Fast GC-ECD Anal
chlorine Pesticide

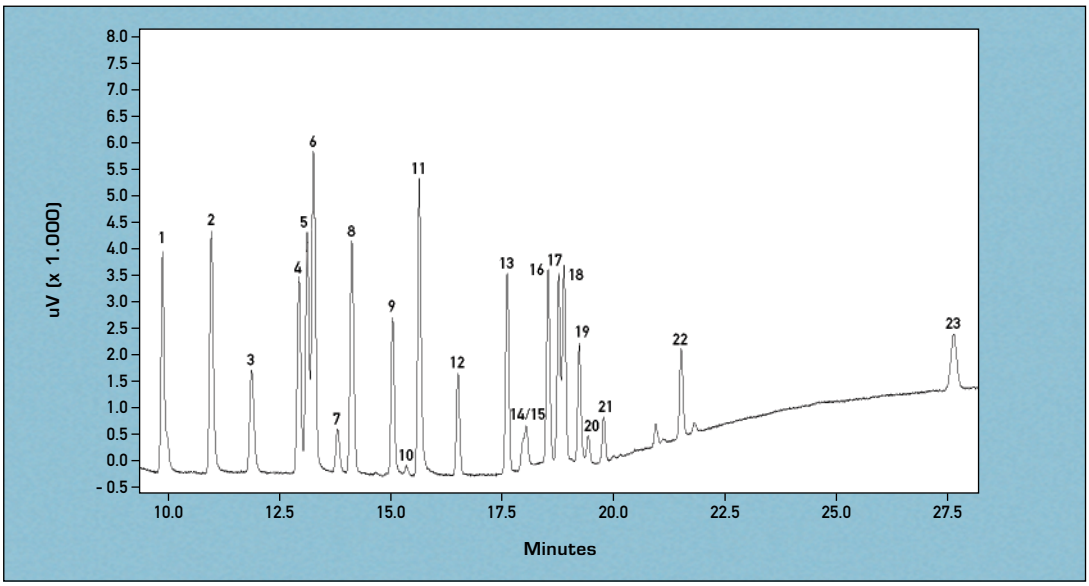

Figure 1: Standard analysis of an OCP standard (23 compounds) using an RTX-5 30 m, 0.25 mm ID, 0.25 µm film

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-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 1min, then 5 °C/min to 220 °C, then 10 °C/min to 260 °C, then 20 °C/min to 280 °C 10 min with N_2 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 H_2 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

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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.

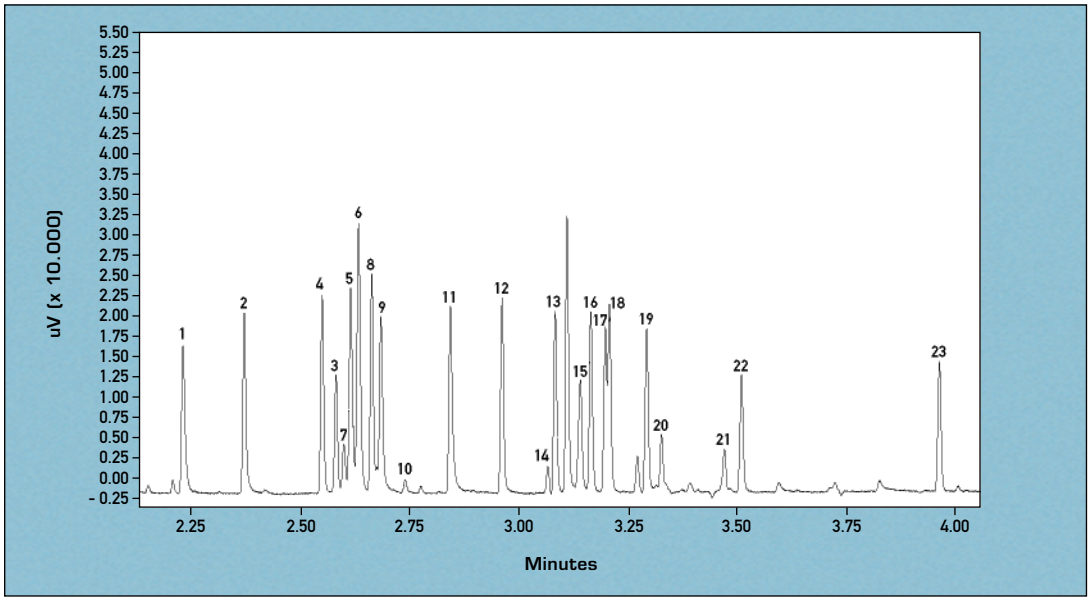

Figure 2: Fast analysis of the OCP standard containing 23 compounds (Injection 1 µL, split 40:1, temperature program: 80 °C, 1 min, 60 °C/min to 280 °C 3 min. H_2 linear velocity 100 cm/s, ECD: make up gas: 80 mL/min, acquisition 16 ms, filter time constant 20 ms.

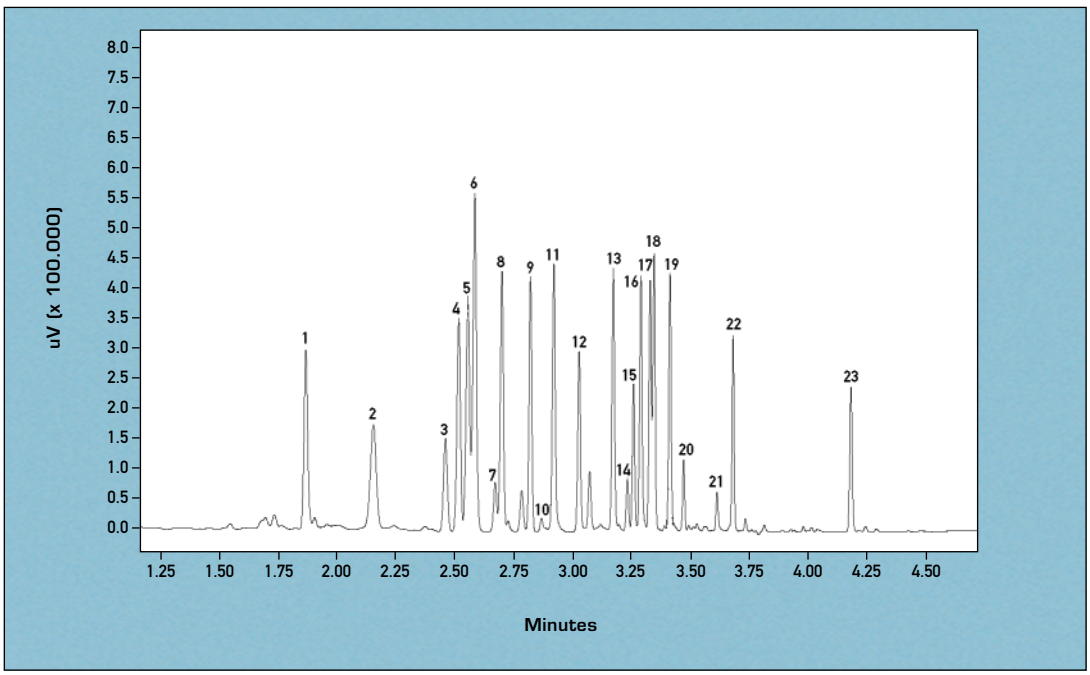

Figure 3: Chromatogram recorded with the OCP standard mix. Injection 1 µL splitless, high pressure pulse 400 kPa. Column RTX-5 10 m, 0.18 mm, 0.4 µm. Temperature program: 100 °C, 1 min, 60 °C/min to 280 °C 3 min. H_2 120 cm/s.

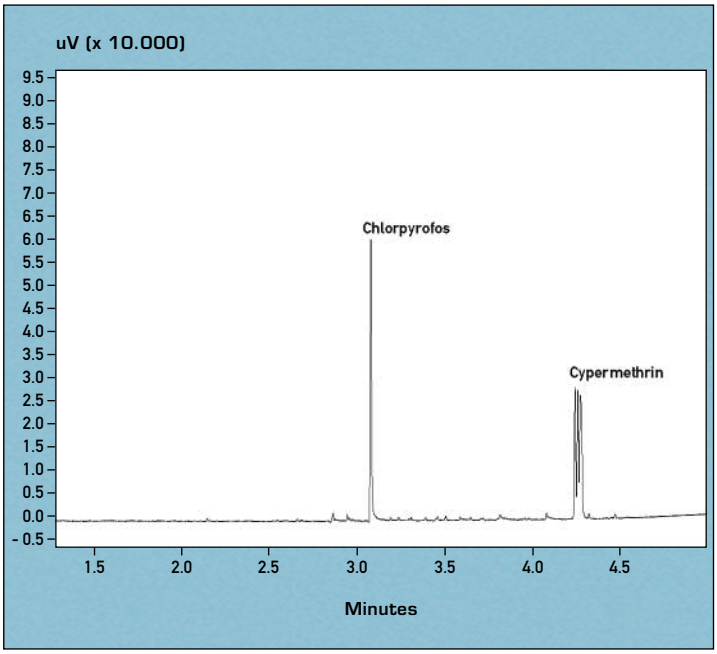

Figure 4: GPC eluate (e2 S 19) of a grape sample measured with fast GC-ECD: Chlorpyrofos 0.53 ng/mL (corresponds to 0.48 ng/kg grapes)and cypermethrin 0.55 ng/mL (corresponds to 0.5 ng/kg).

		RT	Conc (ppb)
01 pentachlorobenzole	Target	2.23	21.3
02 Tecnazene	Target	2.37	22.5
03 Benfluraline	Target	2.58	52.8
04 alpha-HCH	Target	2.548	22.1
05 HCB	Target	2.613	24.1
06 Pentachloroanisole	Target	2.631	20.6
07 beta-HCH	Target	2.598	20.4
08 Lindane	Target	2.662	28.8
09 delta-HCH	Target	2.818	23.2
10 epsilon-HCH	Target	2.683	1
11 Pentachloroaniline	Target	2.842	26
12 Heptachlor	Target	2.96	30.4
13 Aldrine	Target	3.109	21.7
14 Isobenzane	Target	3.065	5
15 Bromophosmethyle	Target	3.139	22.6
16 Isodrine	Target	3.163	22.04
17 cis-Heptachloroepoxide	Target	3.196	25
18 trans-Heptachloroepoxide	Target	3.206	25
19 Bromophosethyle	Target	3.291	50.36
20 trans-Chlordane	Target	3.325	5
21 cis-Chlordane	Target	3.469	5
22 p,p`DDD	Target	3.508	22.4
23 Mirex	Target	3.961	21.84

Table 1: Concentration of the OCP standard

The full with half maximum of a HCH as an example is about 0.5 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 with a split ratio of 40:1, requiring that the signal to noise level be at least 3:1.

To apply a splitless injection technique, a high pressure injection in combination with slightly thicker film on the column has to be used. This is demonstrated in figure 3.

Here a 10 m, 0.18 mm, 0.4 µm (5 % Phenyl) was used with 100 °C initial temperature and 120 cm/s. All other parameters were unchanged. Looking again at a HCH, the detection limit calculated from the signal to noise ratio is about 0.01 ppb in this case.

The analysis of pesticides is regulated by the well known multiresidue method refered 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 chlorpyrofos and cypermethrin. This was measured using the thin film column (see figure 2).

The determination of organophosphorous and organochlorinated pesticides in food matrices can be performed well using Fast-GC-FPD, GC-FPD and GC-ECD. With the chorinated compounds the detection limit of this method is below 0.1 ppb for several compounds using a split of 40:1 and about 0.01 ppb using the splitless technique with a column of increased film thickness in combination with high pressure injection.

Literature:

[1] Van Es, A.: High Speed Narrow Bore Capillary Gas Chromatography, Hüthig, Heidelberg 1992

[2] Baier, H.-U. and Mondello L.: Die schnelle Gaschromatographie in der Lebensmittelanalytik in Schnellmethoden zur Beurteilung von Lebensmitteln und deren Rohstoffen Kap. 3.2, Behrs Verlag 2004. Im Druck.

[3] Hinshaw. J.: LCGC (2002) vol 15 p. 152