APPLICATION PRESENTATION

PESTICIDES

Application Presentation

LC MS and Pesticides

Applications - Pesticides

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Jeremiah D. Tipton, Ph.D.
Director and Applications Manager
Applied Omics & Life Sciences LLC
Agilent Technologies Applications Contractor

BASE OUTLINE OF THE DOCUMENT

- Introduction to Pesticides
- Organophosphates
- Carbamates
- Pyrethroids
- Neonicotinoids
- Organochlorines
- Phenoxy Herbicides
- Triazines
- Glyphosate
- Dinitroanilines
- Biological Pesticides
- Important Notes and Considerations

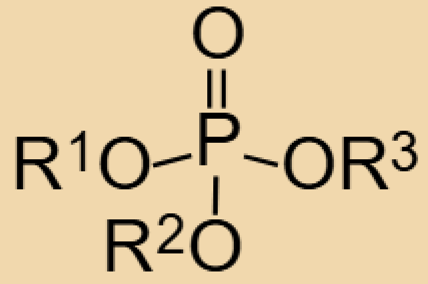
INTRODUCTION TO PESTICIDES

Pesticides are substances used to prevent, destroy, or control pests that can harm crops, livestock, and human health. They play a crucial role in agriculture by enhancing crop yields and protecting plants from diseases and pests.

Pesticides can be classified into various categories, including herbicides, insecticides, and fungicides, each serving specific functions in pest management. Understanding their use and impact is essential for sustainable agriculture and environmental protection.

Pesticide Classes

ORGANOPHOSPHATES



Key Molecules and Characteristics

- Molecules include Chlorpyrifos, Malathion, Diazinon.
- Characteristics: Inhibit acetylcholinesterase, affecting the nervous system.
- Used extensively in agriculture for pest control.
- Can be highly toxic to humans and wildlife if misused.

Impact and Usage

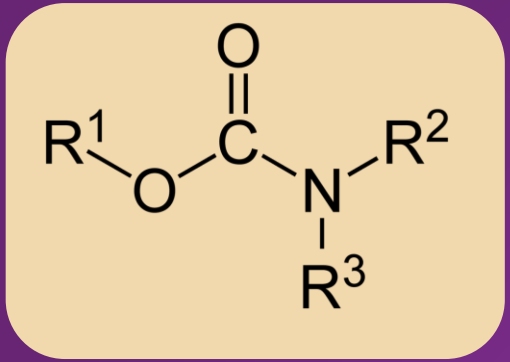
- Widely used in various crops such as corn and soybeans.
- Potential risks include toxicity to non-target organisms and environmental persistence.
- Regulations have tightened due to health concerns and environmental impact.

- Mechanism of Action

These molecules inhibit acetylcholinesterase, which affects the nervous system by preventing the breakdown of acetylcholine, leading to overstimulation of nerve cells.

Pesticide Classes

CARBAMATES



Molecules and Characteristics

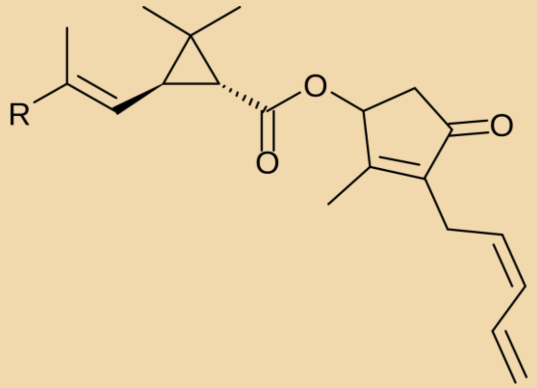
- Molecules include Carbaryl, Aldicarb, and Carbofuran.
- Carbamates inhibit acetylcholinesterase, impacting nervous system function.
- They are generally less persistent in the environment compared to organophosphates.

Impact and Usage

- Reduced toxicity and environmental persistence compared to organophosphates.
- Used widely in agriculture due to their effectiveness and lower long-term effects.
- Important to follow safety guidelines to minimize health risks.

- **Mechanism of Action** Carbamates inhibit acetylcholinesterase, like organophosphates, affecting neurotransmission.

PYRETHROIDS



Molecules and Characteristics

- Molecules include Permethrin, Cypermethrin, and Deltamethrin.
- Synthetic versions of natural pyrethrins derived from chrysanthemum flowers.
- Affect sodium channels in nerve cells, impacting insect nervous systems.

Impact and Usage

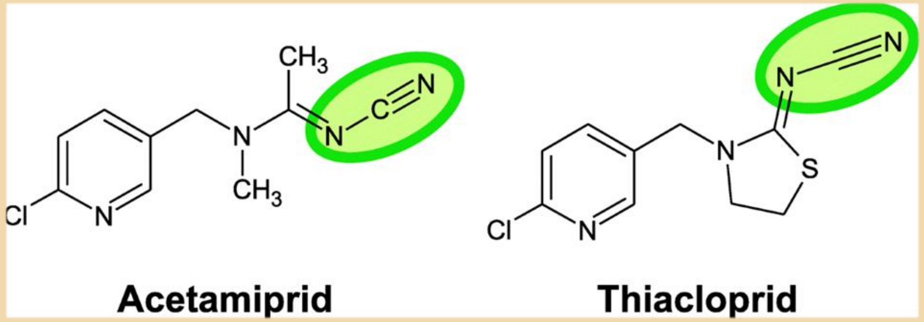
- Commonly used in agricultural and domestic pest control.
- Effective against a wide range of pests, including mosquitoes and agricultural insects.
- Low toxicity to humans and animals when used correctly.

- **Note -- Natural Derivation** Pyrethroids are synthetic versions of natural pyrethrins derived from chrysanthemum flowers.
- **Mechanism of Action** They affect sodium channels in nerve cells, leading to paralysis and death in insects.

Pesticide Classes

NEONICOTINOIDS

Examples



Molecules and Characteristics

- Imidacloprid: A widely used neonicotinoid affecting insect nervous systems.
- Thiamethoxam: Known for its systemic properties, impacting target pests through ingestion.
- Clothianidin: Similar to Imidacloprid, affects the nervous system of insects.

Impact and Usage

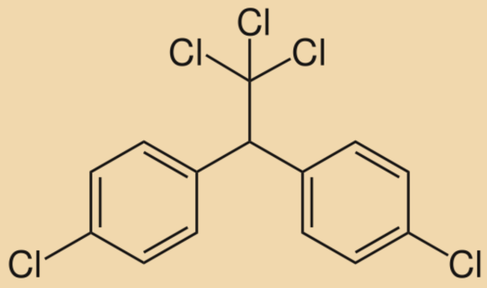
- Affect nicotinic acetylcholine receptors in insects, disrupting normal signaling.
- Lead to paralysis and death of target pests, making them effective insecticides.
- Concerns over their impact on non-target species and pollinators.

- Mechanism of Action

Neonicotinoids affect nicotinic acetylcholine receptors in insects, disrupting their nervous system function.

ORGANOCHLORINES

Example - DTT



Key Molecules and Characteristics

- Notable for their long-lasting presence in ecosystems.
- Bioaccumulation leads to significant ecological risks.
- Regulations implemented to restrict use due to health concerns.

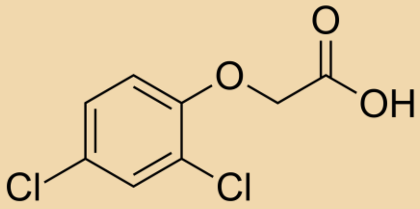
Environmental Impact and Regulations

- Molecules include DDT, Lindane, and Aldrin.
- Persistent in the environment, accumulating in fatty tissues.
- Have been largely banned due to their harmful effects.

- **Environmental Persistence** These compounds are persistent in the environment, often accumulating in fatty tissues.
- **Regulatory Actions** Organochlorines have been largely banned due to their harmful effects.

PHENOXY HERBICIDES

Example – 2,4-D



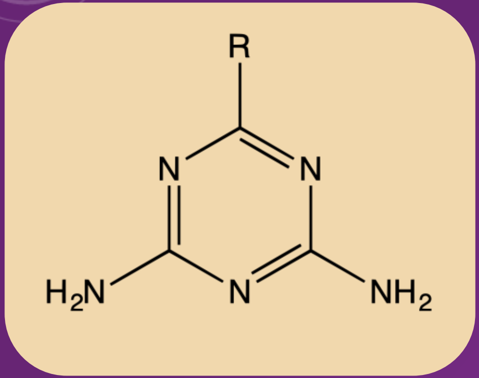
Key Molecules and Characteristics

- 2,4-D and MCPA are primary molecules used in phenoxy herbicides.
- 2,4-D is widely used for controlling broadleaf weeds in various crops.
- MCPA is commonly used in cereal crops and lawns to manage weeds.

Usage and Mechanism of Action

- Phenoxy herbicides disrupt plant hormone function, specifically auxins.
- They mimic natural plant hormones, leading to uncontrolled growth in target weeds.
- This disruption causes broadleaf weeds to grow erratically and die off, allowing crops to thrive.

TRIAZINES



Molecules and Characteristics

- Commonly used in agriculture for weed control.
- Can have residual effects in soil and water, impacting non-target species.
- Regulations exist to manage their application due to potential environmental concerns.

Environmental Impact and Use

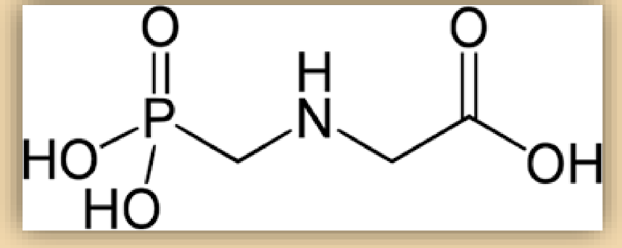
- Molecules include Atrazine and Simazine.
- Triazines inhibit photosynthesis in plants, affecting their growth and health.
- They function by blocking the photosynthetic pathway, leading to reduced energy production.

- Mechanism of Action

Both Atrazine and Simazine target the photosynthetic process, blocking the electron transport chain, which leads to plant death.

Pesticides

GLYPHOSATE



- Glyphosate is the active ingredient in Roundup, one of the most widely used herbicides worldwide.
- It functions by inhibiting an enzyme essential for plant growth called EPSP synthase, which is crucial for the biosynthesis of aromatic amino acids.
- This inhibition affects the growth and survival of plants, making it effective for controlling weeds in agricultural practices.

Usage and Impact

- Its application has led to significant reductions in weed populations, but it has also raised concerns regarding environmental and health effects.

Active Ingredient in Roundup

- Glyphosate is the active ingredient in Roundup, widely used for its effectiveness in controlling weeds.

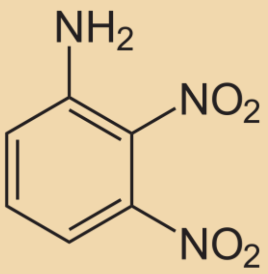
Mechanism of Action

- Glyphosate inhibits an enzyme essential for plant growth, specifically the shikimic acid pathway, which is not found in animals, making it selectively toxic to plants.

Pesticide Classes

DINITROANILINES

Example: 2,3-Dinitroaniline



Molecules and Characteristics

- Molecules include Trifluralin and Pendimethalin.
- Used as pre-emergent herbicides to inhibit root growth in plants.
- Effective in preventing the germination of weeds before they emerge from the soil.

Application and Usage

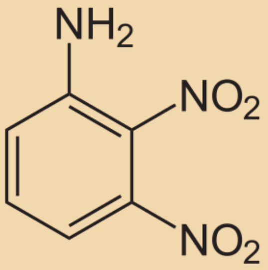
- Applied to soil prior to planting to control weed populations.
- Minimizes competition for nutrients and water from crops.
- Important to follow application guidelines to ensure effectiveness and safety.

- **Mechanism of Action** Dinitroanilines inhibit root growth in plants, impacting their establishment and development.

Pesticide Classes

DINITROANILINES

Example: 2,3-Dinitroaniline



Molecules and Characteristics

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Application and Usage

- Applied to soil prior to planting to control weed populations.
- Minimizes competition for nutrients and water from crops.
- Important to follow application guidelines to ensure effectiveness and safety.

- **Mechanism of Action** Dinitroanilines inhibit root growth in plants, impacting their establishment and development.

NOTE ON BIOLOGICAL PESTICIDES

Bacterial Pesticides

Includes bacteria like Bacillus thuringiensis, which produces toxins that specifically target and kill certain insects, making it a valuable tool in pest control.

Fungal Pesticides

Utilizes fungi that can infect and control pest populations. These biological agents often have a narrow host range, minimizing harm to non-target species.

Viral Pesticides

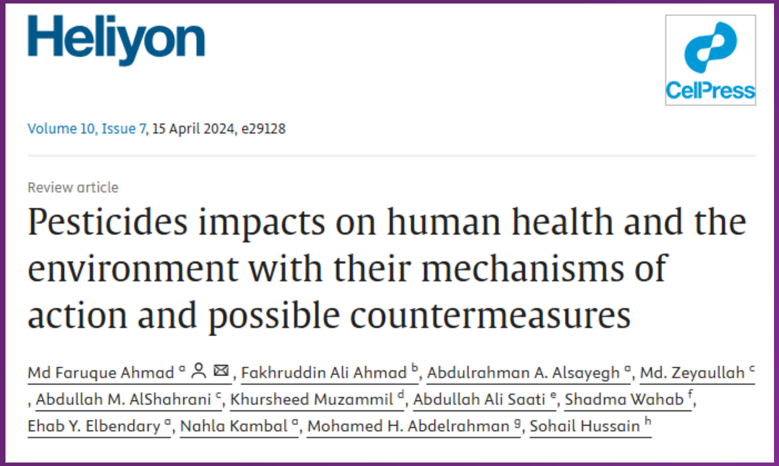
Involves viruses that specifically infect pests, leading to their death. These agents are derived from natural sources and are used for their specificity and reduced environmental impact.

IMPORTANT NOTES AND CONSIDERATIONS

- This is not an exhaustive list, and there are other pesticide classes and molecules.
- The specific molecules within a class can have varying degrees of toxicity and environmental impact.
- Always follow label instructions when using pesticides.
- Consider integrated pest management strategies to minimize pesticide use.

There is variability in toxicity and environmental impact among different pesticide molecules. The specific molecules within a class can have varying degrees of toxicity and environmental impact. It is crucial to always follow label instructions when using pesticides, and to consider integrated pest management strategies to minimize their use.

Web resources and Literature



Heliyon

CellPress

Volume 10, Issue 7, 15 April 2024, e29128

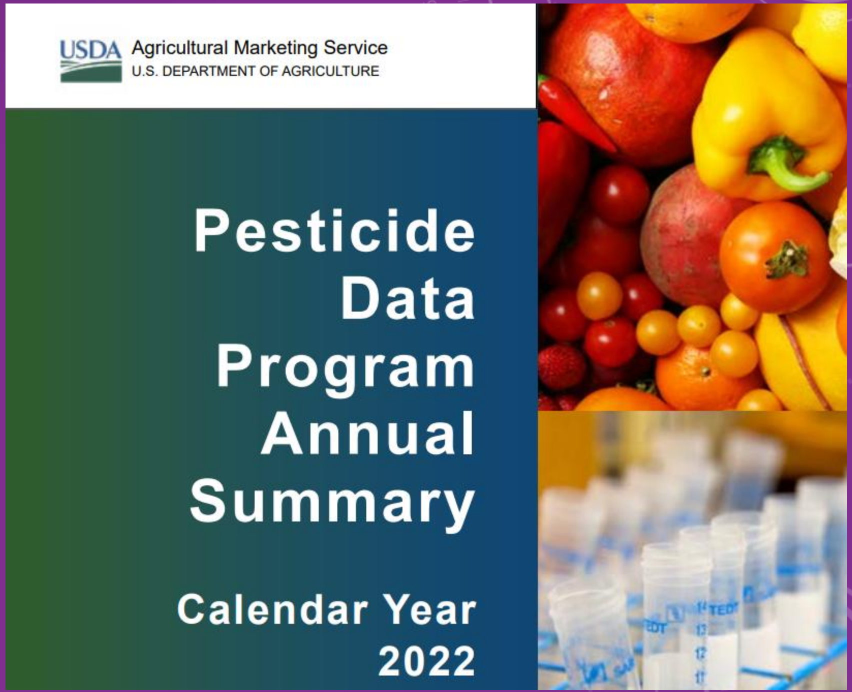
Review article

Pesticides impacts on human health and the environment with their mechanisms of action and possible countermeasures

Md Faruque Ahmad[a], Fakhruddin Ali Ahmad[b], Abdulrahman A. Alsayegh[a], Md. Zeyaullah[c], Abdullah M. AlShahrani[c], Khursheed Muzammil[d], Abdullah Ali Saati[e], Shadma Wahab[f], Ehab Y. Elbendary[a], Nahla Kambal[a], Mohamed H. Abdelrahman[g], Sohail Hussain[h]

Examples in this Presentation

- Organophosphates
- Carbamates
- Pyrethroids
- Neonicotinoids
- Organochlorines
- Phenoxy Herbicides
- Triazines
- Glyphosate
- Dinitroanilines
- Biological Pesticides



LC MS ANALYSIS OF PESTICIDES – EXAMPLES OF EXISTING METHODS

EPA United States Environmental Protection Agency

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Home / Pesticide Analytical Methods

Pesticide Analytical Methods

- **Pesticide Laboratories**
- National Pesticide Standard Repository
- Analyzing Antimicrobials
- Environmental Chemistry Methods and Index
- Analyzing Pesticide Residues

Contact Us About Analytical Methods for Pesticides

Overview of EPA Pesticide Laboratories and Methods

EPA operates two pesticide laboratories that provide a variety of technical services to the Agency, other federal and state agencies, tribal groups and other organizations:

- Analytical Chemistry Laboratory
- Microbiology Laboratory

The labs assist EPA and state enforcement labs by:

- providing:
  - reference standards,
  - analytical methods development,
  - training,
  - assistance with laboratory audits; and
- developing analytical methods for risk assessment and enforcement projects;
- performing chemical and efficacy analyses when needed; and
- assisting in investigations of incidents such as crop damage or illegal pesticide residues.

Our laboratories develop methods and procedures to measure the effectiveness of hard surface disinfectants. They use testing methods to identify pesticides in food, feed, water, and soil. Pesticide residue amounts in a sample are measured, including any significant chemical metabolites and degradates (break-down products).

Pesticide manufacturers must develop environmental chemistry and residue analytical methods and provide them to EPA as a requirement of product registration.

Find methods:

- Antimicrobial testing methods and standard operating procedures
- Environmental chemistry methods test soil and water samples to determine the fate of pesticides in the environment.
- Residue analytical methods test samples of food, feed, and animal commodities. Residues may not exceed our maximum allowable limits (i.e., tolerances).

Application Note

Food Testing and Agriculture

Agilent

Trusted Answers

Quantitation of 764 Pesticide Residues in Tomato by LC/MS according to SANTE 11312/2021 Guidelines

Authors

Peter Kornas and Marcus Chadha

Agilent Technologies, Inc.

Abstract

A comprehensive, quantitative LC/MS/MS workflow was developed for the quantitation of 764 pesticide residues within a 20-minute LC runtime to accelerate and simplify routine laboratory food testing. Compound transitions and optimized parameters were developed based on the Agilent Pesticide Dynamic MRM Database, including curated parameters for fast and easy transfer into the analytical method. The workflow included sample preparation, chromatographic separation, mass spectrometry (MS) detection, and data analysis and interpretation. The workflow applicability was demonstrated using an Agilent 1290 Infinity II LC system coupled to an Agilent 6470 triple quadrupole LC/MS on tomato samples. For sample preparation, an Agilent QuEChERS extraction kit was used without further cleanup.

Workflow performance was evaluated and verified according to SANTE 11312/2021 based on instrument limit of detection (LOD), calibration curve linearity, recovery, and precision using matrix-matched calibration standards from 0.5 to 100 µg/L. Over 98% of analytes demonstrated linearity with $R^2 \geq 0.99$, with calibration curves plotted from 0.5 to 50 or 100 µg/L. Method precision was assessed using recovery repeatability (RSD_r). At 10 µg/kg level, RSD_r values of 96% of compounds were within the limit of 20%. The mean recoveries of the six technical replicates were within the limits of 40 to 120% for 95% of target analytes.

LC MS ANALYSIS OF PESTICIDES – EXAMPLES OF EXISTING METHODS

Application Note

Agilent
Trusted Answers

High-Throughput Pesticide Residue Analysis Using an Agilent Ultivo Triple Quadrupole LC/MS and the MassHunter Productivity App

Authors

Mahsan Miladi,
Dan-Hui Dorothy Yang,
Tanner Stevenson, and
Dan Smith

Abstract

There are >1,000 pesticides used globally, and food safety laboratories are under pressure to widen the scope of their analytical methods for routine pesticide monitoring. As a result, method development and data analysis have become a time-consuming and labor-intensive task for analytical laboratories. To address this growing issue, Agilent has developed the MassHunter Productivity App, which streamlines routine, high-throughput quantitation workflows in food testing laboratories. This Application Note demonstrates the capabilities of the software for multiresidue screening of 254 pesticides in two matrices, using the Agilent Ultivo triple quadrupole LC/MS.

Waters™

Application Note

Detection of Anionic Polar Pesticides in Food Samples Using the Xevo™ TQ Absolute With Sub µg/kg Limits of Quantification

Stuart Adams, Gitte Barknowitz, Kari L. Organtini

Waters Corporation

This is an Application Brief and does not contain a detailed Experimental section.

Abstract

The area of anionic polar pesticide analysis has been evolving over the past ten years where the adoption of generic extraction methods, such as the QuPPe method, have enabled laboratories to take a multi-residue approach for the analysis of these challenging analytes. With the enhanced negative ion sensitivity of the Xevo TQ Absolute Tandem Quadrupole Mass Spectrometer, limits of quantification of 0.5 µg/kg in vegetable samples and 2 µg/kg in cereal samples are achievable. Trueness was assessed over ten injections at 1 and 10 µg/kg in cucumber matrix standards and at 10 and 50 µg/kg in wheat flour matrix standards. Trueness in cucumber was between 91 to 117% with RSDs between 0.6 to 8.7% and between 96 to 104% in wheat flour with RSDs between 0.5 to 9.2%.

LC MS ANALYSIS OF PESTICIDES – EXAMPLES OF EXISTING METHODS

Waters™

Application Note

Evaluation of the Performance of a Method for the Determination of Highly Polar, Anionic Pesticides in Foodstuffs Using LC-MS/MS

Simon Hird, Stuart Adams, Janitha De-Alwis

Waters Corporation

This is an Application Brief and does not contain a detailed Experimental section.

Abstract

Waters previously developed a LC-MS/MS method for the determination of anionic polar pesticides in various food commodities. The method is based upon extraction with the established Quick Polar Pesticides method (QuPPe) from the EURL for Single Residue Methods (SRM) in Stuttgart and LC-MS/MS using the Anionic Polar Pesticide Column. This application brief shows the evaluation of the performance of this method in a selection of food commodities using an ACQUITY UPLC H-Class PLUS System and Xevo TQ-S micro Tandem Quadrupole Mass Spectrometer. Samples representing four different commodity groups (cucumber, rice, soyabean, and milk)

Highly sensitive quantification and selective identification of pesticides in food with Zeno MRM^{HR}

Using the SCIEX ZenoTOF 7600 system, powered by SCIEX OS software

Robert A. Di Lorenzo[1], Lukasz Rajski[2], Jianru Stahl-Zeng[3], Jason Causon[1]
[1]SCIEX, Canada; [2]EURL-FV, Universidad de Almeria, Spain; [3]SCIEX, Germany

Abstract

Using the sensitivity enhancements of the Zeno trap, Zeno MRM^{HR} is used to quantify low levels of pesticides in oilve oil and various fruits and vegetables to meet global regulations for pesticide residues. Over the mass range analyzed, the Zeno trap allowed for signal gains of 5-15x, with negligible increase in noise due to the selectivity of MRM^{HR} analysis, hence gains were directly related to improved LLOQs. The selectivity and specificity afforeded by the accurate mass MS/MS quantitation on the ZenoTOF 7600 system allowed for highly confident identifications of pesitcdes in real food samples (MS and MS/MS mass accuracy, library matching, isotope ratio matching), while still maintaining triple quad-like ability to perfom ion ratios for confirmations.

LC MS ANALYSIS OF PESTICIDES – EXAMPLES OF EXISTING METHODS

Precise testing of pesticides in food using the SCIEX Triple Quad™ 7500 LC-MS/MS System – QTRAP® Ready

Highly sensitive analysis of multi-compound panels in various matrices for food regulations

Jianru Stahl-Zeng[1], Ian Moore[2], Thomas Biesenthal[2], Jack Steed[3], Wim Broer[4]
[1]SCIEX, Germany; [2]SCIEX, Canada; [3] SCIEX, UK, [4]Nofagroup, The Netherlands

Abstract

The SCIEX Triple Quad 7500 LC-MS/MS System - QTRAP Ready provides impressive levels of sensitivity, robustness and accuracy for trace level analysis of pesticide residues in food matrices. Here, over 1400 MRM transitions for 700 compounds were analyzed in a single analysis achieving quantification limits of 0.2 ng/mL for the majority of the pesticides tested.

Introduction

The intensive use of pesticides in agriculture has led to the need for rigorous and extensive use of analytical technologies to ensure that there is no impact on human populations. Depending on the class of compounds, this has been primarily achieved through LC-MS/MS. Maximum residue limits (MRL) are set for regulated residues that define the highest level of a pesticide residue that is legally tolerated in food such that it is safe for consumers. Often these MRLs are set very low for some pesticides, to ensure highest safety, requiring very sensitive instrumentation to accurately quantify these compounds down to their MRL. Therefore LC-MS/MS solutions must be robust and sensitive to meet the needs of food testing labs.

Quantitative and Qualitative Confirmation of Pesticides in Beet Extract Using a Hybrid Quadrupole-Orbitrap Mass Spectrometer

Charles Yang and Dipankar Ghosh, Thermo Fisher Scientific, San Jose, CA
Olaf Scheibner, Thermo Fisher Scientific, Bremen, Germany

Application Note 617

Key Words
Q Exactive Focus, Orbitrap, pesticides, high resolution, accurate mass, quantitation, target screening, unknown screening, retrospective data analysis

Goal
To describe a method for the analysis of pesticides, showing the utility of a full-scan data-dependent MS/MS workflow to achieve regulatory levels while providing a complete targeted and screening analysis using a high-resolution, accurate mass (HRAM) spectral library for identification and confirmation.

Here, a method utilizing the Thermo Scientific™ Q Exactive™ Focus hybrid quadrupole-Orbitrap™ mass spectrometer is described. It consists of a generic chromatographic method and a full-scan data-dependent