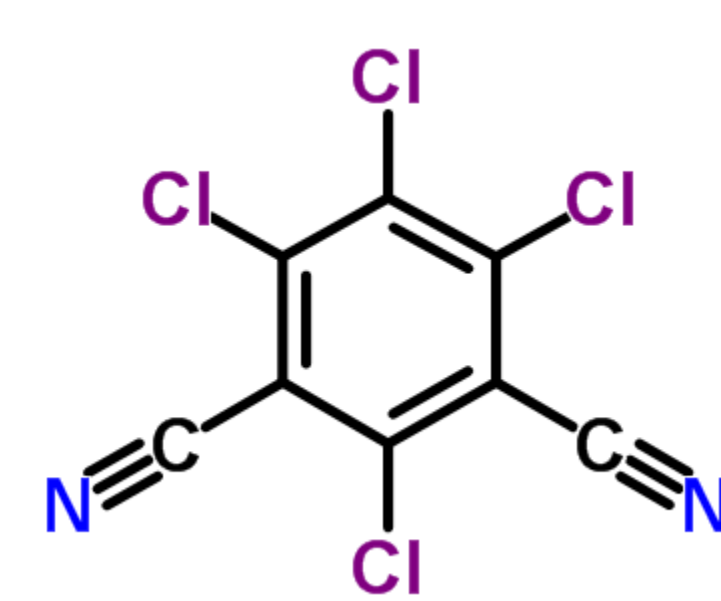


ABSTRACT

Fungicides are applied on turf grass in autumn, to control snow mold in the North-central United States. Fungicides of varying chemical classes have been detected in snow melt runoff from turf. A multi-residue method for simultaneous sample extraction and analysis is needed to process a large quantity of snow melt samples. A method was developed to simultaneously extract three fungicides, quintozene, iprodione, and chlorothalonil, in addition to its major degradation product 4-hydroxychlorothalonil. Water samples were spiked with these four compounds, plus the herbicide acetochlor as a surrogate, and then extracted using a C₁₈ solid phase extraction (SPE) cartridge. The extracts were divided by volume then analyzed by liquid chromatography-mass spectrometry (LC/MS) or gas chromatography-mass spectrometry (GC/MS). The herbicide metazachlor was used as the internal standard for GC/MS analysis of quintozene and chlorothalonil. The insecticide isofenphos was the internal standard for LC/MS analysis of 4-hydroxychlorothalonil and iprodione. The surrogate, acetochlor, was analyzed by both instruments.

CHEMICALS OF INTEREST



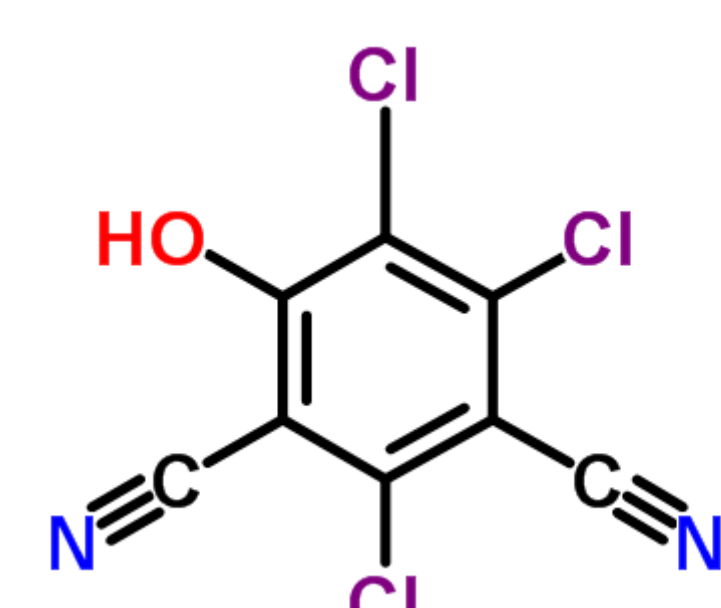
Fungicide: Chlorothalonil

Chemical class: chloronitrile

Molecular weight = 265.9 g mol⁻¹

Water solubility = 0.9 mg L⁻¹

K_{OW} logP = 2.89



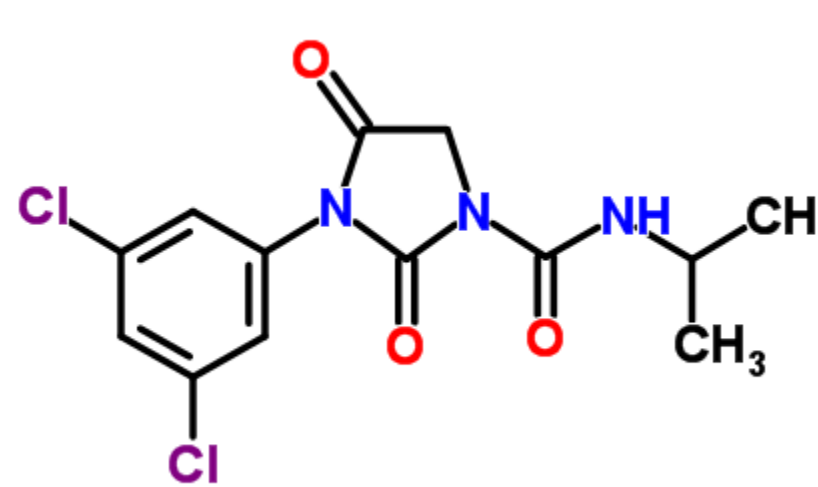
Metabolite: 4-Hydroxychlorothalonil

Chemical class: chloronitrile

Molecular weight = 247.5 g mol⁻¹

Water solubility = not found

K_{OW} logP = not found



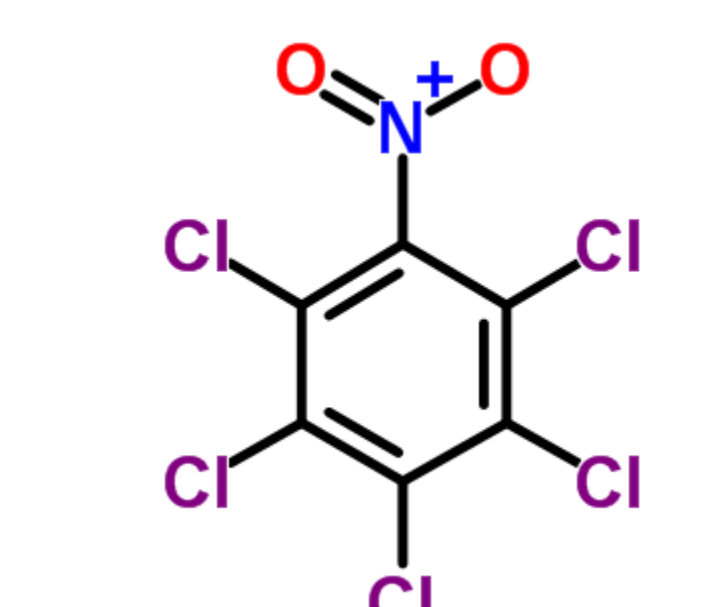
Fungicide: Iprodione

Chemical class: dicarboximide

Molecular weight = 330.2 g mol⁻¹

Water solubility = 13 mg L⁻¹

K_{OW} logP = 3.0



Fungicide: Quintozene

Chemical class: aromatic hydrocarbon derivative

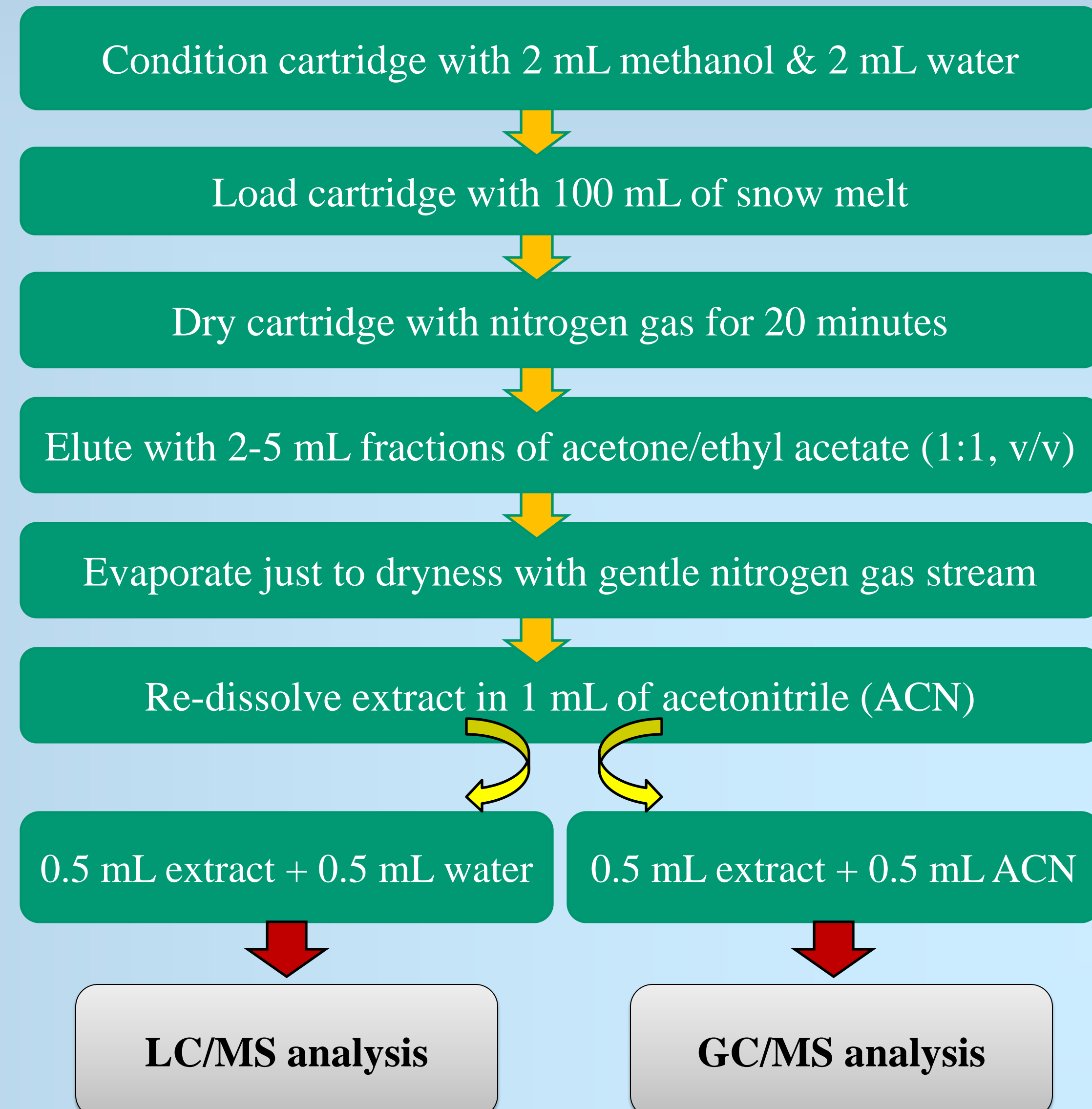
Molecular weight = 295.3 g mol⁻¹

Water solubility = 0.1 mg L⁻¹

K_{OW} logP = 5.1

SOLID PHASE EXTRACTION (SPE)

Fungicides were extracted from snow melt using Supleco Supelclean™ ENVI™-18, 6 mL, 0.5 g SPE cartridges.



LC/MS ANALYTICAL METHOD

LC column (at 40°C) Zorbax RX-C18
5 µm, 2.1 mm x 150 mm

Solvent A 0.1% Formic acid in water
Solvent B Acetonitrile

Injection volume 50 µL

Flow rate 0.20 mL min⁻¹

LC Solvent

0 min.	50 / 50
5 min	50 / 50
7 min	20 / 80
17 min	20 / 80
18 min	50 / 50
25 min	50 / 50

Mass spec conditions

Curtain gas: 30 psi; IS voltage: 4000 V;
Gas 1 & 2: 30 psi; ion source temperature: 500°C; dwell time: 200 ms.
Nominal matrix effects (e.g., signal enhancement or suppression) were observed.

Chemical name	MS ESI mode	Target Ions (m/z)
4-Hydroxychlorothalonil	negative	244.9, 246.9
Iprodione	positive	330.3, 332.3
Acetochlor	positive	226.3, 270.3
Metazachlor	positive	217.0, 287.2

GC/MS ANALYTICAL METHOD

GC column Agilent HP-5ms
30 m x 0.32 mm x 0.25 µm

Carrier gas UPCG Helium

Injection Splitless, 2 µL

Inlet liner Single taper, glass wool
Deactivated

GC Oven Temperature Program

40°C, hold 1 min; 10°C min⁻¹ to 250°C, hold 2 min;
50°C min⁻¹ to 300°C, hold 5 min, for 30 min total run time.

MS Target Ions

Chlorothalonil	m/z = 266; 268; 264
Quintozene	m/z = 295; 237; 142
Acetochlor	m/z = 223; 146
Metazachlor	m/z = 209; 132; 81

Mass spec conditions optimized by daily auto tune with PTFB.

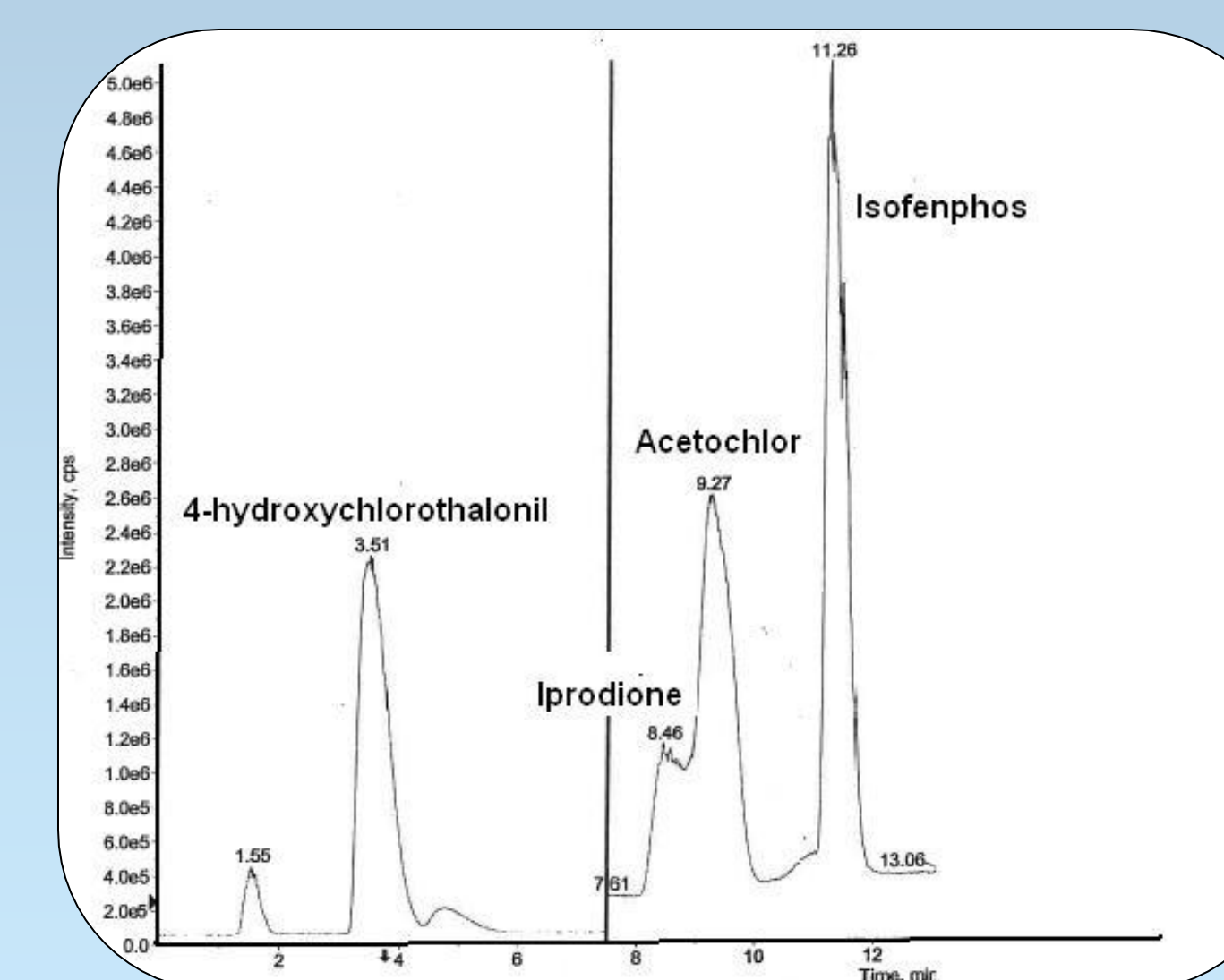
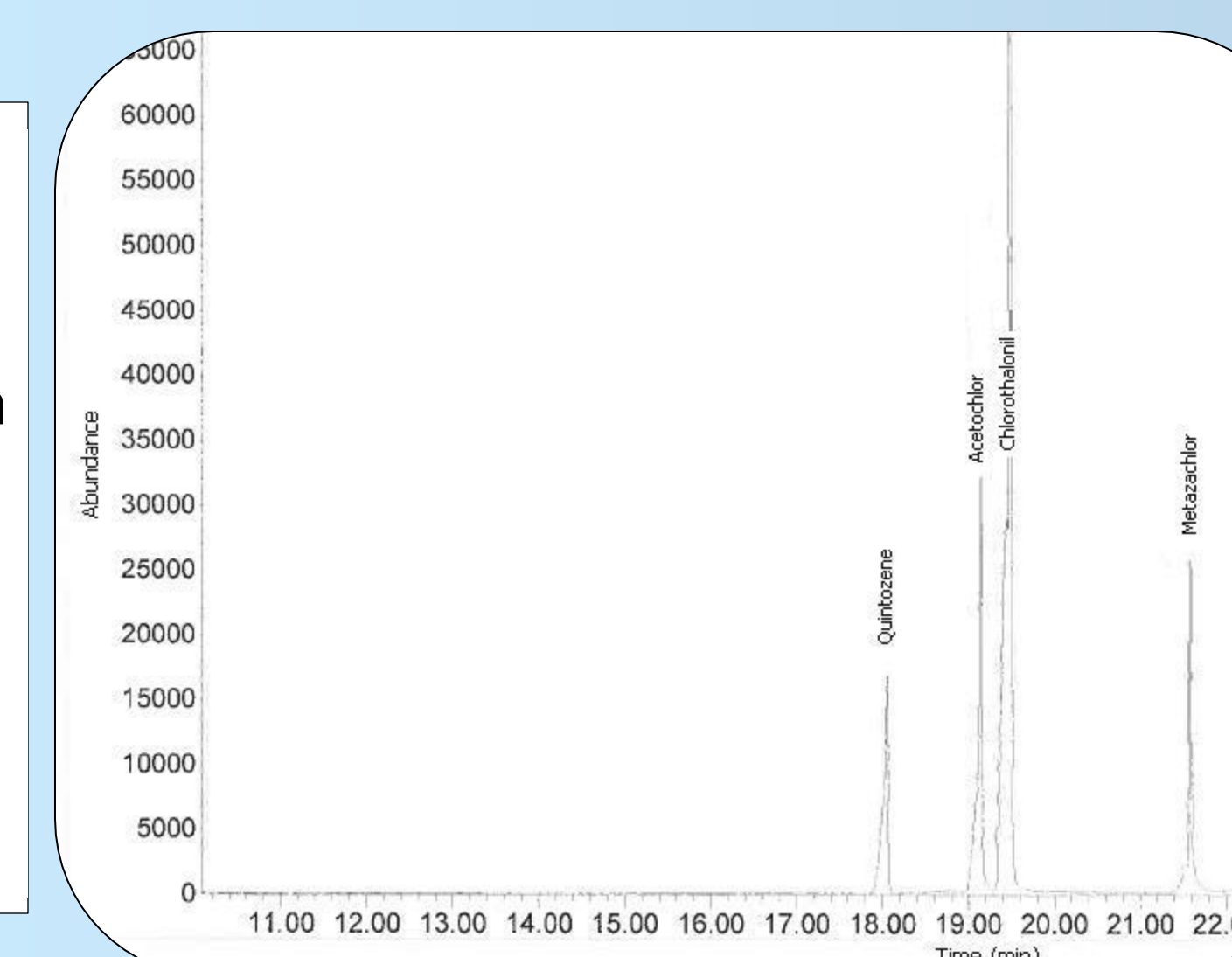


Fig. 1.
LC/MS Snow Melt Analysis

Example of LC/MS chromatogram retention times. Analysis of 4-hydroxychlorothalonil (3.51 min), Iprodione (8.46 min), Acetochlor (9.27 min), and Isofenphos (11.26 min). Total run time is 25 minutes.

Fig. 2.
GC/MS Snow Melt Analysis

Example of GC/MS chromatogram retention times. Analysis of Quintozene (18.02 min), Acetochlor (19.12 min), Chlorothalonil (19.46 min), and Metazachlor (21.59). Total run time is 30 minutes.



RESULTS

Chlorothalonil

- Analyzed by SPE-GC/MS
- Limit of detection is below 10 ppb
- Extraction recovery is 76 %

4-Hydroxychlorothalonil

- Analyzed by SPE-LC/MS
- Limit of detection is below 10 ppb
- Extraction recovery is 44 %

Iprodione

- Analyzed by SPE-LC/MS
- Limit of detection is below 25 ppb
- Extraction recovery is 94 %

Quintozene

- Analyzed by SPE-GC/MS
- Limit of detection is below 25 ppb
- Extraction recovery is 57 %

Acetochlor - surrogate

- Analyzed by SPE-GC/MS
 - Limit of detection is below 25 ppb
 - Extraction recovery is 95 %
- Analyzed by SPE-LC/MS
 - Limit of detection is below 25 ppb
 - Extraction recovery is 108 %

Metazachlor – GC/MS internal standard

- Analyzed by SPE-GC/MS
- Reproducibility within 10%

Isofenphos – LC/MS internal standard

- Analyzed by SPE-LC/MS
- Reproducibility within 1%

REFERENCES

- Chaves, A., D. Shea, and D. Danehower. 2008. Analysis of chlorothalonil and degradation products in soil and water by GC/MS and LC/MS. *Chemosphere* 71:629-638.
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- Tomlin, C. 1994. *The Pesticide Manual*. British Crop Protection Council, Surrey, UK and The Royal Society of Chemistry, Cambridge, UK.

For further information

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