GCxGC-ECD of Organochlorine Pesticides in Cucumber and Tomato

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1. Introduction

Even years after many have been banned from use or have restricted uses, organochlorine pesticides (OCPs) are still detected in fruits and vegetables, albeit usually at very low levels. Endosulfan, because of its value in controlling insects such as whiteflies, armyworms, pinworms, aphids, thrips, Colorado potato beetle, stinkbugs, spider mites, and others, is still used on some vegetables (e.g., tomatoes and cucumbers).

Because OCPs are at low levels in fruits and vegetables, gas chromatography (GC) with a detector that is extremely sensitive (and somewhat selective) for halogenated compounds—the electron capture detector (ECD)—is often used for their analysis. However a food matrix may be so complex that interferences arise and confound the accurate, quantitative determination of OCPs with GC-ECD.

A new way to decrease the potential for interferences through enhanced chromatography is comprehensive two-dimensional GC (GCxGC). In GCxGC, applying two independent separations to a sample in one analysis, with one detector, increases peak capacity. GCxGC involves serially connected columns (differing phases) separated by a thermal modulator. A separation is performed on the first column, and then effluent from the first column is continually (and quickly) focused and "injected" onto the second column. By keeping the second column short, a series of high-speed chromatograms are generated, and the first column separation can be maintained. In addition, GCxGC has the power to improve sensitivity for a compound, since thermal focusing near the detector results in peak sharpening. This increased sensitivity is desirable as concentrations of OCPs in food continue to drop, since the determination of pesticides in food for dietary risk assessments, especially for infants and children, is important.

This application note will demonstrate the potential for determining OCPs in food with GCxGC-ECD. Cucumber and tomato extracts have been quantified for select OCPs, and then spiked with those same OCPs and reanalyzed.

Standards

Organochlorine pesticide mixes were obtained from Restek Corporation (Bellefonte, Pennsylvania, U.S.A.). Pentachloronitrobenzene used as an internal standard was also obtained from Restek.

Sample Preparation

Cucumbers and tomatoes were obtained from a local grocery store. Their extracts were prepared using the Florida-Modified—California Department of Food and Agriculture multiresidue method. To briefly describe the method, a 50 gram sample was homogenized and shaken with 100 mL acetonitrile for 3 minutes, followed by filtration of the extract. A C18 cartridge was used for cleanup, and water removal was accomplished by partitioning with sodium chloride. 15 mL of that extract was evaporated to dryness, followed by reconstitution with 4 mL acetone to give a final extract ready for GCxGC analysis.

2. Experimental Conditions

LECO GCxGC-ECD

Agilent 6890 GC-ECD equipped with a LECO Quad Jet—Dual-Stage Thermal Modulator

Column 1:
10 m x 0.18 mm x 0.20 µm Rtx-5 (Restek)

Column 2:
1.1 m x 0.10 mm x 0.10 µm DB-17 (J&W Scientific)

Carrier:
Helium at 2 mL/minute, constant flow

Injection:
1 µL split at 250°C, split ratio 20:1

Oven 1 Program:
40°C (1 minute), 10°/minute to 290° (1 minute)

Oven 2 Program:
10°C offset from oven 1

Modulation Time: 4 seconds

Detector:
ECD, 325°C, N_2 makeup gas at 148 mL/minute, 50 Hz

3. Results and Discussion

Figure 1 is a GCxGC-ECD contour plot for a group of OCPs in a standard mix and illustrates the separation of compounds in two dimensions.

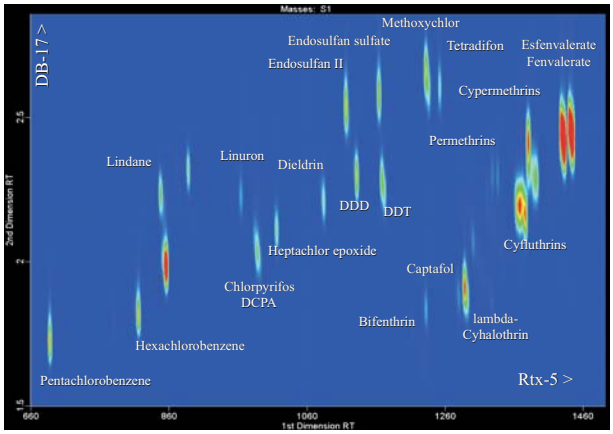

Figure 1. Contour plot of an organochlorine pesticide standard mix analyzed using GCxGC-ECD.

Figure 2 is an example of an internal standard calibration curve plotted from analysis of 0.2, 0.5, 1.0, 10, 20, 100, and 200 pg/µL Endosulfan II standards. The linearity is very good. It is important to note that since a split injection of 20:1 was used, the actual amount of Endosulfan II on

Delivering the Right Results

column for the lowest calibration point is only 10 fg, demonstrating the excellent sensitivity for the GCxGC-ECD method.

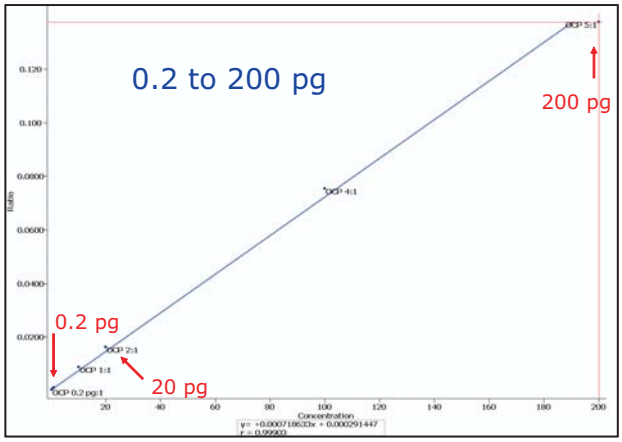

Figure 2. Internal standard calibration curve for Endosulfan II analyzed using GCxGC-ECD.

Tables 1 and 2 show the GCxGC-ECD results (unspiked and spiked) for a representative group of OCPs in cucumber and tomato extracts. (Note that a spike of 20 pg/µL in the extract represents approximately 10 ppb in the vegetable.) The pg/µL levels in the unspiked cucumber are extremely low, and except for DDT, are calculated to be around 250 ppt, or even less in the original cucumber, based on the amount extracted. DDT is estimated to be at 4.4 ppb in the cucumber.

It is not surprising to find Endosulfan II in the unspiked tomato extract. As mentioned in the Introduction, this OCP is often used (and detected) on tomatoes for insect control. Figures 3 and 4 are surface plots (a three-dimensional way to represent GCxGC data) of the unspiked and spiked tomato extracts. The Endosulfan II peak is highlighted in these figures.

Beta-HCH, reported for the tomato extract, is a persistent hexachlorocyclohexane (HCH) isomer formed during the production of Lindane (gamma-HCH), the only HCH to be used as an insecticide. While the value recorded with GCxGC-ECD needs confirmation by mass spectrometry, its presence might not be entirely unexpected.

Even though a split injection was used at a split ratio of 20:1, the signal-to-noise value on the 20 pg/µL (1 pg on column based on split ratio) Endosulfan II spike into the cucumber extract was over 600:1.

Table 1. GCxGC-ECD OCP results in pg/µL for a cucumber extract.

Pesticide	Unspiked	Spiked
beta-HCH	ND	24
Aldrin	0.47	23
Heptachlor epoxide	0.39	24
gamma-Chlordane	0.43	24
Endosulfan II	0.16	26
4,4′-DDT	8.3	37

The spike amount is 20 pg/µL. ND = Not Detected.

Table 2. GCxGC-ECD OCP results in pg/µL for a tomato extract.

Pesticide	*Unspiked*	*Spiked*
beta-HCH	*16*	*34*
Aldrin	*ND*	*25*
Heptachlor epoxide	*0.85*	*24*
gamma-Chlordane	*ND*	*24*
Endosulfan II	*23*	*48*
4,4′-DDT	*ND*	*29*

The spike amount is 20 pg/µL. ND = Not Detected.

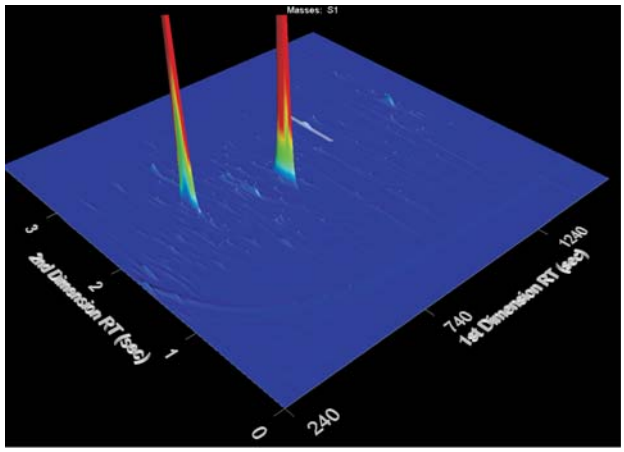

Figure 3. GCxGC-ECD surface plot of unspiked tomato extract. The two largest peaks are internal standards, including pentachloronitrobenzene. The highlighted peak is Endosulfan II.

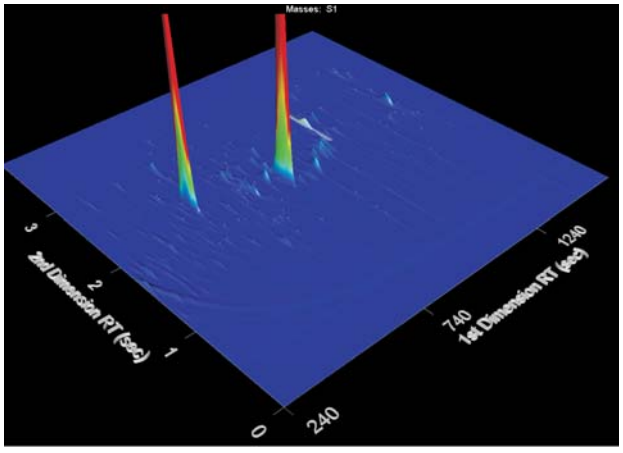

Figure 4. GCxGC-ECD surface plot of a tomato extract spiked with 20 pg/µL of an organochlorine pesticide standard mix. The two largest peaks are internal standards, including pentachloronitrobenzene. The highlighted peak is Endosulfan II. Compare this figure to Figure 3, and other pesticides can be seen in this chromatogram.

4. Conclusions

GCxGC-ECD has great potential for determining organochlorine pesticides in food extracts at low levels. GCxGC—with its increased peak capacity—can decrease the potential for coelutions, both for pesticides coeluting with each other, and for pesticides coeluting with matrix components in extracts. The sensitivity enhancement afforded by GCxGC-ECD will allow better detection limits, important as OCP levels continue to decrease in food.

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