Pesticides in My Beverage—Screening (and Subsequent Quantification) of Pesticides in Beverages Originating from Leaves, Grapes, Grasses, and the Hydrologic Cycle (Tea, Wine, Milk, and Water) Using Automated SPE

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Overview

Purpose: To demonstrate that automated solid-phase extraction (SPE) is an efficient technique for concentrating pesticide residues from beverages and other aqueous samples.

Methods: The Thermo Scientific™ Dionex™ AutoTrace™ 280 Solid-Phase Extraction (SPE) instrument was used for sample pre-treatment, and analysis was performed using gas chromatography (GC) with electron-capture detection (ECD).

Results: Automated SPE using the Dionex AutoTrace 280 cartridge or disk system extracts pesticide residues from large volume beverage samples for analysis with high efficiency, reproducibility, and recovery rate.

Introduction

Pesticides are used on agricultural commodities, animal feeds, and fruits (wine grapes, apples, oranges, etc.) to protect against insects, fungi, molds, and other agents.

Use of pesticides is regulated by the following legislation:

- United Nations Food and Agriculture Organization (FAO) adopted an International Code of Conduct on the Distribution and Use of Pesticides in 1985.
- U.S. EPA regulates pesticides under Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and Food Quality Protection Act (FQPA).
- European Union has published the Thematic Strategy on the Sustainable Use of Pesticides.

Public concern over pesticide residues in food and beverages has been increasing such that it has become a significant food safety issue. For example:

- An Albert Einstein College of Medicine (New York, NY) study suggests pesticides in drinking water are linked to food allergy risks.[1]
- A United Kingdom study found that pesticides in fruit-based soft drinks are 300 times higher than those in tap water.[2]

U.S. EPA Methods for Pesticide Testing:

- **EPA Method 505:** Organohalide Pesticides and Commercial Polychlorinated Biphenyl (PCB) Products in Water
- **EPA Method 507:** Nitrogen- and Phosphorus-Containing Pesticides in Water
- **EPA Method 508:** Chlorinated Pesticides in Drinking Water
- **EPA Method 527:** Selected Pesticides and Flame Retardants in Drinking Water
- **EPA Method 553:** Benzidines and Nitrogen-Containing Pesticides in water
- **EPA Method 608:** Organochlorine Pesticides and PCBs in wastewater
- **EPA Method 614:** Organophosphorus Pesticides in Municipal and Industrial Wastewater
- **EPA Method 619:** Triazine Pesticides in Municipal and Industrial Wastewater
- **EPA Method 622:** Organophosphorus Pesticides in Municipal and Industrial Wastewater
- **EPA Method 1618:** Organo-Halide, -Phosphorus Pesticides, and Phenoxy-acid Herbicides
- **EPA Method 1699:** Pesticides in Water, Soil, Sediment, Biosolids, and Tissue
- **EPA Method 8081A:** Organochlorine Pesticides in Water
- **EPA Method 8141B:** Organophosphorus (OPs) Pesticides in Water

Methods

Sample extraction equipments for U.S. EPA Method 508

- Dionex AutoTrace 280 SPE instrument
  - 6 mL cartridge system
  - 47 mm disk system
- Thermo Scientific™ Dionex™ SolEx™ SPE Cartridges, 6 mL C-18
- 3M Empore™ SPE Disks, 47 mm, C18
- Deionized (DI) water, Type 1 reagent trade, 18 MΩ-cm
- Collection Vials, 60 mL
- Nitrogen Evaporator (or equivalent)
- Analytical Balance (read to the nearest 0.001 g or better)

FIGURE 1. Dionex AutoTrace 280 SPE instrument cartridge system (left) and disk system (right).

Overview of Dionex AutoTrace 280 Instrument

- Automates sample preparation for liquid samples using SPE
- Processes one to six samples
  - Sample volumes of 20 mL to 20 L
- Uses normal or reverse-phase cartridges and disks
- Accepts 1, 3 and 6 mL cartridges or 47 mm disks
- Saves time and reduces costs
- Automatically loads and elutes SPE cartridges/disks
  - Unattended operation
- Uses positive pressure to load and elute samples
  - Provides constant, reproducible flow of liquids
  - Independently controls flow for each channel
  - No hood is required—closed system with fan to vent solvent vapors

Sample Pretreatment

1. Add 50 mg sodium sulfite to 1 L of sample.
2. Add organochlorine pesticide Mix AB # 3, Restek®.
3. Adjust water to pH 2 with HCl.

Condition Rinse and Load Program:

1. Condition cartridge with 5 mL ethyl acetate into solvent waste.
2. Condition cartridge with 5 mL dichloromethane into solvent waste.
3. Condition cartridge with 10 mL methanol into solvent waste.
4. Condition column with 10 mL of DI water (pH 2) into aqueous waste.
5. Load 1200 mL of sample onto column.
6. Dry column with gas for 5 min.

Sample Elution Program:

1. Manually rinse sample container with 20 mL ethyl acetate to collect
2. Manually rinse sample container with 20 mL dichloromethane to collect
3. Collect 5 mL of fraction into a second sample tube using ethyl acetate
4. Collect 5 mL of fraction into a second sample tube using dichloromethane

Dry extracts using a solvent-rinse drying column. Concentrate each extract to 1 mL for GC/ECD analysis.

Analysis of Extracts

GC with ECD was used to separate and identify chlorinated pesticides with the Restek Rtx-PCB fused silica column.

GC-ECD Conditions	
Column	PCB Column 40 mm × 0.18 mm i.d. x 0.18 µm
Injection Port Temperature	250 °C
Flow Rate:	1.5 (mL/min) constant flow
Injection Volume	1 µL
Makeup Gas	Nitrogen
Oven Temperature	100 °C (hold for 1 min) to 200 °C at 30 °C/min to 320 °C at 2 °C/min (hold for 2 min)

Results

Sample Extraction Issues

- Sample handling is the primary source of errors
- Sample extraction causes the biggest bottleneck for most analysis methods
- Costs are increasing for solvent purchase and disposal
- The data is only as good as the sample preparation:
  - High-price chromatography and data systems do not improve the quality of data from poorly-prepared samples
- The Dionex AutoTrace 280 Automated SPE Instrument was designed to address these issues.

Why Use Automated SPE?

- Compatible with U.S. EPA-approved clean water and groundwater methods
- Replaces tedious manual liquid-liquid extraction (LLE)
- Automates all four steps of SPE
- Runs unattended
- Removes sample interferences
- Isolates and concentrates analytes from liquid matrix
- Reduces solvent consumption
- Reduces exposure to solvents
- Increases productivity
  - Chemists or technicians can load six samples using only 15 minutes of their time.
  - 6 samples completed and ready for injection onto GC or LC in just 2-3 hours.

Analysis Result of Chlorinated Pesticides

Both automated and manual extraction showed good recovery of all analytes.

TABLE 1. Extraction of pesticides (50 ppb) from water samples.

Pesticide (50 ppb)	Automated SPE % RSD (n = 6)	LLE % RSD (n = 3)	SPE/LLE % Recovery
Alpha-BHC	13	13	113
Gamma-BHC	12	12	135
Beta-BHC	11	11	113
Heptachlor	12	13	64
Delta-BHN	12	12	128
Aldrin	13	11	134
Heptachlor Epoxide	11	13	102
Cis-Chlordane	12	11	138
Endosulfan	11	12	99
4,4'-DDE	12	12	135
Dieldrin	12	10	107
Trans-Chlordane	11	13	134
Endrin	13	11	125
4,4'-DDD	11	15	115
Endosulfate II	12	16	134
4,4'-DDT	11	11	135
Endrin Aldehyde	10	11	94
Endosulfan Sulfate	16	23	131
Methoxychlor	9	15	143
Endrin Ketone	10	26	138

The Dionex AutoTrace 280 SPE instrument saves more than 60% in both time and solvent consumption:

- Dionex AutoTrace 280 can obtain quantitative recovery of target pesticide compounds at ppb levels.
- Automated SPE instruments have the advantages of minimizing operator interaction, saving time, and reducing solvent consumption
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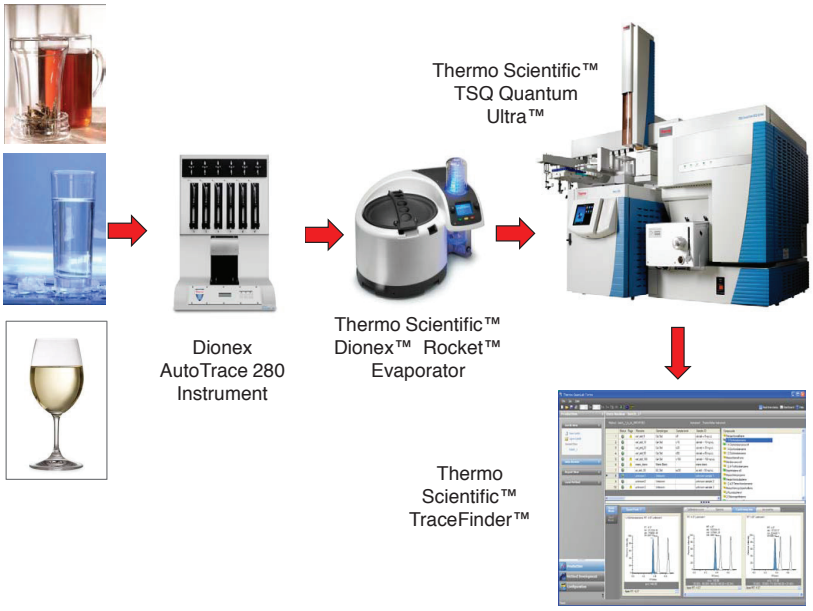
FIGURE 2. The Thermo Scientific Total Workflow Solutions (Sample Preparation, Evaporation, Analysis, and Data Management).



Conclusion

Extraction of pesticides from drinking water and beverage samples can be made easier and faster by using the Dionex AutoTrace 280 SPE instrument. The data shows that the Dionex AutoTrace 280 system can automatically extract pesticide residues among other contaminants from aqueous samples with high efficiency and recovery.

The Dionex AutoTrace 280 instrument can help reduce sample extraction cost by reducing solvent consumption and labor cost, as well as minimizing exposure to hazardous solvents. With this improved productivity, chemists can load six samples, which are then extracted automatically. The samples are completed and ready. The Dionex AutoTrace 280 instrument provides improved analytical precision due to automated sample loading and elution using positive pressure.

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References

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