Analysis of Chlordane by DUIS (Dual Electrospray/Atmospheric Pressure Chemical Ionization) Liquid Chromatography Mass Spectrometry

MP 268

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1. Introduction

The legalization of cannabis has led to many laboratories developing methods to meet local cannabis testing regulatory requirements. One of the challenging residual pesticides to quantitate is chlordane, an organochlorine compound used as a pesticide on crops until 1983 and for termite treatment in homes until 1988. Chlordane is highly persistent in the environment and has been linked to cancers. Gas chromatography mass spectrometry and atmospheric pressure chemical ionization (APCI) – liquid chromatography mass spectrometry (LCMS) methods were published for analysis of chlordane. However, for laboratories without APCI functionality or who prefer not to switch between two different ionization sources, chlordane remains a challenging target for LCMS analysis. This study demonstrates the successful quantitation of chlordane using additive-free DUIS electrospray ionization – LCMS at concentrations below the New York State testing limits.

2. Methods

Technical chlordane (CAS 57-74-9) was obtained from Restek, diluted in water, and analyzed on a Shimadzu LCMS-8060 triple quadrupole mass spectrometer equipped with a DUIS ionization source. The DUIS source was utilized in APCI mode. Technical chlordane is a mixture of *trans*-chlordane, *cis*-chlordane, and related chemicals. The LC parameters shown in Table 1 allowed separation of the *cis*- and *trans*-chlordane isomers.

Table 1. LC parameters.

Parameter	Value
Column	Shim-pack Scepter C18-120, 1.9 µm, 3.0 mm x 50mm
Mobile Phase A	LCMS Grade Water
Mobile Phase B	LCMS Grade Methanol
Flow Rate	0.3 mL/min
Elution Scheme	Isocratic elution at 92% B
Run Time	3.5 min

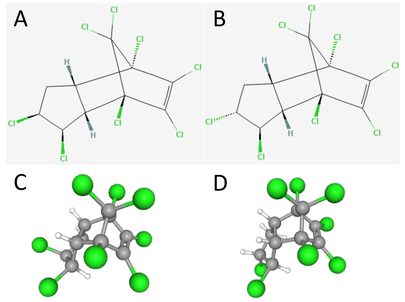

Figure 1. A) 2D Structure of *cis*-chlordane B) 2D structure of *trans*-chlordane C) Ball and stick model of *cis*-chlordane D) Ball and stick model of *trans*-chlordane

3. Results

Initial MS data was collected in Q1 and Q3 Scan mode. Due to the 8 chlorine atoms per chlordane molecule, a distribution of isomers is expected in the mass spectrum. LabSolutions Insight Explore was used to predict isotopic distributions for chlordane with and without adducts. The predicted spectra for the [M-H]- and [M+CH3OH]- are shown in Figure 1A and 1B, respectively. The experimentally observed isotopic distributions for the [M-H]- and [M+CH3OH]- ions are shown in Figure 1C and 1D, respectively. Figure 1E shows the relative intensity of the [M+CH3OH]- versus the [M-H]- isotope clusters. As the [M+CH3OH]- showed the greatest intensity, it was selected for optimization.

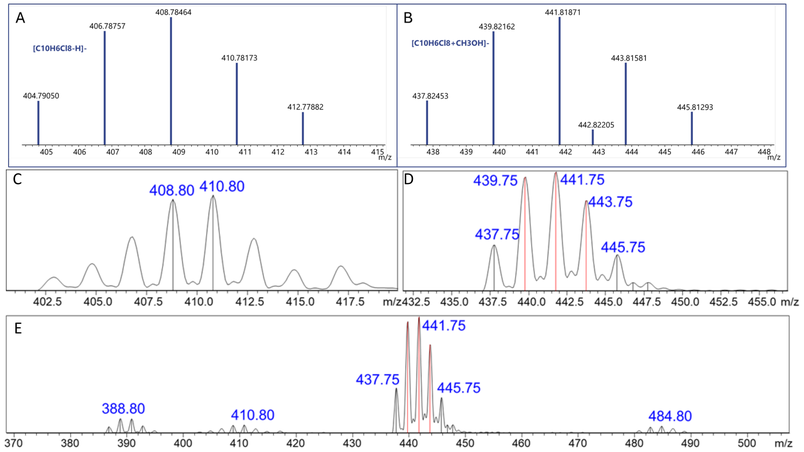

Figure 2. A) Isotopic distribution as predicted by LabSolutions Insight Explore for the negative mode molecular ion of chlordane. B) Isotopic distribution as predicted by LabSolutions Insight Explore for the negative mode chlordane with a methanol adduct. C) Experimentally observed isotopic distribution for the negative mode molecular ion of chlordane. D) Experimentally observed isotopic distribution for the negative mode chlordane with a methanol adduct. E) The chlordane with methanol adduct ion was observed with significantly higher intensity than the molecular ion.

Voltage optimization was performed for the 441.80 to 441.80 MRM with the CID gas turned off. Even after voltage optimization, the signal-to-noise from the primary species in the technical chlordane (in this case, *trans*-chlordane) was insufficient. Automated source optimization using LabSolutions MRM Connect was used to improve signal by optimizing Interface Temperature, Heating Gas Flow, Nebulizing Gas Flow, Drying Gas Flow, DL Temperature, Heat Block Temperature, and Interface Voltage. As a representative example, Figure 3 shows the impact of Interface Temperature on the MRM intensity for the 441.80 m/z.

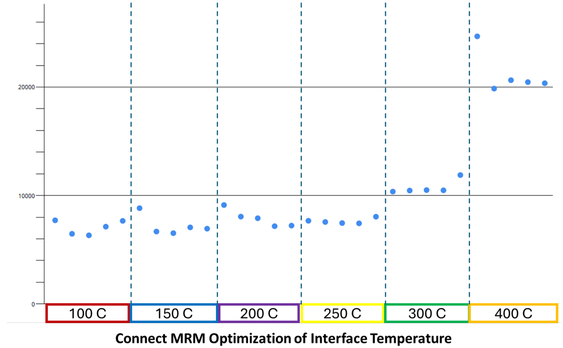

Figure 3. Connect MRM Data Browser display of Interface Temperature Optimization

Technical chlordane was diluted in LCMS grade water to 0.25, 0.5, 1, 10, and 100 ppm. Injections of each standard (2 µL) were repeated 5 times to give the calibration curve shown in Figure 4 below. Representative chromatograms at each concentration are shown in Figure 4. The retention time of the integrated peak is consistent with *trans*-chlordane, and the peak immediately following it at 2.35 min is consistent with *cis*-chlordane.

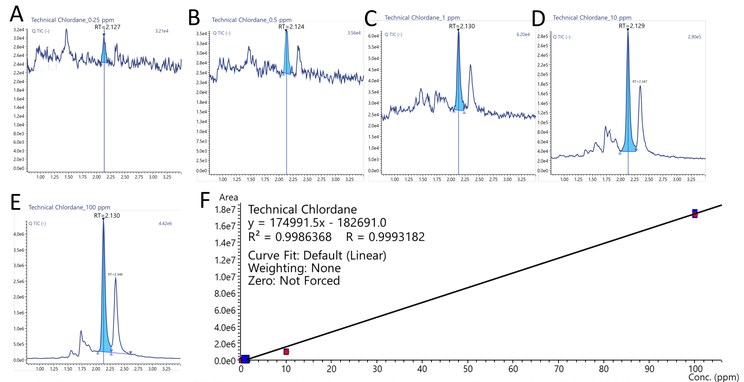

Figure 4. Representative TIC of technical chlordane monitored by Q3 SIM for the 5 [M+CH3OH]- isotopic m/z at each concentration level A) 0.25 ppm, B) 0.5 ppm, C) 1 ppm, D) 10 ppm, and E) 100 ppm. F) Calibration curve of 5 replicates of Technical Chlordane with equation and R^2 values displayed.

National Center for Biotechnology Information (2025). PubChem Compound Summary for CID 1550472, cis-Chlordane. Retrieved May 23, 2025 from https://pubchem.ncbi.nlm.nih.gov/compound/cis-Chlordane.
National Center for Biotechnology Information (2025). PubChem Compound Summary for CID 45356234, trans-Chlordane. Retrieved May 23, 2025 from https://pubchem.ncbi.nlm.nih.gov/compound/trans-Chlordane.