Pesticide Analysis Guide

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The U.S. Environmental Protection Agency (USEPA) definition of a pesticide is "any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest". Pests are defined as "living organisms that occur where they are not wanted or that cause damage to crops or humans or other animals." Insects, mice and animals, unwanted plants, fungi and microorganisms are cited as examples.[1]

The USEPA recognizes four classes of chemical pesticides; organophosphorus, organochlorine, carbamate, and pyrethroid pesticides.[2]

Organophosphorus pesticides irreversibly inactivate the neurotransmitter enzyme aceytlcholinesterase. Organophosphorus pesticides degrade upon exposure to sunlight and air. Commonly used organophosphorus pesticides include; Parathion, Malathion, Chlorpyrifos, and Diazinon.

Organochlorine pesticides act by interfering with ion channel receptors in insect neurons. Commonly used organochlorine pesticides include; Heptachlor, Chlordane, Endosulfan, and Mirex.

Carbamate pesticides are N-substituted esters of carbamic acid. Carbamates are employed as insecticides, herbicides, and fungicides. Commonly used carbamate pesticides include; Aldicarb, Carbaryl, Carbofuran, Methiocarb, and Methomyl.

Pyrethroid pesticides are synthetic analogs of natural pyrethrins from chrysanthemum flowers. Permethrin and Fenvalerate are common pyrethroid pesticides.






Pesticide Analysis Methods

An extensive list of pesticide analysis methods have been issued by the United States Environmental Protection Agency (USEPA), the European Community (EC), United States Department of Agriculture (USDA), Association of Official Analytical Chemists (AOAC), United States Food & Drug Administration (USFDA), and the World Health Organization (WHO). [3,4]

Some representative gas chromatography methods include:

USEPA Method 8141B –Organophosphorus Compounds by Gas Chromatography

This method is used for analyzing organophosphorus pesticides in aqueous and solid samples.

USEPA Method 1618: Organo-halide Pesticides, Organo-phosphorus Pesticides, and Phenoxy-acid Herbicides by Gas Chromatography with Selective Detectors

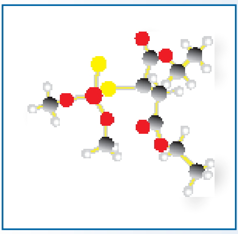
This method is used to test for pesticide residues in water, soil, sediment, and sludge samples. Organo-halide compounds, including derivatized phenoxy-acid herbicides, are detected using an electron capture detector, or an electrolytic conductivity detector. Organo-phosphorus pesticides are detected using a flame photometric detector.

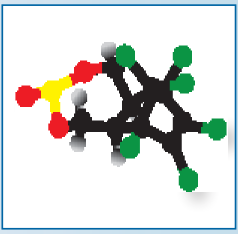
EN 12393:1998, Parts 1,2,3

This European norm covers methods for extraction, clean-up, and gas chromatographic determination of pesticide residues in non-fatty foods.

California Department of Food and Agriculture Multi-Residue Method

This method is used to screen fruits and vegetables for pesticide residues. A number of techniques are employed depending upon the chemical structures of the target pesticides. Instrumentation used includes; GC-electrolytic conductivity detector (ELCD), GC-halogen specific detector (XSD), GC-flame photometric detector (FPD), liquid chromatography with pre- or post-column derivatization and fluorescence detection, and LC-mass spectrometry (MS or MS-MS).





Pesticide Analysis Methods

Florida Department of Agriculture Multi-Residue Method
This method is for analyzing residues of all major classes (organophosphate, organochlorine, pyrethroids, carbamates, triazines,etc.) of pesticides on fruits and vegetables. Techniques employed for analysis include; GC-halogen specific detector (XSD), GC-flame photometric detector (FPD), GC-mass selective detector (MSD), GC-mass spectrometer (MS) ion trap, and LC-tandem mass spectrometer (MS-MS).

QuEChERS Multi-Residue Method
The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method was developed by the USDA Eastern Regional Research Center in Pennsylvania for screening fruits and vegetables for pesticide residues. Following solvent extraction and solid phase extraction (SPE) cleanup steps, analysis is performed by several techniques. Instrumentation used includes; GC-halogen specific detector (XSD), GC-pulsed flame photometric detector, GC-mass spectrometry (MS or MS-MS), LC with pre- or post- column derivatization, and LC-mass spectrometry (MS or MS-MS).

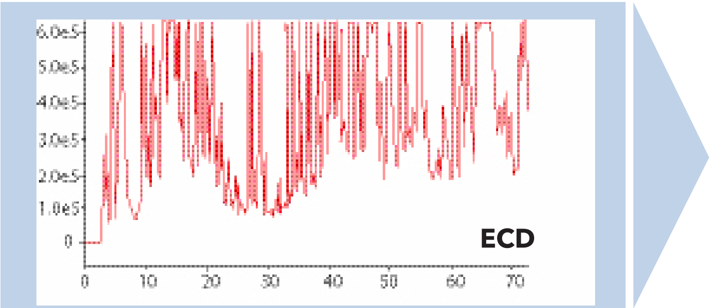
USDA Pesticide Data Program Method for Pesticide Residue Testing in Dairy Products
This method is applicable to the analysis of pesticide residues in milk, cream, and butter. Techniques employed for analysis include; GC-pulsed flame photometric detector (PFPD), GC-electron capture detector (ECD), GC-mass spectrometry, and LC-post column derivatization/fluorescence detection.

USEPA Method 3640A – Gel Permeation Cleanup
This method removes lipids, pigments, natural resins and polymers, cellular components, proteins, and high molecular weight compounds from sample extracts. Both polar and nonpolar compounds can be isolated and recovered for analysis. The method is applicable to organophosphate and organochlorine pesticides, herbicides, phthalates, and other endocrine disrupting chemicals (EDCs).

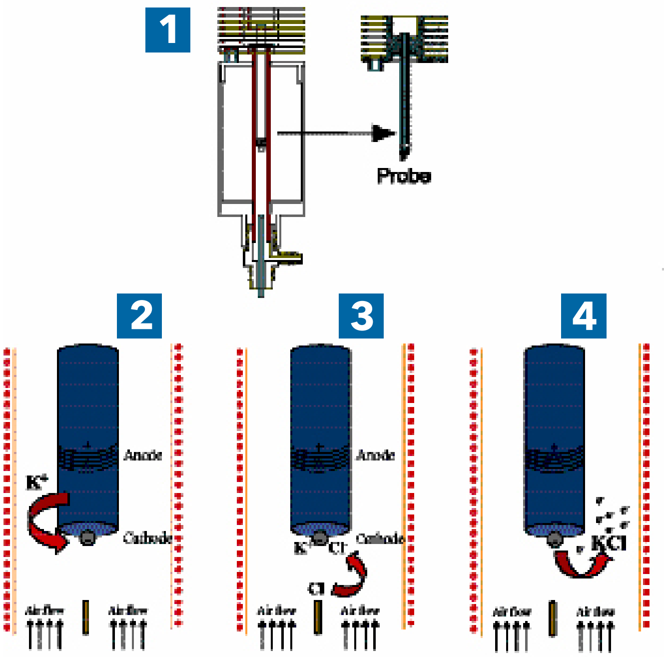
Selective GC Detectors

XSD™ – Halogen Specific Detector

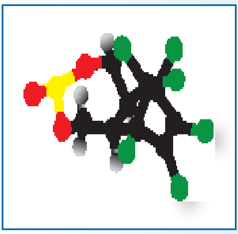
The XSD halogen specific detector is designed for selective detection of halogenated compounds eluting from a capillary gas chromatography column in the sub-picogram to microgram range. While the XSD is not quite as sensitive as an electron capture detector it exhibits virtually no response to matrix interferences. The XSD is particularly effective in pesticide residue analysis because it responds to chlorinated pesticides but not to sulfur interferences.[5] Significantly greater selectivity is achieved, and less extensive sample preparation is required to remove interferences.

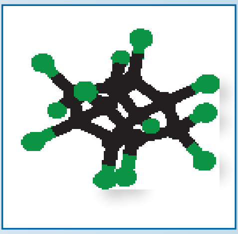


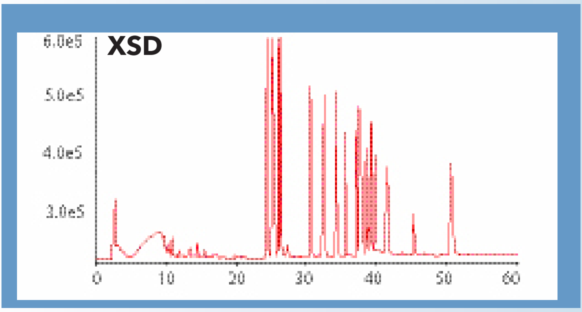
Chromatogram of Lemon Oil spiked with chlorinated pesticides obtained by ECD – electron capture detector.



Selective GC Detectors







Chromatogram of Lemon Oil spiked with chlorinated pesticides obtained by XSD – halogen specific detector.

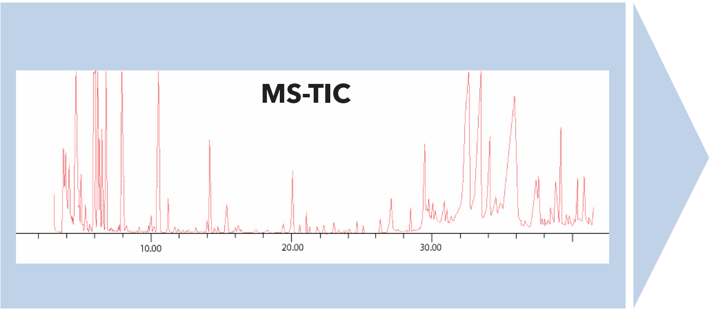
Principle of Operation

GC column effluent is mixed with air or oxygen and analytes undergo oxidative pyrolysis in the XSD reactor core, converting halogenated compounds to oxidation products and free halogen atoms (1). Within the reactor core is a ceramic probe with a platinum anode and cathode. The cathode is activated by alkali ions emitted from the anodic surface (2). Free chlorine atoms react with the monolayer of alkali ions on the cathode (3). The energy of this reaction raises the surface temperature of cathode causing increased thermionic emission of free electrons (4). Changes in the total cathodic current are measured by an electrometer and converted to a 0-1 V or 0-10 V output signal to a chromatographic data handling system.

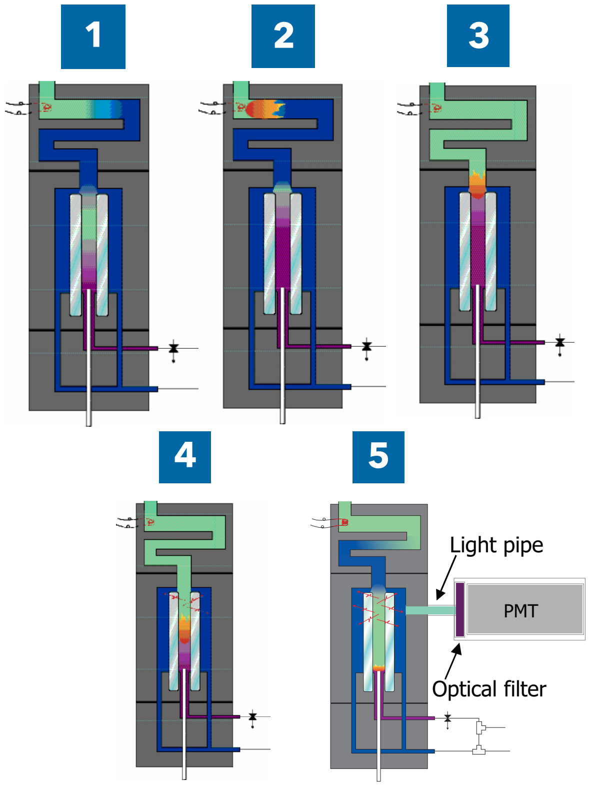
Selective GC Detectors

PFPD – Pulsed Flame Photometric Detector

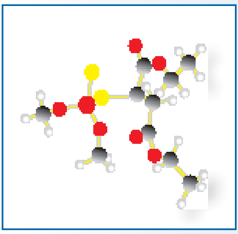
The PFPD pulsed flame photometric detector is designed for selective detection of sulfur and phosphorus compounds. The PFPD is regularly used for analyzing organophosphorus pesticides because it provides both excellent selectivity and extremely low detection limits.[6,7] The operating conditions of a PFPD can be optimized to selectively analyze for phosphorus and/or sulfur and eliminate matrix interferences from other heteroatoms.

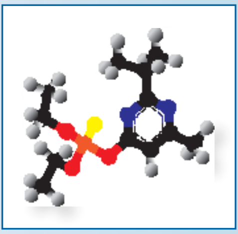


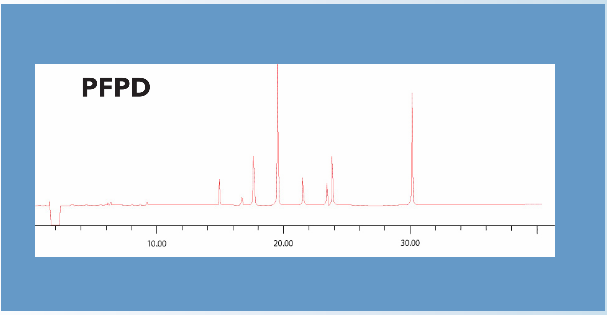
GC-MS total ion chromatogram (TIC) of Broccoli extract spiked with organophosphorus pesticides.



Selective GC Detectors







Chromatogram of Broccoli extract spiked with organophosphorus pesticides obtained by PFPD – pulsed flame photometric detector.

Principle of Operation

A combustible mixture of H_2 and air is introduced and fills the detector body and cap from the bottom up (1). The combustion mixture is ignited in the cap (2). The resulting flame propagates along the pathway consuming the H_2/air mixture (3). Compounds eluting from the GC column are combusted within a quartz combustor and emit light at element-specific wavelengths (4). The flame is extinguished when it reaches the bottom of the detector and excited species continue to fluoresce for up to 25 milliseconds. Emissions from the excited species pass along a light pipe and selected emissions are transmitted through an optical filter to a photomultiplier tube for detection (5). The entire pulsed flame cycle is repeated approximately 3 to 4 times per second.

Selective Detectors & GC-MS

Gas chromatography coupled with mass spectrometry (GC-MS) is the preferred technique for pesticide residue analysis. Nevertheless there are significant advantages to employing a selective GC detector in tandem with a MS detector.

Extracts of food and environmental samples frequently contain complex mixtures of organic components that were co-extracted along with pesticide residues. These co-extracted matrix interferences can make identification and confirmation of pesticide residues difficult. Selective detectors such as the PFPD and XSD facilitate pesticide identification when used in conjunction with a mass spectrometer.

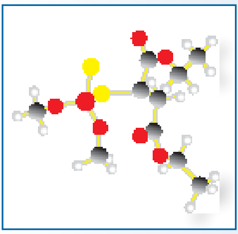
The GC-MS total ion chromatogram of an oregano extract spiked with organophosphorus pesticides is an example of a sample where the presence of co-extracted organic components hinders detection of pesticides.

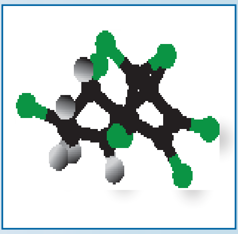
A simultaneous phosphorus mode PFPD chromatogram of the oregano extract is able to pinpoint the organophosphorus pesticides that are present in the extract.

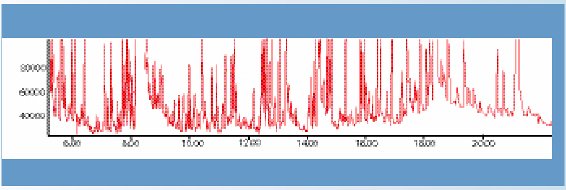
A poor MS library match for the organopshosphorus pesticides present in the oregano extract is obtained without simultaneous pulsed flame photometric detection. Selective GC detectors provide precise retention time marking for improved MS library matching and identification of pesticide residues.

Selective GC detectors also allow detection of unexpected pesticides or other residues that may not be on a normal screening list.

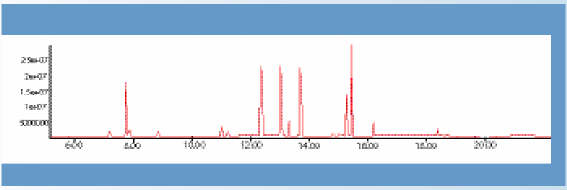
Selective Detectors & GC-MS Systems



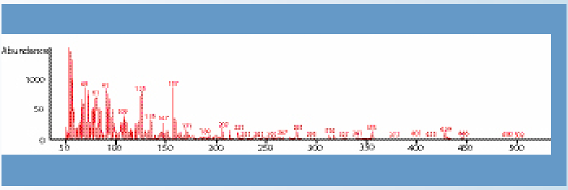




GC-MS total ion chromatogram of an Oregano extract spiked with organophosphorus pesticides.



Simultaneous phosphorus mode PFPD chromatogram of Oregano extract spiked with organophosphorus pesticides.



Poor library match of organophosphorus pesticides due to matrix interferences.

GPC Sample Cleanup

The use of Gel Permeation Chromatography (GPC) for cleanup of crude extracts prior to pesticide residue analysis was pioneered in 1972 by Dr. David Stalling, Chief Chemist at the U.S. Department of Interior's Fish-Pesticide Research Center.

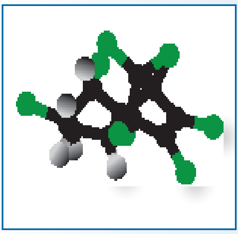
GPC is a size exclusion cleanup technique employing organic solvents and hydrophobic gels to remove co-extracted high and medium molecular weight organic components such as lipids, pigments, and proteins from crude extracts. GPC allows pesticide residues to be isolated and concentrated for high sensitivity measurement by GC or GC/MS.[8, 9, 10, 11]

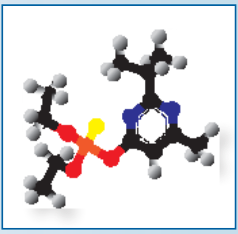
The presence of co-extracted organic components in samples interferes with GC inlet systems, and can cause increased GC/MS downtime or a high measurement bias in some detectors (GC-ECD). The cleaner sample extracts obtained by GPC help analysts achieve improved analytical results and avoid problems arising from continual introduction of excess matrix components into GC and GC/MS instruments.

OI Analytical offers a GPC Sample Cleanup System and a selection of GPC columns to support laboratories performing pesticide residue analysis.

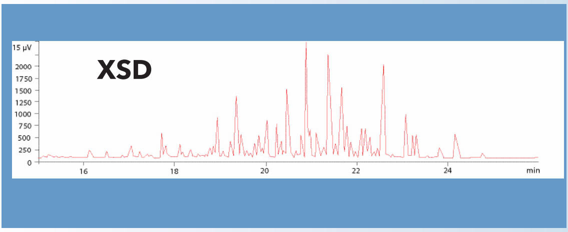
The SP 2000 GPC system is a compact, manually operated instrument for laboratories cleaning up and analyzing a limited numbers of samples. The system consists of an isocratic HPLC pump, sample injector, switching valve, and control module.

GPC Sample Cleanup

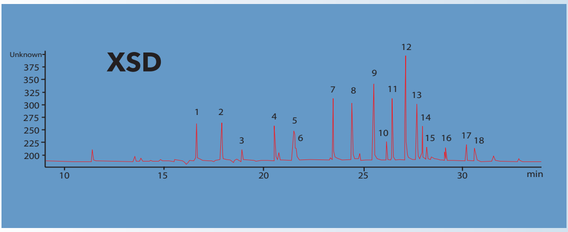




SP 2000 GPC Sample Cleanup System



Chromatogram of a Fish sample extract, obtained by XSD – halogen specific detector following GPC sample cleanup, that tested positive for Aroclor 1016 and 1260.



Chromatogram of a Black Pepper extract fortified with 1 ppm of 18 organochlorine pesticides, obtained by XSD – halogen specific detector following GPC sample cleanup. Interferences from essential oils and lipids were eliminated by GPC. The capsaicin component was detected in the extract but did not interfere with pesticide detection using the XSD.

References & Links

References

[1]Pesticides in the Nations' Streams and Ground Water, 1992-2001, U.S. Geological Survey, Circular 1291, 2006

[2] Types of Pesticides; http://www.epa.gov/pesticides/about/types.htm

[3] Pesticide Analytical Manual, Volume 1, U.S. Food and Drug Administration, 2002

[4]FAO/WHO Food Standards, Codex Alimentarius, Analysis of Pesticide Residues: Recommended Methods, CODEX Standard 229-1993, Rev. 1-2003

[5]Fipronil Analysis by GC/XSD following Post-Extraction Gel Permeation Chromatography Cleanup, OI Analytical Application Note # 25570306

[6]Using the Pulsed Flame Photometric Detector for Low-Level Analysis of Organophosphorus Pesticides, OI Analytical Application Note # 25390206

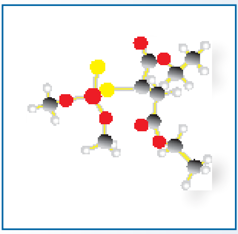
[7]Selective and Sensitive Analysis of Organophosphorus Pesticides in Baby Food Using an Inexpensive GC Detector, OI Analytical Application Note # 37841111

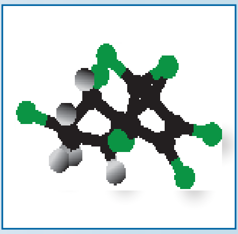
[8]Automated Gel Permeation Chromatographic Preparation of Vegetables, Fruits, and Crops for Organophosphate Residue Determination Using Flame Photometric Detection, J.A. Ault, et al., J. Agric. Food Chem., Vol. 27, No. 4, 1979

[9]Clean-up of Baby Food Samples Using Gel Permeation Chromatography, OI Analytical Application Note # 36790111

[10]GPC Cleanup of Black Pepper Prior to Analysis for Organochlorine (OC) Pesticides by GC/XSD, OI Analytical Application Note # 225850407

[11]Using the GPC AutoPrep 2000 System for Cleanup of Olive Oil Prior to Pesticides Analysis by GC/XSD or GC/PFPD, OI Analytical Application Note # 20540204





References & Links

Links

Association of Official Analytical Chemists (AOAC); www.aoac.org

Association of American Pesticide Control Officials (AAPCO); www.aapco.org

Pesticide Properties Database; www.ars.usda.gov/services

Pesticide Data Program (Analytical Methods); www.ams.usda.gov/science/pdp/Methods.htm

Compendium of Pesticide Common Names; www.alanwood.net/pesticides

Environmental Resource Associates; www.eraqc.com

USEPA Index of Residue Analytical Methods (RAM); www.epa.gov/opp00001/methods/ram12b.htm

Pesticides Safety Directorate; http://www.pesticides.gov.uk

FAO/WHO Food Standards, Codex Alimentarius; http://www.codexalimentarius.net

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