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Quadrupole mass spectrometer operating in the electron-capture negative ion mode as detector for comprehensive two-dimensional gas chromatography

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Abstract

A recently introduced rapid-scanning quadrupole mass spectrometer (qMS) with an electron-capture negative ion (ECNI) option, the Perkin-Elmer Clarus 500, was tested as a detector for comprehensive two-dimensional gas chromatography (GC × GC). The parameters influencing the data acquisition rate in the scan mode, such as scan time and inter-scan delay, and in the selected ion monitoring mode, such as dwell time and inter-channel delay, were evaluated. In the scan mode, good-quality mass spectra covering a range of 300 Da can be obtained at an acquisition rate of 23 Hz; in selected ion monitoring, an acquisition rate of 90 Hz can be achieved when monitoring a single ion. Compared with electron ionisation, the use of electron-capture negative ionisation causes no extra peak broadening. As applications, mixtures of polychlorinated *n*-alkanes (PCAs), polybrominated diphenyl ethers (PBDEs) and polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) were analysed. The separation of PCAs based on their number of chlorine substituents was confirmed for the first time by using GC × GC–ECNI qMS in the scan mode and a significantly improved limit of detection was achieved for BDEs (10–150 fg injected) and CDD/Fs (10–700 fg injected) in the selected ion monitoring mode.
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1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is a powerful separation technique for the analysis of highly complex mixtures. Since its introduction in 1991 [1], it has become a research tool of growing interest: several instruments are commercially available today and over 150 papers have been published in this area. The principles and instrumental requirements of GC × GC have been extensively discussed, e.g. in [2,3]. For the present study, it is relevant to emphasize that the outcome of a GC × GC run is a series of high-speed second-column chromatograms with peaks having widths of 120–600 ms at the baseline [3]. In order to properly describe these very narrow peaks and avoid extra peak broadening caused by the detector, GC × GC has to be coupled to detectors with a high data acquisition rate and small internal volume. Therefore, it does not come as a surprise that virtually all early studies were done with flame ionisation detectors (FID), which have data acquisition rates up to 200 Hz and dead volumes which are effectively zero [4]. More recently, the combination of GC × GC with a micro electron-capture detector (μECD) has shown very good results, in particular for the analysis of polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) [5–7]. The μECD is fast enough (up to 100 Hz) but some peak broadening due to a still too large cell volume was observed even with this smallest commercially available model of ECDs [8]. However, whenever identification and/or confirmation of identity are required, the

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use of a mass spectrometric detector is mandatory. At present, time-of-flight mass spectrometers (ToF MS) with data acquisition rates of up to 200 Hz are available and – as has been demonstrated in numerous studies (e.g. [9–11]) – they are fully compatible with GC × GC. However, as yet there is no commercially available instrument with a chemical ionisation option (although there briefly was a prototype on the market a short while ago), which is a highly desirable option when organohalogenated compounds have to be analysed. In addition, ToF MS instruments are very expensive. Consequently, using a quadrupole MS, preferably with electron-capture negative ionisation, as a GC × GC detector instead, is of decided interest.

The main limitation of a quadrupole MS (qMS) is its relatively slow scan speed. To overcome the limiting value of 2.43 scan/s of the Hewlett-Packard, Model 5972 instrument, Frysinger and Gaines [12] proposed to broaden the chromatographic peaks (from 0.2 to 1 s in the second dimension) by increasing the run time, when marine fuel was analysed by thermally modulated GC × GC–qMS. Shellie et al. [13], for the analysis of essential oils, and Kallio et al. [14], for the analysis of polycyclic aromatic hydrocarbons in urban aerosols, using the up-graded Hewlett-Packard, Model 5973 instrument, preferred to limit the scan range to ca. 200 Da to achieve a rate of 20 scan/s, while Debonneville and Chaintreau [15] opted to monitor a single ion in a study of allergens in fragrances and achieved a frequency of 30.7 Hz. In the present study, a recently introduced fast-scanning quadrupole mass spectrometer, the Perkin-Elmer Clarus 500, has been evaluated as a detector for GC × GC. Our focus was on its use in the electron-capture negative ion (ECNI) mode, which has not been studied so far. Its applicability is demonstrated by means of analyses in which soft ionization is highly required, viz. those of polychlorinated *n*-alkanes (PCAs), polybrominated diphenylethers (PBDEs) and PCDD/Fs.

2. Experimental

2.1. Samples and chemicals

3,3′,4,4′,5-Pentachlorobiphenyl (CB 126; Promochem, Wesel, Germany) with concentrations of 540 and 54 pg/μl in isooctane, and 1,1,1,3,9,11,11,11-octachloroundecane (Chiron, Trondheim, Norway) with a concentration of 15 pg/μl in isooctane, were used to evaluate the qMS system. Three standard mixtures and an eel sample were used for the applications. A mixture of chlorinated decanes with 65% chlorination and a total concentration of 10 ng/μl was purchased from Dr. Ehrenstorfer (Augsburg, Germany). A standard solution containing 2,3,7,8-TCDD and 2,3,7,8-TCDF, both with a concentration of 100 fg/μl, 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, all with a concentration of 500 fg/μl, and OCDD and OCDF, both with a concentration of 1000 fg/μl, was prepared by diluting the commercial standard mixture EDF 7999 (CIL, Andover, MA, USA) in iso-octane. A 100-fold concentrated mixture was used to optimize the qMS conditions. A standard mixture containing BDE congeners 28, 75, 71, 47, 66, 77, 100, 119, 99, 116, 154, 153, 138 and 190 (numbering identical to PCBs [16,17]), all with concentrations of 150 fg/μl, and congeners 49, 85 and 183, each with a concentration of 50 fg/μl, was prepared by mixing standard solutions of each congener (AccuStandard, New Haven, CT, USA) in iso-octane.

An aliquot of an eel sample containing ca. 1 g of fat was mixed with sodium sulphate, allowed to dry for 3 h and Soxhlet-extracted for 12 h with hexane/acetone (3:1, v/v) at 70 °C [18]. The solvents used were of nanograde quality, and were obtained from Promochem. The extract was concentrated on a rotary evaporator, dissolved in 2 ml of dichloromethane, and cleaned by gel permeation chromatography over two Polymer Laboratories (Church Stretton, UK) gel columns (300 × 25 mm, pore size 10 μm), using dichloromethane at 10 ml/min. The 18–23 min fraction was collected, concentrated under nitrogen, dissolved in iso-octane and further purified by shaking with sulphuric acid. After separation of the iso-octane phase, the sulphuric acid phase was washed twice with pentane to extract all BDEs. Finally, the pentane/iso-octane mixture was concentrated under nitrogen to 2 ml (iso-octane) and eluted over a 1.6 g silica column (2% deactivated) with 11 ml iso-octane and 10 ml 20% diethyl ether in iso-octane. The fractions were combined and concentrated to 1 ml (iso-octane).

2.2. GC × GC–qMS

The GC × GC system was built from a Clarus 500 MS (Perkin-Elmer, Shelton, CT, USA) equipped with a dual-jet liquid CO_2 modulator system. The principles and operation of the dual-jet modulator are discussed in [19]. It is relevant to mention here that the oven of the instrument used is rather small (at least compared to Agilent or Thermo Electron GCs). Therefore, the position of the CO_2 jets plays an important role in the retention-time repeatability. The best repeatability was obtained when the jets were mounted just behind the door, i.e. as far as possible from the thermocouple. A DB-1 (100% methylpolysiloxane) and a DB-XLB (proprietary) fused-silica column, both with dimensions of 30 m × 0.25 mm × 0.25 μm and purchased from J&W Scientific (Folsom, CA, USA), were used as first-dimension columns. A 1 m × 0.10 mm × 0.10 μm 007-65HT (65% phenyl-methylpolysiloxane) from Quadrex (New Haven, CT, USA) and a 0.9 m × 0.10 mm × 0.10 μm LC-50 (50% liquid crystalline-methylpolysiloxane) from J&K Environmental (Milton, ONT, Canada) were used as second-dimension columns. In the DB-1 × 007-65HT set-up, which was used for system evaluation and the analysis of the PCAs and PBDEs, one end of the second-dimension col-

umn was coupled directly to the first-dimension column and the other one mounted in the GC–MS interface. In the DB-XLB × LC-50 set-up, used for the analysis of the PCDD/Fs, one end of the second-dimension column was coupled to the first-dimension column via a 10 cm × 0.1 mm piece of retention gap and the other end to the 40 cm × 0.1 mm retention gap mounted in the GC–MS interface. This set-up was required in order to avoid crystallization of the LC-50 phase during modulation and overheating in the GC–MS interface. All column connections were made by means of a press-fit connector (Techrom, Purmerend, The Netherlands).

Helium (Hoek Loos, Schiedam, The Netherlands) with a purity of 99.999% was used as carrier gas at a constant flow of 1.2 ml/min. Injections (1 μl) were made by using an autosampler with the injector operated in the splitless mode at 280 °C; the purge time was 2 min. With the PCDD/Fs, 2-μl samples were injected manually. The modulation period was 7 s, except with the PBDEs, when a 5-s modulation was used. The temperature of the GC–MS transfer line was 290 °C. The mass spectrometer was tuned and calibrated in the electron ionisation (EI) and ECNI modes using heptacosafluorotributylamine (Fluka Chemie, Buchs, Switzerland) as the reference gas according to the recommendations of the manufacturer. The electron energy was 70 eV and the emission current 180 μA. In ECNI qMS, methane was used as reagent gas and the pressure in the mass analyzer region of the vacuum manifold was measured by means of the pressure of the penning pump. Data acquisition was performed using TurboMass software (Perkin-Elmer). Then the data file in 'Mass lab 2 file' format was converted into 'Xcalibur file' format by Xcalibur software (Thermo Electron, Rodano Milan, Italy) and, subsequently, imported into HyperChrom software (Thermo Electron) used for GC × GC transformation, evaluation, visualization and identification. Transform software (Fortner Research, Sterling, VA, USA) was used for producing 2D chromatograms.

3. Results and discussion

3.1. Data acquisition rate in scan mode

In a quadrupole mass spectrometer, the data acquisition rate (Hz), expressed as the number of spectra acquired per second, is determined by two parameters, the scan time and the inter-scan delay:

$$\text{data acquisition rate (Hz)} = \frac{1}{\text{scan time (s)} + \text{inter-scan delay (s)}} \quad (1)$$

The scan time is the time spent on scanning the specified mass range, while the inter-scan delay gives the time between one scan ending and the next scan starting. Eq. (1) clearly shows that, in order to achieve the high data acquisition rates required for GC × GC (at least 20–30 Hz, depending on the application), both parameters have to be kept as low as possible. With the present instrument, the parameters can easily be varied. For example, the scan time can be set down to 0.01 s for mass ranges up to 449 Da, and down to 0.02 s for mass ranges above 450 Da; the inter-scan delay can be set even to 0.00 s. Evaluation of instrument performance was done by varying the parameter settings while working in the EI rather than the ECNI mode. This has the distinct advantage that the quality of the mass spectra of the analytes can be studied in much more detail because of the higher fragmentation. All evaluation experiments were carried out without modulation. Under this condition, a 1D peak was acquired with a baseline width of about 30 s. This is broad enough for the peak to be properly described even at very slow data acquisition rates, which were used as a reference for the comparison with the higher acquisition rates.

As regards the scan time, this depends on the mass range that is scanned and the scan speed:

$$\text{scan time (s)} = \frac{\text{mass range scanned (Da)}}{\text{scan speed (Da/s)}} \quad (2)$$

The mass range scanned depends solely on the application of interest; that is, it is not a limiting factor of the mass spectrometer. In other words, no evaluation of this parameter is required, but its influence has to be considered when the maximum data acquisition rate is calculated.

The scan speed is the main limiting factor of the instrument. As is demonstrated in Fig. 1, in which the averaged continuum mass spectra recorded for the test analyte, CB 126, are shown at four scan speeds, an increasing scan speed reduces resolution, which results in a significant loss (nominal Rs > 1 Da) above about 9 000 Da/s. In order to select the maximum speed at which satisfactory mass spectra can still be obtained, the quality of the averaged mass spectra and the stability of the mass ratios across the chromatographic peak were evaluated in the range 3500–35 000 Da/s. The quality of the averaged mass spectra (Fig. 2) was found to be essentially constant up to 7000 Da/s. This was evaluated by comparing the spectra and also by comparing so-called Rev values, which express the match of the spectra with NIST library spectra. At the next higher value, 8750 Da/s, acceptable averaged mass spectra were still obtained although some point-to-point variation in mass spectra was observed (e.g. the ^{13}C isotope masses *m/z* 325, 327 and 329 were absent in some data points of the peak). At still higher scan speeds of over about 10 000 Da/s, the loss of resolution was so significant that the averaged mass spectra became distorted. The best examples are the ^{13}C isotope masses of the molecular cluster which were now invariably absent and the masses *m/z* 109, 110 and 111 which essentially existed as *m/z* 110 only, creating the new dominant mass of the spectra. This is clearly observed in Fig. 2 for data collected at 35 000 Da/s. The Rev values included in Fig. 2 show the same trend.

As regards the stability of the mass ratios across the CB 126 peak, this parameter was evaluated by calculating the RSDs of three mass ratios, *m/z* 326/324, 326/328 and

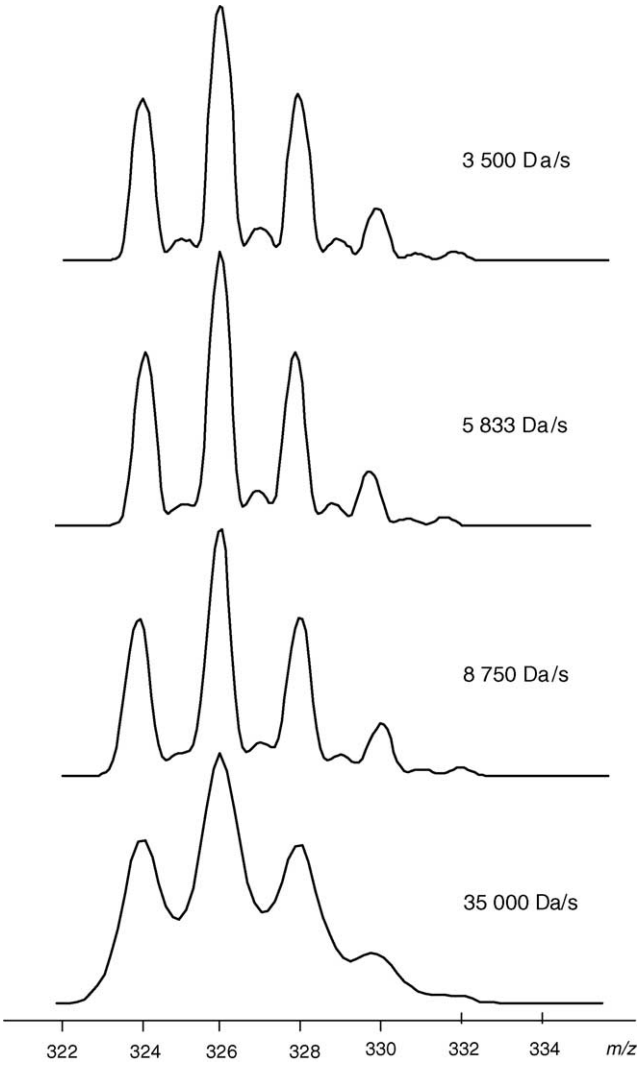

Fig. 1. Part of the averaged continuum mass spectra of CB 126 for four scan speeds (3500–35 000 Da/s). Scan time, 0.1–0.01 s; scanned mass range, 350 Da (*m*/*z* 40–390); inter-scan delay, 0.1 s; number of points per mass, 16.

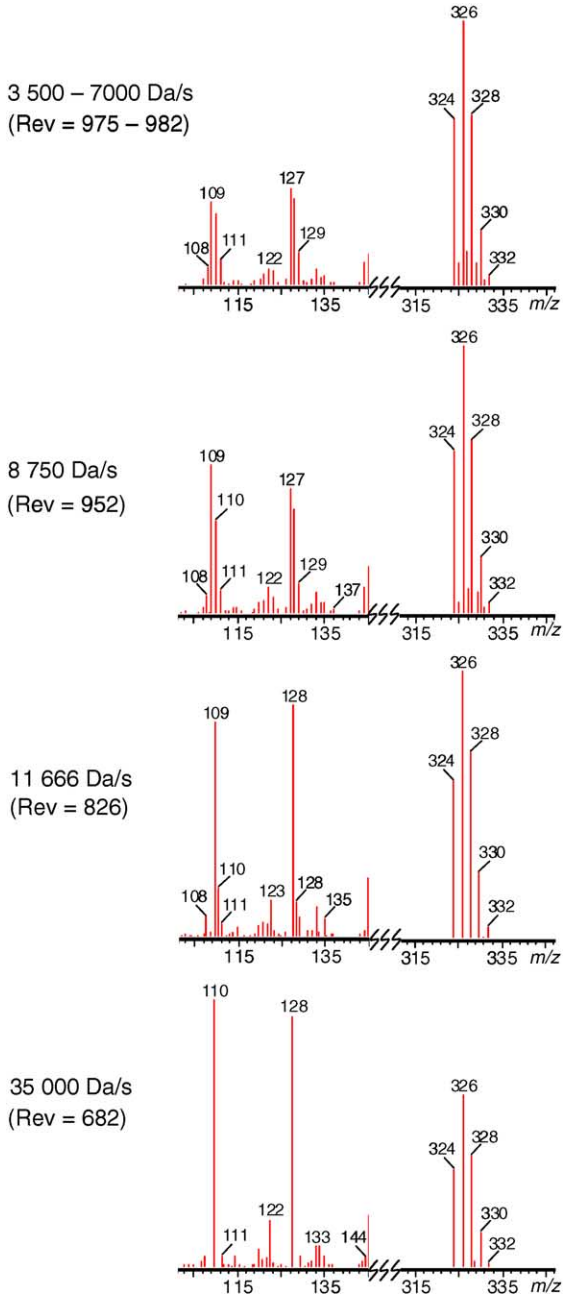

Fig. 2. Part of the averaged mass spectra (no background subtraction) of CB 126 at different scan speeds. Scan time, 0.1–0.01 s; scanned mass range, 350 Da (*m*/*z* 40–390); inter-scan delay, 0.1 s.

324/328 from all data points above a quarter of the peak height. Since varying the scan speed influences the data acquisition rate and, thus, the number of points which describe the peak, the number of points from which the RSDs were calculated, *n*, varied from 19 to 34. The results, which are shown in Fig. 3, again indicate no apparent change up to about 7000 Da/s (RSDs, 5–6%), with a subsequent increase to about 10% at 11 666 Da/s, and RSDs of 15–20% at 35 000 Da/s. Chromatographic noise also increased with increasing scan speed. In this instance, there was a continuous increase over the entire test range. The combined results indicate that fully satisfactory results can be expected for scan speeds of up to 7000–8000 Da/s. This agrees with the upper limit of 6700 Da/s declared by the manufacturer which is, obviously, a fairly conservative value. Actually, our experience showed that good-quality averaged mass spectra can be obtained up to 9000 Da/s, although quantification will then become somewhat less precise.

The other parameter which influences the data acquisition rate and is also a limiting factor of the mass spectrometer is the inter-scan delay—the time which is required to re-set the voltages to the starting values and to process the data of the previous scan. We observed that, if the delay is too short, proper processing and recording of the acquired spectrum cannot be achieved. Since the mass spectrometer scans from higher towards lower masses, the first effect is a loss of information—i.e. initially lower intensities of, and, next, a complete loss of the pertinent peaks in the averaged mass spectrum. In Fig. 4, this is clearly visible for masses

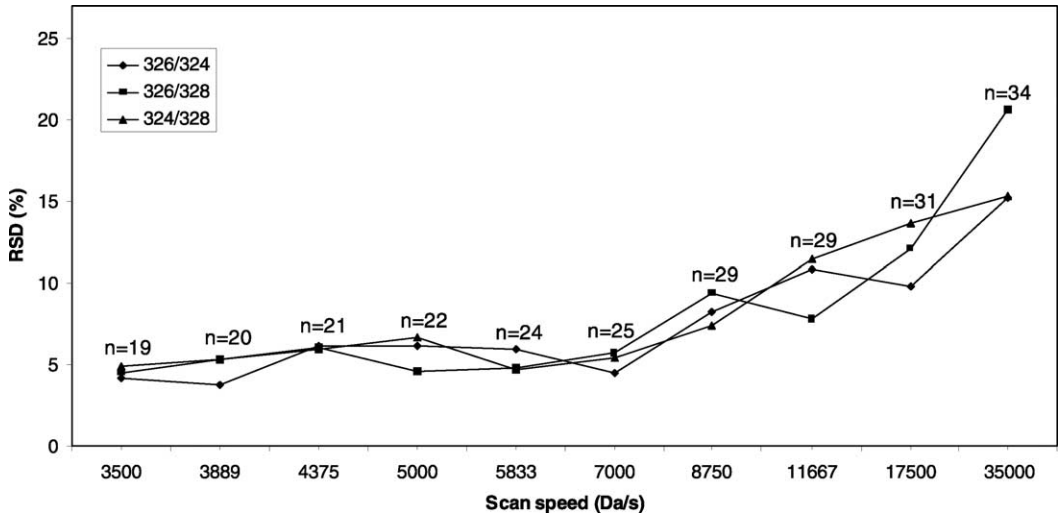

Fig. 3. RSD of mass ratios (n = 19–34, depending on scan speed) through the chromatographic peak of CB 126 vs. scan speed. Scan time, 0.1–0.01 s; scanned mass range, 350 Da (m/z 40–390); inter-scan delay, 0.1 s.

in the m/z 40–50 range, with 0.01 s being a safe lower limit (also see Table 1 below). One consequence is that TIC chromatograms will become noisier because of this gradual loss of spectral information. Since the required inter-scan delay is mass-range dependent, the minimum values were studied for ranges of 50–400 Da; they are listed in Table 1. Obviously, for most practically relevant applications, a delay of 5–15 ms is required.

With the information now available on the limiting factors of the mass spectrometer, scan speed and inter-scan delay, the maximum data acquisition rates were calculated by means of Eq. (1) for five selected mass ranges (Table 1). If we assume that recording seven data points is enough to properly describe a peak, as was shown amongst others by Dallüge et al. [20], it is obvious that high-quality mass spectra can be obtained even if a 300 Da scan range is used: most analytes—and certainly the organohalogens—are sufficiently retained in the second dimension of a GC × GC run to end up with baseline peak widths of, at least, some 300 ms. The present result compares favourably with literature data, where the mass range that can be scanned under conditions similar to those reported here, are sometimes two-fold shorter [13,14].

3.2. Data acquisition rate in SIM mode

The data acquisition rate in the SIM mode is determined by the number of ions that is monitored, n, the dwell time per ion, and the inter-channel delay:

$$\text{data acquisition rate (Hz)} = \frac{1}{\sum_{i=1}^{n}(\text{dwell time})_i + n(\text{inter-channel delay})} \quad (3)$$

The dwell time (s) is the time the system spends on acquiring the selected mass and its value can be different for each mass. The inter-channel delay (s) specifies the time between ending one mass acquisition and starting the next one. Eq. (3) clearly shows that in order to achieve a high data acquisition rate, these two parameters must be kept at their lowest

Table 1
Minimum inter-scan delay required for different mass ranges plus maximum achievable data acquisition rates and minimum detectable peak widths for two scan speeds

Mass range scanned (Da)	Minimum inter-scan delay (s)	Maximum scan speed: 6700 Da/s			Maximum scan speed: 9000 Da/s		
		Scan time[a] (s)	Max. data acquisition rate[b] (Hz)	Min. detectable peak width[c] (ms)	Scan time[a] (s)	Max. data acquisition rate[b] (Hz)	Min. detectable peak width[c] (ms)
400	0.014	0.060	14	510	0.044	17	410
300	0.011	0.045	18	380	0.033	23	300
200	0.010	0.030	25	280	0.022	31	230
100	0.005	0.015	50	140	0.011	63	110
50	0.001	0.007	125	56	0.006	143	50

[a] From Eq. (2).
[b] From Eq. (1).
[c] Calculated for seven points per peak from: detectable peak width = 7/maximum data acquisition rate.

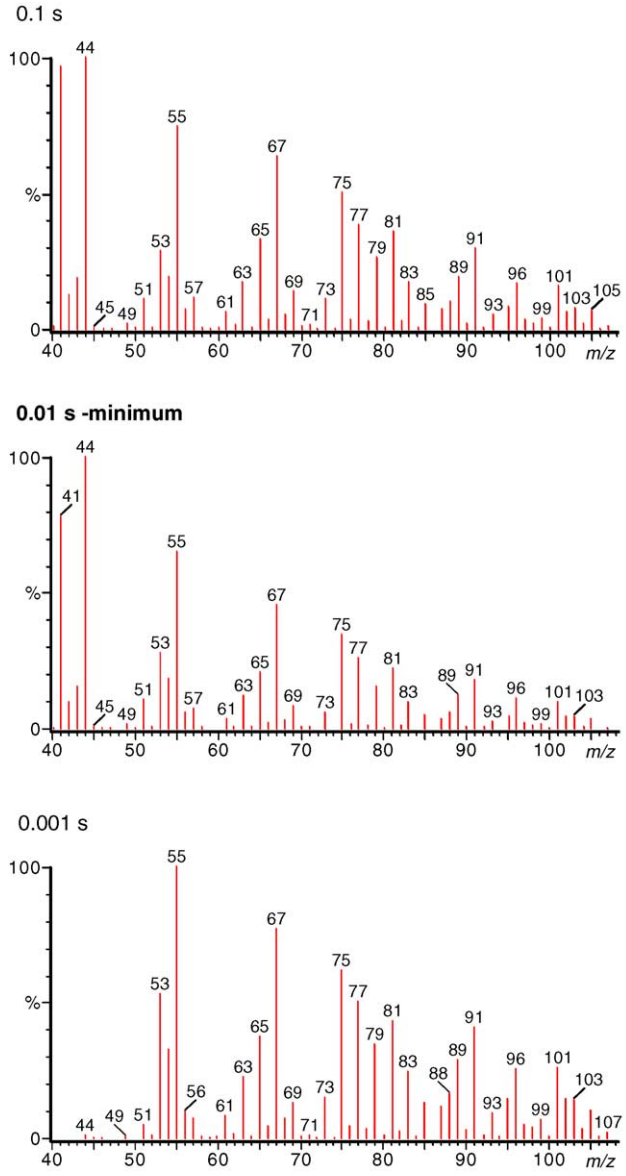

Fig. 4. Part of the averaged mass spectra of 1,1,1,3,9,11,11,11-octachloroundecane acquired at different inter-scan delays. Inter-scan delay, 0.1–0.001 s; scanned mass range, 200 Da (*m*/*z* 40–240); scan time, 0.1 s.

values. As regards the inter-channel delay, here the software allows 'zero' as the lowest value. Its influence on the stability of the mass ratio across the peak of CB 126 was studied by calculating the RSDs of the *m*/*z* 326/324 mass ratio. The RSDs were found to be constant over the whole range tested, 0.1–0.0001 s. To be on the safe side, a delay time of 0.001 s was selected for further work. This is 10-fold less than the minimum dwell time that is allowed by the software (and was used by us), which is 0.01 s and, consequently, has little influence on the data acquisition rate. One should mention here, that the RSD in the SIM mode was higher than in the scan mode (13% versus 5%). This is due to a higher spectral skewing caused by working in the SIM mode.

Table 2
Maximum data acquisition rates and minimum detectable peak widths for SIM of up to four monitoring ions

Number of ions	Dwell time (s)	Max. data acquisition rate[a] (Hz)	Min. detectable peak width[b] (ms)
1	0.01	91	80
	0.02	48	150
	0.03	32	220
	0.04	24	290
2	0.01	45	160
	0.02	24	290
3	0.01	30	230
4	0.01	23	300

[a] From Eq. (3) with dwell time of 0.01–0.04 s and inter-scan delay of 0.001 s.
[b] Calculated as in Table 1.

Using the selected dwell and inter-channel delay times, the maximum data acquisition rates and the minimum detectable peak widths (for at least seven data points across a peak) were calculated. Typical results for up to four selected ions are shown in Table 2. When monitoring a single ion, an acquisition rate of 90 Hz can be achieved, which is much faster than the earlier published value of 30.7 Hz [14]. More importantly, Table 2 shows that for the many applications in which peaks have baseline widths of at least 300 ms, up to four ions can be monitored without sacrificing the seven-data points-per-peak rule.

3.3. EI versus CI peak width

As was mentioned before, all experiments discussed so far were carried out in the EI mode. Consequently, it had to be verified whether working in the CI mode instead would cause additional peak broadening due to the higher pressure of the CI source and/or the presence of a reagent gas in the ionisation volume. With CB 126 as the test compound, raw chromatograms of GC × GC–qMS runs in the EI and ECNI modes, made under otherwise identical conditions, were overlaid. Comparison of peaks from individual modulations showed that no extra band broadening could be observed. In other words, the CI and EI sources are equally suitable for application in GC × GC.

3.4. Applications

One interesting application of GC × GC–ECNI qMS in the scan mode is the analysis of polychlorinated *n*-alkanes (PCAs), which are complex technical mixtures with carbon chain lengths varying from C_{10} to C_{30} and chlorine contents between 30 and 70 wt.%. Analysis of PCAs is a difficult task because these mixtures contain at least several thousand individual congeners [21–23]. Not unexpectedly, complete separation of the individual compounds cannot be accomplished by means of conventional, i.e. 1D-GC: chromatograms display a characteristic broad envelope indica-

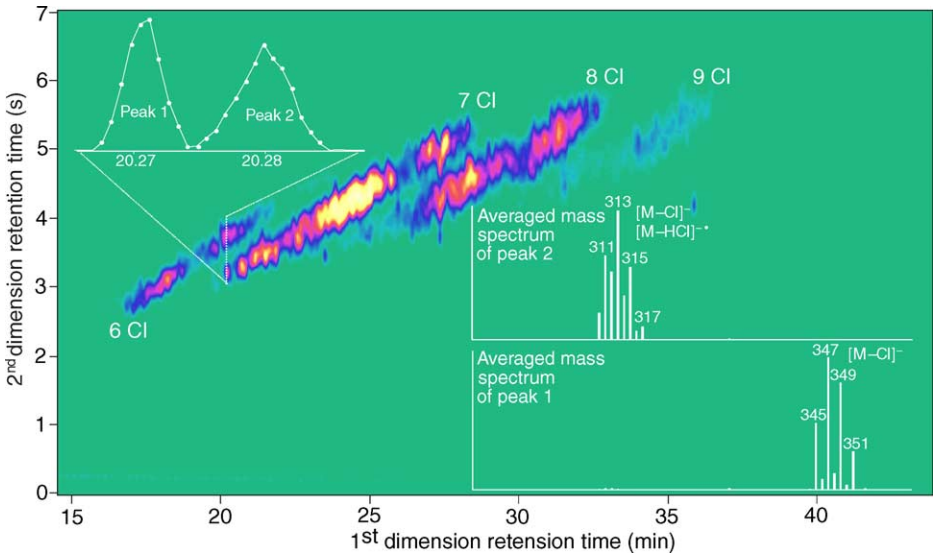

Fig. 5. Full-scan (*m/z* 210–490 Da) GC × GC–ECNI qMS of a mixture of polychlorinated decanes with average chlorine content of 65 wt.% on DB-1 × 007-65HT column combination. Temperature programme: 90 °C (2 min), at 30 °C/min to 170 °C, then at 2 °C/min to 300 °C. Interface temperature, 280 °C. Scan time, 0.032 s (8750 Da/s); inter-scan delay, 0.011 s; source temperature, 150 °C. Left-hand-side insert: separation of hexa- and hepta-chlorinated decanes in second dimension and number of data points per peak. Right-hand-side insert: part of averaged mass spectra of peaks 1 and 2.

tive of a large number of co-eluting peaks. In other words, this is an area in which the use of GC × GC should be rewarding. As an example, Fig. 5 shows a GC × GC–ECNI qMS chromatogram of a mixture of polychlorinated decanes with an average chlorine content of 65 wt.%. The most striking observation is the much improved (though certainly not yet complete) overall separation, and the ordered structure with the four parallel groups of peaks. On the basis of the ECNI mass spectra that were recorded, the presence of hexa- to nona-chlorinated decanes and a separation based on the number of chlorine substituents was confirmed. Mass spectra recorded for a hexa- and a hepta-substituted congener, which are shown in the right-hand-side insert of Fig. 5, show the well-known dominance of $[M - Cl]^-$ and $[M - HCl]^{\bullet -}$ ions [21,24]. It is interesting to add that such a structure assignment would not be possible when using EI ionisation, because the spectra are then highly fragmented and there is, consequently, little or no structural information. The left-hand-side insert of Fig. 5 demonstrates that the rapid-scanning qMS instrument provides spectra of good quality at the scan speed of 8750 Da/s used in this experiment: there are enough data points for satisfactory peak description. That is, the present instrumental set-up can be considered a promising tool for the further unravelling of the composition of PCA mixtures and their trace-level analysis in environmental samples [25].

As a second application, GC × GC–ECNI qMS, this time in the SIM mode, was used to analyse PBDEs, a group of brominated flame retardants with a theoretical maximum of 209 congeners. In environmental samples, some 20–25 BDEs are typically detected, but additional congeners are expected to show up when processes such as photolytic or metabolic debromination play a role and change the initial composition of a technical mixture. Congener-specific GC × GC analysis is, therefore, an interesting approach, specifically in combination with ECNI MS detection of the $[Br]^-$ ion at *m/z* 79 and 81; this yields much better detectability than EI MS. In this instance, the inter-channel delay was 0.001 s, and the dwell time used for each ion was 0.02 s, which is the highest value allowed if two ions have to be monitored (cf. Table 2). Under these conditions, the limits of detection (LODs) of a selected number of tetra- to hepta-BDEs were found to be excellent, with values of 10–40 fg injected for all congeners except one (Table 3). Actually, these LODs are 10- to 20-fold lower than those obtained with the 1D-GC method currently running in our laboratory. This can be explained by the combined effect of the well-known focusing occurring during modulation in GC × GC and the higher sensitivity of the new mass spectrometer. As a real-life example, Fig. 6

Table 3
LODs (fg) of selected BDE congeners in GC × GC–ECNI qMS when monitoring $[Br]^-$ ion at *m/z* 79 and 81

BDE congener		LOD[a] (fg)
No.	Structure	
47	2,2′,4,4′	10
71	2,3′,4′,6	10
77	3,3′,4,4′	10
85	2,2′,3,4,4′	20
100	2,2′,4,4′,6	10
119	2,3′,4,4′,6	10
138	2,2′,3,4,4′,5′	20
153	2,2′,4,4′,5,5′	30
154	2,2′,4,4′,5,6′	15
183	2,2′,3,4,4′,5′,6	40
190	2,3,3′,4,4′,5,6	150

[a] Column combination, DB-1 × 007-65HT; dwell time, 0.02 s; inter-channel delay, 0.001 s.

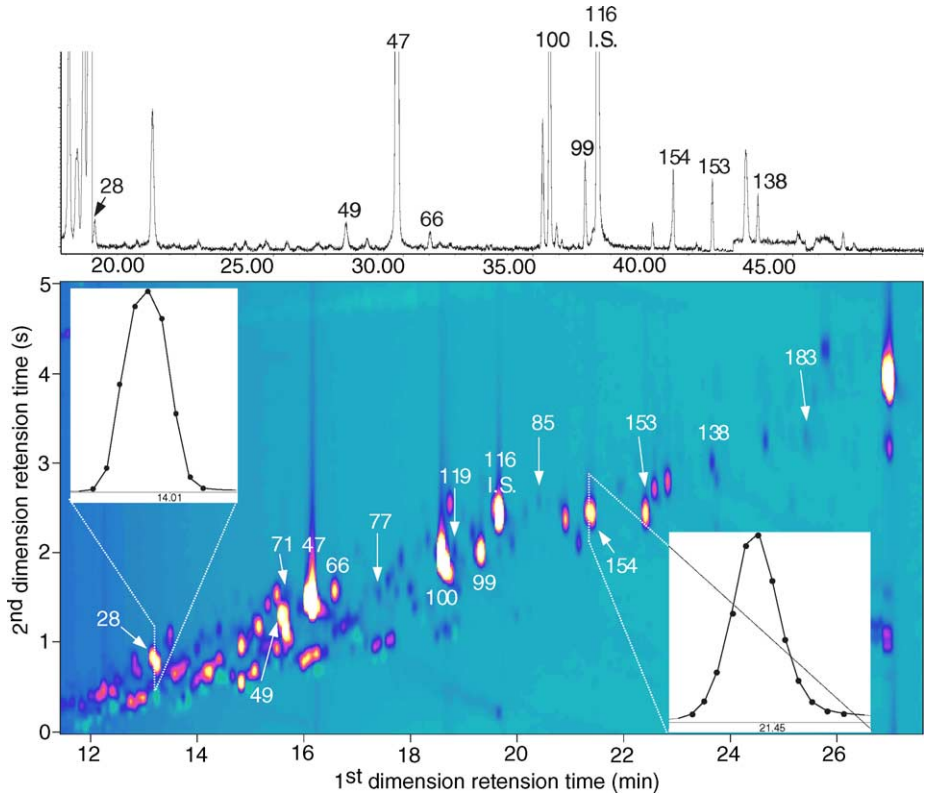

Fig. 6. Upper frame: SIM-mode GC–ECNI qMS (Agilent) of an eel BDE extract on CP-Sil 8 (50 m × 0.25 mm × 0.25 μm) column. Temperature programme: 90 °C (3 min), at 30 °C/min to 210 °C (20 min), then at 5 °C/min to 290 °C (20 min). Interface temperature, 290 °C. MS conditions: SIM of *m/z* 79, 81, 159 and 161 with dwell of 50 for each mass; source temperature, 200 °C. Lower frame: SIM-mode GC × GC–ECNI qMS (Perkin-Elmer) of an eel BDE extract on DB-1 × 007-65HT column combination. Temperature programme: 90 °C (2 min), at 30 °C/min to 210 °C, then at 5 °C/min to 320 °C (5 min). Interface temperature, 300 °C. MS conditions: SIM of *m/z* 79 and 81, both with dwell time of 0.02 s and inter-channel delay of 0.001 s; source temperature, 200 °C. Inserts show second-dimension chromatograms of BDE 28 and 154 and number of data points per peak.

Table 4
LODs (fg) of priority CDD/Fs in GC × GC–ECNI qMS and GC × GC–μECD

Compound	Ions monitored		LODs (fg)	
			GC × GC –ECNI qMS	GC × GC –μECD[a]
2,3,7,8-TCDD	$[M]^{\bullet -}$	320 + 322	710	90
1,2,3,7,8-PeCDD	$[M]^{\bullet -}$	354 + 356	40	70
1,2,3,4,7,8-HxCDD	$[M - Cl]^{-}$	355 + 353	30	60
1,2,3,6,7,8-HxCDD	$[M]^{\bullet -}$	390 + 392	20	50
1,2,3,7,8,9-HxCDD	$[M - Cl]^{-}$	355 + 353	50	40
1,2,3,4,6,7,8-HpCDD	$[M - Cl]^{-}$	389 + 391	70	70
OCDD	$[M - Cl]^{-}$	423 + 425	430	150
2,3,7,8-TCDF	$[M]^{\bullet -}$	304 + 306	100	70
1,2,3,7,8-PeCDF	$[M]^{\bullet -}$	338 + 340	30	70
2,3,4,7,8-PeCDF	$[M]^{\bullet -}$	338 + 340	10	70
1,2,3,4,7,8-HxCDF	$[M]^{\bullet -}$	374 + 376	10	40
1,2,3,6,7,8-HxCDF	$[M]^{\bullet -}$	374 + 376	10	50
1,2,3,7,8,9-HxCDF	$[M]^{\bullet -}$	374 + 376	10	50
2,3,4,6,7,8-HxCDF	$[M]^{\bullet -}$	374 + 376	100	40
1,2,3,4,6,7,8-HpCDF	$[M]^{\bullet -}$	408 + 410	10	70
1,2,3,4,7,8,9-HpCDF	$[M]^{\bullet -}$	408 + 410	50	80
OCDF	$[M]^{\bullet -}$	442 + 444	110	150

[a] From [7].

shows the GC × GC–ECNI qMS chromatogram of an eel extract, in which fourteen BDE congeners were identified. As becomes evident from a comparison with the 1D-GC trace (top of Fig. 6), the presence of five additional congeners (i.e. 71, 77, 119, 85, 183) was confirmed. Inspection of Fig. 6 reveals that some of these added confirmations are caused by the improved 2D separation (e.g. BDEs 71 and 119) and others by the enhanced detectability (e.g. BDE 183). The clear recognition of a rather large number of Br-containing compounds in the early part of the chromatogram, which were not seen in 1D-GC, is another aspect of interest. Finally, the inserts to Fig. 6 show that a sufficient number of data points per peak (at least nine) was recorded throughout the chromatogram, as is illustrated for BDEs 28 and 154.

Finally, the practicability of the present set-up was briefly tested for the notorious priority CDD/Fs, for which compounds very low LODs are required. In this case, a DB-XLB × LC-50 column combination was installed, because of its excellent selectivity for the analytes of interest [7]. In order to obtain maximum sensitivity, the source temperature and the pressure of the ionisation gas in the MS source were optimised. It was found that the source temperature must be kept above 200 °C in order to avoid peak broadening. This was rather surprising, because no such effect was observed for the PCAs. The optimum value of the ionisation gas pressure was found to be 9×10^{-5} kPa. Under these conditions, the mass spectra of all CDFs were characterized by a high intensity of the molecular ion, $[M]^{\bullet -}$, while with some CDD congeners, $[M - \mathrm{Cl}]^-$ was the dominant ion. Consequently, analyses were carried out and LODs determined by recording the two masses listed in Table 4. Very low LODs were obtained for the penta- and higher substituted congeners, which are in most cases better than those published for GC × GC–μECD [7]. The LOD of 2,3,7,8-TCDF is slightly worse, but still satisfactory for all real-life applications. Unfortunately, the LODs of OCDD and, more so, 2,3,7,8-TCDD are much higher and, actually, too high for the present instrumental set-up to replace GC–HRMS.

4. Conclusions

The Perkin-Elmer Clarus 500 rapid-scanning quadrupole mass spectrometer, operated in the EI or ECNI mode, is an excellent detector for GC × GC. As for acquisition, in the scan mode good-quality mass spectra covering a mass range of 300 Da can be obtained at an acquisition rate of 20 Hz. This is suitable for peaks with a baseline width of at least 300 ms, which implies that it can be used for many, and certainly for most organohalogen applications. In the SIM mode, acquisition rates of up to 90 Hz can be used when only one ion is monitored. This allows the adequate recording (at least seven data points) of peaks having baseline widths as low as 80 ms.

The present GC × GC–ECNI qMS set-up is, consequently, highly suitable for the trace-level analysis of a variety of organohalogenated compound mixtures. The examples given here include PCAs, for which ordered structures were found and interpreted, and selected BDEs, which showed LODs of 10–40 fg (SIM mode: *m/z* 79 + 81). In the latter case, the improved detectability allowed the identification of several additional congeners in an eel sample. Similarly low LODs were found for most priority CDD/Fs. Here, however, there were two exceptions, OCDD and 2,3,7,8-TCDD, for which the ECNI mechanism does not provide enough sensitivity (LODs of 450–710 fg). This means that further work is needed before the present technique can be recommended as a replacement for GC–HRMS in dioxin analysis.

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