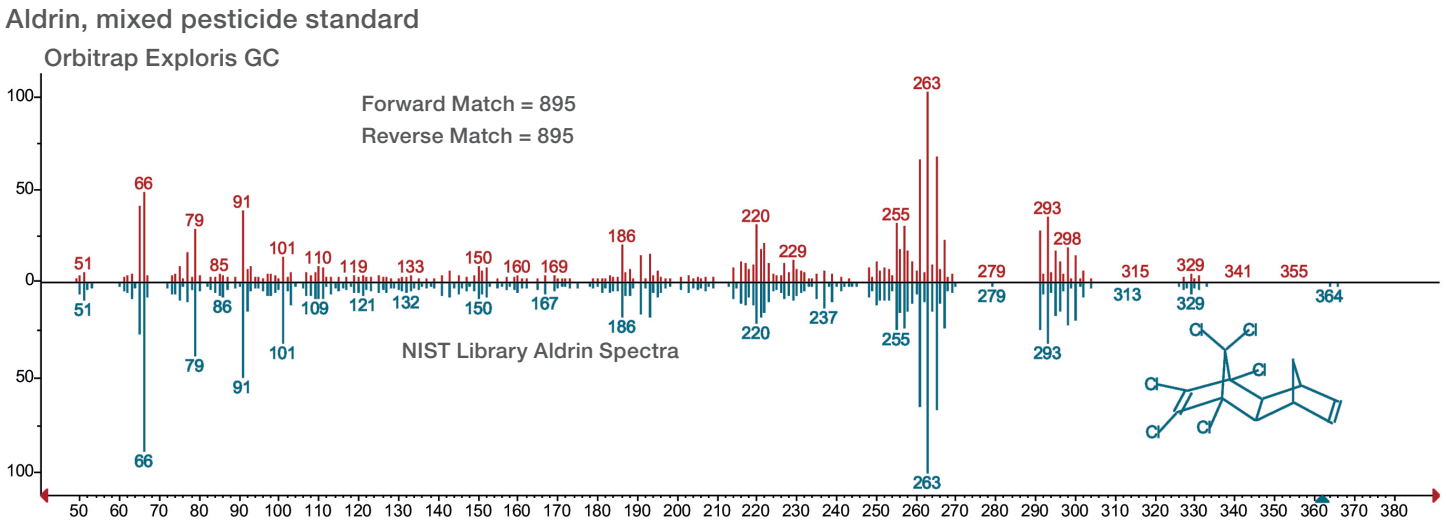


Figure 2. NIST library search mass spectra and match results achieved for the analysis of aldrin in a mixed pesticide standard using an Orbitrap Exploris GC operated in full scan at 60k resolution (FWHM at *m/z* 200)

Additional results achieved using the Orbitrap Exploris GC are shown in Figure 3 for a selection of pesticides in a mixed pesticide standard in whole flour matrix, where similar NIST library results were obtained considering both reverse and forward search results.

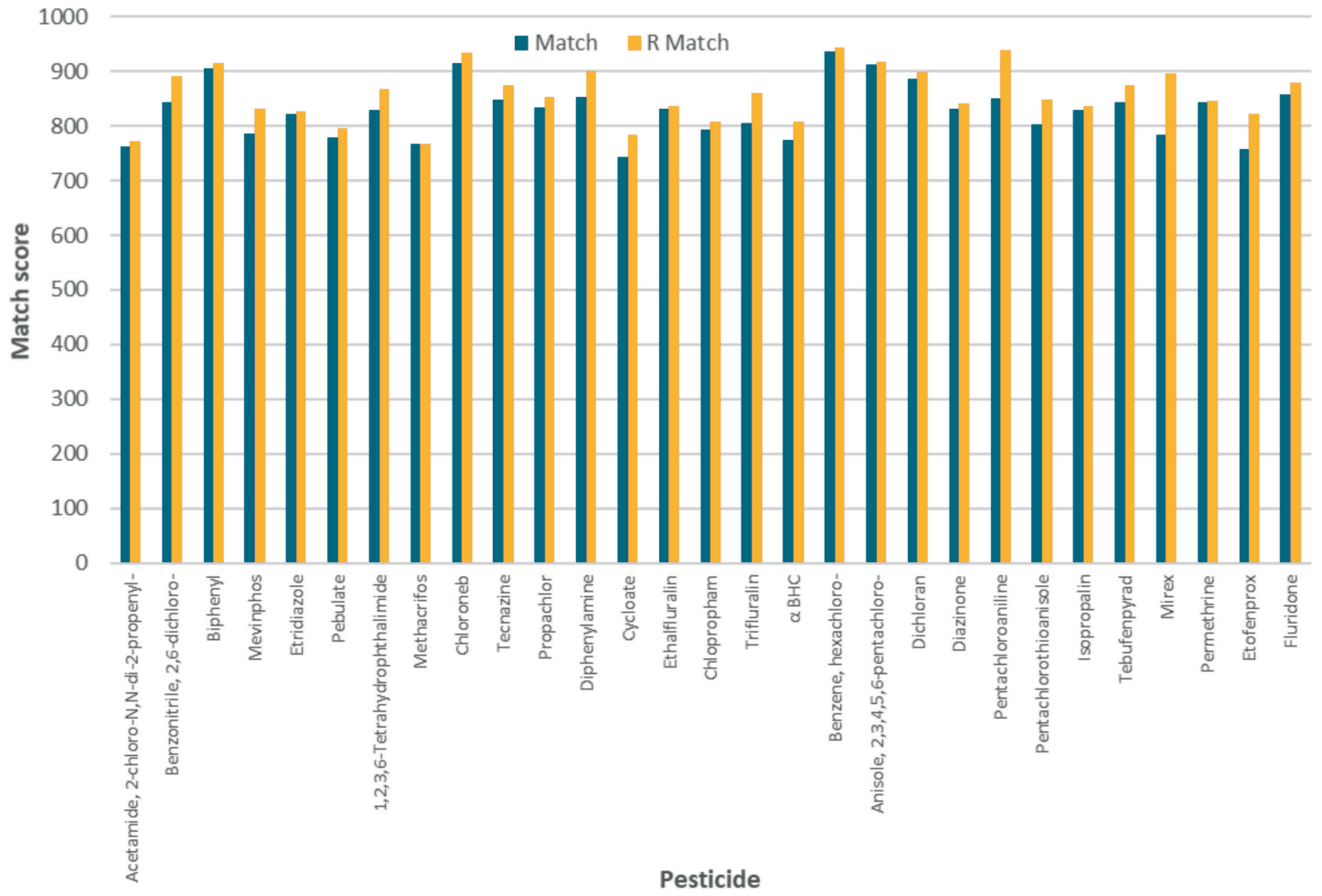


Figure 3. Library search scores achieved using an Orbitrap Exploris GC for a selection of pesticides in a mixed pesticide standard in a whole flour matrix (a score of 1,000 equals a perfect match). Forward search scores (Match) and reverse search scores (R Match) given for each pesticide, when searched against the NIST library. The Orbitrap Exploris GC was operated in full scan at 60k resolution (FWHM at *m/z* 200).

Linear dynamic range

A wide linear dynamic range is essential, especially when dealing with applications where the samples analyzed contain a complex chemical background that could potentially interfere with the analytes of interest (e.g., pesticide screening and quantification, metabolomics). To test the linear dynamic range using the Orbitrap Exploris GC, repeat injections (n=3) of increasing concentration levels (0.1 pg to 10,000 pg on column) of mixed solvent standards were performed. An example of compound linearity obtained using log(10) is shown in Figure 4 for hexachloroethane, the results demonstrating linear dynamic range extending to six orders of magnitude (0.1–10,000 pg on-column) making the Orbitrap Exploris GC an ideal platform for quantitative analysis.

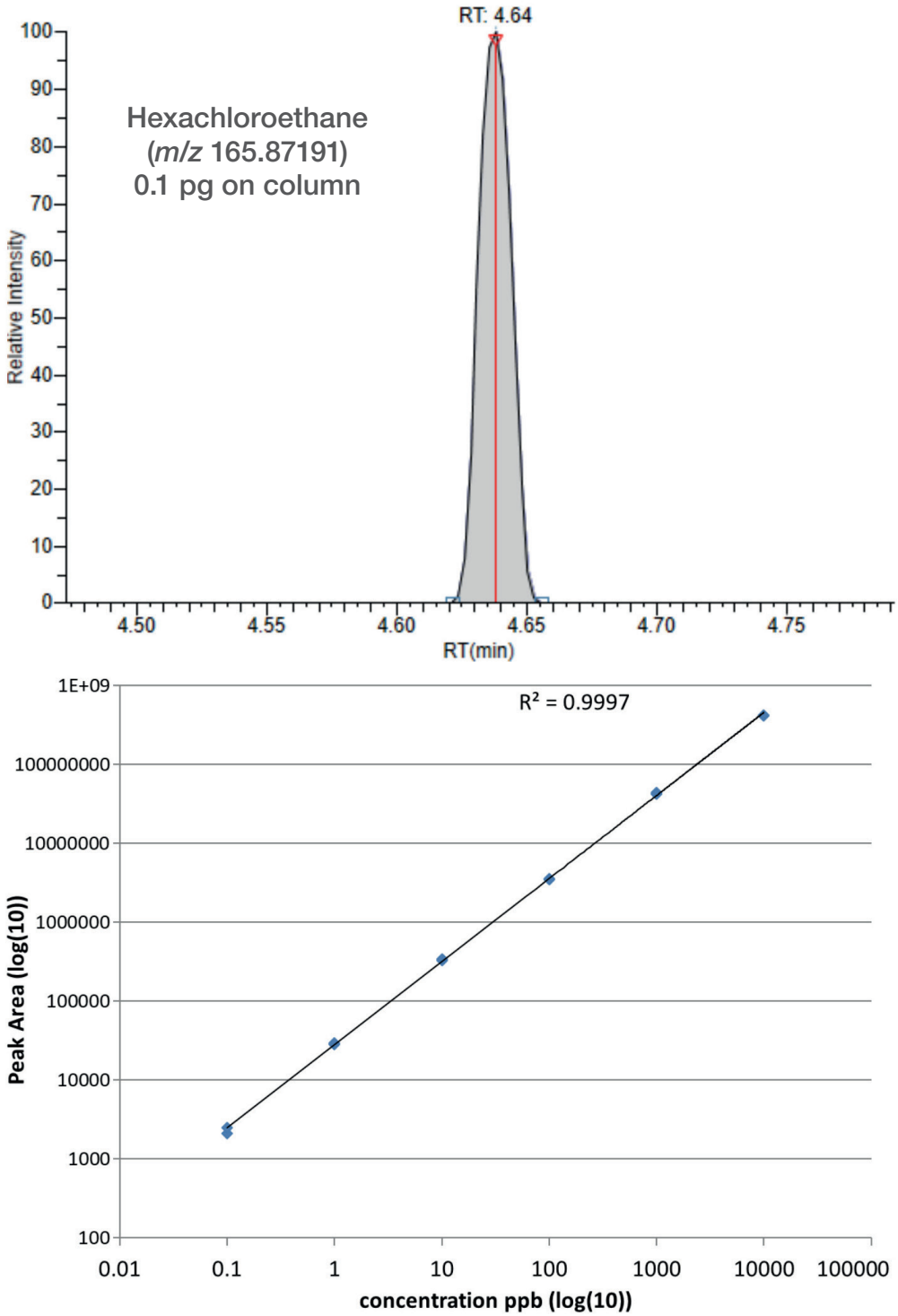


Figure 4. Linear dynamic range of the Orbitrap Exploris GC is demonstrated using hexachloroethane solvent standards injected over six orders of magnitude. The extracted ion chromatogram (*m/z* 165.87191) corresponding to hexachloroethane at 0.1 pg on column is shown together with the coefficient of determination (R^2) values determined over a concentration range of 0.1–10,000 pg on column.

Moreover, excellent peak area repeatability (n=3 injections) was obtained at each concentration level as demonstrated for hexachloroethane in Table 1 which shows %RSD ranged from 1.0 to 4.9 across the six orders of magnitude.

Table 1. Calculated %RSD from n=3 repeat injections of hexachloroethane solvent standard at various on column concentrations. Data from the Orbitrap Exploris GC shown.

Hexachloroethane concentration (pg on column)	Orbitrap Exploris GC %RSD (n=3)
10000	1.7
1000	1.5
100	1.0
10	2.4
1	2.4
0.1	4.9

Sensitivity

The sensitivity achievable with the Orbitrap Exploris GC was evaluated for the analysis of whole flour spiked with pesticides. For this a whole flour sample extract was spiked with pesticides at 10 pg/µL level (equivalent to the European Union (EU) default maximum residue level (MRL) set at 10 µg/kg) and repeat injections (n=10) were performed.

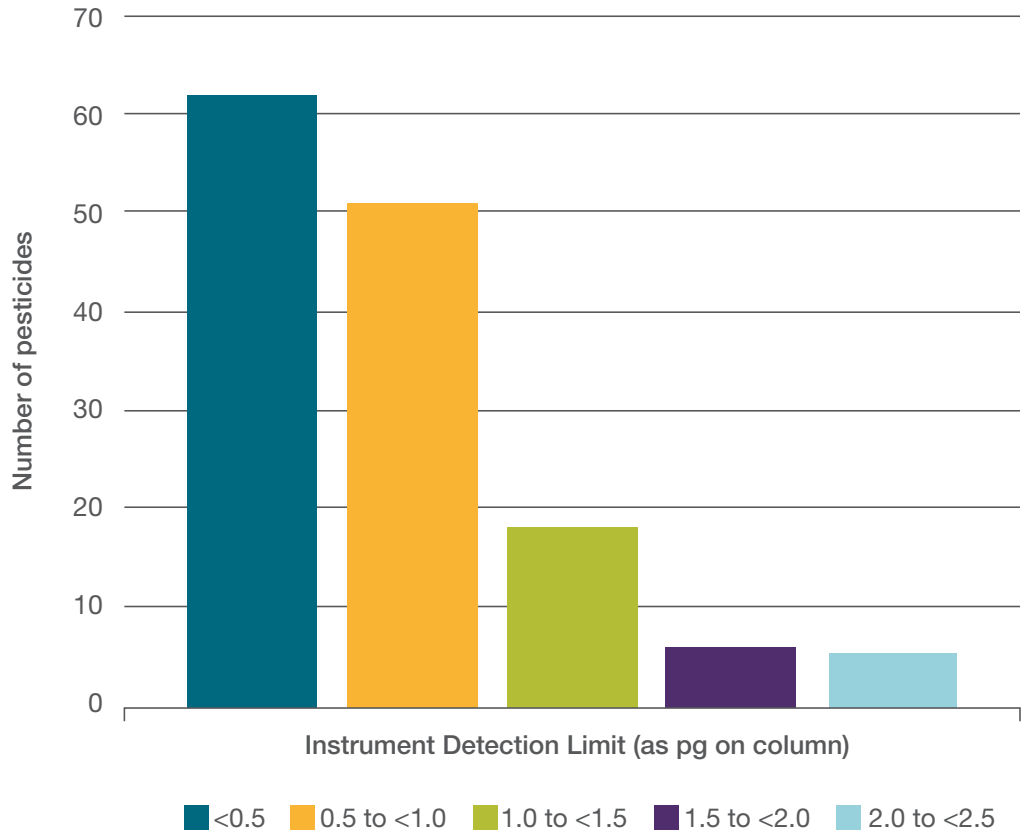
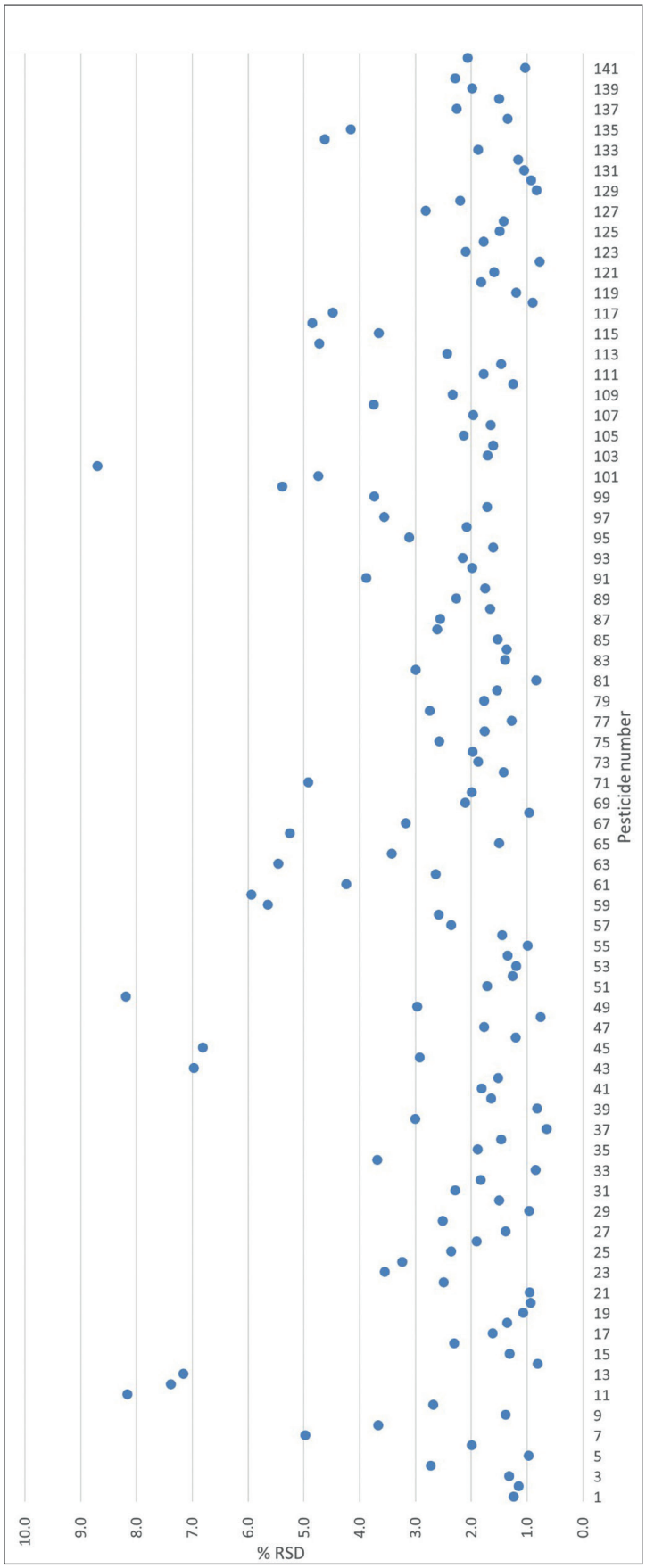


Figure 5. Sensitivity instrument detection limit (IDL as pg on column) determined for 142 pesticides in whole flour using an Orbitrap Exploris GC. Data was obtained by taking into account the amount on column, the Student's-*t* value corresponding degrees of freedom for repeat injections (n=10) of a 10 pg/µL whole flour matrix matched pesticide standard.

Sensitivity expressed as instrument detection limits (IDL) for all the pesticides analyzed was calculated and is reported in Figure 5, and the associated %RSD values are shown in Figure 6. The IDL was calculated taking into account the Student's-*t* critical values for the corresponding degrees of freedom (99% confidence). Excellent sensitivity with IDL values ranging from 0.18 to 2.45 pg/µL was achieved, with an average value of 0.7 pg/µL. The results confirmed that the Orbitrap Exploris GC has the sensitivity levels to meet the regulatory analysis of pesticides in matrix matched standards.

Orbitrap Exploris GC pesticide %RSD in whole flour



No	Compound	No	Compound
1	2-phenylphenol	72	Fenthion
2	3,4-Dichloroaniline	73	Fluquinconazole
3	4,4'-Dichlorobenzophenone	74	Fluridone
4	9,10-Anthracenedione	75	Flutolanil
5	Acetamide, 2-chloro-N-(2,6-dimethylphenyl)-N-(2-methoxyethyl)-	76	Heptachlor epoxide
6	Acetamide, 2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)-	77	Hexazinone
7	Acetamide, 2-chloro-N,N-di-2-propenyl-	78	Iodofenphos
8	Acrinathrin	79	Isazofos
9	Alachlor	80	Isodrin
10	Aldrin/Aldrin-r	81	Isopropalin
11	Azinphos-ethyl	82	Lenacil
12	Azinphos-methyl	83	Leptophos
13	Benfluralin	84	Metazachlor
14	Benzenamine, 2,3,5,6-tetrachloro-	85	Methacrifos
15	Benzene, hexachloro-	86	Methyl parathion
16	Benzonitrile, 2,6-dichloro-	87	Mevinphos
17	Benzonitrile, pentachloro-	88	Mirex
18	BHC, alpha	89	Mitotane
19	BHC, beta	90	N-(2-Ethylhexyl)-5-norbornene-2,3-dicarboximide
20	BHC, delta	91	Nitralin
21	BHC, gamma	92	Nitrofen
22	Bifenthrin	93	Norflurazon
23	Bioallethrin	94	o,p'-DDE
24	Biphenyl	95	o,p'-Methoxychlor
25	Bromfenvinphos-methyl	96	Oxadiazone
26	Bromophos	97	Oxyfluorfen
27	Bromophos-ethyl	98	p,p'-DDE
28	Bromopropylate	99	p,p'-DDT
29	Bupirimate	100	Parathion
30	Carbamothioic acid, bis(1-methylethyl)-, S-(2,3-dichloro-2-propenyl) ester	101	Pebulate
31	Carbophenothion	102	Penconazole
32	Carfentrazone-ethyl	103	Pendimethalin
33	Chlorbenside	104	Pentachloroaniline
34	Chlorfenapyr	105	Pentachlorothioanisole
35	Chlorfenson /Ovex	106	Permethrin
36	Chlorfenvinphos	107	Phosalone
37	Chlorobenzilate	108	Phosmet
38	Chloroneb	109	Phosphonothioic acid, phenyl-, O-ethyl O-(4-nitrophenyl) ester
39	Chlorpropham	110	Piperonyl butoxide
40	Chlorpyrifos(-ethyl)	111	Pirimiphos methyl
41	Chlorpyriphos-methyl	112	Pirimiphos-ethyl
42	Chlorthiophos	113	Pretilachlor
43	Chlorthiophos II	114	Prochloraz
44	Chlozolinate	115	Prodiamine
45	Cis-1,2,3,6-Tetrahydrophthalimide	116	Profenofos
46	cis-Chlordane	117	Profluralin
47	cis-Nonachlor	118	Propanil
48	Clomazone/Dimethazone	119	Propyzamide
49	Coumaphos	120	Pyrazophos
50	Cycloate	121	Pyridaphenthion
51	Cyprodinil	122	Pyrimethanil
52	Diazinone	123	Pyriproxyfen
53	Dichloran	124	Quintozene
54	Diphenamid	125	Sulfotep
55	Diphenylamine	126	Sulprofos
56	Disulfoton	127	Tebuconazole
57	Endosulfan (beta)	128	Tebufenpyrad
58	Endosulfan ether	129	Tecnazene
59	Endosulfan sulfate	130	Tefluthrin
60	Endosulfan, (alpha)	131	Terbacil
61	Endrin	132	Terbufos
62	Endrin ketone	133	Terbuthylazine
63	Endrin-aldehyde	134	Tetrachlorvinphos
64	Ethalfluralin	135	Tetramethrin
65	Ethion	136	Tolclofos-methyl
66	Etofenprox	137	trans-Chlordane
67	Fenamiphos	138	Transfluthrin
68	Fenarimol	139	trans-Nonachlor
69	Fenchlorphos/Ronnel	140	Triadimefon
70	Fenitrothion	141	Triallate
71	Fenson	142	Vinclozolin

Figure 6. IDL repeatability expressed as % RSD achieved for the analysis of 142 pesticides using an Orbitrap Exploris GC, for repeat injections (n=10) of a 10 pg/µL whole flour matrix matched pesticide standard

Spectral fidelity irrespective of concentration

Maintaining spectral fidelity over the full analytical concentration range in matrix is critical to maintain confidence in compound identification, even at low levels, as illustrated in Figure 7 for pentachloroaniline in whole flour matrix. The mass accuracy for every ion in the isotopic cluster is <1 ppm giving high confidence in the identification.

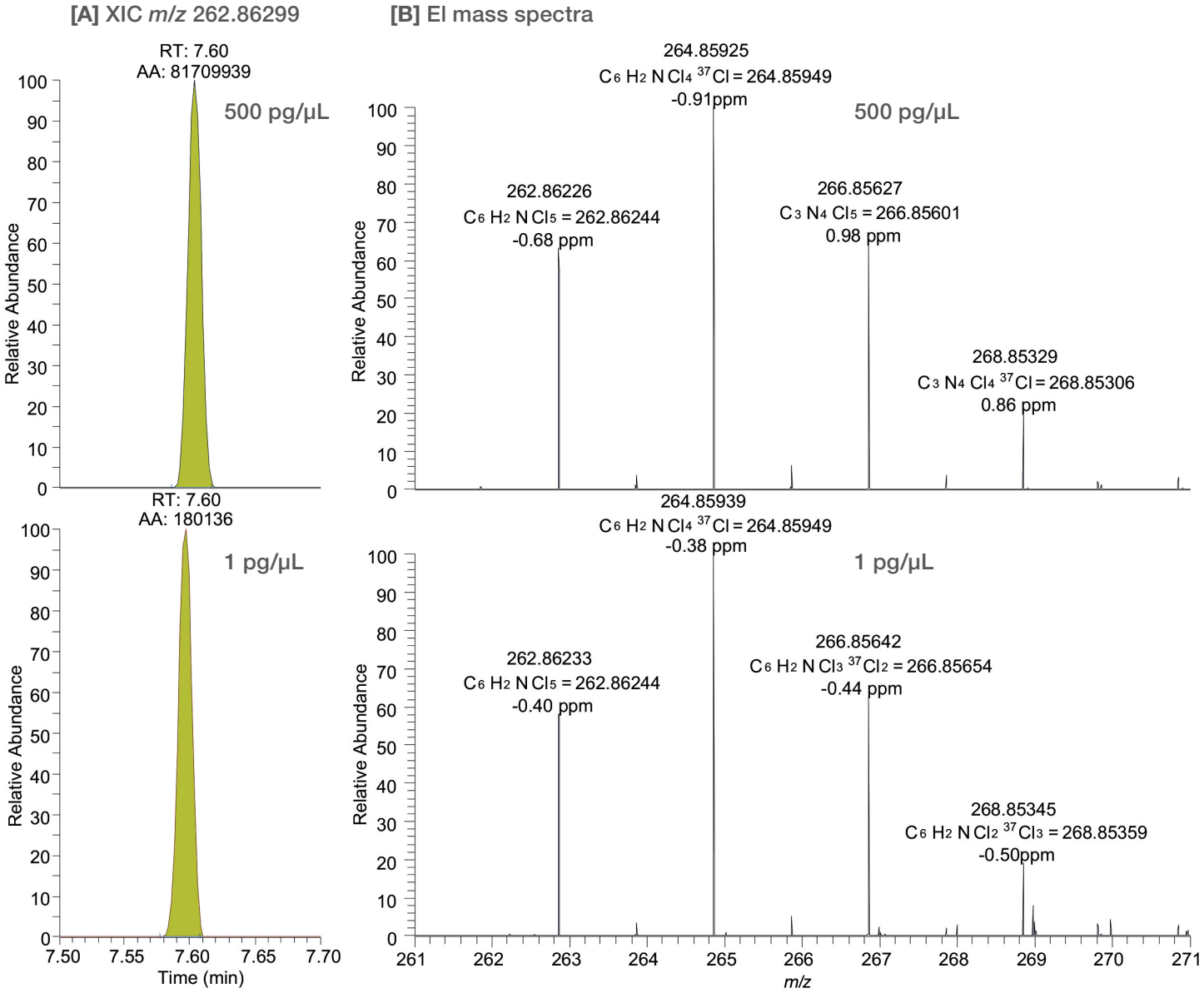
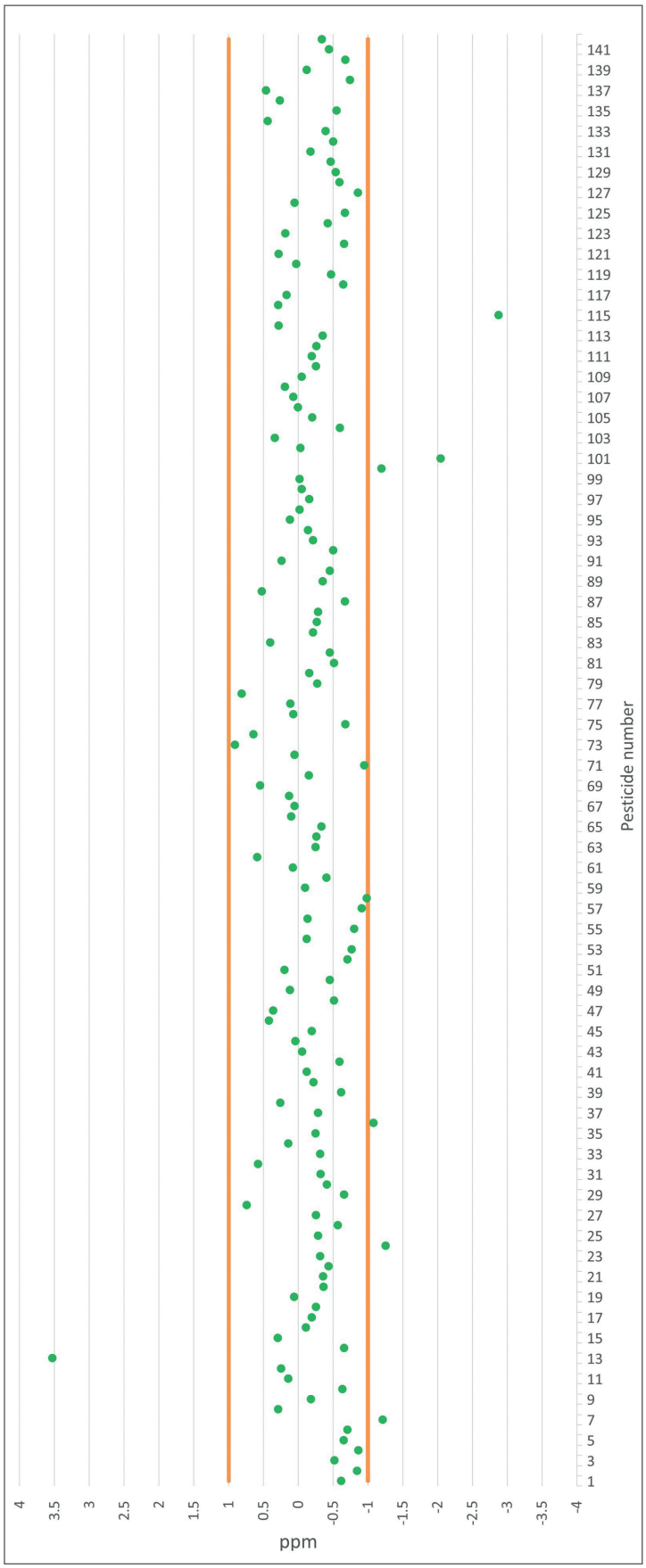


Figure 7. Spectral fidelity illustrated for pentachloroaniline for two levels (1 and 500 pg/µL) in whole flour matrix using an Orbitrap Exploris GC. [A]: Extracted ion chromatograms (XIC) for pentachloroaniline at each level annotated with peak retention time (RT) and peak area (AA); [B]: EI mass spectra zoomed at the molecular ion cluster at each level, annotated with measured mass, elemental composition, theoretical mass and mass accuracy (ppm).

Mass accuracy

To have a high degree of confidence in compound identification, low (<1 ppm) mass accuracy is critical. To test the mass accuracy that can be achieved using the Orbitrap Exploris GC, repeat injections (n=10) of mixed pesticides standards (10 pg/µL) were carried out. Examples are reported in Figure 8, with an average mass accuracy of -0.2 ppm.



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6	Acetamide, 2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)-	77	Hexazinone
7	Acetamide, 2-chloro-N,N-di-2-propenyl-	78	Iodofenphos
8	Acrinathrin	79	Isazofos
9	Alachlor	80	Isodrin
10	Aldrin/Aldrin-r	81	Isopropalin
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12	Azinphos-methyl	83	Leptophos
13	Benfluralin	84	Metazachlor
14	Benzenamine, 2,3,5,6-tetrachloro-	85	Methacrifos
15	Benzene, hexachloro-	86	Methyl parathion
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17	Benzonitrile, pentachloro-	88	Mirex
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21	BHC, gamma	92	Nitrofen
22	Bifenthrin	93	Norflurazon
23	Bioallethrin	94	o,p'-DDE
24	Biphenyl	95	o,p'-Methoxychlor
25	Bromfenvinphos-methyl	96	Oxadiazone
26	Bromophos	97	Oxyfluorfen
27	Bromophos-ethyl	98	p,p'-DDE
28	Bromopropylate	99	p,p'-DDT
29	Bupirimate	100	Parathion
30	Carbamothioic acid, bis(1-methylethyl)-, S-(2,3-dichloro-2-propenyl) ester	101	Pebulate
31	Carbophenothion	102	Penconazole
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33	Chlorbenside	104	Pentachloroaniline
34	Chlorfenapyr	105	Pentachlorothioanisole
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41	Chlorpyriphos-methyl	112	Pirimiphos-ethyl
42	Chlorthiophos	113	Pretilachlor
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46	cis-Chlordane	117	Profluralin
47	cis-Nonachlor	118	Propanil
48	Clomazone/Dimethazone	119	Propyzamide
49	Coumaphos	120	Pyrazophos
50	Cycloate	121	Pyridaphenthion
51	Cyprodinil	122	Pyrimethanil
52	Diazinone	123	Pyriproxyfen
53	Dichloran	124	Quintozene
54	Diphenamid	125	Sulfotep
55	Diphenylamine	126	Sulprofos
56	Disulfoton	127	Tebuconazole
57	Endosulfan (beta)	128	Tebufenpyrad
58	Endosulfan ether	129	Tecnazene
59	Endosulfan sulfate	130	Tefluthrin
60	Endosulfan, (alpha)	131	Terbacil
61	Endrin	132	Terbufos
62	Endrin ketone	133	Terbuthylazine
63	Endrin-aldehyde	134	Tetrachlorvinphos
64	Ethalfluralin	135	Tetramethrin
65	Ethion	136	Tolclofos-methyl
66	Etofenprox	137	trans-Chlordane
67	Fenamiphos	138	Transfluthrin
68	Fenarimol	139	trans-Nonachlor
69	Fenchlorphos/Ronnel	140	Triadimefon
70	Fenitrothion	141	Triallate
71	Fenson	142	Vinclozolin

Figure 8. Mass accuracy (ppm) in matrix is illustrated for repeat injections (n=10) of mixed pesticides standards (10 pg/µL)

Maintaining sub-ppm mass accuracy irrespective of compound concentration

Sub-ppm mass accuracy was maintained across compound concentrations using an Orbitrap Exploris GC, as exemplified for hexachloroethane (Table 2). In all cases, irrespective of the *m/z* and concentration level, <1 ppm values were observed. This is essential as any compromise in accuracy of mass measurements can result in false identification and non-detection of toxic chemicals such as pesticides in a screening experiment.[2] It is also necessary to maintain this performance at all concentration levels as any level can be encountered in real world samples.

Mass accuracy repeatability

To evaluate repeatability of mass accuracy over long analysis runs at low concentrations when using the Orbitrap Exploris GC, 140 injections of mixed solvent standards containing octafluoronaphtalene (OFN) (0.1 pg oc) and hexachlorobenzene (HCB) (10 pg oc) were performed, as reported in Figure 9. The results confirmed that by using the Orbitrap Exploris GC, high levels of mass accuracy (<1.1 ppm) over 2 days unattended analysis can confidently be achieved, without instrument maintenance, calibration, or tuning.

Table 2. Mass accuracy (ppm) over six orders of magnitude for five selected ions of hexachloroethane measured using the Orbitrap Exploris GC

Level	Orbitrap Exploris GC				
ppb on column	*m/z* 118.90306	*m/z* 116.90601	*m/z* 120.90011	*m/z* 165.87191	*m/z* 202.83781
0.1	0.1	0.4	0.7	0.1	-0.3
1	0.0	0.0	0.2	0.1	-0.1
10	0.4	0.6	0.5	0.6	0.3
100	0.4	0.5	0.4	0.5	0.3
1000	0.7	0.8	0.7	0.8	0.5
10000	0.5	0.6	0.5	0.6	0.3
average Δppm	**0.4**	**0.5**	**0.5**	**0.4**	**0.2**

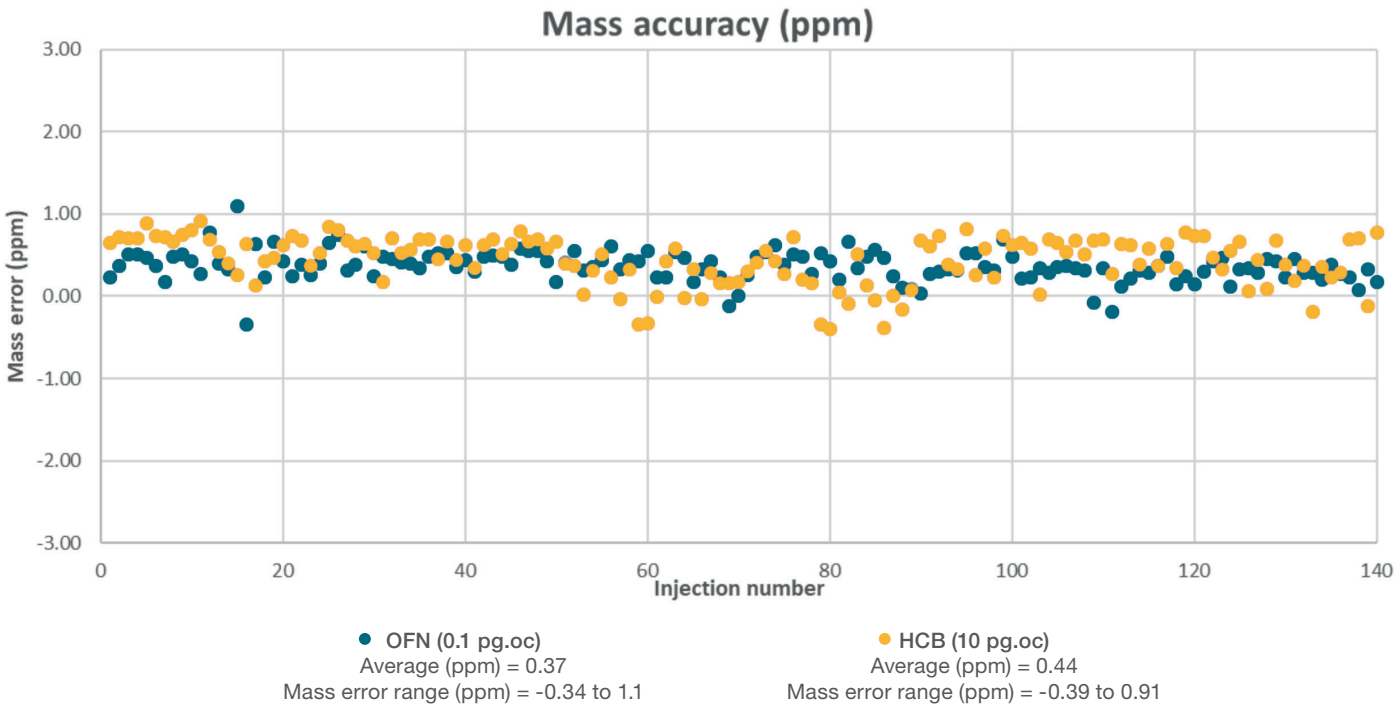

Figure 9. Repeatability of mass accuracy (ppm), illustrated with 140 injections of a solvent standard, containing OFN (0.1 pg on-column) and HCB (10 pg on-column), annotated with average mass accuracy and range achieved using an Orbitrap Exploris GC

Compound confirmation using PCI

When the spectral library match from the EI spectrum is inconclusive, or additional confirmation is required, positive chemical ionization (PCI) data can be used to confirm the elemental composition of the parent molecule using accurate mass information. In PCI experiments using methane as the reagent gas three adducts are typically observed: $[M+H]^+$, $[M+C_2H_5]^+$, and $[M+C_3H_5]^+$. As an example, EI and PCI spectra of camphene in a sample of thyme are reported in Figure 10. The observed molecular ion corresponding to *m/z* 136.12468 is present in the EI spectrum with a mass difference of 0.2 ppm from the theoretical *m/z* 136.12465 for the formula $C_{10}H_{16}$. The presence of the methane adducts in the PCI spectrum with sub-1 ppm mass accuracy confirmed *m/z* 136.12468 as the molecular ion for camphene (RT=9.04 min) and supported the elemental composition of the proposed molecule.

Resolving power

Acquiring reliable accurate mass measurements is critical when detecting low level pesticides in complex matrices. Through the high-mass resolving power of the Orbitrap Exploris GC 240, discrimination between matrix interferences and target analyte ions can be confidently achieved. When the resolution is insufficient, the mass profile of ions overlaps, which could result in high mass error and incorrect assignment of the mass of the target ion. This is demonstrated in Figure 11 where an oat matrix standard (500 pg/µL) was analyzed at resolving powers of 30K, 60K, 120K, and 240K using the Orbitrap Exploris GC 240. The zoomed in mass spectra show the quantifier ion and a matrix ion of a similar mass causing interference. The diphenylamine ion at 30K and 60K is not resolved resulting in poor mass accuracies of -6.38 and -6.18 ppm, respectively, and is resolved at 120K and even further resolved at 240K with mass accuracies of 1.10 and 0.56 ppm, respectively.

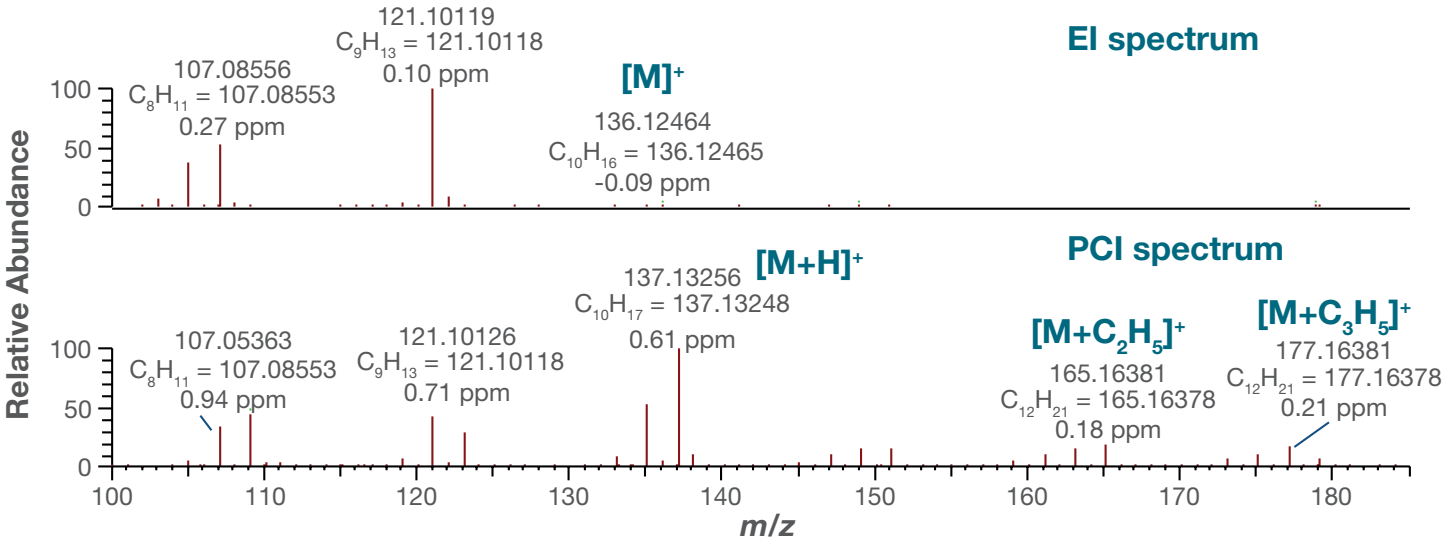

Figure 10. Comparison between EI and PCI spectrum for camphene in a sample of thyme (RT=9.04 min). The molecular ion (*m/z* 136.12468) is visible in the EI spectrum with sub ppm mass accuracy annotated. In the PCI spectrum the typical adducts observed when methane gas is used are clearly visible confirming the molecular ion and the proposed molecular formula for camphene.

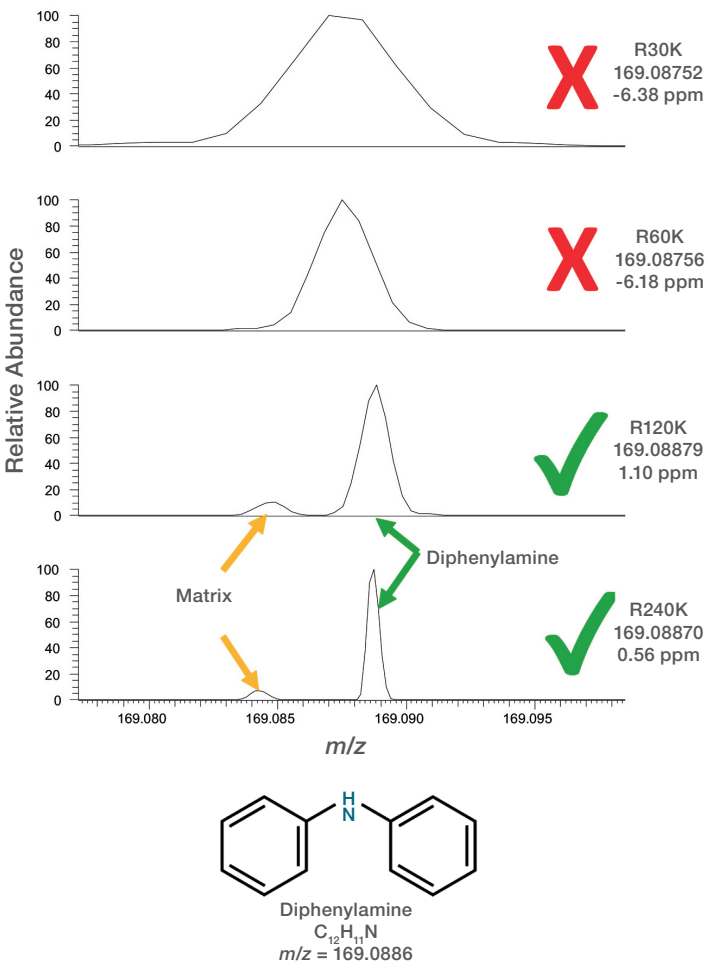

Figure 11. Effects of resolving power on the mass accuracy using the Orbitrap Exploris GC 240 for the detection of diphenylamine in an oat matrix standard (500 pg/µL) acquired at 30K, 60K, 120K, and 240K. The diphenylamine ion at 30K and 60K is not resolved; however, at 120K and 240K the quantifier ion for diphenylamine and a matrix interference ion are sufficiently resolved. Zoomed in mass spectra are annotated with the resolving power, the measured mass, as well as the mass accuracy (ppm).

Conclusions

The data shown here demonstrate that the Orbitrap Exploris GC mass spectrometers deliver exceptional high-quality analytical performance using full scan acquisition for both analytical testing and scientific research applications.

The fast scan speeds available allow sufficient data points across narrow chromatographic peaks to accurately describe the peak area and to ensure signal and spectra reproducibility. The linear dynamic range extending to six orders of magnitude and the sensitivity demonstrated for >140 pesticides in whole flour (IDL values of between 0.18 and 2.45 pg/µL) make the Orbitrap Exploris GC ideal for analytical testing.

NIST library searchable accurate mass spectra are achievable, enabling confident identification of unknown compounds and confirmation of knowns. Spectral fidelity irrespective of concentration can also be achieved, which is critical to maintain confidence in compound identification.

When the spectral library match from the EI spectrum is inconclusive, or additional confirmation is required, the Orbitrap Exploris GC positive chemical ionization (PCI) data can be used to confirm the elemental composition of the parent molecule using accurate mass information.

Sub-ppm mass accuracy is achievable for the analysis of pesticides in whole flour spiked with pesticides. In addition, the high mass resolving power of the Orbitrap Exploris GC 240 enables superior discrimination between matrix interferences and target analyte ions.

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Enhanced quantitative performance for analytical testing laboratories with Orbitrap Exploris GC

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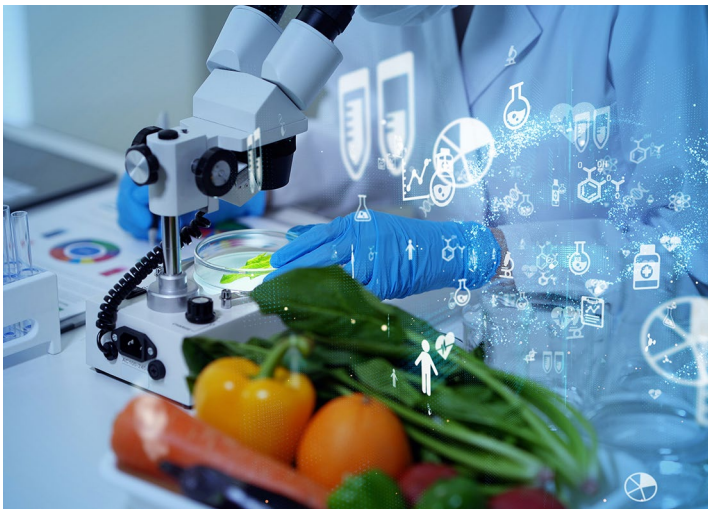
Keywords: Orbitrap Exploris GC, Orbitrap technology, high resolution, accurate mass, sensitivity, robustness, gas chromatography, analytical testing, pesticides, PCBs, fruits and vegetables, quantitation, TraceFinder



Goal

To demonstrate the benefits of the Thermo Scientific™ Orbitrap Exploris™ GC mass spectrometer for the analysis of pesticide residues and polychlorinated biphenyls (PCBs) at trace levels in food, in compliance with SANTE method performance criteria.

Introduction

In high-throughput analytical testing laboratories, robust streamlined analytical and data processing workflows are key requirements for the accurate and reliable determination of trace level residues and contaminants (such as pesticides and PCBs) in food. These methods must overcome the challenges of an ever-growing list of compounds and diversity of sample matrices, in addition to ever-demanding sensitivity and identification requirements. Typically, gas chromatography coupled to low resolution, nominal mass triple quadruple mass spectrometers (GC-MS/MS) has been the system of choice for the sensitive and selective detection of a wide range of target compounds. A GC-MS/MS acquisition method requires at least two precursor ions for product selected reaction monitoring (SRM) transitions to be optimized for selectivity and sensitivity for each analyte. Furthermore, the retention time for each analyte has to be pre-programmed into the acquistion method. This initial method development can be a time-consuming process.

The development of additional hyphenated GC-MS analytical systems such as high-resolution accurate mass (HRAM) Orbitrap mass spectrometry coupled to GC has proved to be a valuable alternative to triple quadrupole GC-MS.[1-5] With HRAM mass spectrometry, the default acquisition mode is untargeted (full-scan) meaning that all the ions are acquired with high selectivity at the same time

across a specified mass range, making the method setup and data acquisition simple to manage and giving the analyst the flexibility to decide which compounds to focus on. This can extend into retrospective analysis of data to evaluate for the presence/absence of other contaminants not necessarily of interest at the time of acquisition.

In the European Union (EU), the default maximum pesticide residues level (MRL) is regulated at 10 µg/kg.[6,7] The guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed is SANTE/12682/2019,[7] which includes quantitative and identification criteria for HRAM MS data:

- At least two ions per target compound, measured with mass accuracy of ≤5 ppm (≤5 mDa for masses below 200 Da)
- Retention time tolerance of ±0.1 min
- Precision for bracketed (beginning and end of the run) matrix-matched calibration standards % RSD ≤20% for each calibration level is required
- The lowest standard ≤ the reporting limit
- Recoveries within the range 60% to 140%, or ± 2× RSD (determined from validation data or ongoing QC results)
- For HRAM compared to nominal mass analysis, ion ratio guidelines state matching ion ratios are not necessary, but could be used for additional confirmation

In the experiments described below, the analytical performance and suitability of a benchtop HRAM Orbitrap GC-MS for analytical testing laboratories was assessed. System setup simplicity and method setup as well as typical method performance parameters were tested including sensitivity, linearity, quantitation, recovery, accurate mass, and ion ratios.

Experimental

Sample and standard preparation

Homogenized test-portions of fruit and vegetable samples were extracted using the mini-Luke procedure,[8] and prepared as detailed in a previously published Application Note.[9] A series of matrix-matched calibration standards containing pesticides and PCBs, over varying concentration ranges, were prepared by spiking apple and carrot extracts.

Instrument and method setup

Automatic sample injection was performed using a Thermo Scientific™ TriPlus™ RSH autosampler, and chromatographic separation was performed using a Thermo Scientific™ TRACE™ 1310 GC system equipped with a PTV injector and fitted with a Thermo Scientific™ TraceGOLD™ TG-5SilMS 30 m × 0.25 mm I.D. × 0.25 µm film capillary column with a 5 m integrated guard (P/N 26096-1425). Finally, a Thermo Scientific Orbitrap Exploris GC mass spectrometer was used for accurate mass measurements in full-scan mode at 60,000 mass resolution (FWHM *m/z* 200). Ease of use maintenance features, such as changing columns or removing the source that can be carried out without venting the MS, can save valuable time and add flexibility with increased efficiency. Additional details of instrument parameters are as detailed in previously published Application Note.[9]

Data processing

Data were acquired and quickly processed using Thermo Scientific™ TraceFinder™ software, which allows intuitive instrument control, method development, and data processing capabilities. Ready-to-go templates for instrument and processing method setup allowing walk up and use capability. For targeted analysis, a compound database was prepared containing compound name, accurate masses for the quantification and qualifying ions, retention times, and the elemental compositions of the molecular ion. To generate the extracted ion chromatograms (EIC), a mass window of ±5 ppm was used, meaning that only ions with a mass accuracy ≤5 ppm were extracted.

Results and discussion

The objective of this study was to evaluate the quantitative, ease of use, and performance of the Exploris GC system for the analysis of pesticides and PCBs in fruit and vegetable matrices with varying complexity considering the performance requirements detailed in the SANTE guidelines.[3]

Pesticides were assessed in typical food matrices such as apples and carrots. Chromatographic separation was achieved in under 33 min with the TRACE GC system, which comes with modular injectors that allow for PTV and SSL selection. A typical TIC chromatogram in an apple matrix is shown in Figure 1, versus overlaid EICs for a selection of pesticides. The results achieved demonstrate excellent selectivity for the analysis of pesticides and PCBs even in complex samples.

The Orbitrap Exploris GC-MS, with markedly reduced footprint, can be tuned and calibrated very quickly (~1.5 min) and efficiently, using a next generation tune software designed for ease of use, while offering maximum functionality, see Figure 2.

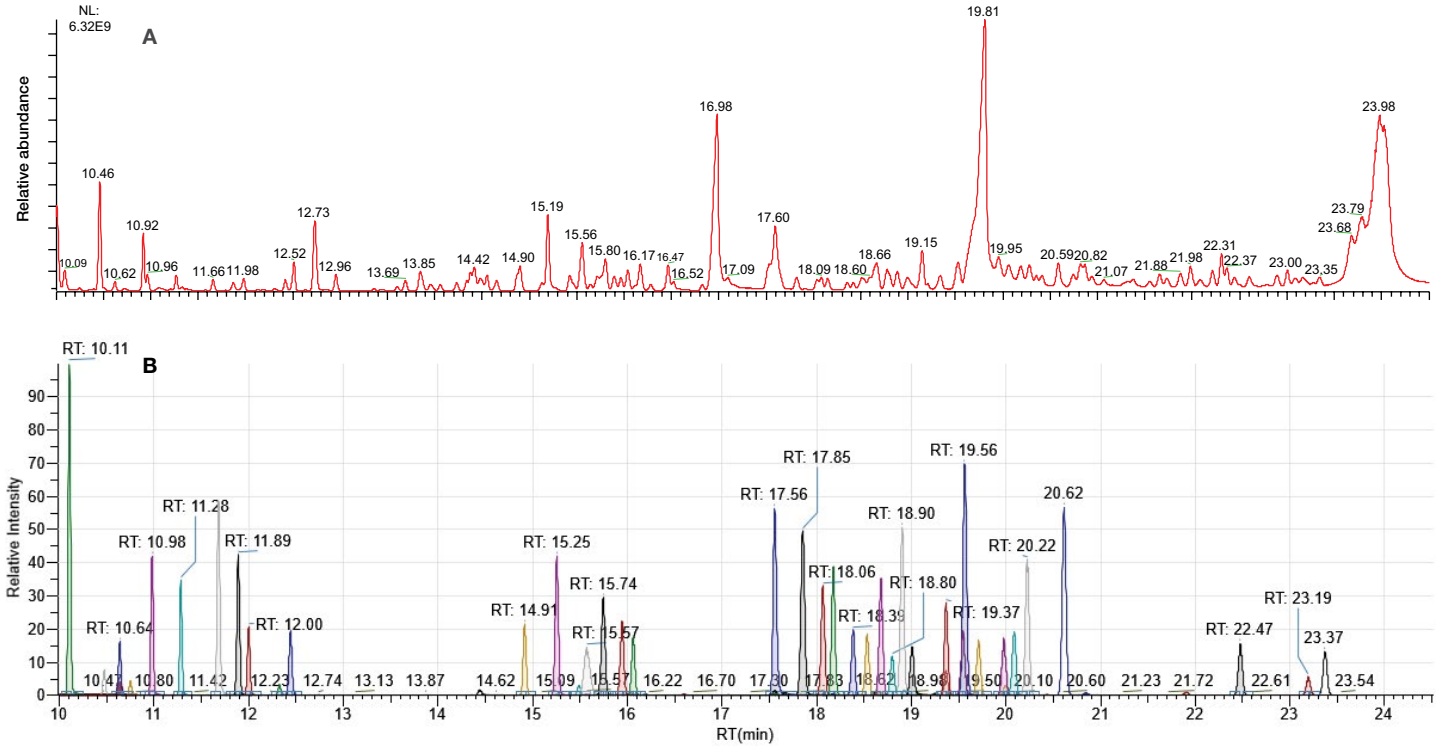


Figure 1. Apple sample chromatogram (spiked 100 µg/kg): [A] TIC full scan; [B] EICs for a selection of pesticides

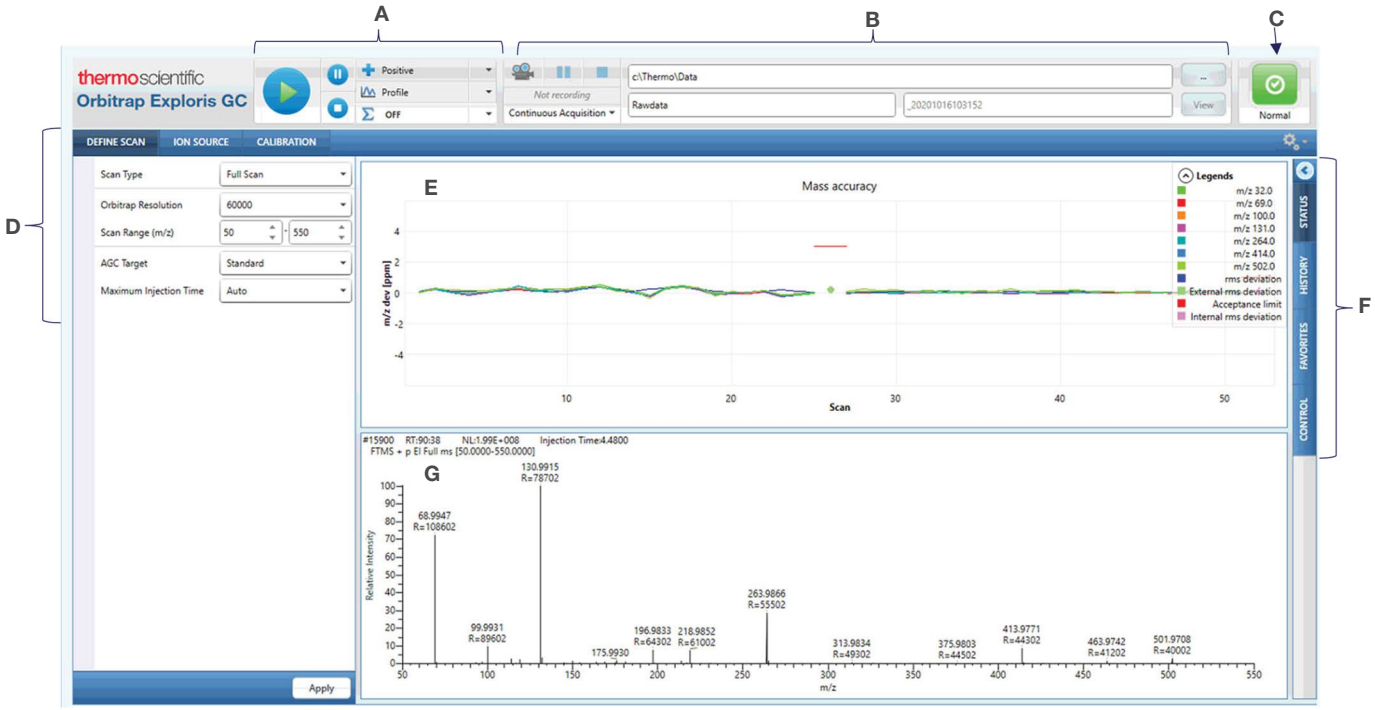


Figure 2. Orbitrap Exploris GC-MS tune page user interface developed for simplicity of use while offering maximum functionality to enable fast and efficient system setup. System calibration and tuning take ~1.5 minutes and are stable for a week or longer. The tune page includes: [A] power and instrument icons; [B] data acquisition buttons; [C] instrument status icon; [D] scan, ion source, and calibration panes; [E] plot view; [F] status panes, and [G] spectrum view.

The method editor is simple and intuitive and features ready to use, pre-optimized method templates for a wide range of typical application, including food safety (Figure 3).

Linearity and sensitivity

A wide linear dynamic range is essential, especially when dealing with applications where the samples analyzed contain a complex chemical background that could potentially interfere with the analytes of interest.[10] The sensitivity of target compounds in matrix is a key parameter when assessing the suitability of a quantitative analytical technique.

The SANTE guidelines[7] specify that precision and sensitivity for bracketed (beginning and end of the run) matrix-matched calibration standards % RSD ≤20% for each calibration level is required, with the lowest standard less than or equal to the reporting limit (RL).

An external matrix-matched five-point calibration covering a 5 to 250 ppb range was used, with a linear curve fit, a standard weighting of 1/×, and with curves not forced through the origin. The residual values variation (as %RSD) and coefficient of determination (R^2) were used to assess linearity. R^2 values of ≥0.95 and residuals ≤30% are considered acceptable. Figure 4 summarizes the linearity achieved for pesticides in apple and carrot matrices.

Achieving sufficient sensitivity when analyzing food contaminants is critical. With increasing resolution, the Orbitrap Exploris GC signal intensity is not affected unlike other types of high-resolution mass spectrometers where doubling the resolution will result in a significant drop in sensitivity.[12] Therefore when operating at a resolving power of 60,000, the established RL exceed the detection requirements for pesticide residue monitoring.

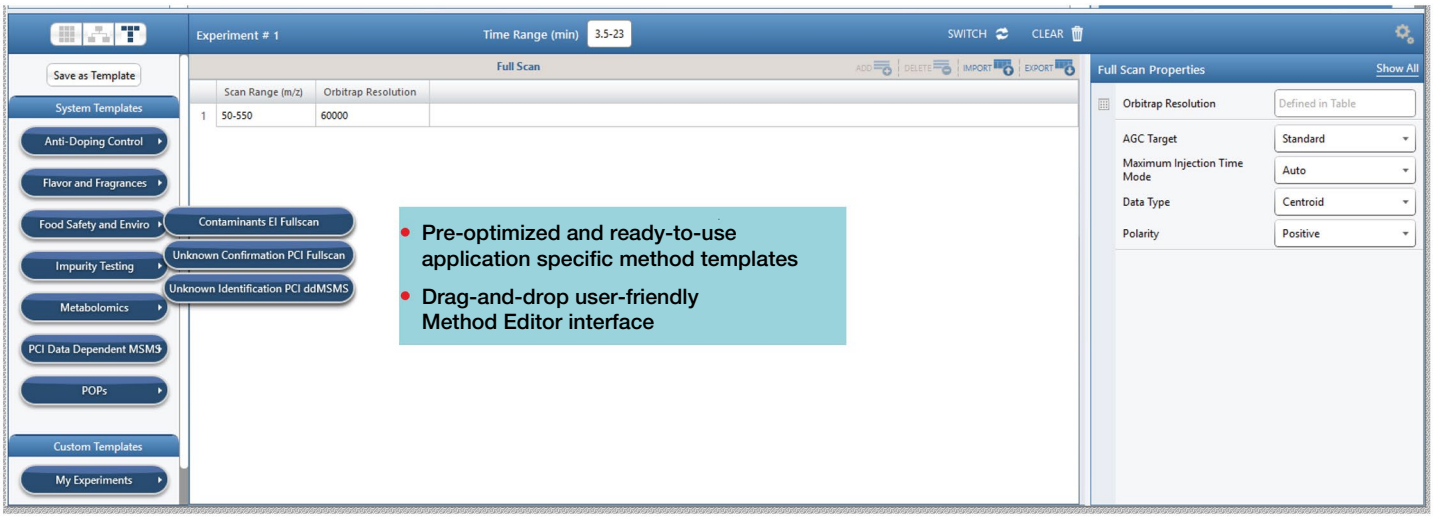


Figure 3. Orbitrap Exploris GC method editor system templates, enabling user friendly method setup using pre-optimized application specific method templates

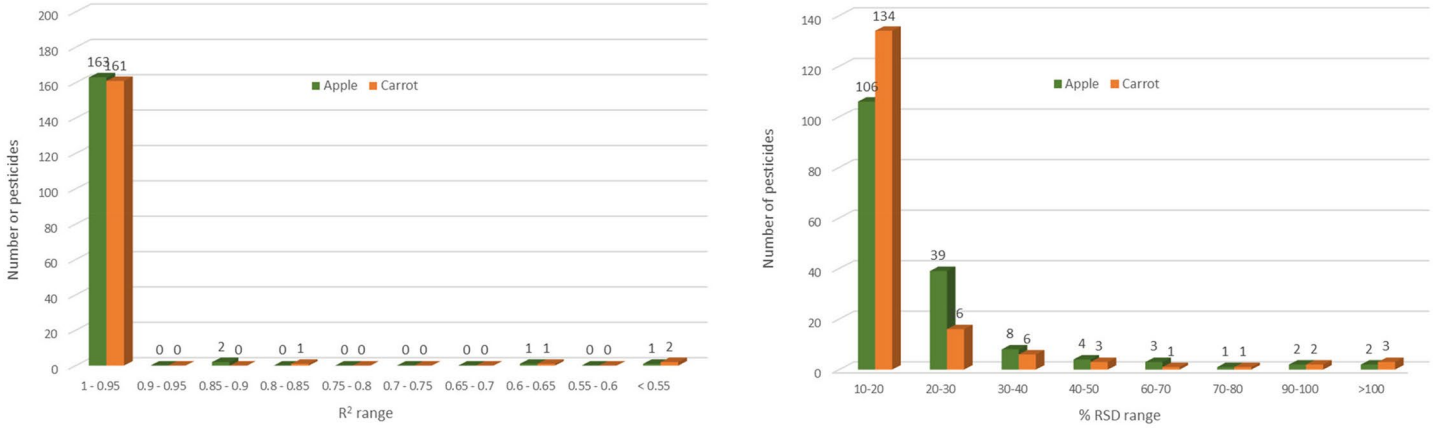


Figure 4. Summary of linearity achieved for pesticides in apple and carrot matrices, expressed as (A) R^2 and (B) % RSD

An example of compound sensitivity is shown in Figure 5 for bifenthrin in carrot. Overlay of the diagnostic ions at 10 µg/kg and the linear response for this compound are shown in the customizable views in TraceFinder software, which allows the user to quickly review the key detection criteria and any parameters outside of specified tolerances can be flagged automatically.

Accurate quantitation

For accurate compound identification and quantitation, at least 10 data points (scans) across a chromatographic peak are usually considered necessary. Figure 6 shows biphenyl peak in apple at 10 pg on column with ~33 scans across a 4.8 s wide peak.

To assess the detectability and accuracy of quantitation, spiked apple and carrot samples were analyzed. Figure 7 summarizes these recovery results for 167 pesticides, which show good agreement between the spiked and calculated concentrations, with 97% of pesticides within the SANTE guidelines[8] (60–140% for routine recoveries) for compounds outside this range quoted include pesticides that are a challenge for GC-MS and typically are also analyzed using LC-MS.

High accurate mass for confident compound identification

With the Orbitrap Exploris GC system operated routinely at 60,000 resolving power, consistent high mass accuracy information is always obtained, which is essential to increase the confidence in compound identification and avoid reporting false positive results. The SANTE guideline[8] recommends a criterion of <5 ppm for mass accuracy for identification of target pesticides in food and feed samples. As shown in Figure 8, this was achived for all pesticides analyzed, with ~90% of compounds showing <2 ppm mass accuracy for both the quantification and qualifier ions and 100% of compounds <5 ppm. This was achieved by performing a mass calibration at the start of the anlytical run, with no additional calibrations performed during the analytical sequence.

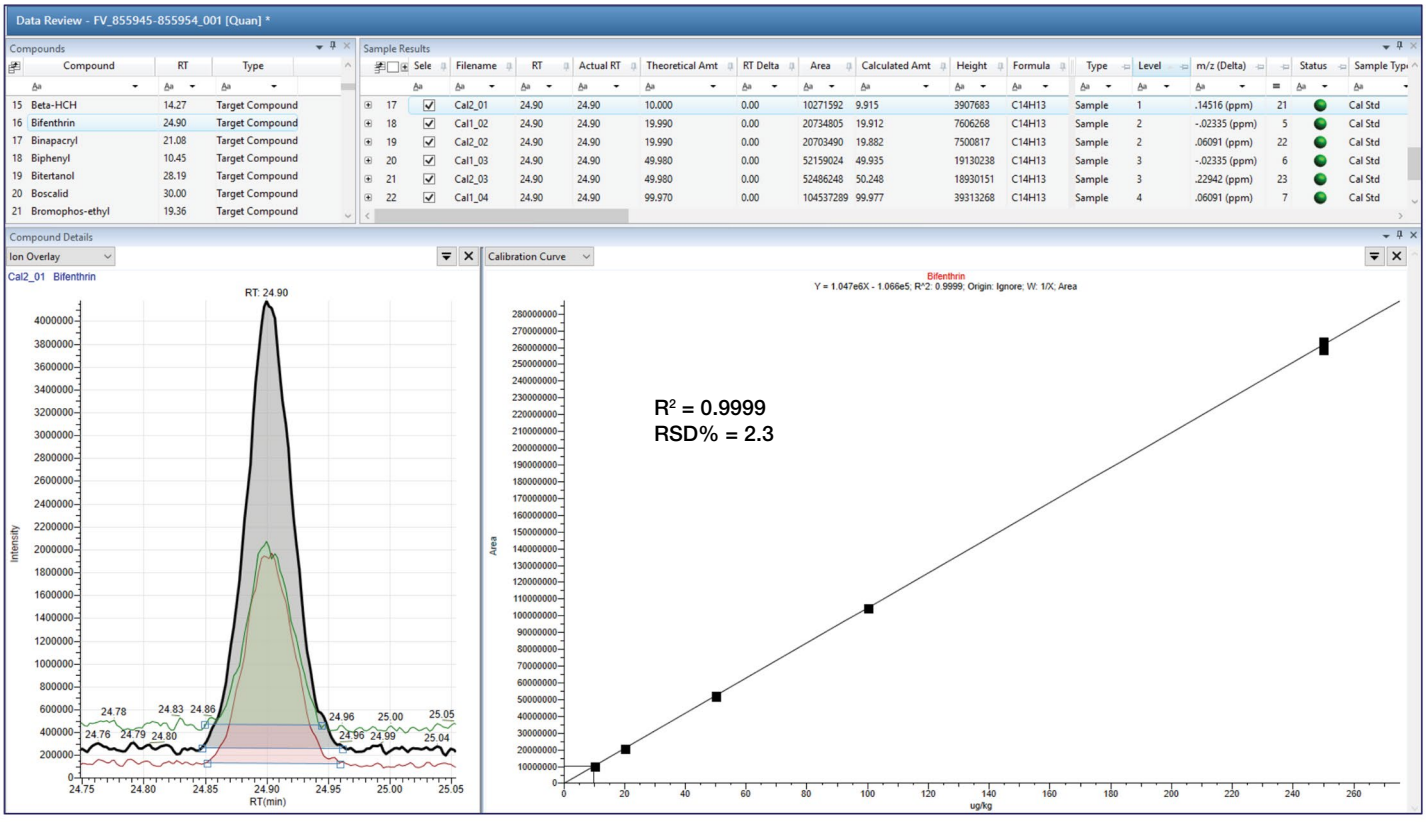


Figure 5. TraceFinder quantification results browser showing bifenthrin as an example. The overlay of extracted ion chromatograms for the quantification and two confirmatory ions as well as the linear response for bifenthrin over a concentration range of 10 to 250 ppb (equivalent to 10–250 µg/kg in matrix) with R^2 = 0.9999 and residual value as RSD% = 2.3 are shown.

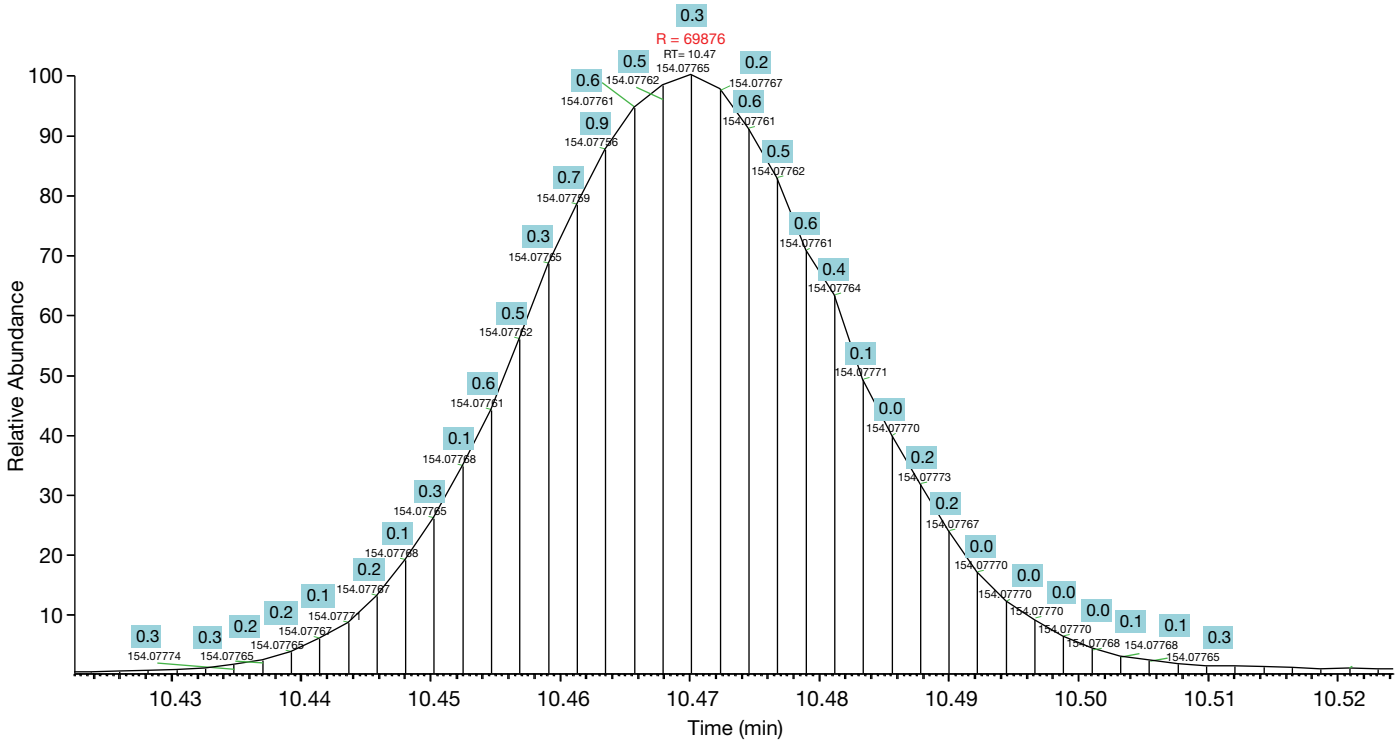


Figure 6. Biphenyl acquired in full scan at 60k resolution in an apple sample at 10 pg on column (corresponding to 10 µg/kg level), showing ~33 scans/peak (4.8 s peak width). Consistent sub 1-ppm accuracy was obtained for each individual scan.

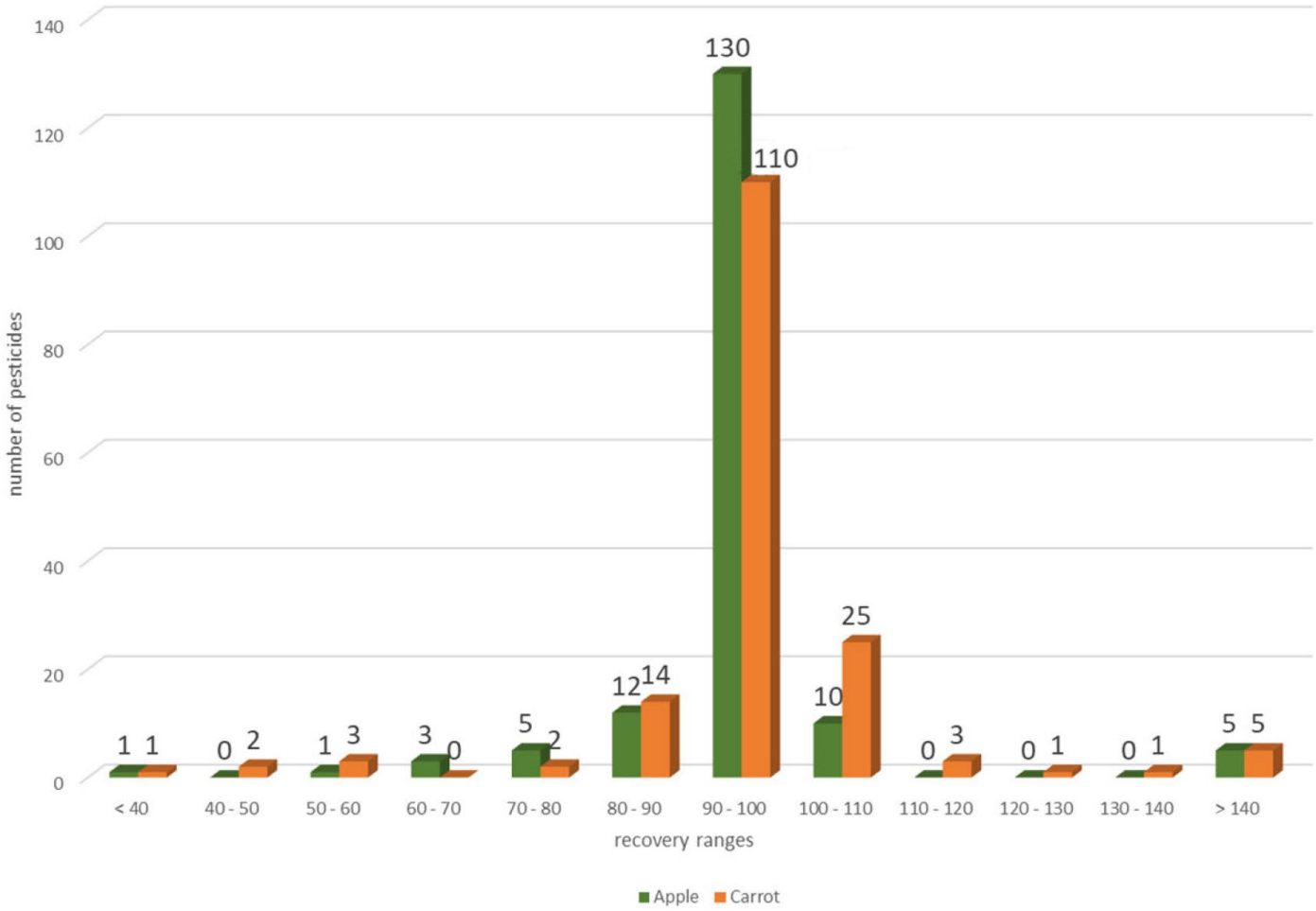


Figure 7. Summary of the % recoveries for 167 pesticides spiked at 100 ppb level (equivalent to 100 µg/kg) in apple and carrot matrices

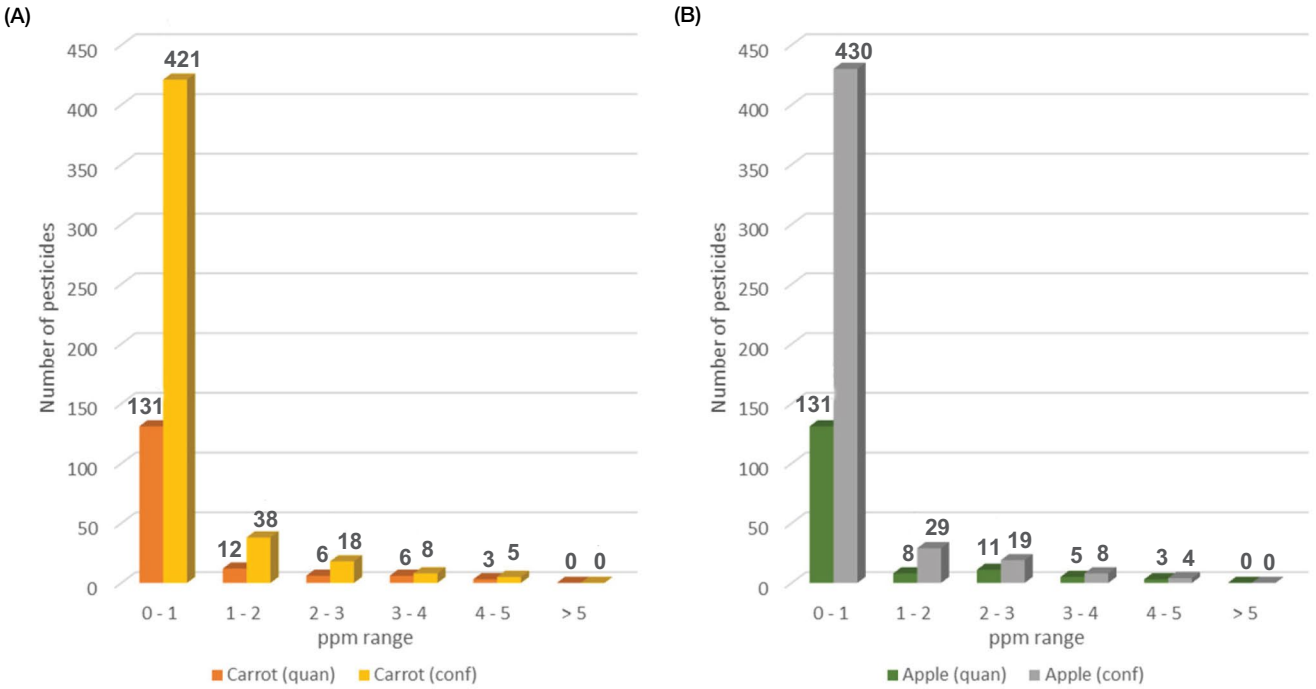


Figure 8. Summary of mass accuracy (as ppm) results for the quantification and qualifier ions in pesticides and PCBS spiked in (A) carrot and (B) apple

Ion ratios for additional compound identification

When evaluating mass spectrometry data, considering ion ratios achieved can provide additional verification. The SANTE guideline document allows a variation of 30% between ion ratios of the standards and the sample, but it also documents when using HRAM ion ratios are of secondary importance. A summary of the ion ratios results achieved is shown in Figure 9, which shows that for apple and carrots 93% of ion ratios differences are ≤30%.

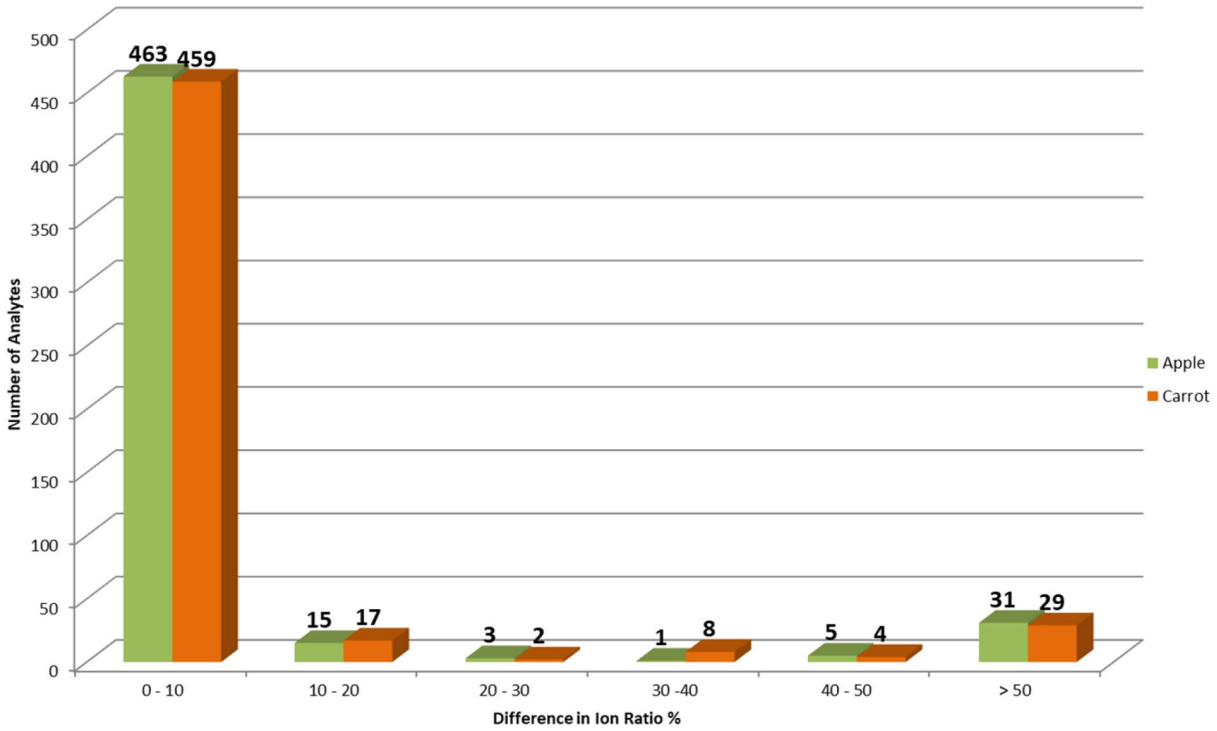


Figure 9. Summary of the difference in ion ratios between standards and recovery spikes by matrix

Compound identification against spectral NIST libraries

Where additional confirmation is required, the Exploris Orbitrap GC with full scan range mass accuracy and sensitivity enables accurate and reliable commercial library (e.g., NIST/Wiley) matching. Figure 10 shows the NIST library search results achieved using the Orbitrap Exploris GC for the analysis of biphenyl and hexachlorobenzene in a mixed pesticide standard, with both forward and reverse library match scores of >900 achieved.

Ensuring consistency of results across daily sample batches

Consistent instrument performance is key to ensure quality of results. This was evaluated for the analysis of pesticides and PCBs in food using n=35 apple matrix injections over two days of continuous operation by repeatedly injecting an apple extract (10 µg/kg). Response of pesticides and PCBs were consistently stable, illustrated in Figure 11, for a selection of pesticide and PCBS with % RSDs <11, demonstrating a robust system performance critical for analytical testing.

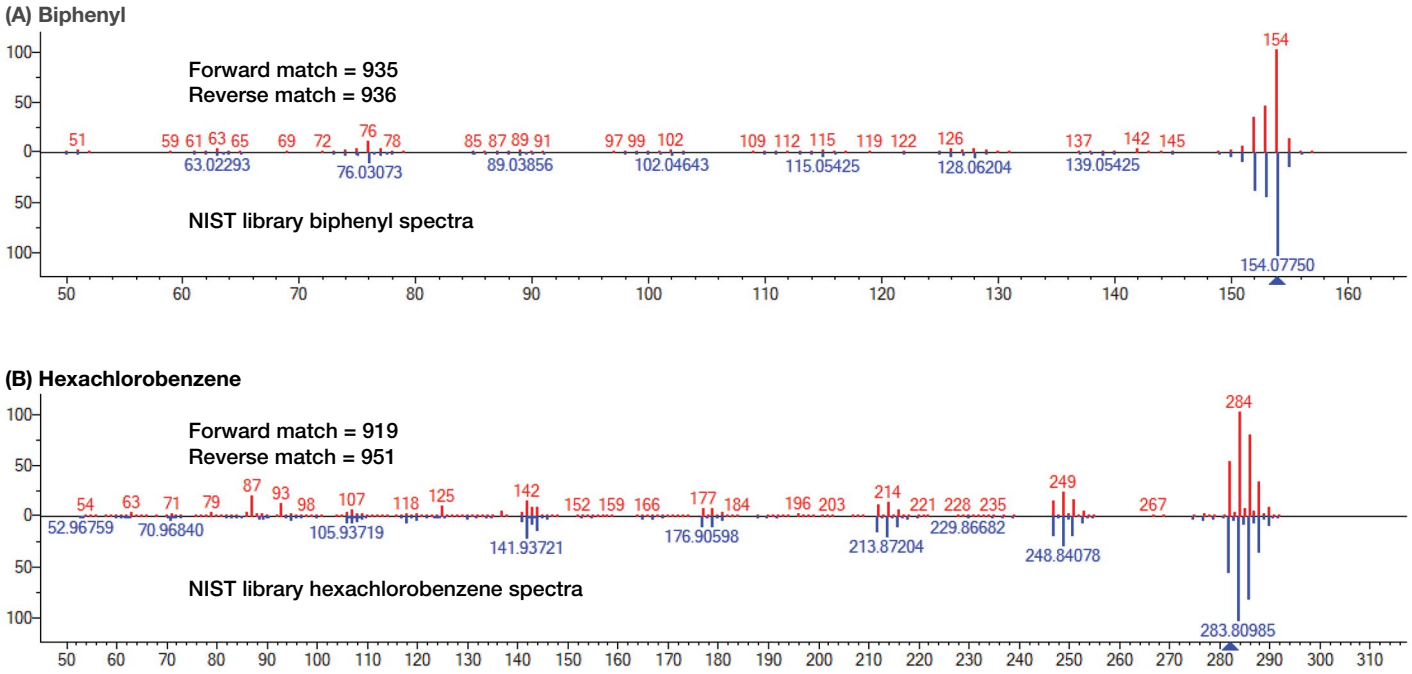


Figure 10. NIST library search results achieved using the Exploris Orbitrap GC for the analysis of biphenyl and hexachlorobenzene in a mixed pesticide standard (10 µg/kg), with both forward and reverse library match scores of >900 achieved

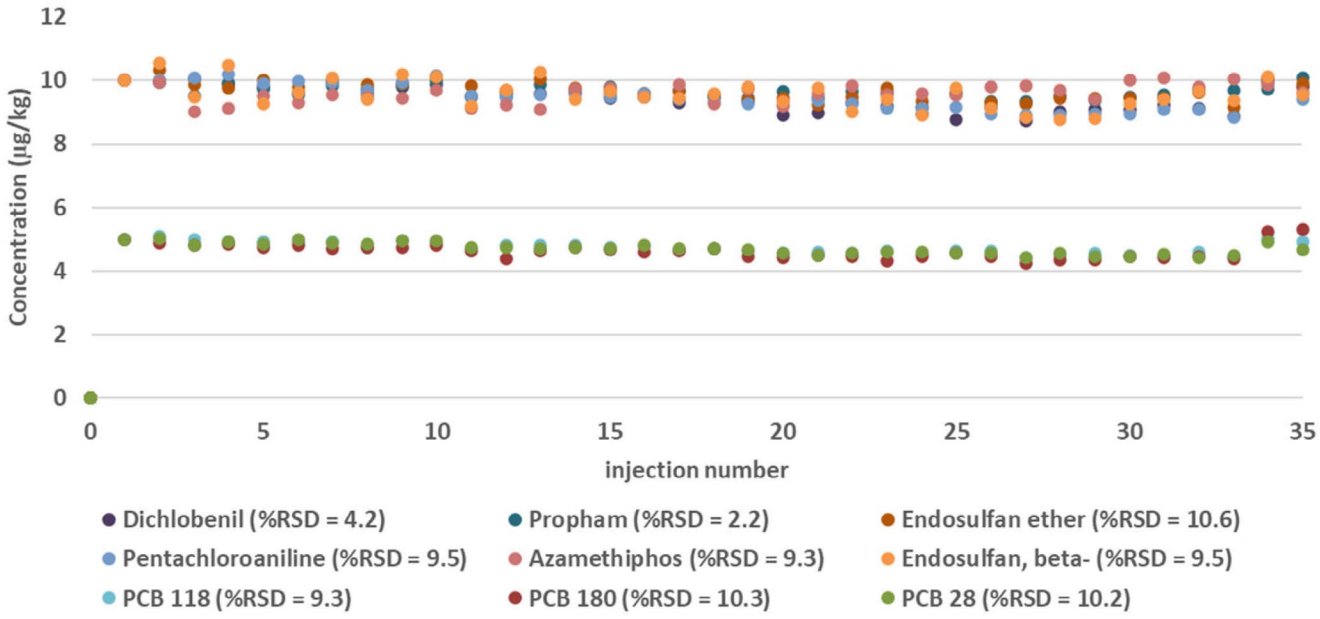


Figure 11. Robustness data achieved for the analysis of a selection of pesticides and PCBs in apples and carrots using the Exploris Orbitrap GC, with %RSD <11 (n=35), demonstrating consistent system performance, essential for analytical testing application

Summary

The results summarized in this application note demonstrate that the Orbitrap Exploris GC mass spectrometer coupled to the TRACE 1310 GC represents a suitable alternative to traditional GC-MS/MS approaches for the analysis of trace level contaminants in food. The smaller instrument footprint and simplified system setup enables operational use while offering powerful gains in quantitative performance, ease of use, simplicity, and productivity in line with regulatory requirements such as SANTE/12682/2019.

Sensitive and robust full-scan analysis allows for easy and flexible method setup, data acquisition, and processing, meeting SANTE guidelines for the analysis of pesticides and PCBs:

- Sensitivity below the MRL; the majority of mass accuracy <2 ppm; 93% of ion ratios with differences of ≤30% between ion ratios of standards and samples achieved; excellent linearity with $R^2 > 0.95$; average response factors RSD% < 20 across the 5-point (5–1250 µg/kg) matrix-matched calibration series; recoveries for pesticides spiked in apple and carrot samples showed reliable detection and accurate quantitation of spiked compounds, with >92% of pesticides tested within 70–120% recovery obtained.
- A compact footprint offering regulated testing with robust quantitative performance with results confidently reportable with fast turnarounds, all at a competitive cost
- Ease of use features enabling maintenance such as changing columns or removing the source to be carried out without venting the MS, saving valuable time, adding flexibility with increased efficiency
- Quick and efficient tuning and calibration using Orbitrap Exploris tune software designed for ease of use, while offering maximum functionality
- Options for retrospective addition of compounds enhance productivity.
- Method editor incorporated with System Templates, enabling user friendly method setup using pre-optimized application specific method templates
- The TRACE 1310 GC brings the power to the user through its instant connect modular injectors and analogue detectors, which can be interchanged within minutes, and fast cooling capability, reducing the time between injections.

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Can the Orbitrap Exploris GC drive profitability in analytical testing laboratories?

Expands analytical power through simplicity

For analytical testing laboratories, the efficiency of operations from sample receipt to report is what drives profitability. Every step in the process is critical and every instrument needs to make a return on investment. The Thermo Scientific™ Orbitrap Exploris™ GC mass spectrometer delivers new possibilities for analytical services to boost productivity and ultimately profitability. With outstanding real-world performance and analytical flexibility, the system can reduce the costs but increase the quality of results.

Analytical testing laboratories can explore new business opportunities, keep pace with changing regulations, and streamline processes through simplified, consolidated multi-class methods and secure the very highest confidence in compound detections.

Maximum system uptime is delivered through robust performance and automation, and with a compact footprint, the instrument conserves laboratory bench space.

Transforms efficiency

Lab managers in analytical testing laboratories are faced with unique challenges. Such challenges include an ever-growing list of target compounds to be analyzed with faster turnaround times and at a competitive cost. Essentially it comes down to the efficiency of operations to increase sample throughput and minimize instrument downtime.

The Orbitrap Exploris GC mass spectrometer brings new opportunities and data certainty to laboratories performing analyses in applications such as food safety, environmental, industrial, forensics, and anti-doping. The system enables highly selective screening and quantitation of both targeted and non-targeted compounds in complex matrices with minimal method development to ensure confident analysis and increasing lab productivity.

In this smart note a closer look at the key benefits of deploying Orbitrap Exploris GC is taken to answer how this system allows for unique advantages to drive profitability in analytical testing.

Provides high confidence in results

The Orbitrap Exploris GC mass spectrometers provide the capability to acquire accurate mass data in full scan, overcoming the limitations of triple quadrupoles without compromising quantitative performance. Additionally, due to its high and ultra-high resolutions, from 60,000 up to 240,000 (FWHM at *m/z* 200), the Orbitrap Exploris GC systems can resolve almost any matrix interference from analytes of interest, as well as determine fine isotopes (^{34}S, ^{18}O, ^{15}N, etc.) for easier and faster identification. High resolving power together with excellent mass accuracy increases analytical selectivity, which means less time is spent on data interpretation and sample results can be quickly reviewed and reported. The consequence of reporting a false positive or negative result can have serious implications. From full scan data, multiple points of identification can be used to quickly confirm or reject detections to give peace of mind. In addition to the retention time of target accurate mass ions, compound detection can be confirmed using spectral matching (Figure 1), isotope pattern, retention indices, and elemental compositions to provide detection certainty and deal with the tentative identifications that exist today with other technology.[1-5]

Maximizes return on investment

To comprehensively screen a sample for a wide range of chemical classes, multiple methods are often required. In a high-throughput environment this can involve multiple GC-MS/MS systems to address each of the compound classes, for example, PAHs, PBDEs, OCPs, SCCPs, etc. Having multiple instruments is costly as they require their own maintenance programs, service arrangements, consumables, and operators. These all increase the cost of analysis and impact efficiency.

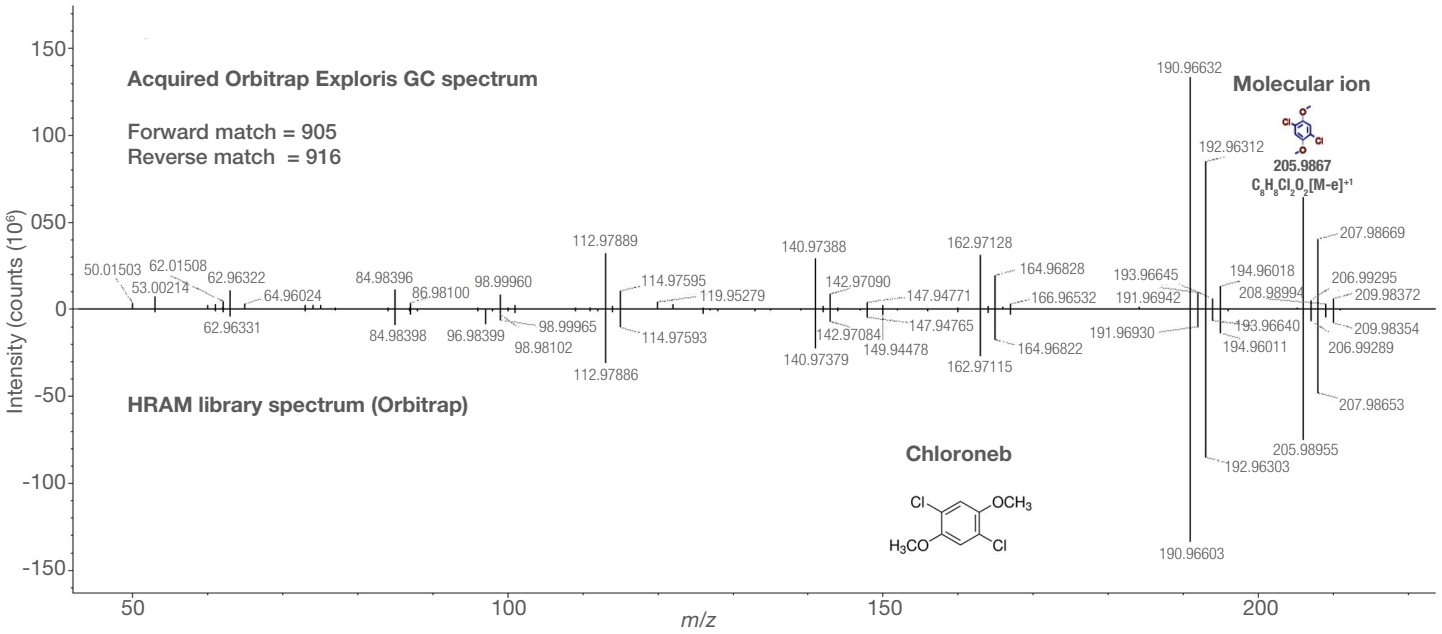

Figure 1. Full scan allows multiple compound identification points, such as multiple accurate mass ions, spectral matching, isotope pattern comparison (measured versus theoretical), and ion ratio confirmation. Example spectrum library match for chloroneb in a mixed pesticide standard using an Orbitrap Exploris GC 240 system operated in full scan at 240,000 resolution (FWHM at *m/z* 200).

This approach of multiple systems has developed through extraction and instrument capability, rather than by design. Through high resolution mass spectrometry, it is possible to take advantage of a full scan untargeted acquisition, but with the required selectivity and sensitivity that is demanded by quantitative applications (Figure 2). This enables a single data file to be acquired and processing methods then customized to extract the requested target compounds or even expand to a wider scope of analysis.

Operating one instrument instead of multiple single or tandem quadrupole systems, there is less time spent on routine daily maintenance and system set up. In addition, there is a significantly reduced bench space and instrument consumable requirements. The result is a much simpler operation that is efficient and flexible to adapt to changing laboratory needs. Furthermore, with fewer systems to maintain, instrument uptime is much higher and potentially all analytical personnel are able to process compounds from any chemical class.

Reduces method setup time

The Orbitrap Exploris GC system is designed to reduce training needs, while empowering staff of all skill levels through easy to use operation software and pre-defined method templates. The intuitive and standardized instrument control of the Orbitrap Exploris GC system guarantees that it is always performing at its best for both expert and non-expert users alike. It is now possible to initiate, tune and calibrate in under five minutes with full confidence that the system is at optimal performance. With full scan data across the entire chromatographic run, there is no need to spend time verifying that SRM windows are correct, as is the case with GC-MS/MS. This untargeted acquisition also enables the system to be quickly set up so that analysts can focus on results and not setup.

Increases the scope of analysis

Ever-changing regulations mean that analytical testing laboratories face an expanding list of analytes to be included in their scope of analysis, and they must also have the ability to respond to emerging food and environmental safety matters. Currently most laboratories rely on targeted analytical approaches using triple quadrupole mass spectrometry (MS) instrumentation to analyze a

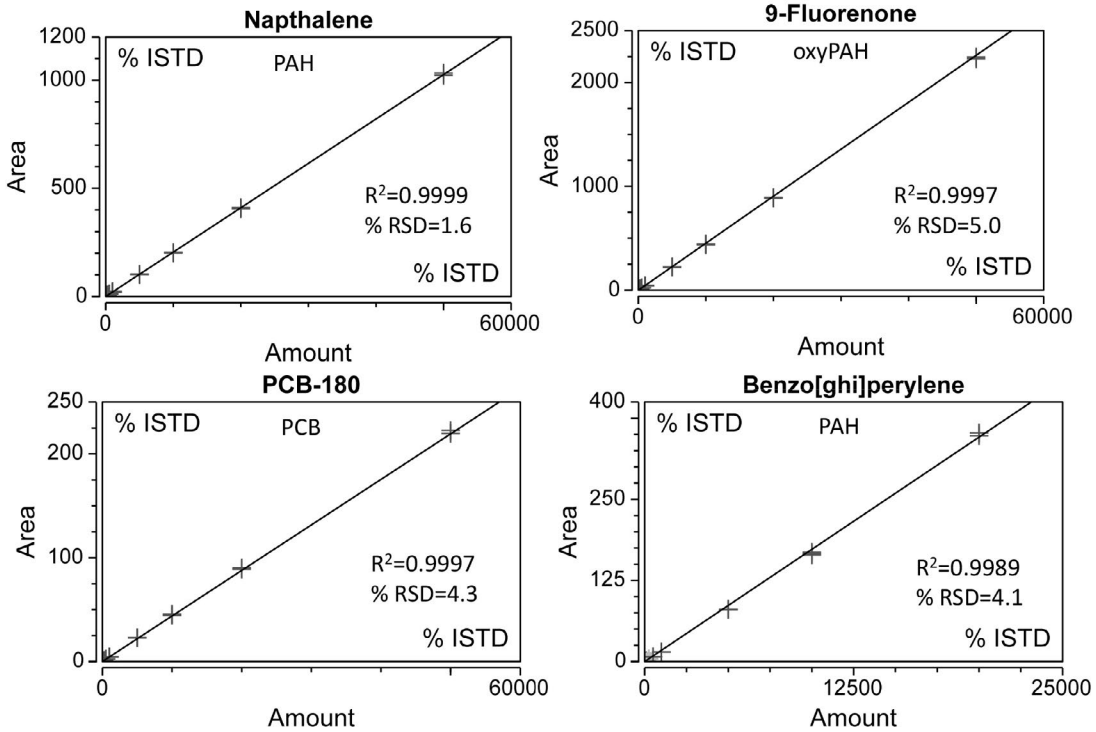

Figure 2. Quantitative capability for example PAHs and PCBs using solvent-based calibration curves ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in soil sample). Average calibration factor function (AvCF) was used in Chromeleon CDS and three replicate injections at each concentration with internal standard adjustment were performed.

target list of compounds. This technology covers a wide range of chemical classes and provides the required level of sensitivity and selectivity. However, they are limited to only detect those compounds in the method acquisition list. When new compounds are to be added, they require careful optimization of acquisition parameters and the checking of acquisition time windows to ensure detection of the target analyte. With an untargeted full scan acquisition, it is simply a case of updating the processing method with the appropriate ions of interest and retention time. With accurate mass selectivity, it is possible to extract target compound from a complex chemical background, and retrospective analysis of data allows the lab to investigate the presence of contaminants in samples collected and analyzed years ago.

Supports expansion into emerging applications and services

Food fraud and emerging environmental contamination is predicted to increase, and this is likely to raise concern for global regulatory authorities and consumers alike. This presents an opportunity for analytical testing laboratories to explore new services such as sample profiling and fingerprinting to observe what is normal and what is different. This is enabled through comprehensive data to allow additional questions to be asked of a sample, such as what is in my sample beyond a target list, when did it start appearing, what's different between sample groups, is my sample similar to others, and is there a marker of authenticity? You have the data, just ask the question.

Summary

Orbitrap mass analyzer technology has been successfully used to drive productivity gains in a wide range of environmental analysis, food testing applications, clinical, and anti-doping applications. The popularity of performing quantitative, qualitative, and screening analyses in a single injection is growing rapidly and provides a solution to ever-changing demands in analytical science. This is due to the Orbitrap mass analyzer's unique ability to provide high resolution accurate mass and both quantitation and qualification (accurate screening) data in a single analytical run. The quality and flexibility of data produced provides ultimate confidence in the results obtained. High resolving power increases analytical selectivity for compounds in complex matrices and thus reduces the uncertainty associated with the misassignment of positive results. The unique ability to capture all relevant data using full scan allows retrospective data analysis, reducing the need for additional sample injections.

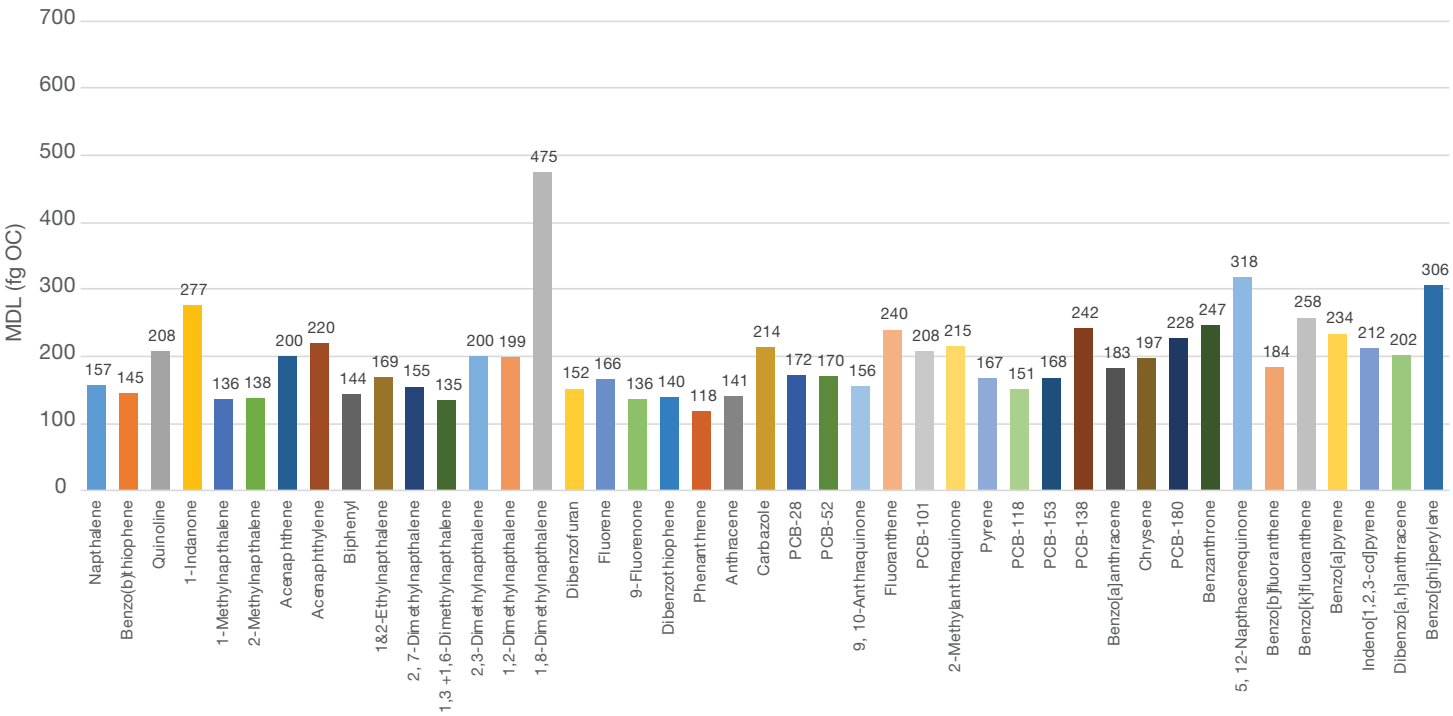

Figure 3. Sensitivity is a key factor in trace contaminant analysis. Graph showing individual method detection limit (MDLs) (as detectable fg on column) for 45 native PCB, PAH, methyl PAH, oxyPAH, and NSO-PAHs calculated from n=18 replicate injections of the lowest serially diluted matrix-matched standards.

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Furthermore, Orbitrap mass analyzers are enabling analytical scientists to raise their productivity and profitability to new levels. Compared to triple quadrupole MS-based quantitation methods that involve time consuming optimization of hundreds of SIM or SRM transitions in numerous time windows, Orbitrap mass analyzer methods enable the quantitation of virtually unlimited numbers of compounds that is fast and easy to set up. The Orbitrap Exploris GC provides unmatched versatility to meet the needs of analytical testing laboratories today and into the future.

References

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4. Technical Note 10730: Mass resolving power of 240,000: For confident compound identification. Thermo Fisher Scientific.
5. Technical Note 10728: Robust analysis of PAHs and PCBs in soil with over 500 repeat injections using Orbitrap Exploris GC. Thermo Fisher Scientific.

Find out more at **thermofisher.com/OrbitrapExplorisGC**

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CASE STUDY
Department of Agriculture, Food and the Marine

GC Orbitrap MS delivers increased productivity to analytical testing

Thermo Scientific™ Exploris GC

"To ensure our food is safe there is a continual demand to detect more compounds and to do so with the very highest confidence. GC triple quadrupole instruments have served us well for many years, but to meet the need for increased scope and to accurately quantify over a wide range, then we have turned to GC high resolution mass spectrometry for the solution"

—Dr Jim Garvey,
Department of Agriculture, Food and the Marine

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Food safety and environmental analytical testing laboratories are under ever-increasing pressure to screen samples for more pesticides in a single injection, with a fast turnaround time and at a competitive cost. These challenges are ones faced by Jim Garvey, the Head of Food Chemistry at the Department of Agriculture, Food and the Marine, in Celbridge, Ireland. They are a European Union National reference Laboratory accredited for the measurement of pesticide residues in a wide range of food commodities. One of their primary functions is the implementation of European Union (EU) law within Ireland. This means that each year they face an increasing list of pesticides and metabolites to be included in their scope of analysis and they must also have the ability to respond to emerging food safety matters.

Most laboratories rely on targeted analytical approaches using triple quadrupole mass spectrometry (MS) instrumentation. This technology covers a wide range of chemical classes and provides the required level of sensitivity and selectivity. However, they are limited to only detect those compounds in the method acquisition list. When new compounds are to be added they require careful optimization of acquisition parameters and the daily monitoring of acquisition time windows to ensure detection of the target analyte. An alternative approach to address these demands is to develop methods that use high-resolution accurate mass (HRAM) mass spectrometry (MS). This technology brings distinct advantages, to meet the ever-changing demands in pesticide analysis.

The laboratory has been developing pesticide residue analysis using the Thermo Scientific Orbitrap Exploris GC system. The team value the high specificity, sensitivity and flexibility of this system to increase the scope of analysis without the need for compound optimization. According to Dr Jim Garvey, “The aim is to cover more than 90% of the regulated pesticides and metabolites using multi-residue methods. This means that our current methods are constantly expanding; for example, we have a plan to add another 45 pesticides to our existing methods by the end of the year. To cope with this, we have had to look at alternatives to our existing triple-quadrupole MS systems and at different workflows such as the introduction of screening methods. For this reason, we have started to develop and validate methods using high-resolution accurate mass (HRAM)-MS systems”.

The priority of the team was to develop a multi-residue method for the analysis of pesticides and polychlorinated biphenyls (PCBs) in fruit and vegetables using GC–HRAM-MS. They had used triple-quadrupole instruments for almost 15 years, but the demand for an increase in scope means that they will have to anticipate methods with scopes of up to 1000 pesticides and metabolites in the near future. There is also the desire to consolidate separate methods onto a single system. Jim explained, “I think methods using triple-quadrupole instruments will struggle to cope with this demand for a number of reasons. We need to find transitions for every new compound added to a method, and these transitions need to be optimized for the instrument being used, which is a considerable amount of work. Once we have done this, the scanning speed of the instruments then limits the number of transitions that we can fit into the method, and this in turn puts a limit on how far we can develop triple-quadrupole methods. These limitations

> “Compared to existing triple-quadrupole methods, the selectivity of GC Orbitrap is much higher, the sensitivity is at least comparable and the repeatability and reproducibility are better”
>
> — Dr Jim Garvey

don't exist with high-resolution MS systems operating in full scan, and these systems also give the advantage of high resolution and mass accuracy, which gives us greater confidence in our results".

To develop the protocol, the laboratory built a HRAM database that includes the retention times, exact masses, and confirmatory ions for target compounds of interest. Using the database, the laboratory can quickly set up a method for a confirmatory analysis. The confirmatory method uses an average of four ions—one for quantification and three for confirmation to compare at least two ion ratios—exceeding the SANTE guidelines that require two ions measured by HR MS and one ion ratio.

Following this the method was validated following criteria in the SANTE/2019/12682 guidance document used in the EU. The method was validated for fruit and vegetables - a high water content matrix (cucumber), a high acid content matrix (lemon), and a high chlorophyll content matrix (broccoli). Recovery experiments were carried out across the linear range of the method (5–250 µg/l) using two different analysts, and the repeatability was calculated and the within-laboratory reproducibility. Mass accuracy and the confirmatory ion ratios were also evaluated, and finally they looked at matrix effects. The method contains 167 pesticides, PCBs, and metabolites, and was successfully validated for 94% of these with recoveries within 60–140% with a repeatability and within-laboratory reproducibility of <20%.

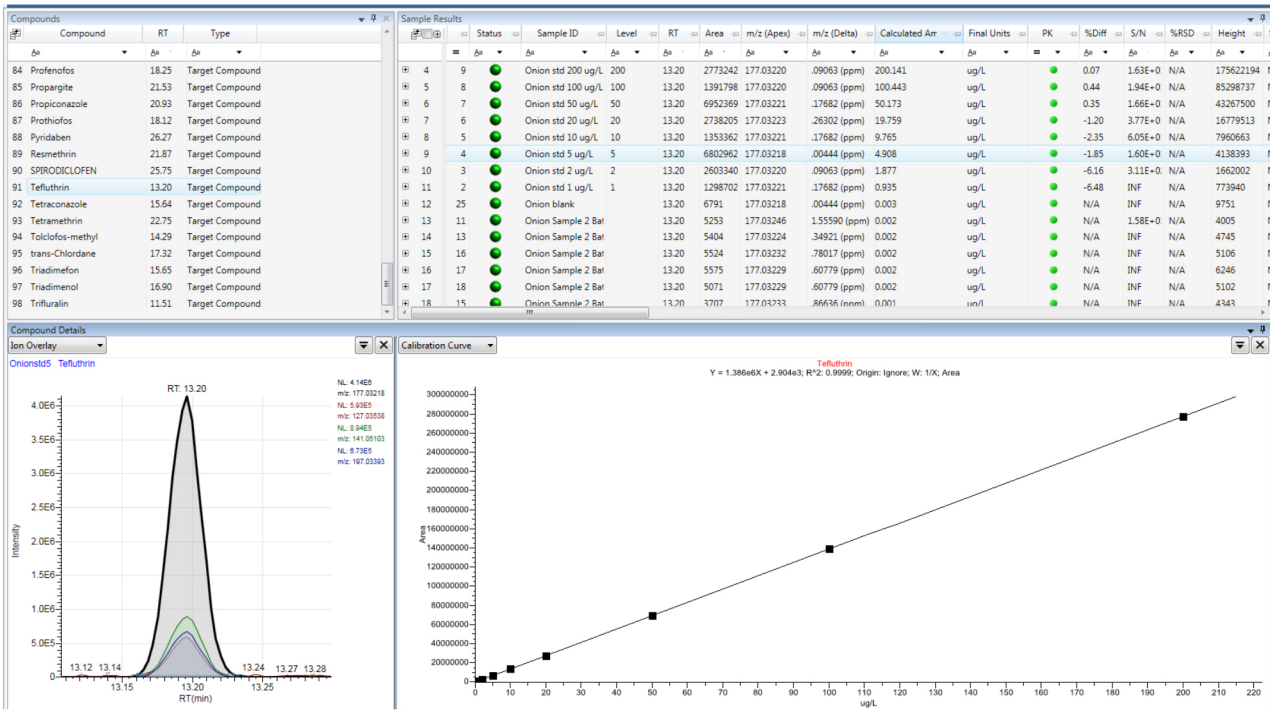

Figure 1. TraceFinder data review. Example showing 5 µg/L Tefluthrin in onion with extracted ion overlay of quan ion and three confirming ions (±5ppm window) and matrix matched calibration series

"For laboratories working in high-throughput analysis of food samples, using HRAM is a good choice and enables the lab to adapt to changing demands"

— Dr Jim Garvey

The sensitivity in full scan mode easily meets the default MRLs of 10 µg/l for 90% of the analytes. The mass accuracy for the target ion and confirmatory ions is less than 2 parts per million (ppm) for most of the analytes. Although it's only an indicative criterion, we evaluated the ratios of confirmatory ion to target ion, and again the majority of these meet the 30% level set in the SANTE document.

In addition to increasing the scope of analysis there are some clear advantages to using HRAM in a high throughput environment. One of those is that the system is very quick to set up with tuning and calibration taking minutes to perform and with data acquired in full scan, there is no need to spend time verifying that SRM windows are correct. It is the data processing options that provide the most significant advantages. With GC-QQQ-MS the analyst is limited to using only 2 or 3 SRM transitions to detect and confirm positive results. With data acquired at 60,000 mass resolution in full scan the user has additional points of identification and therefore the bottle neck of data processing and peak verification is faster. Full scan allows any ion to be used for confirmation and can be changed according to sample matrix. Spectral matching and isotope pattern score matching can also be used to confirm detections and therefore reduce false positives and negatives. The final benefit is that the retrospective analysis can be performed, enabling compounds to be measured post acquisition or the samples profiled and compared to samples from different time points. This capability can be very useful during method validation where methods can be tweaked without the need to re-analyse samples.

Confirming suspect positives

A recent case highlighted the benefits of having full scan high resolution data, where a suspect positive for molinate from a GC-MS/MS system was proved false by high resolution data. The two molinate targeted SRM transitions produced a peak at the correct retention time and even had acceptable ion ratios. The suspect sample was re-analysed on the GC Orbitrap where the selectivity and flexibility to look at a full spectrum and multiple identification points ruled out the presence of molinate.

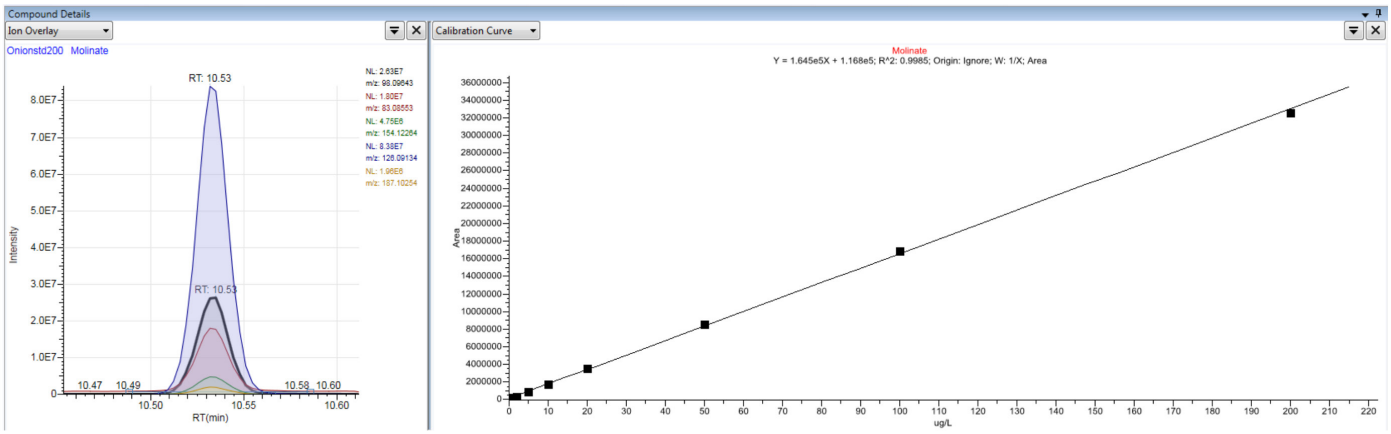

Figure 2. TraceFinder extracted ion overlay of quan ion and four confirming ions for molinate (±5ppm window) and matrix matched calibration series

"The sensitivity in full scan mode easily meets the default MRLs of 10 ppb for 90% of the analytes. The mass accuracy for the target ion and confirmatory ions is less than 2 ppm for most of the analytes"

— Dr Jim Garvey

About Dr Jim Garvey

Dr Jim Garvey graduated from The National University of Ireland (Galway) with a Ph.D. in organic chemistry. He developed his career in the pharmaceutical industry as a Research Chemist, before becoming a process development manager in industry. Since 1999, he has been at the Pesticide Control Laboratory where he is currently managing the introduction of HRAM technology to the residues laboratory. He was recently appointed Head of Food Chemistry at the department of Agriculture, Food and the Marine. As well as pesticides the Food Chemistry division also covers veterinary drugs, compositional analysis of dairy products, contaminants and elemental analysis.

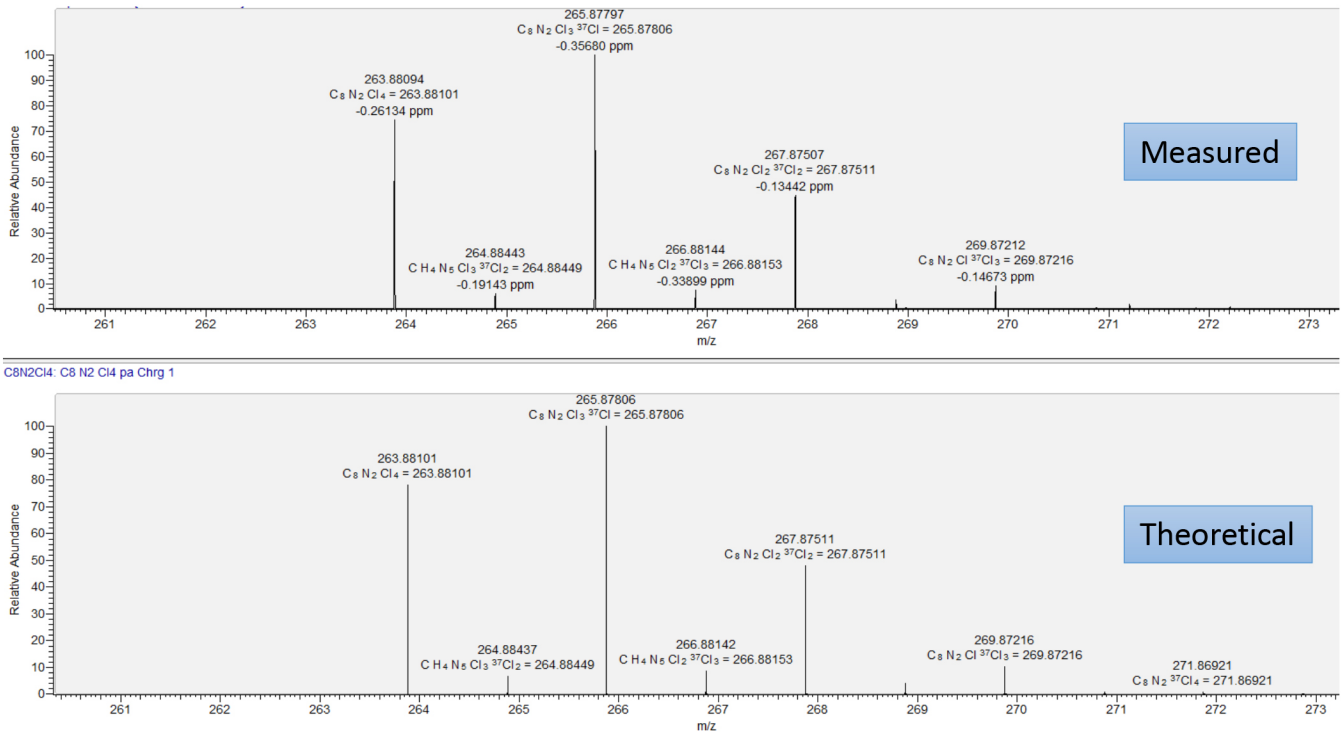

Figure 3. Comparison of measured and theoretical isotope pattern of chlorthalonil molecular ion $C_8N_2C_{l4}$. All isotopes measured with correct abundance and excellent mass accuracy

Conclusion

Confidence in the results of food safety and environmental testing is of utmost importance. The Exploris GC system brings the power of HRAM Orbitrap MS to provide the required specificity, sensitivity for target compound analyses in high throughput analytical testing. HRAM brings significant advantages compared with targeted methods including:

- Increased confidence in positive detections.
- Easily increases the scope of analysis.
- Method consolidation options.
- Faster and more confident data processing.
- Retrospective analysis.

All of these enable analytical testing and scientific research laboratories to adapt to ever changing demands.

About Pesticide Control Laboratory at DAFM

The Pesticide Control Laboratory (PCL) at DAFM is the national monitoring laboratory for the analysis of pesticide residues in food and animal feed and for the analysis of formulated products. PCL is also the designated National Reference Laboratory for the analysis of pesticide residues. The laboratory implements the monitoring program for pesticide residues in food, in compliance with EU legislation. The PCL is a fully accredited laboratory, which means that the EU Commission and our customers can have complete confidence in our laboratory's ability to analyse samples for pesticide residues.

The Pesticide Residue laboratory analyses samples of fruit, vegetables, cereals, food of animal origin including animal fat, milk and other dairy products, honey, infant and follow on formula and processed foods (including wine, juices, tinned foods and oils). Ssampling of fruit and vegetables is biased in favour of food commodities that are of greater dietary importance. In excess of 800 samples of domestic and imported fruit and vegetables are taken annually. Baby food, fruit and vegetable juices as well as wine fall under this category. Samples are analysed annually for ~460 pesticides and their metabolites.

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TECHNICAL NOTE 10728

Robust analysis of PAHs and PCBs in soil with over 500 repeat injections using Orbitrap Exploris GC

Authors: Aaron Lamb, Dominic Roberts, and Cristian Cojocariu

Thermo Fisher Scientific, Runcorn, UK

Keywords: Routine, robust, gas chromatography, Orbitrap, high resolution mass spectrometry, environmental analysis, method consolidation, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), QuEChERS, Orbitrap Exploris GC, Chromeleon

Goal

The scope of this study was to test a simplified GC-Orbitrap™ analytical method over a large number of consecutive injections of soil samples to assess if it can meet the demands of routine trace analysis in soil samples.

Introduction

Polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) are toxic organic pollutants that can contaminate soils, air, sediments, and water as a result of natural and human processes. PCBs and PAHs are resistant to environmental degradation and can be transported over long distances. PAHs and PCBs from the environment can enter food chains where they are very persistent and very bioaccumulative (vPvB).[1]

PAHs and PCBs have numerous congeners, many of which have identical masses. For this reason, gas chromatography-mass spectrometry is the analytical technique of choice for their separation and quantification. Higher mass PAHs are prone to poor peak shape in gas chromatography, making peak integration challenging by impacting chromatographic resolution and sensitivity, leading to higher limits of detection and quantification. Also, the routine analysis of PAHs and PCBs in complex soil matrices requires consumables and instrumentation that deliver exceptional degrees of stability in terms of peak areas, response factors, ion ratios, and mass accuracy so that multiple batches of samples can be analyzed day in and day out with minimal instrument maintenance, such as liner change, column trimming, MS maintenance, or tuning.

In this work the performance of the Thermo Scientific™ Orbitrap Exploris™ GC was demonstrated for the analysis of PAH and PCBs in complex soil matrices by 500 repeat injections. Orbitrap Exploris GC is ideal for routine environmental screening methods because of its ability to meet the required sensitivity and in full scan, which enables consolidation of methods through combining compound classes into a single acquisition. Robustness and suitability for routine analysis was assessed by looking at the relative response factor, ion ratio, and mass accuracy stability for a low-level calibration QC standard (40 pg/µL in *n*-hexane) interspaced throughout the injection sequence of 500 samples, standards, and blanks over a total period of three weeks of continual high-throughput analysis. The system robustness was assessed by examining the peak area stability of 500 injections of a spiked QuEChERS soil extract (10 pg/µL) over this time period.

Experimental

Calibration standards containing 45 native PCBs and PAHs at twelve concentration levels (full details can be found in Application Note 10731[2]), and 14 (^{13}C-labeled) internal standards were acquired from Fisher Scientific, AccuStandards, and Wellington Laboratories Inc. (Ontario, Canada). For the assessment of relative response factor (RRF) stability, a low-level QC standard (40 pg/µL) was injected directly after every 20 sample injections.

An Orbitrap Exploris GC with mass resolving powers of up to 60k (*m/z* 219, FWHM) equipped with an electron ionization (EI) source and vacuum probe interlock (VPI) was fitted with an Instant-Connect SSL injector. The Thermo Scientific™ ExtractaBrite™ EI source is fully removable without needing to break the vacuum during source cleaning and column changing, and the patented RF lens leads to an excellent level of sensitivity and robustness.

Liquid injections (1 µL) of the QuEChERS soil extracts were performed using a Thermo Scientific™ TriPlus™ RSH™ Autosampler and Thermo Scientific™ LinerGOLD™ single taper with glass wool SSL liner (P/N 453A1925-UI). Chromatographic separation was achieved by a Thermo Scientific™ TraceGOLD™ TG-5 SilMS™ 30 m × 0.25 mm I.D. × 0.25 µm (P/N 26096-1420) film capillary column. Full experimental details, instrument parameters, and consumables used can be found in the Application Note 10731.[2]

Data were acquired using full scan (FS) acquisition mode, processed and reported using Thermo Scientific™ Chromeleon™ 7.3 software, which allows instrument control, method development, quantitative/qualitative analysis, and customizable reporting all within one platform.[3] With Automated System Suitability Testing (SST) and Intelligent Run Control (IRC), real time batches can be analyzed and the sequence can be stopped should a QC criterion fall outside of the set limits, saving precious samples from being injected.[4]

Results and discussion

PAH and PCB robustness were assessed based on absolute peak area response for 500 injections of a soil QuEChERS extract spiked at 10 pg/µL (ppb) level. The Orbitrap Exploris GC suitability for routine PAH and PCB analysis was also assessed continuously over three weeks with measurements of analytical parameters, such as stability of relative response factors, ion ratios, and compound mass accuracy. The batch included blanks, calibration standards, and soil sample extracts as well as quality control (QC) low level (40 pg/µL) solvent standards injected every 20 soil sample injections. Additional details of chromatography, sensitivity, linearity, and sample analysis can be found in the supporting application note.

Routine GC-MS analysis

Matrix complexity

Due to the diversity of matrices with various degrees of complexity, achieving enough selectivity can be challenging in routine GC-MS analysis of environmental samples. An example of soil sample complexity is shown in Figure 1 as a TIC of a sonicated unspiked QuEChERS soil extract containing many environmental contaminants including linear and branched alkanes.

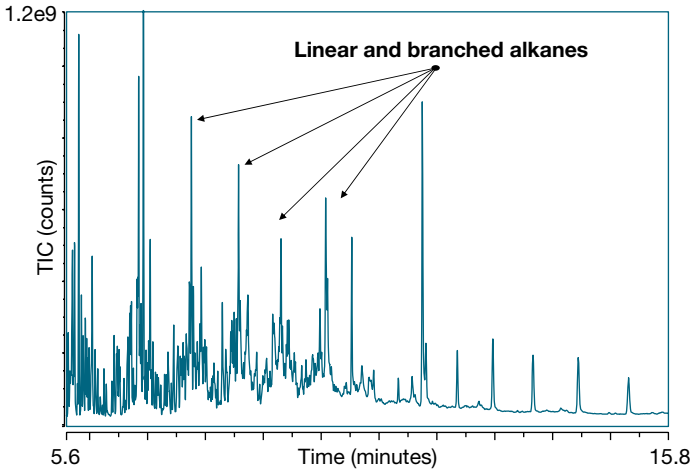
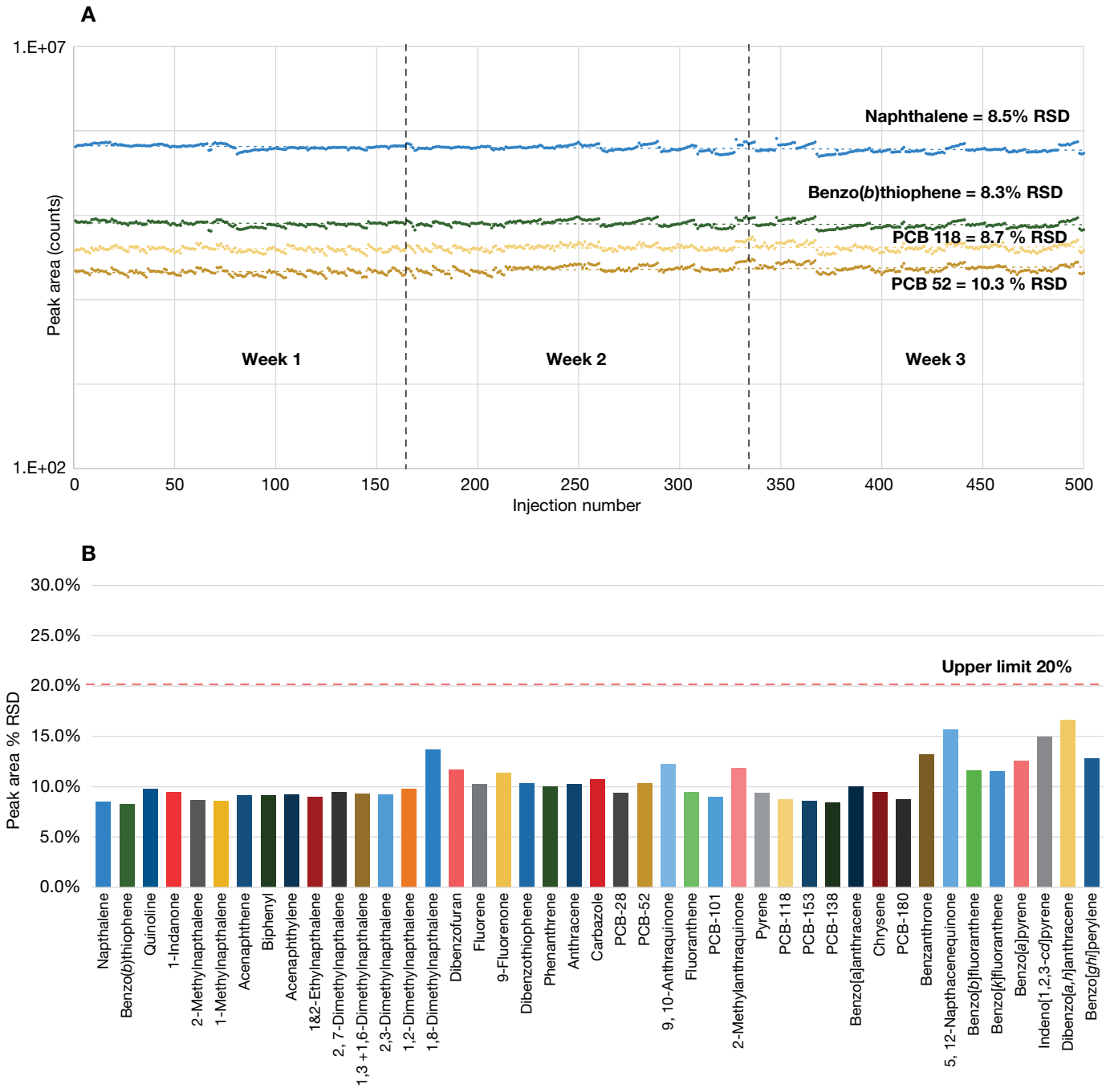


Figure 1. Total ion chromatogram of a QuEChERS soil extract (unspiked) acquired using an Orbitrap Exploris GC in electron ionization (EI), full scan (FS) over a mass range of *m/z* 50–550

Assessment of robustness

To evaluate system robustness, a QuEChERS soil extract post-spiked at 10 pg/µL (ppb) was injected 500 times. The absolute peak areas of target compounds were plotted and used to calculate the stability of response over time (as %RSD) as demonstrated for certain PAHs and PCBs (Figure 2A). The results demonstrate the system robustness with peak area repeatabilities for the incurred residues were <20% RSD over the 500 injections and three weeks of continuous analysis with an average of 10.5% across all compounds. (Figure 2B). Importantly minimal inlet maintenance (septa change every 100 injections) was performed with no liner change, column trimming, MS maintenance, or tuning were performed over the analysis period (the inlet septa were replaced every 100 injections and the Orbitrap system was calibrated weekly).



*Inlet septa were replaced every 100 injections. Apart from this no other inlet maintenance was undertaken.

Figure 2. (A) Repeatability %RSD of absolute peak area response (no internal standard correction), for example PAHs and PCBs from n=500 injections of a QuEChERS soil extract post-spiked at 10 pg/µL (ppb); (B) Absolute peak area %RSDs (no internal standard adjustment) for all PAHs and PCBs from n=500 injections of a QuEChERS soil extract as described in part (A)

Response factor stability in matrix samples

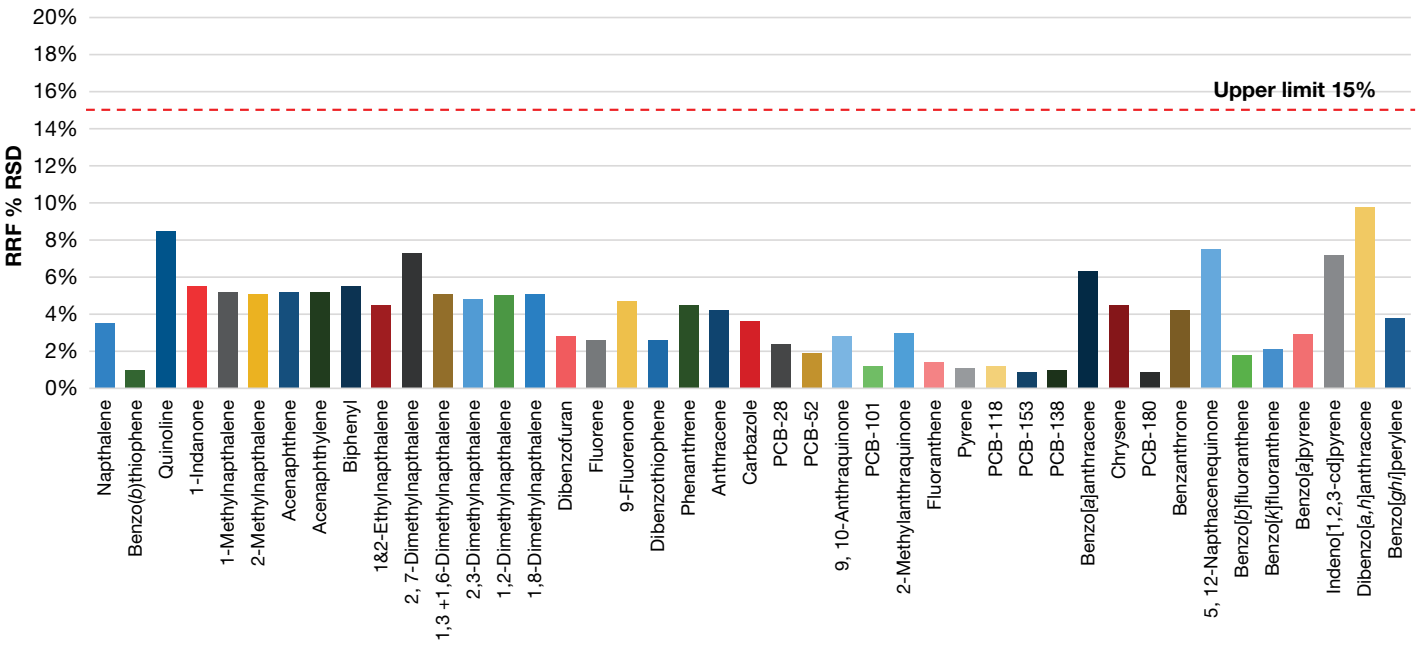
Relative response factor (RRF) is defined as the ratio between the response factors (RF) of both the analyte of interest and the associated internal standard. It can be used to calculate an unknown amount of an analyte in a sample of interest with high accuracy and precision, providing the system of interest is stable in nature, i.e., generating consistent RRFs across an analytical batch. Many labs choose to do this continuously throughout an analytical sequence without having to run an expensive and time-consuming calibration by instead running a quality control (QC) standard to check the RRF %RSD i.e. the precision and accuracy of measurements and the RRF % deviation from the calibration average. For these reasons, a low-level QC standard (40 pg/µL) was injected every 20 injections and the average RRF %RSDs were monitored for each PAH and PCB congener (Figure 3).

The RRF %RSDs were ≤15% for all the targeted PAHs and PCBs calculated over a sequence with an average of 4% across all compounds (which included over 500 sample injections). This demonstrates the excellent system stability with minimal inlet maintenance (septa change every 100 injections), no column trimming, MS maintenance, or system tuning.

RRF % deviation from the calibration average was also calculated for all PAHs and PCBs in the QC standards across the batch including 500 samples. All results were within a tolerance window of ±15%, in the calculated benzo(a)pyrene and PCB 153 examples (Figure 4) the RRF % deviation for n=35 QC injections were 1.2% and 0.5%, respectively.

Ion ratio stability in matrix samples

Another analytical parameter used for confident confirmation of compounds detected in samples is the ion ratio between quantification and qualifier ions. Stability of ion ratios is essential for any mass spectrometer in a routine laboratory setting in order to safeguard against false positive results. One way to indicate how stable the measurements are is the ion ratio of each analyte and its potential deviation from the initially determined value (usually determined as an average value over an external calibration curve injected at the beginning of a sequence). The ion ratio values obtained for all PAHs and PCBs for a low-level QC standard (40 pg/µL) were within ±15% of the expected values calculated as an average across a calibration curve ranging from 0.1-500 pg/µL (corresponding to 0.1–500 µg/kg in extracted soil). (Figure 5). This demonstrates excellent system stability and applicability for routine analysis.



*Inlet septa were replaced every 100 injections. Apart from this no other inlet maintenance was undertaken.

Figure 3. Response factor %RSD for a low-level standard QC standard (40 pg/µL) (n=35) run every 20 sample injections, injection sequence containing blanks, standards, and over 500 matrix (QuEChERS soil extract) injections

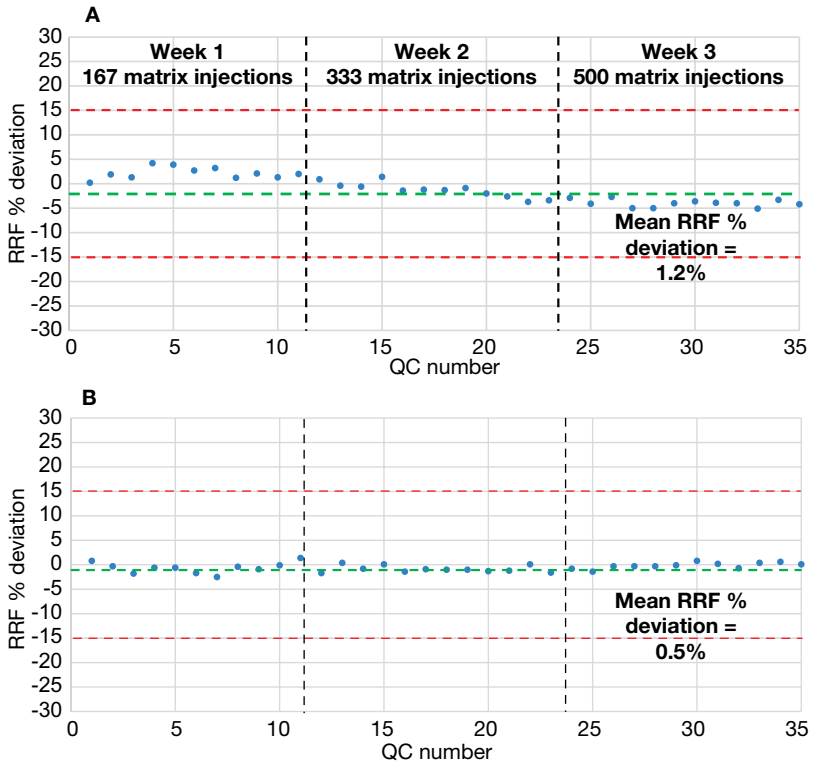


Figure 4. Chart showing the individual RRF % deviation values for benzo(a) pyrene (A) and PCB 153 (B) calculated for a low-level standard QC standard (40 pg/µL) (n=35) run every 20 sample injections. The ±15% tolerance RRF % deviation from the calibration average upper and lower limits are annotated using the red dotted lines and the mean RRF % deviation for the QCs is displayed using the green dotted line.

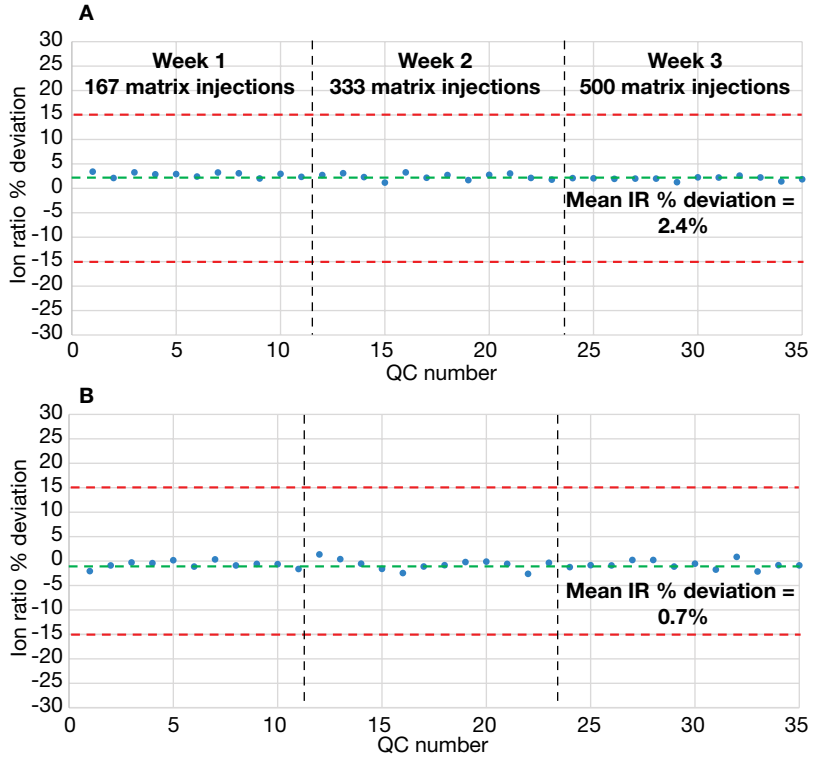


Figure 5. Example of ion ratio stability for benzo(a)pyrene (A) and PCB 153 (B) calculated for a low-level standard QC standard (40 pg/µL) (n=35) run every 20 injections. The ±15% tolerance ion ratio % deviation upper and lower limits are annotated using the red dotted lines and the mean ion ratio % deviation for the QCs is displayed using the green dotted line.

Mass accuracy stability in matrix samples

For high resolution accurate mass spectrometers operating in routine environments, stable mass accuracy is a cornerstone of system stability. Mass accuracy stability was assessed by monitoring the ppm mass error of a QC standard. The results obtained for all PAHs and PCBs for a low-level QC standard (40 pg/µL) were within ±1 ppm of the expected values. A few examples of the mass accuracy stability are shown in Figure 6.

The mass accuracy stability was also demonstrated in matrix (n=500 injections, 10 pg/µL soil QuEChERS extract) where accurate mass data was plotted for low, high, and medium mass compounds 1-indanone, PCB 180, and bezno(*g,h,i*)perylene (*m/z*=132.05697, 393.80195, and 276.09335, respectively), which eluted in the early, mid, and late range of the chromatogram (RT=6.0, 10.8, and 15.5 min) (Figure 7 – A, B, C). The average mass accuracies were 0.3, 0.1, and 0.0 ppm, respectively, which is well within 1 ppm mass accuracy criteria for the Orbitrap system. A QC standard was also used to monitor system performance over the three-week robustness study (40 pg/µL) injected (n=35) every 20 soil samples with mass calibration performed on a weekly basis. Average measured mass accuracy in ppm is denoted by a colored dot for each compound and the associated standard deviation is displayed as error bars. Annotated also is the combined mean mass accuracy and standard error for measurements made for all compounds (Figure 7 – D).

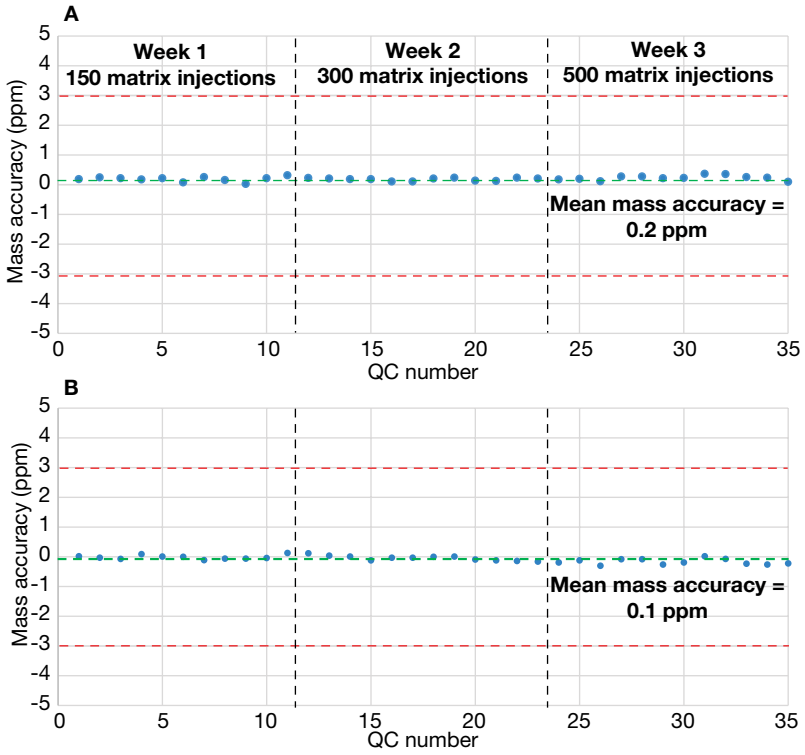


Figure 6. Example of mass accuracy stability for benzo(a)pyrene (A) and PCB 153 (B) calculated for a low-level standard QC standard (40 pg/µL) (n=35) run every 20 injections.

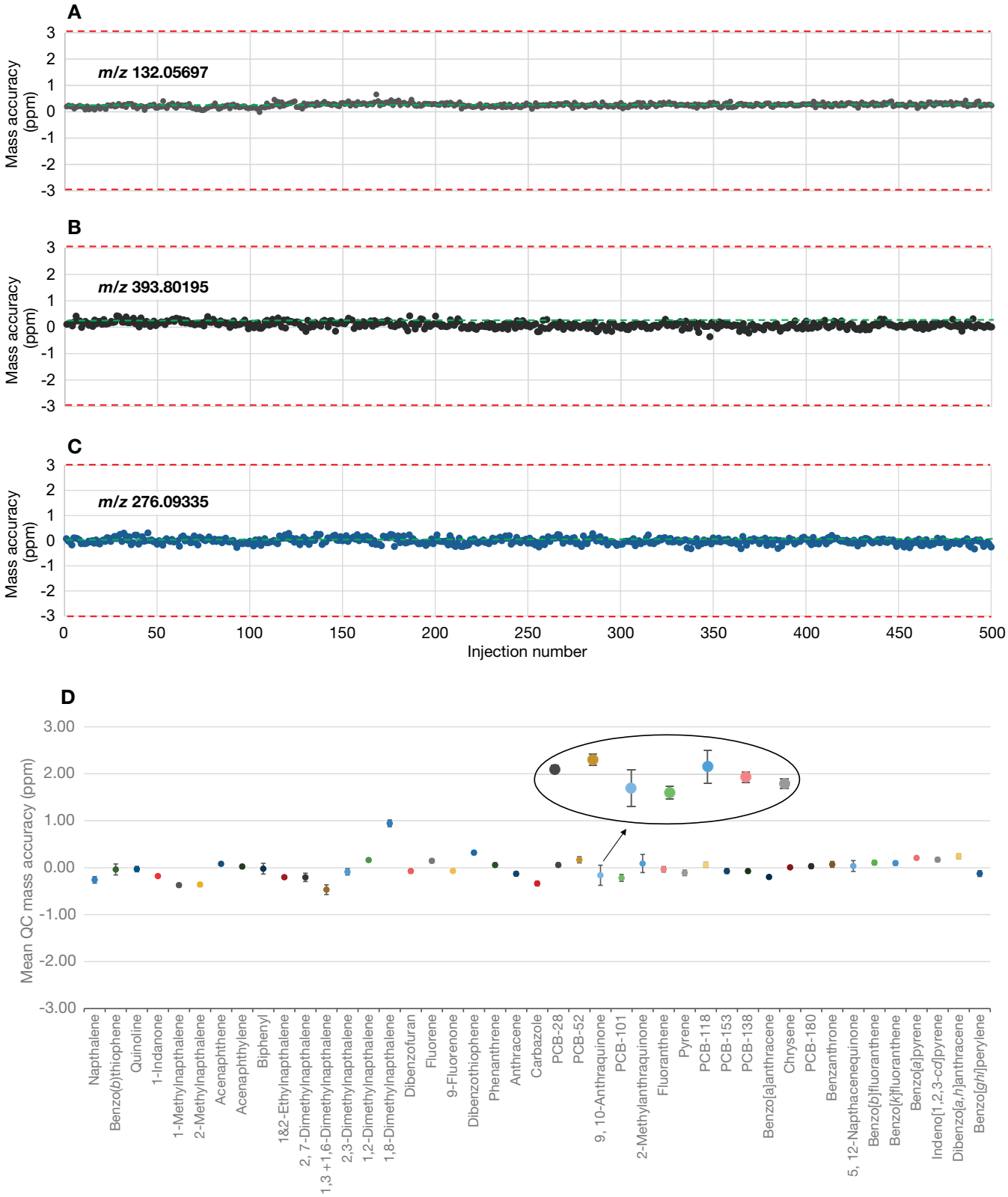


Figure 7. (A) Mass accuracy stability of low mass, early eluting (oxyPAH) 1-indanone, n=500 injections of a 10 pg/µL spiked soil QuEChERS extract (RT=6.0 min, *m/z* 132.05697, average mass accuracy=0.3 ppm); (B) Mass accuracy stability of high mass, mid-eluting PCB 180, n=500 injections of a 10 pg/µL spiked soil QuEChERS extract (RT=10.8 min, *m/z* 393.80195, average mass accuracy = 0.1 ppm); (C) Mass accuracy stability of mid mass, late eluting (PAH) benzo(*g,h,i*)perylene, n=500 injections of a 10 pg/µL spiked soil QuEChERS extract (RT=15.5 min, *m/z* 276.09335, average mass accuracy = 0.0 ppm); (D) Example of mass accuracy stability for all target compounds analyzed in a low-level standard QC standard used to monitor system performance over the three-week robustness study (40 pg/µL) (n=35) injected every 20 soil samples throughout the injection sequence including 500 matrix injections with mass calibration performed on a weekly basis. Average measured mass accuracy in ppm is donated by a colored dot for each compound and the associated standard deviation is displayed as error bars. Annotated also is the combined mean mass accuracy and standard error for measurements made for all compounds.

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Conclusions

These results demonstrate that the Orbitrap Exploris GC-MS system provides the consistent, uninterrupted performance needed in fast-paced routine environments looking at increasing productivity while reducing instrument downtime and the cost per sample. In summary, the following performance was demonstrated:

- Excellent system repeatability in routine use. When analyzing modified QuEChERS soil extracts, the peak area repeatabilities for the incurred residues were <20% RSD over the 500 complex soil sample injections and three weeks of continuous analysis with an average of 10.5% across all compounds.
- High RRF stability of low-level QC standards throughout an injection sequence containing 500 sample injections was demonstrated with the RRF %RSDs for all compounds being ≤15% with an average of 4%. This shows long term system stability and applicability for routine GC-MS analysis of PAHs and PCBs in soil.
- Outstanding RRF agreement of QC standards with the measured RRFs % deviation of the n=35 injected QC standards were all within ±15% of the measured value across the calibration curve with minimal inlet maintenance, column trimming, MS maintenance, or tuning.
- Stable QC ion ratios where all were within ±15% of the expected values calculated as an average across a calibration curve ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in extracted soil).
- Excellent mass accuracy stability was demonstrated for all compounds measured in the 35 QC standards, which had mass accuracies that were within ±1 ppm of the expected values with only weekly calibration of the MS disrupting the instrument up-time.
- Further mass accuracy was demonstrated with the average of all compounds in a QC standard being <1ppm over three weeks of analysis.
- Examples of mass accuracy in matrix were demonstrated for low, high, and medium (m/z)/ early, mid, and late eluting compounds 1-indanone, PCB 180, and benzo(g,h,i)perylene with average (n=500) mass accuracies of 0.3, 0.1, and 0.0 ppm, respectively.

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APPLICATION NOTE 10731

Consolidated analysis of soil contaminants

Four-fold increase in the sample throughput with GC-Orbitrap

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Keywords: Analytical environmental testing, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), QuEChERS, targeted quantification, screening, unknowns, gas chromatography, high resolution mass spectrometry, full scan (FS), sensitivity, Orbitrap Exploris GC, electron ionization (EI), chemical ionization (CI), Chromeleon, Compound Discoverer

Goal

The purpose of this study was to assess the quantitative performance and advantages of PAHs and PCBs using the Thermo Scientific™ Orbitrap Exploris™ GC in addition to screening of unknown soil contaminants.

Introduction

Polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) are toxic organic compounds that can contaminate soils, air, sediments, and water as a result of natural and anthropogenic processes. PCBs and PAHs are resistant to environmental degradation and can be transported over long distances. Moreover, due to their lipophilicity these chemicals can undergo biomagnification and accumulation in the food chain and can pose significant health risks to humans. Their toxicity even at very low concentrations means that their presence in the environment needs to be monitored so that the risk of uptake of these compounds into to the food chain and subsequently into human populations is minimized.

More recently it has become apparent that oxidized and substituted derivatives of PAHs (such as oxy and methyl PAHs) have similar or increased toxicities compared to non-substituted versions; therefore, governments have already began monitoring them in soil and particulate matter.[1, 2] Nitrogen, sulfur, and oxygen-containing polyaromatic heterocycles (NSO-PAHs) are another class of compounds that have gained interest due to their ubiquitous presence in the environment and lack of data on their toxicities.[2, 3]

PCBs and PAHs (and derivatives) are typically analyzed by gas chromatography (GC) coupled to mass spectrometry (MS). The challenges for the analysis of PAHs and PCBs are the requirement for complicated and costly sample preparation such as Sohxlet extraction. Often long chromatographic separations (>40 min per sample) are required, which overall will result in low sample throughput and high cost of analysis.

To comprehensively characterize an environmental sample, multiple methods are employed for both the sample preparation and GC-MS analysis of these compounds. Having multiple chromatographic methods for the same sample increases the requirement for both labor and instrumentation. Multiple methods and chemists to review the process and report the data add to the time and cost of analysis.

In this application note a consolidated approach for the rapid and cost-effective analysis of sixteen EPA PAHs, seven marker PCBs, three oxyPAHs, ten methylPAHs, and nine NSO-PAHs in soil samples using a sensitive HRMS instrument was employed. For this, a modified QuEChERS sample extraction and clean up was investigated. Chromatographic separation of target compounds was optimized for a <20 min/sample method and detection was achieved using the Orbitrap Exploris GC system.

The evaluation of system robustness and method suitability for PAH and PCB GC-MS analysis was outside of the scope of this application but is discussed in a supporting technical note (TN10728).

Experimental

Sample preparation

Calibration standards containing 45 native PCB, PAHs, methyl PAHs, oxyPAHs, PANHs, PASHs, and PAOHs at twelve concentration levels (Appendix 1 – Table 1), and 14 (^{13}C-labeled) internal standards (Appendix 2 – Table 2), were acquired from Fisher Scientific, AccuStandards, and Wellington Laboratories Inc. (Ontario, Canada).

For the calculation of MDLs and LOQs QuEChERS soil extract was spiked at 0.5, 1.0, 1.5, 2.5, and 5.0 pg/µL. Soil was freeze dried, homogenized, and sieved prior to a modified QuEChERS extraction and clean up procedure. A summary of the QuEChERS methodology can be seen in a recent application note (AN10720).

GC-MS analysis

An Orbitrap Exploris GC instrument equipped with the ExtractaBrite™ electron ionization source was used for this analysis. This configuration allows vent-free column changes and ionization source maintenance in under 2 minutes representing a 98% time saving versus traditional venting approaches, which take up to 4 hours. This is achieved using state of the art NeverVent technology, which increases laboratory productivity through the minimization of instrument downtime.

Liquid injections of the sample extracts were performed using a Thermo Scientific™ TriPlus™ RSH series autosampler and chromatographic separation was achieved by a Thermo Scientific™ TraceGOLD™ TG-5 SilMS 30 m × 0.25 mm i.d. × 0.25 µm film (P/N 26096-1420) capillary column. Additional details of instrument parameters are displayed in Tables 1 and 2. Full details of all consumables used can be found in the Thermo Scientific™ AppsLab™ library.

Table 1. GC conditions. Full list of consumables and instrument can be found in the AppsLab library.

TRACE 1310 GC parameters	
Injection volume (µL)	1.0
Liner	Single gooseneck with glass wool LinerGOLD™ (P/N 453A1925-UI)
Inlet (˚C)	300
Inlet module and mode	SSL, Splitless
Splitless time (min)	1.0
Split flow (mL/min)	50.0
Septum purge flow (mL/min)	5.0
Carrier gas, flow rate (mL/min)	He, 1.2
Oven temperature program	
Temperature 1 (˚C)	40
Hold time (min)	1.0
Temperature 2 (˚C)	285
Rate (˚C/min)	28
Hold time (min)	0
Temperature 3 (˚C)	305
Rate (˚C/min)	3
Hold time (min)	0
Temperature 4 (˚C)	350
Rate (˚C/min)	30
Hold time (min)	5
Total GC run time (min)	20

Table 2. Mass spectrometer conditions

Orbitrap Exploris GC EI GC-MS parameters	
Transfer line (˚C)	320
Ion source (ionization type)	ExtractaBrite (EI)
Ion source (˚C)	350
Electron energy (eV)	70
Emission current (µA)	50
Acquisition mode	Full scan (FS)
Mass range (*m/z*)	50–550
Mass resolution	60,000 (FWHM @ *m/z* 200, scan speed 7.4 Hz):
Lock mass (*m/z*)	207.03235

Table 2 continued. Mass spectrometer conditions

Orbitrap Exploris GC CI GC-MS parameters	
Transfer line (˚C)	320
Ion source (ionization type)	ExtractaBrite (PCI)
Reagent gas type	10% ammonia in methane
Flow rate (mL/min)	0.6
Ion source (˚C)	190
Electron energy (eV)	70
Emission current (µA)	100
Acquisition mode	Full scan (FS)
Mass range (*m/z*)	65–690
Mass resolution (FWHM @ *m/z* 200)	60,000 (scan speed 7.4 Hz)
Lock mass	None

Data processing

Data were acquired using full scan (FS) mode, processed, and reported using Thermo Scientific™ Chromeleon™ 7.3 chromatography data system (CDS). Additional screening of unknowns was performed using Compound Discover software. Thermo Scientific™ Compound Discoverer™ software, version 3.2, was also used for spectral deconvolution, NIST library searching, and compound identification using the EI and CI nodes.

Results and discussion

Chromatography, selectivity, and linearity were evaluated using solvent based standards. Assessment of sensitivity (as matrix detection limits and limits of quantitation), recovery, and selectivity were performed in soil using a modified QuEChERS extraction method, which is described in the experimental section.

Chromatography

All compounds were analyzed in <20 min and excellent separation of the critical pairs was obtained for the 16 EPA PAH standard (i) phenanthrene/anthracene, (ii) benzo(a) anthracene/chrysene, (iii) benzo(b)fluoranthene/benzo(k) fluoranthene (Figure 1, A-D). As expected, with fast multiresidue methods of this nature, some coelution did occur in which case the data was reported as a sum of the combined area (ex: included (i) 1-ethylnapthanalene/ 2-ethylnapthalene, (ii) 1,3-dimethylnapthalene/ 1,6-dimethylnapthalene). Due to the superior inertness of the TraceGOLD silphenylene GC columns, excellent peak shape was observed for all compounds including the strongly basic compound quinoline which had a European Pharmacopeia (EP) asymmetry value of 1.0[3].

Due to the diversity of sample matrices with various degrees of complexity, selectivity can be challenging in GC-MS analysis of soils. An example of sample complexity is shown in Figure 1, E-F as an overlay of the TIC EI full scan of a sonicated unspiked QuEChERS soil extract (top chromatogram) and of a FS XIC (bottom chromatogram) showing the incurred residues.

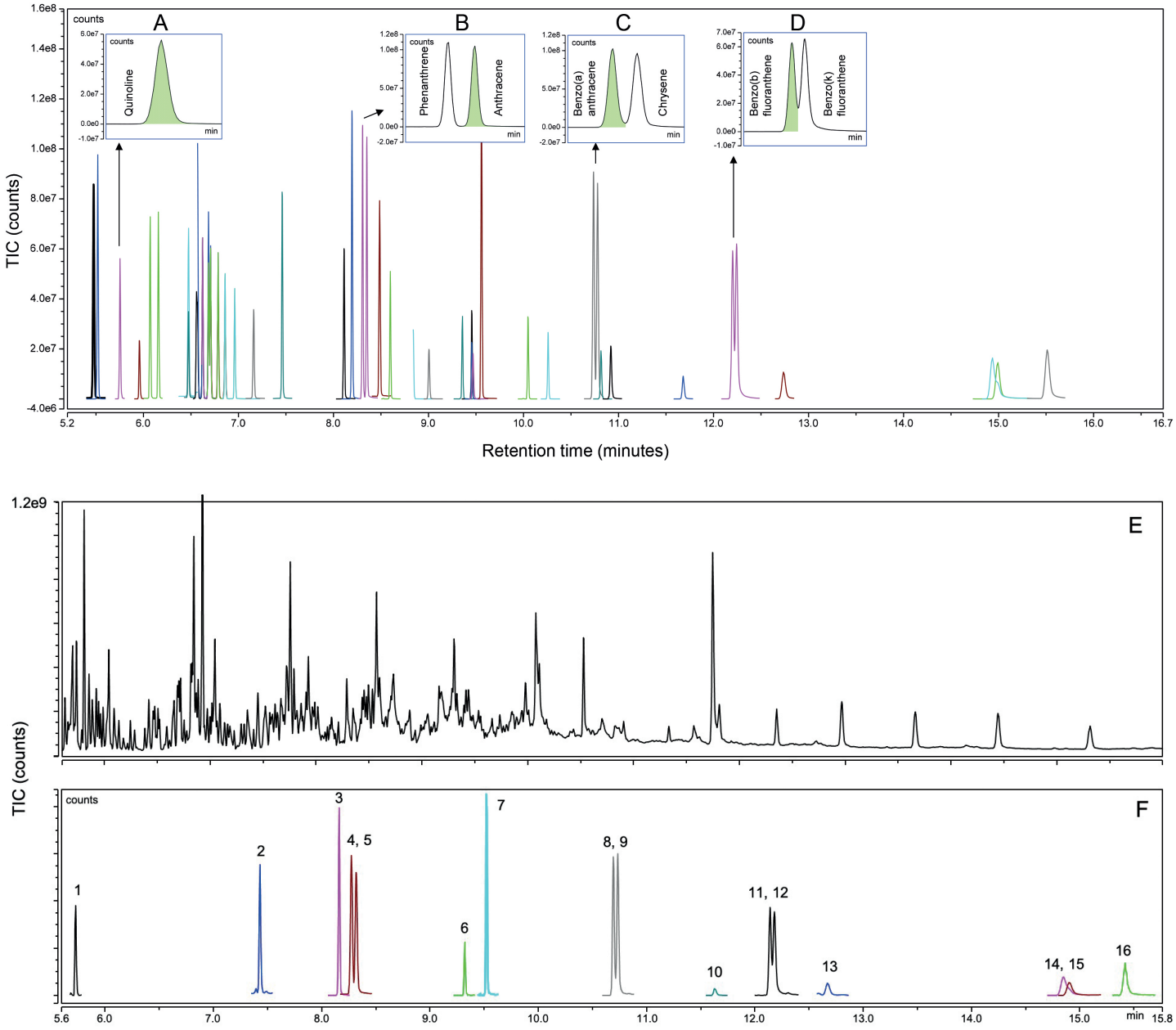


Figure 1. Example chromatograms showing overlaid native PAHs and PCBs FS XICs for a 50 pg/µL (50 pg on column (OC)) solvent standard in *n*-hexane with excellent chromatographic peak shapes for all compounds in <20 min. A) Peak shape for nitrogen containing polyaromatic heterocycle quinoline with peak asymmetry of 1.0; (B) Resolution of critical components phenanthrene and anthracene with EP resolution of 1.5; (C) Resolution of critical components benzo(a)anthracene and chrysene with chromatographic resolution of 1.3; (D) Resolution of critical components benzo(b)fluoranthene and benzo(k)fluoranthene with EP resolution of 1.0. (E) QuEChERS soil extract unspiked, FS, *m/z*=50–550; (F) QuEChERS soil extract unspiked, native incurred residue XICs; Compounds: 1= Quinoline, 2=Fluorene, 3=Dibenzothiophene, 4, 5=Phenanthrene/Anthracene 6=Fluoranthene, 7=Pyrene, 8, 9=Benzo[a]anthracene,Chrysene, 10=5,12-Napthacenequinone, 11, 12=Benzo[b/k]fluoranthene, 13=Benzo[a]pyrene, 14=Indeno[1,2,3-cd]pyrene, 15=Dibenzo[a,h]anthracene, 16=Benzo[ghi]perylene. C^{13}-labeled internal standards were not displayed to show native peak shapes clearly.

Sensitivity: determination of method detection limits (MDLs)

To practically assess the MDLs, n=18 replicate injections of the lowest serially diluted matrix-matched standard (0.5, 1.0, 2.5 pg/uL) with a peak area % RSD of <15% were used. The MDL was then calculated by considering the injected amount, peak area % RSD, and t-score of 2.567, corresponding to 17 (n-1) degrees of freedom at the 99% confidence interval (Figure 2). The MDL values calculated ranged from 118 to 475 fg on column (corresponding to 0.1–0.5 µg/kg in sample).

Sensitivity: determination of limit of quantitation (LOQ)

Method LOQs were calculated using serially diluted matrix-matched standards at 0.5, 1.0, 2.5, and 5.0 pg/µL. Eighteen (n=18) replicate injections of each of the diluted standards ranging between 0.5 pg/µL and 5.0 pg/µL were performed (0.5–5.0 µg/kg in sample) (Appendix 3 – Table 3).

The criteria used to assess individual LOQs were:

- Ion ratios within ±30% of the expected values calculated as an average across a calibration curve ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in sample, Figure 3)
- Peak area repeatability of <15% RSD

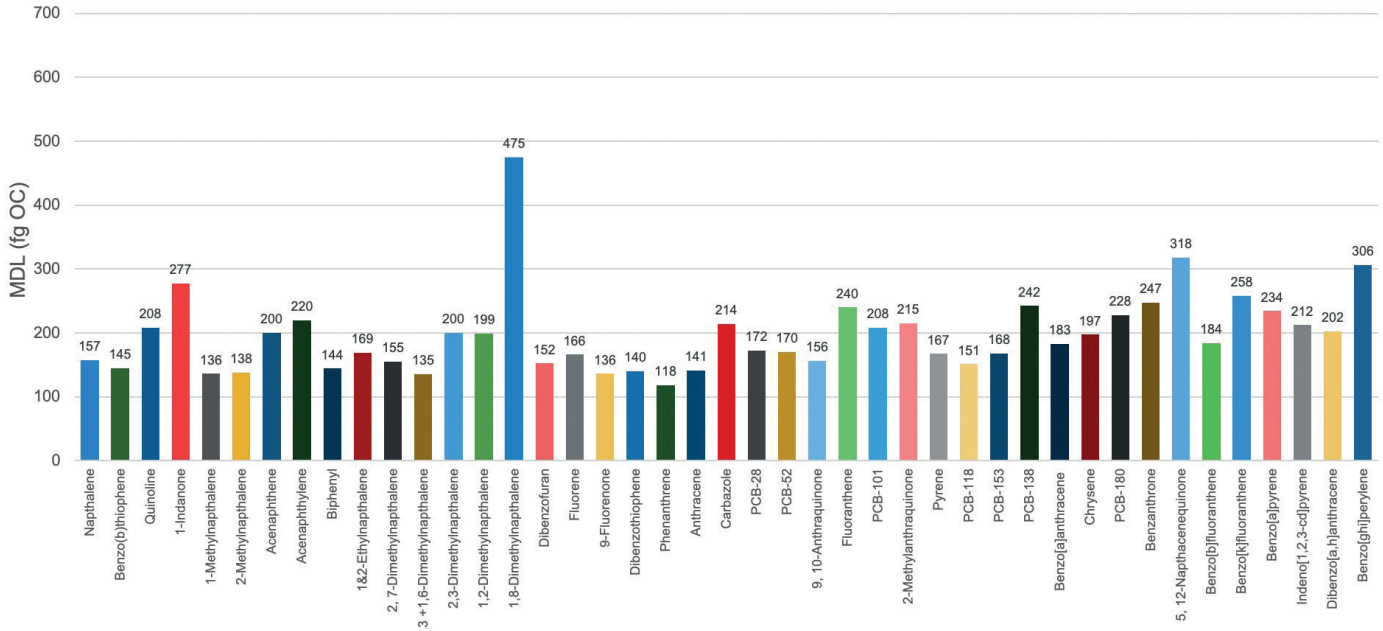


Figure 2. Graph showing individual MDLs (as detectable fg on column) for 45 native PCB, PAH, methyl PAH, oxyPAH, and NSO-PAHs calculated from n=18 replicate injections of the lowest serially diluted matrix-matched standards. *1,8-Dimethyl naphthalene 1.0 pg OC had a peak area % RSD >15% so the nearest standard 2.5 pg OC was used giving a higher MDL; however, by using a lower amount OC ~1.5 pg the true MDL value would be expected to be lower.

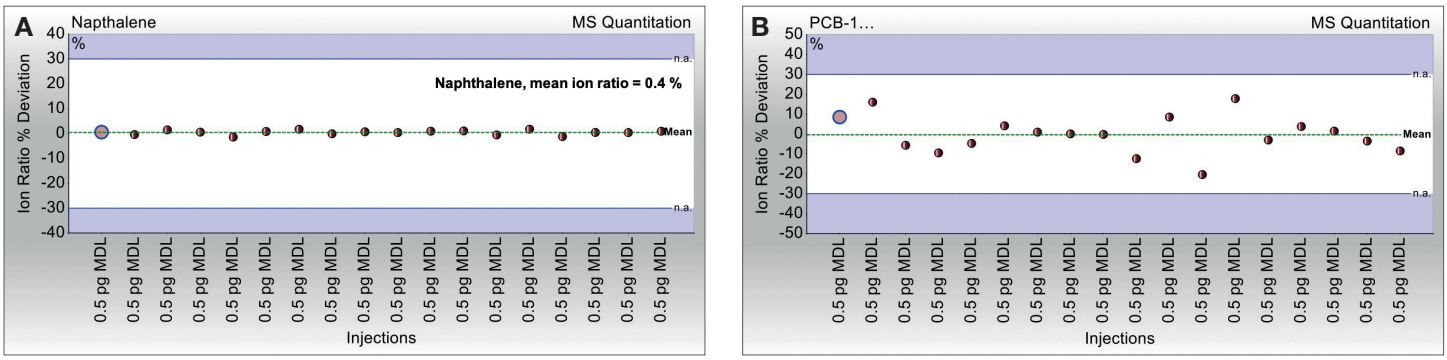


Figure 3. Graphs showing ion ratio consistency for selected PAHs and PCBs. (A) Naphthalene; (B) PCB 118, over n=18 replicate injections at the LOQ level. The average ion ratio % deviation calculated from the calibration range is displayed as a green dotted line in the center. The ±30% upper and lower ion ratio tolerance windows are also defined, and for all PAHs and PCBs the ion ratio % deviation for injections were within specification. This also illustrates how using Chromeleon CDS interactive charts allows the user to easily handle and interpret MS data.

Linearity

Linearity was determined using solvent standards at concentrations 0.1–500 pg/µL. The calibration of each compound was performed using the linear/average calibration factor function in Chromeleon CDS (AvCF) over three injections at each concentration level (Figure 4).

All compounds show excellent linear responses with coefficients of determination R^2 ≥0.995, and average calibration factors %RSD across the calibration range being <13%. The R^2 values ranged from 0.9951 to 1.0000 with an average value of 0.999. (Appendix 4 – Table 4).

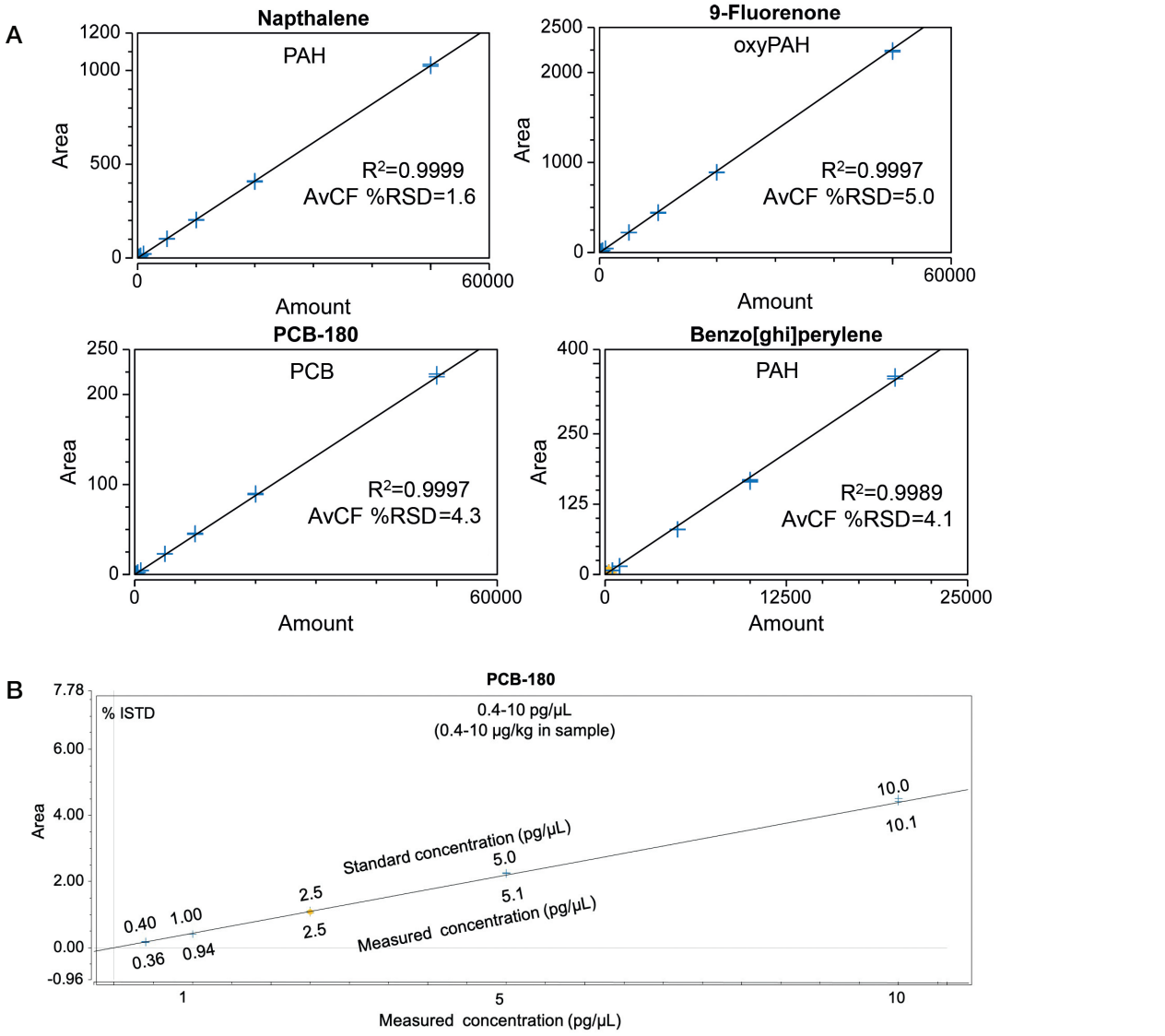


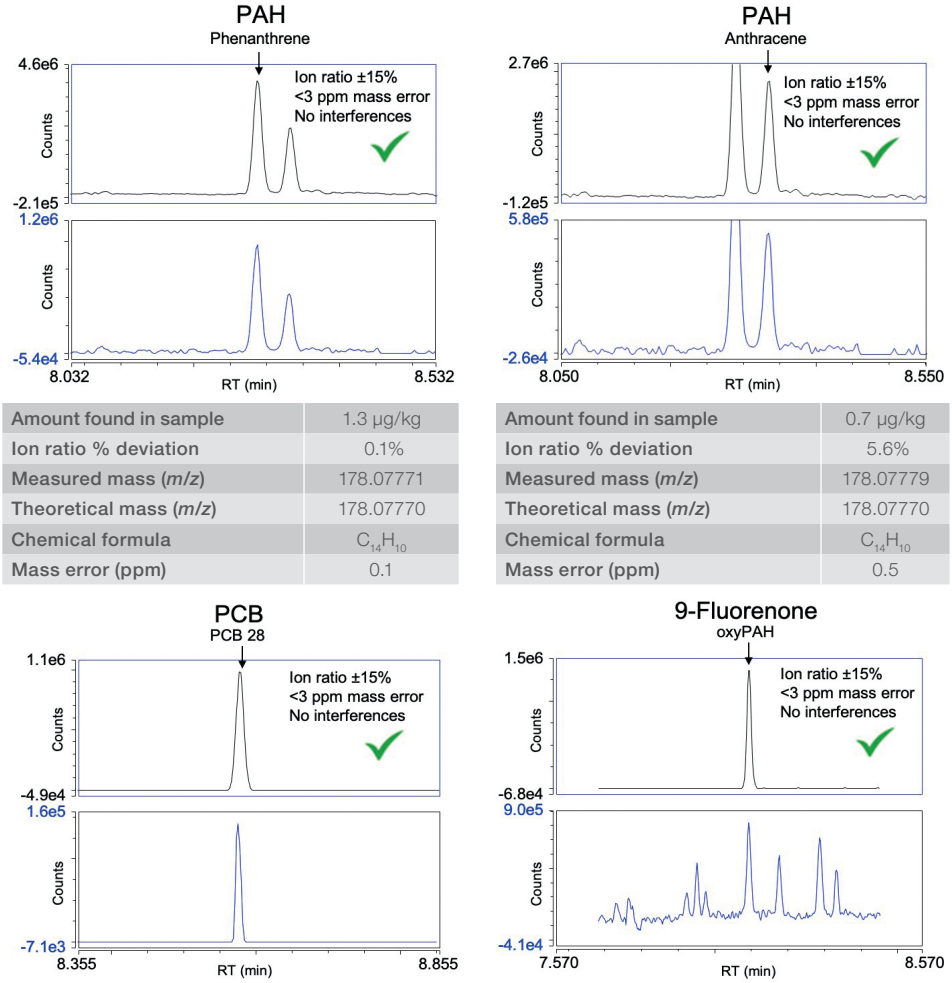
Figure 4. (A) Linearity of example PAHs and PCBs as demonstrated using solvent-based calibration curves ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in sample). Average calibration factor function (AvCF) was used in Chromeleon CDS and three replicate injections at each concentration with internal standard adjustment were performed. Coefficient of determination (R^2) and average calibration factor values (AvCF %RSD) are displayed. (B) A magnified region of the calibration for PCB 180 ranging from 0.4 to 10 pg/µL is shown (corresponding to 0.4–500 µg/kg in sample) showing excellent precision and accuracy for triplicate injections per point.

Recoveries

Seven replicate QuEChERS extractions, performed on soil spiked with deuterated internal standards at 50 ng/g added prior to extraction, were used to assess the compound recovery (details of sample preparation given in a recent application note (AN10720). Triphenyl phosphate at 100 ng/g was added post extraction and used as internal standard to adjust for potential injection variability (Appendix 5 – Table 5). All compounds show good recoveries with the average values of 79% (Appendix 5 – Table 5). Lower boiling point compounds, such as naphthalene-d_8, had lower recoveries that could be explained by losses during the solvent evaporation phase. Although the recovery of such compounds is low, precision of measurement over n=7 replicate extractions was <15% RSD for all compounds and the majority being <5%. This clearly demonstrates that the QuEChERS extraction and dSPE procedure method is highly reproducible and therefore suitable for analytical testing laboratories. The total sample preparation time was <2 hours, which compared to typical Soxhlet extractions of 24–48 hours, and is a significant time (and cost) savings of 10–20×.

Quantification of PAHs and PCBs in QuEChERS soil extracts

Soil samples, extracted as described in AN10720, were analyzed for their native incurred residues. The quantitative performance of the method in terms of sensitivity and selectivity is highlighted below with examples of low level native incurred residues (Figure 5).



Amount found in sample	1.3 µg/kg
Ion ratio % deviation	0.1%
Measured mass (*m/z*)	178.07771
Theoretical mass (*m/z*)	178.07770
Chemical formula	$C_{14}H_{10}$
Mass error (ppm)	0.1

Amount found in sample	0.7 µg/kg
Ion ratio % deviation	5.6%
Measured mass (*m/z*)	178.07779
Theoretical mass (*m/z*)	178.07770
Chemical formula	$C_{14}H_{10}$
Mass error (ppm)	0.5

Amount found in sample	0.6 µg/kg
Ion ratio % deviation	0.7%
Measured mass (*m/z*)	255.96074
Theoretical mass (*m/z*)	255.96078
Chemical formula	$C_{12}H_7C_{l3}$
Mass error (ppm)	0.2

Amount found in sample	0.8 µg/kg
Ion ratio % deviation	4.8%
Measured mass (*m/z*)	180.05698
Theoretical mass (*m/z*)	180.05697
Chemical formula	$C_{13}H_8O$
Mass error (ppm)	0.1

Figure 5. Examples of FS XIC chromatograms (quantification in black, and confirmation ions in blue) for phenanthrene in soil (top left), anthracene in soil (top right), PCB-28 in soil (bottom left), and 9-fluroenone in soil (bottom right). Below each of the FS XIC chromatograms the following is annotated: (i) amount found in sample as µg/kg, (ii) ion ratio deviation from the calibration average, (iii) measured mass (*m/z*), (iv) theoretical mass (*m/z*), (v) chemical formula, and (vi) mass error (ppm).

In summary, the results obtained in these experiments demonstrate that a consolidated compound class method using a modified QuEChERS sample preparation can be used to quantify PAHs and PCBs in soils. In the case of PCB-28, low levels of incurred residues of 0.6 µg/kg were detected and quantified within an ion ratio deviation from the calibration of only 0.7% and a mass error of the theoretical exact mass of 0.2 ppm with minimal matrix interferences all while in FS.

Screening for additional soil contaminants

The advantages of acquiring data in FS with high resolution and accurate mass were leveraged through retrospective analysis of samples and additional screening of unknown contaminants with confirmation by chemical ionization (CI). The Compound Discoverer platform includes a streamlined workflow for GC EI data allowing for extraction, deconvolution, and putative identification of the unknowns based on mass spectral library matching (NIST 2017). The software first performed spectral deconvolution above a customizable signal to noise (S/N) followed by compounds detection and grouping to consider compounds that elute at the same retention time (within ±6 s window). The deconvoluted spectra were then searched against mass spectral libraries (such as NIST), and the hits were scored based on the total score derived from a combination of library search index (SI) score and presence/absence of the molecular ions as well as percentage of fragment ions that can be explained from the NIST elemental composition. The use of a retention index acquired under the same conditions used for sample analysis helped to increase the confidence in compound identification. Compounds detected with NIST SI scores >750 can be seen in (Figure 6A). With the Compound Discoverer browser an overlaid XIC of the peak eluting at 10.95 min (*m/z* 136.07579) was identified as the top hit versus NIST library (Figure 6B). The peak was putatively identified as pyriproxyfen with a SI score of 953; however, the molecular ion of *m/z* 321.135945 was not observed, which demonstrates the requirement for additional chemical ionization and mass accuracy confirmation of molecular ions. Full results of the EI NIST matches for the deconvoluted data can be found in the (Appendix 6 – Table 6).

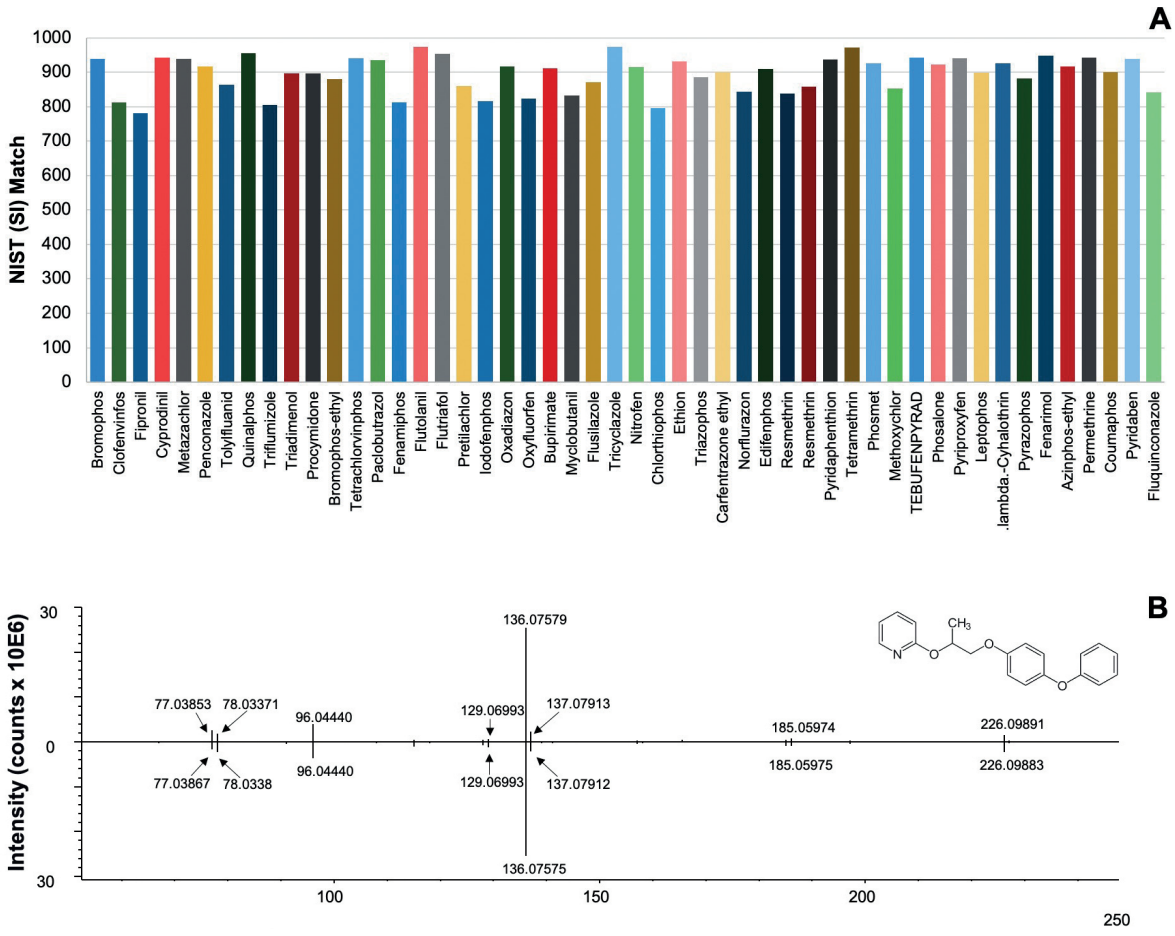


Figure 6. (A) Example NIST SI match scores for compounds detected in the deconvoluted EI spectra QuEChERS soil extract spiked at 100 pg/µL. (B) Compound Discoverer software EI spectrum of a spiked QuEChERS soil extract – deconvoluted versus NIST library of the peak eluting at 10.95 min (*m/z* 136.07579), with the structure of the top SI match pyriproxyfen from the result table.

Full-scan data for blank and spiked QuEChERS soil extracts (100 pg/µL) were analyzed with Compound Discoverer 3.2 software for putative identification of peaks. A complete workflow was used to identify compounds with a high degree of confidence using deconvoluted EI spectra based on search index scores (SI) and confirmation of the corresponding molecular ion and or adducts using positive chemical ionization. FS data was acquired using Chromeleon 7.3 in EI and PCI modes at 60,000 FWHM resolution and then imported in Compound Discoverer 3.2 software. The software was used to deconvolute, align, and filter the peaks to putatively identify the compounds using mass spectral library match (NIST 17). The power of the deconvolution algorithms become clear when overlaying both the FS TIC and deconvoluted spectra for analytes eluting in a crowded area of the chromatogram (Figure 7).

Confirmation of suspect contaminants using positive chemical ionization

Further confirmation used in the identification of compounds was achieved by assessing the PCI spectra to identify the elemental composition of the parent ion by looking at common adducts. In PCI experiments using methane as the reagent gas, three adducts are typically observed: $[M+H]^+$, $[M+C_2H_5]^+$, and $[M+C_3H_5]^+$. An example was shown for a peak at 9.44 min, which was identified as flutolanil versus the NIST library; however, the molecular ion *m/z* 323.11276 was not giving a significant response (Figure 8 A). When looking at the PCI data for this compound a significant boost in the molecular ion was observed with minimal mass error of 0.09 ppm (Figure 13B). Two additional adducts $[M+H]^+$ and $[M+C_2H_5]^+$ were also observed with ppm mass errors of -0.1 and -0.03 ppm respectively. Full results of the PCI confirmation can be found in Appendix 7 – Table 7.

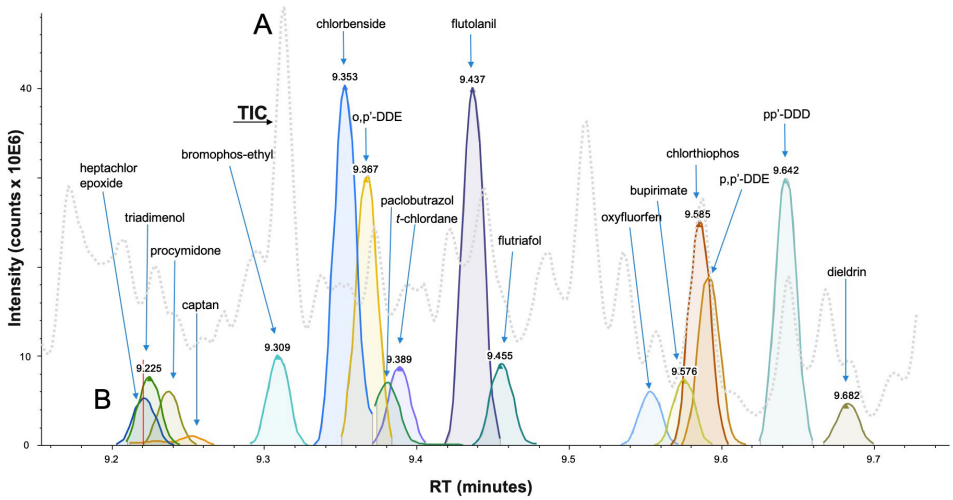


Figure 7. (A) Overlaid FS (*m/z* = 50–550) TIC for a soil QuEChERS extract spiked with pesticides at 100 pg/µL. (B) Compound Discoverer 3.2 software deconvoluted EI spectrum showing closely eluting compounds extracted from the complex TIC FS data.

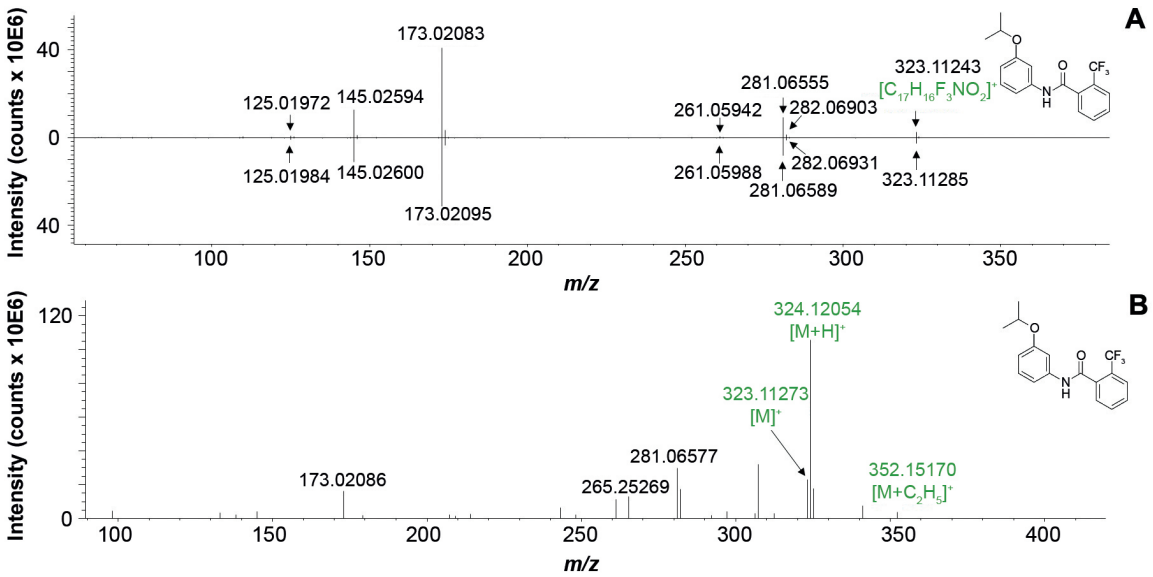


Figure 8. (A) Compound Discoverer software EI spectrum of a spiked QuEChERS soil extract – deconvoluted versus NIST library of the peak eluting at 9.437 min (*m/z* 323.11243), with the structure from the top SI match flutolanil from the result table. (B) PCI mass spectrum for flutolanil displaying adducts $[M+H]^+$ and $[M+C_2H_5]^+$ used for confirmation of this compound in conjunction with the EI data.

Conclusions

The results of the experiments presented demonstrate that modified QuEChERS methods and the TriPlus RSH autosampler in combination with the Orbitrap Exploris GC provides an ideal solution for **analytical testing laboratories looking to improve productivity and deliver confident results.**

- Comprehensive method consolidation with chromatographic separation and overall analytical performance was achieved for the analysis of PAHs and PCBs in soil in <20 min.
- Increased throughput of up to 20× can be realized by using a modified QuEChERS method compared to tradition Sohxlet extraction methods, saving cost and time.
- Femtogram level sensitivity was achieved using the Orbitrap Exploris GC, with the MDLs values calculated for 45 native compounds ranging from 115 to 475 fg OC (corresponding to 0.1–0.5 µg/kg in sample).
- LOQs ranged from 0.5 to 5.0 µg/kg in soil as determined from n=18 repeat injections of the lowest serially diluted matrix-matched standard that satisfied the acceptance criteria defined below:
  - Ion ratios within ±30% of the expected values calculated as an average across a calibration curve ranging from 0.1 to 500 pg/µL (equivalent to 0.4–5.0 µg/kg in sample)
  - Peak area repeatability of <15% RSD
- Linearity was achieved across a calibration range of 0.1–500 pg/µL (corresponding to 0.1–500 µg/kg in soil) showed coefficient of determination values of R^2 ≥0.995, and residuals <13%.
- All compounds show good recovery overall with the average internal standard recovery being 79%, and precision of the seven technical replicate extractions <5% RSD.
- Quantitative performance with soil samples was excellent as demonstrated by the closeness of the ion ratios and mass error compared to expected values when used for confirmation of low-level incurred residues in soil such as PAHs, PCBs, and oxyPAHs.
- Rapid change-over from EI (for spectral library search) to softer ionization such as PCI (for molecular ion confirmation using adduct information) is possible.
- The streamlined GC-EI data processing workflow with Compound Discoverer software allows for quick extraction, deconvolution, and identification of unknown compounds.

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Appendix 1 – Table 1. Details of 45 native compounds analyzed, including compound type, CAS number, and calibration range

Native standard	Compound type	CAS Number	Calibration range (ng/mL)
Napthalene	PAH	91-20-3	0.1–500
Benzo(b)thiophene	PASH	95-15-8	
Quinoline	PANH	91-22-5	
1-Indanone	PAOH	83-33-0	
2-Methylnapthalene	methylPAH	91-57-6	
1-Methylnapthalene	methylPAH	90-12-0	
Biphenyl	aromatic	92-52-4	
Acenaphthylene	PAH	208-96-8	
1-Ethylnapthalene	methylPAH	1127-76-0	
2-Ethylnapthalene	methylPAH	939-27-5	
Acenaphthene	PAH	83-32-9	
2,7-Dimethylnapthalene	methylPAH	582-16-1	
1,3-Dimethylnapthalene	methylPAH	575-41-7	
1,6-Dimethylnapthalene	methylPAH	575-43-9	
2,3-Dimethylnapthalene	methylPAH	581-40-8	
1,2-Dimethylnapthalene	methylPAH	573-98-8	
1,8-Dimethylnapthalene	methylPAH	569-41-5	
Dibenzofuran	PAOH	132-64-9	
Fluorene	PAH	86-73-7	
9-Fluorenone	oxyPAH	486-25-9	
Dibenzothiophene	PASH	132-65-0	
Phenanthrene	PAH	85-01-8	
Anthracene	PAH	120-12-7	
Carbazole	PAOH	86-74-8	
PCB-28	PCB	7012-37-5	
PCB-52	PCB	35693-99-3	
9,10-Anthraquinone	PAOH	84-65-1	
Fluoranthene	PAH	206-44-0	
PCB-101	PCB	37680-73-2	
2-Methylanthraquinone	PAOH	84-54-8	
Pyrene	PAH	129-00-0	
PCB-118	PCB	31508-00-6	
PCB-153	PCB	35065-27-1	
PCB-138	PCB	35065-28-2	
Benzo[a]anthracene	PAH	56-55-3	
Chrysene	PAH	218-01-9	
PCB-180	PCB	35065-29-3	
Benzanthrone	oxyPAH	82-05-3	
5,12-Napthacenequinone	oxyPAH	1090-13-7	
Benzo[b]fluoranthene	PAH	205-99-2	
Benzo[k]fluoranthene	PAH	207-08-9	
Benzo[a]pyrene	PAH	50-32-8	
Indeno[1,2,3-cd]pyrene	PAH	193-39-5	
Dibenzo[a,h]anthracene	PAH	53-70-3	
Benzo[ghi]perylene	PAH	191-24-2	

Appendix 2 – Table 2. Details of the 14 internal standards, including compound type, CAS number, and concentration (suffix "L" indicates mass-labeled)

Internal standard	Compound type	CAS Number	Concentration (ng/mL)
Napthalene-d-8	PAH	1146-65-2	100
Dibenzofuran-d8	PAOH	93952-04-6	
9-Fluorenone-d8	oxyPAH	137219-34-2	
Pyrene-d-10	PAH	1718-52-1	
PCB-28L	PCB	7012-37-5	
PCB-52L	PCB	35693-99-3	
PCB-101L	PCB	37680-73-2	
PCB-118L	PCB	31508-00-6	
PCB-153L	PCB	35065-27-1	
PCB-138L	PCB	35065-28-2	
PCB-180L	PCB	35065-29-3	
Quinoline-d7	PANH	34071-94-8	
o-Terphenyl	aromatic	84-15-1	
Perylene-d-12	PAH	1520-96-3	

Appendix 3 – Table 3. Method LOQs were determined from the lowest serially diluted spiked QuEChERS extract solution prepared as detailed in the experimental section, which pass the criteria. Eighteen replicate injections of each of the diluted standards ranging between 0.5 pg/µL and 5.0 pg/µL were performed. The criteria used to assess individual LOQs were (i) measured ion ratio (IR) ±30% compared to the target ion ratio calculated from the average ion ratio across the calibration range and (ii) peak area <15 % RSD.

Compound	Injected amount (pg OC)	Min IR % dev	Max IR % dev	Mean IR % dev	Peak area % RSD	LOQ (pg OC)	LOQ (µg/kg)
Napthalene	0.5	-1.4	1.7	0.4	4.5%	0.5	0.5
Benzo(b)thiophene	1.0	-0.8	-13.3	1.0	5.7%	1.0	1.0
Quinoline	1.0	10.9	-0.7	1.0	8.1%	1.0	1.0
1-Indanone	2.5	-10.9	13.0	2.6	6.2%	2.5	2.5
1-Methylnapthalene	0.5	6.9	10.3	8.8	2.2%	0.5	0.5
2-Methylnapthalene	0.5	4.6	7.3	6.0	2.2%	0.5	0.5
Acenaphthene	0.5	-5.8	13.5	4.4	5.6%	0.5	0.5
Acenaphthylene	0.5	-10.2	14.7	2.8	6.6%	0.5	0.5
Biphenyl	0.5	-12.0	1.6	-5.2	3.6%	0.5	0.5
1 & 2-Ethylnapthalene	0.5	-9.1	9.9	3.0	2.9%	0.5	0.5
2, 7-Dimethylnapthalene	0.5	5.6	14.7	10.0	2.2%	0.5	0.5
1,3 & 1,6-Dimethylnapthalene	0.5	10.4	17.5	13.7	3.3%	0.5	0.5
2,3-Dimethylnapthalene	0.5	-13.3	13.2	0.3	10.2%	0.5	0.5
1,2-Dimethylnapthalene	0.5	-24.2	16.1	-12.1	5.8%	0.5	0.5
1,8-Dimethylnapthalene	2.5	-12.5	11.3	-3.1	3.2%	2.5	2.5
Dibenzofuran	0.5	-13.9	2.1	-5.4	2.0%	0.5	0.5
Fluorene	1.0	11.1	5.4	1.0	6.5%	1.0	1.0
9-Fluorenone	1.0	9.1	-2.3	1.0	5.3%	1.0	1.0
Dibenzothiophene	1.0	9.7	-4.4	1.0	5.4%	1.0	1.0
Phenanthrene	0.5	-13.3	2.9	-5.6	2.6%	0.5	0.5
Anthracene	1.0	11.5	0.8	1.0	5.5%	1.0	1.0
Carbazole	1.0	11.3	-1.0	1.0	8.3%	1.0	1.0
PCB-28	2.5	-11.7	9.5	-3.6	3.7%	2.5	2.5
PCB-52	1.0	12.1	0.4	1.0	6.6%	1.0	1.0

Appendix 3 – Table 3 continued. Method LOQs were determined from the lowest serially diluted spiked QuEChERS extract solution prepared as detailed in the experimental section, which pass the criteria. Eighteen replicate injections of each of the diluted standards ranging between 0.5 pg/µL and 5.0 pg/µL were performed. The criteria used to assess individual LOQs were (i) measured ion ratio ±30% compared to the target ion ratio calculated from the average ion ratio across the calibration range and (ii) peak area <15 % RSD.

Compound	Injected amount (pg OC)	Min IR % dev	Max IR % dev	Mean IR % dev	Peak area % RSD	LOQ (pg OC)	LOQ (µg/kg)
9, 10-Anthraquinone	1.0	14.6	8.8	1.0	6.1%	1.0	1.0
Fluoranthene	0.5	-11.3	13.7	4.5	6.7%	0.5	0.5
PCB-101	0.5	-27.9	15.3	-12.9	8.3%	0.5	0.5
2-Methylanthraquinone	1.0	13.5	-1.4	1.0	8.4%	1.0	1.0
Pyrene	0.5	-12.2	2.6	-4.1	3.6%	0.5	0.5
PCB-118	0.5	-20.4	17.8	-0.3	7.0%	0.5	0.5
PCB-153	1.0	19.5	1.5	1.0	6.6%	1.0	1.0
PCB-138	1.0	13.2	1.2	1.0	9.4%	1.0	1.0
Benzo[a]anthracene	1.0	6.8	-0.6	1.0	7.1%	1.0	1.0
Chrysene	1.0	10.7	0.0	1.0	7.7%	1.0	1.0
PCB-180	0.5	-24.2	24.7	-4.5	9.5%	0.5	0.5
Benzanthrone	2.5	-12.3	12.0	1.3	6.3%	2.5	2.5
5, 12-Napthacenequinone	2.5	-12.2	12.8	0.4	8.1%	2.5	2.5
Benzo[b]fluoranthene	1.0	6.3	-2.7	1.0	7.2%	1.0	1.0
Benzo[k]fluoranthene	1.0	7.6	-3.9	1.0	10.1%	1.0	1.0
Benzo[a]pyrene	1.0	8.3	-3.1	1.0	9.1%	1.0	1.0
Indeno[1,2,3-cd]pyrene	1.0	-7.8	-14.6	1.0	8.3%	1.0	1.0
Dibenzo[a,h]anthracene	2.5	-6.4	9.6	1.4	4.6%	2.5	2.5
Benzo[ghi]perylene	2.5	-9.9	11.8	-0.2	3.0%	2.5	2.5

Appendix 4 – Table 4. Coefficient of determination (R^2) and residual average response factor (% RSD)

Compound	Compound type	R^2	AVCF % RSD
Naphthalene	PAH	0.9999	1.6
Acenaphthylene	PAH	0.9987	5.4
Acenaphthene	PAH	0.9995	4.0
Biphenyl	PAH	0.9998	2.6
Fluorene	PAH	0.9981	9.0
Phenanthrene	PAH	0.9995	3.8
Anthracene	PAH	0.9981	4.3
Fluoranthene	PAH	0.9998	3.0
Pyrene	PAH	0.9997	3.2
Benzo[a]anthracene	PAH	0.9999	1.7
Chrysene	PAH	0.9997	3.1
Benzo[b]fluoranthene	PAH	0.9998	2.6
Benzo[k]fluoranthene	PAH	0.9994	4.5
Benzo[a]pyrene	PAH	0.9987	5.4
Indeno[1,2,3-cd]pyrene	PAH	0.9964	9.3
Dibenzo[a,h]anthracene	PAH	0.9978	7.3
Benzo[ghi]perylene	PAH	0.9989	5.1
1-Methylnapthalene	methylPAH	1.0000	1.1
2-Methylnapthalene	methylPAH	0.9999	1.8

Appendix 4 – Table 4 continued. Coefficient of determination (R^2) and residual average response factor (% RSD)

Compound	Compound type	R^2	AVCF % RSD
2, 7-Dimethylnapthalene	methylPAH	0.9999	1.5
1,3 & 1,6-Dimethylnapthalene	methylPAH	0.9999	2.0
2,3-Dimethylnapthalene	methylPAH	0.9999	1.8
1,2-Dimethylnapthalene	methylPAH	0.9993	4.5
1,8-Dimethylnapthalene	methylPAH	0.9998	2.6
PCB-28	PCB	0.9997	2.5
PCB-52	PCB	0.9991	2.8
PCB-101	PCB	0.9998	3.2
PCB-118	PCB	0.9998	3.7
PCB-153	PCB	0.9998	1.6
PCB-138	PCB	0.9991	2.8
PCB-180	PCB	0.9997	4.3
Benzo(b)thiophene	PASH	0.9998	3.2
Dibenzothiophene	PASH	0.9988	3.7
1 & 2-Ethylnapthalene	ethylPAH	0.9996	3.7
Quinoline	PANH	0.9988	4.0
1-Indanone	PAOH	0.9993	4.7
Dibenzofuran	PAOH	0.9993	5.3
Carbazole	PAOH	0.9980	4.7
9, 10-Anthraquinone	PAOH	0.9951	12.9
2-Methylanthraquinone	PAOH	0.9981	6.5
9-Fluorenone	oxyPAH	0.9997	5.0
Benzanthrone	oxyPAH	0.9985	6.0
5, 12-Napthacenequinone	oxyPAH	0.9963	9.6
	Min	**0.9951**	**1.1**
	Max	**1.0000**	**12.9**
	Mean	**0.9991**	**4.2**

Appendix 5 – Table 5. QuEChERS soil extraction IS % recovery data

Compound	Extraction internal standard spiked recovery %							Mean	STDEV	% RSD
	1	2	3	4	5	6	7			
Napthalene d8	70.6	69.3	68.4	69.1	69.1	71.0	64.8	69	2.015	2.9%
Quinoline d7	72.0	71.7	69.9	74.8	72.4	71.9	69.3	72	1.792	2.5%
Dibenzofuran d8	82.0	82.8	80.4	80.7	79.8	82.4	77.4	81	1.847	2.3%
9-Fluorenone d8	81.8	81.4	78.2	82.5	79.1	79.9	78.7	80	1.676	2.1%
PCB 28L	89.2	89.5	90.9	93.7	86.0	92.7	91.2	91	2.546	2.8%
PCB 52L	89.7	88.5	87.0	85.2	85.1	86.5	83.8	87	2.063	2.4%
PCB 101L	85.2	82.6	82.7	78.0	81.6	79.5	80.3	81	2.375	2.9%
Pyrene d10	92.9	91.0	90.0	86.7	88.7	86.0	85.7	89	2.734	3.1%
PCB 118L	83.9	82.1	80.0	78.8	80.0	79.3	77.8	80	2.067	2.6%
PCB 153L	83.0	82.1	78.2	76.9	79.0	77.0	76.1	79	2.685	3.4%
PCB 138L	84.9	83.5	82.6	78.1	82.2	81.9	80.5	82	2.168	2.6%
PCB 180L	75.2	73.8	71.3	68.8	71.9	72.3	70.8	72	2.0735	2.9%
Perylene d12	63.6	63.6	62.3	64.4	66.7	70.4	68.1	66	2.9116	4.4%

Appendix 6 – Table 6. Compound Discoverer 3.2 software QuEChERS soil extract deconvoluted EI data NIST search index

Compound name	Reference RT [min]	Measured *(m/z)*	NIST formula	NIST theoretical *(m/z)*	Mass error (ppm)	Area	Calculated RI	RI Delta	NIST formula	Score	SI	RSI
Benzyl alcohol	4.466	79.05409	C6H7	79.05423	1.78	16069986	1039	5	C7H8O	95.7	937	987
Mevinphos	6.543	127.01549	C2H8O4P	127.01547	0.13	17076195	1429	16	C7H13O6P	99	960	962
Pebulate	6.729	128.10695	C7H14NO	128.10699	0.32	8595860	1469	0	C10H21NOS	95.2	895	936
Phthalimide	6.788	147.03149	C8H5NO2	147.03148	0.10	1242332	1482	0	C8H5NO2	99.4	968	968
Methacrifos	6.874	180.00058	C5H9O3PS	180.00045	0.71	6569371	1501	6	C7H13O5PS	98.5	931	932
Chloroneb	6.945	190.96625	C7H5Cl2O2	190.96611	0.72	17004439	1517	0	C8H8Cl2O2	98.2	960	981
Benzene, pentachloro-	7.084	249.84847	C6HCl5	249.84859	0.50	24762934	1549	0	C6HCl5	94.2	943	973
Tecnazene	7.384	202.87970	C5HCl4	202.87974	0.18	4337238	1609	0	C6HCl4NO2	94.3	975	988
Propachlor	7.411	120.08082	C8H10N	120.08078	0.36	9254651	1612	0	C11H14ClNO	97.2	938	964
Diphenylamine	7.501	169.08841	C12H11N	169.0886	1.13	24878507	1624	2	C12H11N	95.6	954	983
Cycloate	7.537	83.08540	C6H11	83.08553	1.48	12902977	1628	8	C11H21NOS	96.4	859	874
Chlorpropham	7.587	127.01830	C6H6ClN	127.01833	0.20	9390559	1634	0	C10H12ClNO2	97.9	953	976
Trifluralin	7.590	264.02240	C8H5F3N3O4	264.02267	1.01	10518127	1635	0	C13H16F3N3O4	96.9	855	860
Benfluralin	7.612	292.05356	C10H9F3N3O4	292.05397	1.40	11572988	1637	0	C13H16F3N3O4	98.3	915	924
Sulfotep	7.640	293.99060	C6H16O5P2S2	293.99089	0.98	5705056	1641	0	C8H20O5P2S2	98.9	945	948
Phorate	7.764	75.02623	C3H7S	75.0263	0.89	9945770	1656	0	C7H17O2PS3	93.4	858	914
Pentachloroanisole	7.934	264.83575	C6Cl5O	264.83568	0.28	10759890	1677	0	C7H3Cl5O	98.6	950	954
Botran	7.936	123.99490	C6H3ClN	123.99485	0.35	2725458	1677	0	C6H4Cl2N2O2	96	886	907
Atrazine	7.963	200.06975	C7H11ClN5	200.06975	0.00	8074011	1681	67	C8H14ClN5	97.5	947	948
Clomazone	8.022	125.01531	C7H6Cl	125.01525	0.41	24300346	1688	0	C12H14ClNO2	95.9	884	907
Terbuthylazine	8.073	214.08533	C8H13ClN5	214.0854	0.34	9737849	1694	82	C9H16ClN5	98.5	969	969
Diazinone	8.102	137.07097	C7H9N2O	137.07094	0.22	13998989	1698	90	C12H21N2O3PS	98.5	924	926
Propyzamide	8.113	172.95569	C7H3Cl2O	172.95555	0.82	17602860	1699	85	C12H11Cl2NO	98.2	942	944
Fonofos	8.148	108.98717	C2H6OPS	108.98715	0.17	23490821	1708	73	C10H15OPS2	98.3	950	956
Pyrimethanil	8.177	198.10248	C12H12N3	198.10257	0.48	45520948	1715	0	C12H13N3	94.9	918	978
Isazophos	8.203	118.98820	C2H2ClN3O	118.98809	0.90	9010911	1722	0	C9H17ClN3O3PS	98.1	905	915
Disulfoton	8.221	88.03407	C4H8S	88.03412	0.56	8860789	1727	0	C8H19O2PS3	97.2	921	951
Chlorothalonil	8.239	265.87787	C8Cl4N2	265.87806	0.72	19236284	1732	0	C8Cl4N2	97.1	966	971
Anthracene	8.252	178.07787	C14H10	178.0777	0.93	764555	1736	70	C14H10	97.8	909	914
Triallate	8.287	268.03238	C10H16Cl2NOS	268.03242	0.14	6379150	1745	80	C10H16Cl3NOS	97.4	896	897
Dibutyl phthalate	8.386	149.02332	C8H5O3	149.02332	0.03	5881147	1772	181	C16H22O4	98.1	915	916
Propanil	8.464	160.97940	C6H5Cl2N	160.97936	0.28	19471408	1793	0	C9H9Cl2NO	98.7	955	960
Chloropyriphos-methyl	8.514	285.92539	C7H7Cl2NO3PS	285.92558	0.69	20128971	1807	72	C7H7Cl3NO3PS	97.9	940	941
Transfluthrin	8.523	163.01637	C7H3F4	163.01654	1.02	11807916	1809	0	C15H12Cl2F4O2	97.3	897	927
Vinclozoline	8.526	212.00269	C10H8Cl2N	212.00283	0.68	3926786	1810	0	C12H9Cl2NO3	97.6	921	942
Alachlor	8.561	160.11224	C11H14N	160.11208	1.05	8630775	1820	74	C14H20ClNO2	92.8	849	907
Tolclofos-methyl	8.570	264.98505	C9H11ClO3PS	264.98496	0.34	30985887	1822	74	C9H11Cl2O3PS	97	848	848
Fenchlorphos	8.643	284.93015	C8H8Cl2O3PS	284.93033	0.66	22859648	1843	0	C8H8Cl3O3PS	97.4	887	973
Pirimiphos methyl	8.682	290.07211	C10H17N3O3PS	290.07228	0.56	12041239	1853	79	C11H20N3O3PS	98.1	913	914
Fenitrothion	8.726	260.01404	C9H11NO4PS	260.01409	0.20	6776685	1866	0	C9H12NO5PS	97.7	911	918
Malathion	8.755	124.98213	C2H6O2PS	124.98206	0.55	9227531	1874	0	C10H19O6PS2	99	953	954
Linuron	8.786	61.05217	C2H7NO	61.05222	0.67	996941	1882	0	C9H10Cl2N2O2	93.7	754	767
Dichlofluanid	8.801	123.01375	C6H5NS	123.01372	0.22	10765859	1886	71	C9H11Cl2FN2O2S2	98.3	923	924

Appendix 6 – Table 6 continued. Compound Discoverer 3.2 software QuEChERS soil extract deconvoluted EI data NIST search index

Compound name	Reference RT [min]	Measured (*m/z*)	NIST formula	NIST theoretical (*m/z*)	Mass error (ppm)	Area	Calculated RI	RI Delta	NIST formula	Score	SI	RSI
Pentachlorothioanisole	8.839	295.83633	C7H3Cl5S	295.83631	0.08	10450278	1897	58	C7H3Cl5S	98.1	937	954
Parathion	8.894	96.95074	H2O2PS	96.95076	0.27	4484103	1913	75	C10H14NO5PS	97.9	907	912
DCPA	8.901	300.87985	C9H3Cl4O3	300.88013	0.93	23819724	1915	72	C10H6Cl4O4	98.5	944	947
Triadimefon	8.918	208.02710	C9H7ClN3O	208.02722	0.56	4235155	1919	77	C14H16ClN3O2	97.7	896	898
9,10-Anthracenedione	8.949	208.05202	C14H8O2	208.05188	0.65	8399424	1928	55	C14H8O2	97.5	903	919
Pirimiphos ethyl	8.956	168.05891	C7H10N3S	168.05899	0.48	9261908	1930	0	C13H24N3O3PS	98.4	928	945
Isopropalin	9.011	238.08212	C10H12N3O4	238.08223	0.46	11131988	1946	0	C15H23N3O4	97.8	892	902
Bromophos	9.027	330.87711	C8H8BrClO3PS	330.87687	0.72	18301347	1951	68	C8H8BrCl2O3PS	97.9	938	949
Clofenvinfos	9.060	266.93747	C8H6Cl2O4P	266.93753	0.22	423034	1960	0	C12H14Cl3O4P	94.6	813	831
Fipronil	9.080	366.94272	C11H4Cl2F3N4OS	366.94295	0.62	1478777	1966	0	C12H4Cl2F6N4OS	95.6	781	781
Cyprodinil	9.093	224.11832	C14H14N3	224.11822	0.41	40372063	1969	0	C14H15N3	97.3	943	971
Metazachlor	9.117	132.08084	C9H10N	132.08078	0.50	11264282	1976	68	C14H16ClN3O	98.6	939	941
Penconazole	9.137	158.97646	C7H5Cl2	158.97628	1.09	18713951	1982	74	C13H15Cl2N3	98.3	917	918
Tolylfluanid	9.161	137.02948	C3H12Cl2F	137.02946	0.15	13660572	1989	74	C10H13Cl2FN2O2S2	96.6	864	894
Quinalphos	9.201	146.04755	C8H6N2O	146.04746	0.56	10014184	2000	77	C12H15N2O3PS	98.4	956	959
Triflumizole	9.214	205.99829	C8H4ClF3N	205.99789	1.96	3132804	2004	83	C15H15ClF3N3O	96	805	806
Triadimenol	9.225	112.05049	C4H6N3O	112.05054	0.42	8170623	2008	78	C14H18ClN3O2	97.9	897	897
Procymidone	9.238	96.05702	C6H8O	96.05697	0.58	6299842	2012	0	C13H11Cl2NO2	96.9	897	916
Bromophos-ethyl	9.309	302.84604	C7H4BrCl2O2S	302.84574	0.97	10486942	2034	0	C10H12BrCl2O3PS	96.8	880	888
Tetrachlorvinphos	9.342	328.92981	C10H9Cl3O4P	328.92985	0.13	8515425	2044	0	C10H9Cl4O4P	97.8	940	952
Paclobutrazol	9.382	125.01531	C7H6Cl	125.01525	0.41	7793995	2057	0	C15H20ClN3O	98.5	935	979
Fenamiphos	9.417	55.05417	C4H7	55.05423	1.11	8959158	2068	0	C13H22NO3PS	93.4	813	896
Flutolanil	9.437	173.02083	C8H4F3O	173.02088	0.27	42560841	2074	0	C17H16F3NO2	99.5	974	976
Flutriafol	9.455	123.02410	C7H4FO	123.02407	0.26	9903083	2080	50	C16H13F2N3O	98.5	953	960
Pretilachlor	9.508	162.12763	C11H16N	162.12773	0.62	10905234	2096	0	C17H26ClNO2	95.3	860	902
Iodofenphos	9.510	376.86569	C8H8ClIO3PS	376.86595	0.68	21511075	2097	61	C8H8Cl2IO3PS	93.1	816	857
Oxadiazon	9.530	174.95873	C6H3Cl2NO	174.95862	0.60	11688803	2103	0	C15H18Cl2N2O3	98.3	916	918
Oxyfluorfen	9.554	252.03917	C13H7F3O2	252.03927	0.38	6287263	2111	85	C15H11ClF3NO4	95.9	824	826
Bupirimate	9.576	208.14444	C11H18N3O	208.14444	0.01	7679148	2118	0	C13H24N4O3S	98.2	911	915
Myclobutanil	9.583	179.02463	C8H6ClN3	179.02448	0.85	7298452	2120	0	C15H17ClN4	96.1	832	891
Flusilazole	9.592	233.05919	C13H11F2Si	233.05926	0.30	20153005	2123	73	C16H15F2N3Si	90.3	871	891
Tricyclazole	9.614	189.03554	C9H7N3S	189.03552	0.10	3484770	2129	43	C9H7N3S	97.1	973	981
Nitrofen	9.759	282.97965	C12H7Cl2NO3	282.97975	0.37	4113285	2175	60	C12H7Cl2NO3	97	915	922
Chlorthiophos	9.782	268.92563	C7H7ClO3PS2	268.92573	0.36	4905455	2182	0	C11H15Cl2O3PS2	95.5	796	815
Ethion	9.837	230.97318	C5H12O2PS3	230.97315	0.09	17039535	2199	73	C9H22O4P2S4	98.1	932	970
Triazophos	9.934	162.06630	C8H8N3O	162.06619	0.68	4817402	2229	75	C12H16N3O3PS	97.6	886	887
Carfentrazone ethyl	9.974	312.05896	C13H9F3N3O3	312.05905	0.29	7221687	2242	0	C15H14Cl2F3N3O3	97.9	900	922
Norflurazon	10.055	303.03787	C12H9ClF3N3O	303.03808	0.67	5679397	2267	0	C12H9ClF3N3O	96.9	843	845
Carbophenothion	10.062	156.98746	C6H6OPS	156.98715	1.97	11686197	2269	62	C11H16ClO2PS3	98.4	941	946
Edifenphos	10.102	109.01067	C6H5S	109.01065	0.17	11653922	2282	0	C14H15O2PS2	94.3	910	920
Resmethrin	10.214	128.06212	C10H8	128.06205	0.53	3084053	2315	0	C22H26O3	96.4	838	852
Pyridaphenthion	10.422	199.08656	C12H11N2O	199.08659	0.13	4151296	2375	0	C14H17N2O4PS	98.8	937	942
Tetramethrin	10.481	164.07062	C9H10NO2	164.07061	0.08	16344579	2392	0	C19H25NO4	99.4	972	976
Phosmet	10.539	160.03935	C9H6NO2	160.0393	0.30	28822343	2408	0	C11H12NO4PS2	98.4	926	986

Appendix 6 – Table 6 continued. Compound Discoverer 3.2 software QuEChERS soil extract deconvoluted EI data NIST search index

Compound name	Reference RT [min]	Measured *(m/z)*	NIST formula	NIST theoretical *(m/z)*	Mass error (ppm)	Area	Calculated RI	RI Delta	NIST formula	Score	SI	RSI
Methoxychlor	10.574	227.10657	C15H15O2	227.10666	0.39	20536768	2417	69	C16H15Cl3O2	94.2	852	895
Tebufenpyrad	10.609	171.03200	C6H8N2O2P	171.03179	1.22	13061973	2426	76	C18H24ClN3O	96.7	942	956
Phosalone	10.852	182.00035	C8H5ClNO2	182.00033	0.10	11687589	2490	0	C12H15ClNO4PS2	97	922	938
Pyriproxyfen	10.883	136.07579	C8H10NO	136.07569	0.73	30668503	2498	71	C20H19NO3	97.9	940	953
Leptophos	10.885	171.00285	C7H8OPS	171.0028	0.32	13220533	2499	51	C13H10BrCl2O2PS	95.6	899	913
.lambda.-Cyhalothrin	10.921	181.06485	C13H9O	181.06479	0.33	12337809	2507	85	C23H19ClF3NO3	98.2	925	928
Pyrazophos	11.064	221.07954	C10H11N3O3	221.07949	0.24	6802604	2540	0	C14H20N3O5PS	97.6	881	923
Fenarimol	11.177	138.99460	C7H4ClO	138.99452	0.57	7620002	2567	52	C17H12Cl2N2O	97.9	947	950
Azinphos-ethyl	11.214	132.04440	C8H6NO	132.04439	0.10	6897902	2575	0	C12H16N3O3PS2	97.7	916	960
Permethrine	11.503	183.08044	C13H11O	183.08044	0.02	14135701	2639	0	C21H20Cl2O3	98.8	942	952
Pyridaben	11.578	147.11690	C11H15	147.11683	0.48	25077978	2655	0	C19H25ClN2OS	98.5	938	944
Fluquinconazole	11.583	340.03946	C16H8ClFN5O	340.03959	0.39	19132298	2656	62	C16H8Cl2FN5O	87.6	842	941

Appendix 7 – Table 7. Compound Discoverer 3.2 software QuEChERS soil extract PCI confirmation data for [M+], [M+H], [M+C_2H_5], and [C_3H_5] with associated ppm mass error (where detected)

Name	Reference RT [min]	NIST Formula	$[M]^+$	Mass error (ppm)	$[M+H]^+$	Mass error (ppm)	$[M+C_2H_5]^+$	Mass error (ppm)	$[M+C_3H_5]^+$	Mass error (ppm)
Benzyl alcohol	4.466	C7H8O	108.05697	0.83	109.06534	0.88	137.09664	0.19	149.09664	0.04
Mevinphos	6.543	C7H13O6P	224.04443		225.05280	-0.16	253.08410	-1.36	265.08410	
Pebulate	6.729	C10H21NOS	203.13384		204.14221	0.68	232.17351	0.33	244.17351	
Phthalimide	6.788	C8H5NO2	147.03148		148.03986	-0.22	176.07116		188.07116	
Methacrifos	6.874	C7H13O5PS	240.02158	0.06	241.02996	0.15	269.06126	-0.25	281.06126	-0.2
Chloroneb	6.945	C8H8Cl2O2	205.98959	0.5	206.99796	1.42	235.02926	-0.26	247.02926	
Benzene, pentachloro-	7.084	C6HCl5	247.85154	0.21	248.85992	2.63	276.89122		288.89122	
Tecnazene	7.384	C6HCl4NO2	258.87559	0.53	259.88397	0.74	287.91527		299.91527	
Propachlor	7.411	C11H14ClNO	211.07584	0.39	212.08422	0.24	240.11552	0.50	252.11552	-1.15
Diphenylamine	7.501	C12H11N	169.08860	0.65	170.09698	0.19	198.12828	0.50	210.12828	0.57
Cycloate	7.537	C11H21NOS	215.13384		216.14221	0.45	244.17351	0.13	256.17351	
Chlorpropham	7.587	C10H12ClNO2	213.05511	0.21	214.06348	1.39	242.09478		254.09478	
Trifluralin	7.590	C13H16F3N3O4	335.10874	-0.34	336.11712	-0.14	364.14842		376.14842	
Benfluralin	7.612	C13H16F3N3O4	335.10874	-0.34	336.11712	-0.14	364.14842		376.14842	
Sulfotep	7.640	C8H20O5P2S2	322.02219	-0.02	323.03057	-0.46	351.06187	-0.25	363.06187	-0.04
Phorate	7.764	C7H17O2PS3	260.01228	-0.24	261.02066	0.10	289.05196		301.05196	
Pentachloroanisole	7.934	C7H3Cl5O	277.86210	-0.02	278.87048	2.27	306.90178		318.90178	
Botran	7.936	C6H4Cl2N2O2	205.96443	0.34	206.97281	0.94	235.00411		247.00411	
Atrazine	7.963	C8H14ClN5	215.09322	0.46	216.10160	0.44	244.13290	-0.01	256.13290	0.45
Clomazone	8.022	C12H14ClNO2	239.07076		240.07913	0.11	268.11043	0.43	280.11043	-1.17
Terbuthylazine	8.073	C9H16ClN5	229.10887	0.34	230.11725	0.10	258.14855	-0.37	270.14855	-0.27
Diazinone	8.102	C12H21N2O3PS	304.10050	-0.09	305.10888	-0.84	333.14018	-0.37	345.14018	-0.62
Propyzamide	8.113	C12H11Cl2NO	255.02122	0.43	256.02960	-0.02	284.06090	0.84	296.06090	-1.29
Fonofos	8.148	C10H15OPS2	246.02964	-0.11	247.03802	-0.26	275.06932	-0.40	287.06932	-0.41
Pyrimethanil	8.177	C12H13N3	199.11040	0.99	200.11878	0.17	228.15008	-0.11	240.15008	-0.28

Appendix 7 – Table 7 continued. Compound Discoverer 3.2 software QuEChERS soil extract PCI confirmation data for [M+], [M+H], [M+C_2H_5], and [C_3H_5] with associated ppm mass error (where detected)

Name	Reference RT [min]	NIST Formula	$[M]^+$	Mass error (ppm)	$[M+H]^+$	Mass error (ppm)	$[M+C_2H_5]^+$	Mass error (ppm)	$[M+C_3H_5]^+$	Mass error (ppm)
Isazophos	8.203	C9H17ClN3O3PS	313.04113	-0.09	314.04950	-0.37	342.08080	-0.17	354.08080	-0.17
Disulfoton	8.221	C8H19O2PS3	274.02793	-0.74	275.03631	-0.28	303.06761		315.06761	
Chlorothalonil	8.239	C8Cl4N2	263.88101	-0.22	264.88939	1.09	292.92069	-0.58	304.92069	
Anthracene	8.252	C14H10	178.07770	0.03	179.08608	-0.18	207.11738		219.11738	
Triallate	8.287	C10H16Cl3NOS	303.00127		304.00965	-0.33	332.04095	-0.07	344.04095	
Dibutyl phthalate	8.386	C16H22O4	278.15126		279.15964	-0.06	307.19094		319.19094	
Propanil	8.464	C9H9Cl2NO	217.00557	0.06	218.01395	0.21	246.04525	-0.82	258.04525	
Chloropyriphos-methyl	8.514	C7H7Cl3NO3PS	320.89443	0.46	321.90281	-0.29	349.93411	-0.20	361.93411	0.03
Transfluthrin	8.523	C15H12Cl2F4O2	370.01450	-0.04	371.02288	-0.40	399.05418	0.74	411.05418	
Vinclozoline	8.526	C12H9Cl2NO3	284.99540	-0.55	286.00378	1.29	314.03508	-0.34	326.03508	
Alachlor	8.561	C14H20ClNO2	269.11771	0.16	270.12608	0.20	298.15738	0.21	310.15738	
Tolclofos-methyl	8.570	C9H11Cl2O3PS	299.95381		300.96218	-0.21	328.99349	-0.28	340.99349	-0.27
Fenchlorphos	8.643	C8H8Cl3O3PS	319.89919		320.90756	0.10	348.93886	-0.27	360.93886	0.08
Pirimiphos methyl	8.682	C11H20N3O3PS	305.09575	0.41	306.10413	-0.16	334.13543	0.22	346.13543	0.32
Fenitrothion	8.726	C9H12NO5PS	277.01683	0.42	278.02521	0.25	306.05651	0.30	318.05651	
Malathion	8.755	C10H19O6PS2	330.03552		331.04389	0.02	359.07519	-0.50	371.07519	
Linuron	8.786	C9H10Cl2N2O2	248.01138	0.08	249.01976	0.48	277.05106		289.05106	
Dichlofluanid	8.801	C9H11Cl2FN2O2S2	331.96175	-0.08	332.97013	0.39	361.00143		373.00143	
Pentachlorothioanisole	8.839	C7H3Cl5S	293.83926	0.23	294.84764	1.63	322.87894	0.30	334.87894	-0.4
Parathion	8.894	C10H14NO5PS	291.03248	0.27	292.04086	0.35	320.07216		332.07216	
DCPA	8.901	C10H6Cl4O4	329.90147	0.33	330.90985	0.37	358.94115	-0.89	370.94115	
Triadimefon	8.918	C14H16ClN3O2	293.09256		294.10093	-0.06	322.13223	2.74	334.13223	
9,10-Anthracenedione	8.949	C14H8O2	208.05188	0.71	209.06026	0.86	237.09156	0.33	249.09156	
Pirimiphos ethyl	8.956	C13H24N3O3PS	333.12705	0.24	334.13543	-0.34	362.16673	0.27	374.16673	-0.1
Isopropalin	9.011	C15H23N3O4	309.16831		310.17668	0.45	338.20798		350.20798	
Bromophos	9.027	C8H8BrCl2O3PS	363.84867		364.85705	0.54	392.88835	0.33	404.88835	0.92
Clofenvinfos	9.060	C12H14Cl3O4P	357.96898		358.97736	-0.11	387.00866		399.00866	
Fipronil	9.080	C12H4Cl2F6N4OS	435.93816		436.94653	-0.10	464.97783		476.97783	
Cyprodinil	9.093	C14H15N3	225.12605	1.74	226.13443	0.40	254.16573	-0.07	266.16573	0.2
Metazachlor	9.117	C14H16ClN3O	277.09764	0.86	278.10602	-0.23	306.13732		318.13732	
Penconazole	9.137	C13H15Cl2N3	283.06375		284.07213	-0.10	312.10343		324.10343	
Tolylfluanid	9.161	C10H13Cl2FN2O2S2	345.97740	-1.96	346.98578	-0.07	375.01708		387.01708	
Quinalphos	9.201	C12H15N2O3PS	298.05355	-0.05	299.06193	-0.10	327.09323	-0.16	339.09323	-0.31
Triflumizole	9.214	C15H15ClF3N3O	345.08503		346.09340	-0.31	374.12470		386.12470	
Triadimenol	9.225	C14H18ClN3O2	295.10821		296.11658	-0.77	324.14788		336.14788	
Procymidone	9.238	C13H11Cl2NO2	283.01614	-0.08	284.02451	-0.17	312.05581	-0.39	324.05581	-0.16
Bromophos-ethyl	9.309	C10H12BrCl2O3PS	391.87997		392.88835	0.04	420.91965	0.36	432.91965	1.75
Tetrachlorvinphos	9.342	C10H9Cl4O4P	363.89871		364.90708	-0.21	392.93838		404.93838	
Paclobutrazol	9.382	C15H20ClN3O	293.12894		294.13732	-0.13	322.16862		334.16862	
Fenamiphos	9.417	C13H22NO3PS	303.10525	-0.3	304.11363	1.41	332.14493	1.84	344.14493	
Flutolanil	9.437	C17H16F3NO2	323.11276	0.09	324.12114	-0.09	352.15244	0.03	364.15244	
Flutriafol	9.455	C16H13F2N3O	301.10212		302.11050	-0.37	330.14180		342.14180	

Appendix 7 – Table 7 continued. Compound Discoverer 3.2 software QuEChERS soil extract PCI confirmation data for [M+], [M+H], [M+C_2H_5], and [C_3H_5] with associated ppm mass error (where detected)

Name	Reference RT [min]	NIST Formula	$[M]^+$	Mass error (ppm)	$[M+H]^+$	Mass error (ppm)	$[M+C_2H_5]^+$	Mass error (ppm)	$[M+C_3H_5]^+$	Mass error (ppm)
Pretilachlor	9.508	C17H26ClNO2	311.16466	-0.66	312.17303	-0.06	340.20434	0.50	352.20434	0.62
Iodofenphos	9.510	C8H8Cl2IO3PS	411.83480		412.84318	-0.04	440.87448	-0.26	452.87448	-0.01
Oxadiazon	9.530	C15H18Cl2N2O3	344.06890	0.02	345.07728	-0.12	373.10858	1.81	385.10858	
Oxyfluorfen	9.554	C15H11ClF3NO4	361.03232	-1.34	362.04070	-0.02	390.07200		402.07200	
Bupirimate	9.576	C13H24N4O3S	316.15636	0.13	317.16474	-0.03	345.19604	-0.51	357.19604	-0.47
Myclobutanil	9.583	C15H17ClN4	288.11363		289.12200	-0.26	317.15330		329.15330	
Flusilazole	9.592	C16H15F2N3Si	315.09978	0.35	316.10816	0.20	344.13946	1.59	356.13946	
Tricyclazole	9.614	C9H7N3S	189.03552	0.96	190.04390	0.70	218.07520		230.07520	
Nitrofen	9.759	C12H7Cl2NO3	282.97975	-0.57	283.98813	-1.32	312.01943		324.01943	
Chlorthiophos	9.782	C11H15Cl2O3PS2	359.95718	0.17	360.96556	0.28	388.99686	0.22	400.99686	-0.33
Ethion	9.837	C9H22O4P2S4	383.98707	0.19	384.99544	0.29	413.02674		425.02674	
Triazophos	9.934	C12H16N3O3PS	313.06445	-1.35	314.07283	0.18	342.10413	0.02	354.10413	
Carfentrazone ethyl	9.974	C15H14Cl2F3N3O3	411.03588	0.16	412.04426	0.15	440.07556	2.15	452.07556	
Norflurazon	10.055	C12H9ClF3N3O	303.03808	0.52	304.04645	0.41	332.07775	-0.37	344.07775	
Edifenphos	10.102	C14H15O2PS2	310.02456	-0.21	311.03294	0.33	339.06424		351.06424	
Resmethrin	10.214	C22H26O3	338.18765	0.5	339.19602	0.40	367.22732		379.22732	
Resmethrin	10.258	C22H26O3	338.18765	0.5	339.19602	0.40	367.22732		379.22732	
Pyridaphenthion	10.422	C14H17N2O4PS	340.06412	-0.63	341.07249	-0.09	369.10379	-0.99	381.10379	
Tetramethrin	10.481	C19H25NO4	331.17781		332.18619	-0.34	360.21749		372.21749	
Phosmet	10.539	C11H12NO4PS2	316.99399		318.00236	-0.14	346.03366		358.03366	
Methoxychlor	10.574	C16H15Cl3O2	344.01321		345.02159	0.14	373.05289	0.86	385.05289	0.23
Tebufenpyrad	10.609	C18H24ClN3O	333.16024	0.15	334.16862	0.22	362.19992	-0.37	374.19992	
Phosalone	10.852	C12H15ClNO4PS2	366.98632	-0.29	367.99469	0.32	396.02599		408.02599	
Pyriproxyfen	10.883	C20H19NO3	321.13595		322.14432	-0.09	350.17562		362.17562	
Leptophos	10.885	C13H10BrCl2O2PS	409.86941		410.87778	0.22	438.90908	0.15	450.90908	
.lambda.-Cyhalothrin	10.921	C23H19ClF3NO3	449.10001		450.10838	-0.05	478.13968		490.13968	
Pyrazophos	11.064	C14H20N3O5PS	373.08558	-1.03	374.09396	0.10	402.12526	0.09	414.12526	
Fenarimol	11.177	C17H12Cl2N2O	330.03212	-1.22	331.04050	-0.52	359.07180		371.07180	
Azinphos-ethyl	11.214	C12H16N3O3PS2	345.03652		346.04490	-0.31	374.07620		386.07620	
Permethrine	11.503	C21H20Cl2O3	390.07840		391.08678	0.07	419.11808		431.11808	
Coumaphos	11.563	C14H16ClO5PS	362.01391	0.55	363.02229	0.56	391.05359	-0.88	403.05359	
Pyridaben	11.578	C19H25ClN2OS	364.13706	-1.4	365.14544	0.55	393.17674		405.17674	
Fluquinconazole	11.583	C16H8Cl2FN5O	375.00845		376.01682	0.86	404.04812	-0.67	416.04812	

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