Fast GC-ECD Analysis of Organochlorine Pesticides

The analysis of organophosphorous (OPP) and organochlorine (OCP) pesticides in environmental and food matrices is of major importance in routine analysis. The large number of compounds to be detected requires a proper screening method in order to complete the analysis in a reasonable time.

In the search for a method which reduces analysis time while maintaining resolution, the use of narrow bore columns has become significant in routine work [1].

Although many publications exist describing Fast-GC using FID, FTD and FPD, this paper describes the use of ECD. As the peak width at half height (FWHM) in a chromatogram recorded with 0.1 mm ID column are expected to be about 0.5 s [2], the detector needs to have low dead volume, selectable filter time constant, and to supply enough data points across the peak [3]. The latter is referred to as the sampling frequency.

With the GC-2010, it is possible to freely select the filter time constant and the sampling frequency between 4 ms and 250 Hz respectively for all detectors.

In GC analysis using standard columns of about 30 m length with inner diameter 0.25 mm and 0.25 µm film, the typical run time for an OCP standard containing 23 compounds is about 29 minutes. Figure 1 shows the chromatogram of such an standard (for concentration refer to table 1).

The retention time of the p,p-DDE is about 21 minutes. The column used was a 5% phenyl with a temperature program of 100 °C, 1 min, 50 °C/min to 170 °C 1 min, then 5 °C/min to 220 °C, then 10 °C/min to 260 °C, then 20 °C/min to 280 °C 1 min with N₂ and a starting pressure of 77 kPa corresponding to a linear velocity of 23 cm/s. The injection was carried out in splitless mode (1 µL).

This method was then transferred to the Fast-GC method using a CPsil 8,9 m, 0.1 mm, 0.1 µm and H₂ as carrier gas. The result is shown in figure 2. All 23 compounds were better separated and the retention time of p,p DDD was less than 3.6 minutes. The program used was 80 °C 1 min, then 60 °C/min up to 280 °C 3 min with a initial head pressure of 324 kPa and a mean linear velocity of 100 cm/s constant over the entire chromatogram. The filter time constant and the sampling frequency was selected as 20 ms and 63 Hz respectively.

Injection volume was 1 µL with a split ratio of 40 : 1. The signal to noise ratio of a HCH, for example is about 440 : 1 in this analysis, compared to 220 : 1 in the splitless standard measurement, indicating the increased sensitivity due to the sharper peaks.

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Figure 1: Standard analysis of an OCP standard (23 compounds) using an RTX-5 30 m, 0.25 mm ID, 0.25 µm film

Figure 2: Fast analysis of the OCP standard containing 23 compounds (Injection 1 µL, split 40 :1, temperature program: 80 °C, 1 min, 60 °C/min to 280 °C 3 min. H₂ linear velocity 120 cm/s, ECD: make up gas: 80 mL/min, acquisition 16 ms, filter time constant 20 ms.

Figure 3: Chromatogram recorded with the OCP standard mix. Injection 1 µL splitless, high pressure pulse 400 kPa. Column RTX-5 10 m, 0.18 mm, 0.4 µm. Temperature program: 100 °C, 1 min, 60 °C/min to 280 °C 3 min. H₂ 120 cm/s.
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Although many publications exist describing Fast-GC using FID, FTD and FPD, this paper describes the use of ECD. As the peak width at half height (FWHM) in a chromatogram recorded with 0.1 mm ID column are expected to be about 0.5 s [2], the detector needs to have low dead volume, selectable filter time constant, and to supply enough data points across the peak [3]. The latter is referred to as the sampling frequency.

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In GC analysis using standard columns of about 50 m length with inner diameter 0.25 mm and 0.25 µm film, the typical run time for an OCP standard containing 23 compounds is about 29 minutes. Figure 1 shows the chromatogram of such an standard (for concentration refer to table 1).

The retention time of the p,p-DDD is about 21 minutes. The column used was a 5 % phenyl with a temperature program of 100 °C, 1 min, 50 °C/min to 170 °C 1 min, then 5 °C/min to 220 °C, then 10 °C/min to 260 °C, then 20 °C/min to 280 °C 10 min with N₂ and a starting pressure of 77 kPa corresponding to a linear velocity of 23 cm/s. The injection was carried out in splitless mode (1 µL).

This method was then transferred to the Fast-GC method using a CPsil 8,9 m, 0.1 mm, 0.1 µm and H₂ as carrier gas. The result is shown in figure 2. All 23 compounds were better separated and the retention time of p,p-DDD was less than 3.6 minutes. The program used was 80 °C 1 min, then 60 °C/min up to 120 °C 10 min with N₂, a linear velocity of 100 cm/s constant over the entire chromatogram. The filter time constant and the sampling frequency was selected as 20 ms and 63 Hz respectively.

Injection volume was 1 µL with a split ratio of 40 : 1. The signal to noise ratio of a HCH, for example is about 440 : 1 in this analysis, compared to 220 : 1 in the splitless standard measurement, indicating the increased sensitivity due to the sharper peaks.

In GC analysis using standard columns of about 30 m length with inner diameter 0.25 mm and 0.25 µm film, the typical run time for an OPP standard containing 10 compounds is about 15 minutes. Figure 3 shows the chromatogram of such an OPP standard (for concentration refer to table 2).

Although the peak width at half height (FWHM) in a chromatogram recorded with 0.1 mm ID column are expected to be about 0.5 s [4], the detector needs to have low dead volume, selectable filter time constant, and to supply enough data points across the peak [5]. The latter is referred to as the sampling frequency.

With the GC-2010, it is possible to freely select the filter time constant and the sampling frequency between 4 ms and 250 Hz respectively for all detectors.

In GC analysis using standard columns of about 30 m length with inner diameter 0.25 mm and 0.25 µm film, the typical run time for an OPP standard containing 10 compounds is about 15 minutes. Figure 3 shows the chromatogram of such an OPP standard (for concentration refer to table 2).
The full with half maximum of a HCH as an example is about 2.5 s which is the typical FWHM observed with these kind of columns proving the suitability of the ECD-2010 for fast analysis in the field of organochlorine pesticides beyond doubt.

The limit of detection for a HCH, for example, is about 0.1 ppb for a split ratio of 40:1, requiring that the signal to noise level is at least 3:1. To apply a splitless injection with a split ratio of 40:1, requiring that the signal to noise level be at least 3:1.

The analysis of pesticides is regulated by the well-known multiresidue method referred to as S19 in Germany and DIN EN 1528-3, DIN EN 12393-2 in Europe. The method described above was also adapted to measurement of real samples prepared according to this procedure. Figure 4 shows a chromatogram recorded with a grape eluate containing chlorpyrifos and cypermethrin. This was measured using the thin film column in figure 3.

The flexible report generator. The CLASS-Agent database software connects Shimadzu’s diverse analytical systems to a laboratory network. Data of very different analytical instruments such as LC, LCMS, GC, GCMS, TOC, AAS, UV, IR and balances are entered automatically into the database. All relevant information such as analytical methods, date and time of data acquisition, user names and all chromatograms/data are stored and archived with a time stamp. Based on all these entries, the database filter simplifies data retrieval at a later date, for instance of a particular batch, a method or a certain signature status in a defined registration period. All data can be easily administered via a central server in the network.

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