2.3 Evaluating the use of a high-resolution time-of-flight mass spectrometer for the determination of selected environmental contaminants[§]

Summary

A benchtop high-resolution time-of-flight mass spectrometer (TOF MS) was evaluated for the determination of key organic microcontaminants. The major advantage of the TOF MS proved to be the high mass resolution of about 0.002 Da (10 ppm). Consequently, the detectability of polar pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls is excellent, and detection limits are in the order of 1–4 pg injected mass. Best mass spectral resolution was obtained for medium-scale peaks. It is a disadvantage that the calibration range is rather limited, *viz.* to about two orders of magnitude. The high mass spectral resolution was especially useful to improve the selectivity and sensitivity when analyzing target compounds in complex samples and to prevent false-positive identifications.

[§] From *J. Chromatogr. A*, 970 (2002) 213-223, also published in J. Dallüge, PhD thesis, Free University, Amsterdam, the Netherlands, 2003.

2.3.1 Introduction

Today, three types of commercially available mass spectrometers (MS) are mainly used in combination with gas chromatography (GC), quadrupole, ion-trap, and sector instruments. With the introduction of relatively inexpensive and user-friendly benchtop quadrupole and ion-trap instruments, MS detection became available for routine operation in GC. Both types of instrument provide unit mass resolution (R<1000), moderate scan speeds of up to 10 spectra/s and detection limits in the low-pg range. Sector instruments provide a much higher mass resolution (R>10,000). Usually, they are operated in the selected-ion monitoring (SIM) mode or used to scan over a narrow mass range, and are used for the target analysis of, *e.g.*, polychlorinated dibenzodioxins and -furans [2], biphenyls (CBs) [3] or toxaphene [4]. Sector instruments trade sensitivity for resolution – the higher mass resolution is obtained by using narrow slits, which allows only ions in a narrow *m/z* range only to pass through [1]. Detectability is similar to that of quadrupole and ion-trap detectors in the SIM mode at a much higher mass resolution; however, operated in the full-scan mode, the scan speed then is typically 3 scans/s. In addition, they are expensive and bulky, and experienced operators are required.

Some seven years ago, the first commercially available time-of-flight mass spectrometer (TOF MS) was introduced for analytical purposes. In contrast to the above MS systems, which use an electrical or magnetic field to separate ions with different *m/z* values, TOF MS instruments measure the time an ion needs to travel through a field-free region. The ions generated in the ion source, are accelerated as discrete packages into the field-free flight tube by using a pulsed electrical field. Flight times – which are proportional to the square root of the *m/z* of an ion – are in the order of microseconds. Consequently, TOF MS can be operated at very high repetition rates, typically 5–30 kHz, *i.e.* 5000–30,000 raw mass spectra are generated per second. Of course, fast detector electronics (which were not available or too expensive until a few years ago) are required to record the arrival times of the ions at the end of the flight tube. A number of the raw mass spectra are added or averaged and, typically, 10–500 spectra/s are stored in the computer system. [5,6,7]

The fast scan speed makes TOF MS very suitable for fast, flash or comprehensive GC. In addition, because discrete packages of ions are analyzed in the flight tube, analyte concentrations do not change during the 'scan' of one raw mass spectrum; consequently,

TOF MS is not prone to skewing. Due to the high repetition rate, a large fraction of the ions generated in the ion source is pulsed into the flight tube, and during separation in that tube, no ions are lost (which does occur with scanning instruments such as the quadrupole MS). Consequently the duty cycle of a TOF MS is 20–30% as against 0.1–1% for a scanning instrument. As a result, sensitivity will be higher for TOF MS, than for the other instruments when operated in the *scanning* mode.

In TOF MS, there are today two more or less complementary approaches, with instruments that provide high resolution (5–10 ppm) [7] but have a moderate scan speed (ca. 10 Hz), and instruments that feature a high storage speed of, typically, 100–500 spectra/s but usually provide only unit-mass resolution (or, as actually should be said, a resolution of 300–1500; at 50% peak-height definition). In the past few years, high-speed instruments have repeatedly been used successfully as detectors of choice for fast and comprehensive GC [6, 8]. The LECO (St. Joseph, MI, USA) TOF MS Model Pegasus II is the instrument used in most of these studies. Recently, a benchtop high-resolution mass spectrometer has been marketed by Micromass (Manchester, UK). It is, therefore, of distinct interest to study the capabilities of this instrument for the identification/determination of key organic micropollutants and to briefly compare the merits of both approaches.

2.3.2 Experimental

Materials

All chemicals used were of research-grade quality. Methyl acetate was distilled before use. A standard containing 40 nitrogen- and/or phosphorus-containing pesticides (code NPM-525C), a PCB standard (EPA PCB congener calibration check solution), and a mixture of the 16 EPA PAHs were obtained from J.T. Baker (Deventer, the Netherlands).

Methods

Instrumental. Analyses were performed on a HP 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) using a GCT time-of-flight mass spectrometer (Micromass, Manchester, UK) as detector. The GCT TOF MS was equipped with a 1 GHz time-to-digital converter. Injections were done in the on-column mode using a 1 m x 0.53 mm I.D. retention gap. Pesticides and PAHs were separated on a 30 m x 0.25 mm

I.D. x 0.25 μm DB-5 MS column (J&W, Folsom, CA, USA); the PCBs were separated on a 40 m x 0.18 mm I.D. x 0.18 μm DB-5 column (J&W).

The GCT TOF MS was operated at a multi-channel plate voltage of 2500 V, a pusher interval of 40 μs (resulting in 25,000 raw spectra per second), and a scan range of *m/z* 50–500. The spectrum storage rate was 2 Hz. 2,4,6-Tris-trifluoromethyl-[1,3,5]triazine was used as internal standard for mass calibration with *m/z* 284.9950 as internal reference mass. During analysis, the internal standard was continuously introduced into the ion source. MassLynx software version 3.4 was used for data processing.

For comparison, a HP 6890 (Agilent Technologies) equipped with an Optic 2 programmable injector (ATAS, Veldhoven, the Netherlands) and a Pegasus II TOF MS (LECO, St. Joseph, MI, USA) was used. The LECO TOF MS allows spectrum storage rates of 1–500 spectra per second at mass-unit resolution. The LECO TOF MS was operated at a spectrum storage rate of 2 Hz, using a mass range of *m/z* 45–500 and a multi-channel plate voltage of –2000 V. With this set-up, 1-μl injections were performed in the cold splitless mode. Separations were carried out on a 30 m x 0.25 mm I.D. x 0.25 μm DB-5 MS column (J&W).

Wastewater. Solid-phase extraction (SPE) of the wastewater samples was performed on a Prospekt automated sample preparation system (Spark Holland, Emmen, the Netherlands). The Prospekt system consists of three six-port valves, an automated cartridge exchanger and a solvent delivery unit including solvent selection valves and an LC pump. The solvent for the desorption of the SPE cartridges was delivered by a Phoenix CU20 syringe pump (Carlo Erba Strumentazione, Milan, Italy).

Samples of influent water from a municipal sewage water treatment plant were first centrifuged and, then, filtered through a 0.45 μm membrane filter (type HA, Millipore, Etten-Leur, the Netherlands). SPE was carried out as described in [9] using 50 ml of wastewater. In the final desorption step the analytes were eluted with 200 μl of methyl acetate. The samples were spiked with the pesticide mixture at levels of 0.05–0.1 μg/l.

Eel samples. PCB extraction was based on total lipid extraction according to Bligh and Dyer [10]. The extracted lipids, which had been used for the determination of the fat

content, were redissolved in hexane, and this solution was cleaned on a 5% deactivated alumina (Merck, Darmstadt, Germany) and, next, a 5% deactivated silica (Merck) column. Prior to the final concentration step, tetrachloronaphthalene (Promochem, Wesel, Germany) was added as an internal standard.

2.3.3 Results and discussion

Mass accuracy: dependence on signal intensity

According to its specifications, the GCT TOF MS equipped with a 1 GHz time-to-digital converter should be able to achieve a mass accuracy of better than 10 ppm (above *m/z* 200) or 0.002 Da (below *m/z* 200), provided that the peak of interest has a 'sufficient intensity'. The lower relative mass accuracy (expressed in ppm) below *m/z* 200 is caused by limitations of the detector electronics, since at these low masses much smaller flight-time differences have to be measured. Actually, a further improvement *viz.* to 5 ppm and 0.001 Da, respectively, is possible with an optional 3.6 GHz time-to-digital converter which was, however, not available to us. In this section, two aspects will be studied: (i) the influence of the signal intensity on the mass accuracy and (ii) the effects of a reduced mass accuracy on the peak shape.

Figure 2.3.1A shows the dependence of the mass accuracy (difference between calculated and measured mass in ppm) on the signal intensity for a set of 40 pesticides in the range *m/z* 200–300. The data points were obtained by examining more than 80 single mass spectra (at 2 Hz, *i.e.* obtained by averaging 12,500 raw spectra to achieve high mass accuracy) that were acquired across several chromatographic peaks. The mass accuracy clearly improves with the signal intensity. At intensities below 300 counts, an accuracy of better than 10 ppm was obtained for only half of the examined spectra. Clearly, a signal intensity of about 2000–3000 counts in a single mass spectrum (at 2 Hz) is required to achieve a mass accuracy of better than 10 ppm for the pesticides. Translating this result into the minimum mass of an analyte that has to be injected, two typical examples may be quoted: a signal intensity of 2000 counts corresponded to an injected mass of 150 pg atrazine (at the *m/z* 215.0938 trace) or 20 pg pyrene (*m/z* 202.0783 trace).

The lower mass accuracy at low mass intensities limited the possibility of using narrow mass windows when generating selected ion chromatograms in trace-level studies or for less intense masses in the spectrum. In addition, the mass determination on the lower

slopes of a chromatographic peak (with their lower intensities) will be less accurate, as is shown in Figure 2.3.1B. Consequently, in some instances, the edges of a peak were 'cut off' when using too narrow mass windows because the masses measured at the edges were outside the mass window. This is demonstrated in Figure 2.3.1C for a 25 ppm and a 10 ppm mass window, with atrazine as an example. Such behaviour will result in an underestimation of the peak area; a broader mass window had, therefore, to be used for quantification at trace levels.

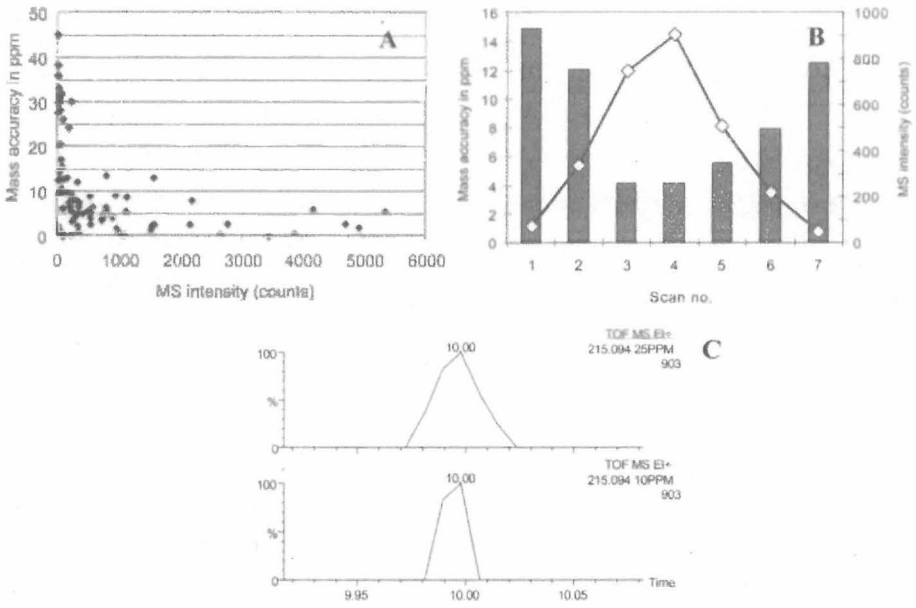

Figure 2.3.1: (A) Dependence of mass accuracy (in ppm) on signal intensity for low concentrations (using 40 test pesticides, mass range m/z 200–300). **(B)** Mass accuracy across a peak with a low intensity. The bars indicate the mass accuracy, the full-drawn line the MS intensity (i.e. peak profile). The example is for a 300 pg injection of atrazine; m/z 215.0938 trace. **(C)** Influence of mass window on peak profile at low concentration. Extract ion chromatogram of atrazine (300 pg); upper trace, 25 ppm mass window; lower trace, 10 ppm mass window.

The lower mass accuracy at these low intensities had, however, little consequence when the accurate mass of a chromatographic peak had to be determined. In that case, usually the mass spectrum at the (intense) peak apex was used. If required, the mass accuracy could be improved by combining (averaging) 3–5 mass spectra across the peak apex, which means that between about 37,000 and 62,000 raw mass spectra were actually

combined. The combined mass spectra feature enhanced signal-to-noise and improved mass accuracy. The algorithm combines peaks in the mass spectrum within a selected mass window (good results were obtained with a window of 0.01 Da) into a single peak. To quote an example, with analytes for which the mass accuracy obtained at the peak maximum was as poor as 28 ppm, the operation effected a distinct improvement to better than 10 ppm.

The data acquisition of the GCT uses a so-called time-to-digital converter (TDC). The TDC is an ion counting system, which can only record the arrival of one ion at a time. After recording such an event, the TDC requires a certain dead time to recover before it can register another ion. At relatively high analyte concentrations and, consequently, higher ion currents it is more likely that one or more ions will arrive within the dead time and, therefore, will not be registered. Quantification will then be incorrect, and the number of non-detected ions will be higher in the higher-*m/z* part of a peak in the mass spectrum. This will cause a shift of the apex towards a lower mass. The software automatically corrects for these effects via a so-called dead-time correction model. However, this dead-time correction does not work at high peak intensities, and the software indicates peaks in the mass spectra that are too intense to use the correction model by a question mark. In our study, this was observed for all peaks that exceeded an intensity of about 6000 counts. The accurate mass can, then, not be determined with sufficient reliability, *i.e.* the identification potential is affected.

The influence of high signal intensities on the measured mass was studied with phthalate esters (*m/z* 149.0239) as an example, because they were present at very high concentrations in some of the samples. As shown in Figure 2.3.2A, the mass accuracy clearly deteriorated at intensities above approx. 50,000 counts. At these high intensities the measured mass was clearly shifted towards lower values, as explained above. However, in the 6000–50,0000 range a mass accuracy of better than 0.006 Da was still achieved. This suggests that accurate masses can still be obtained in, at least, some cases where the software indicates that the dead-time correction model is exceeded. However, the limited information now available does not yet permit us to draw generally valid conclusions.

As an illustration of the decreased mass accuracy across an intense peak, Figure 2.3.2B shows the peak profile and the corresponding mass accuracy across an intense peak of CB 153 in an eel extract. The marked contrast with Figure 2.3.1B is obvious: mass spectra should now be obtained from slopes of the peak because of the higher mass accuracy there. In order to show what can also happen in such situations, Figure 2.3.2C demonstrates that decreased mass accuracy at the peak apex of a very intense peak may lead to split peaks when using narrow mass windows. Therefore, quantification masses should be chosen such that also at high analyte amounts, they are still within the dead-time model. This may imply that, in some cases, a less intense quantification ion has to be selected.

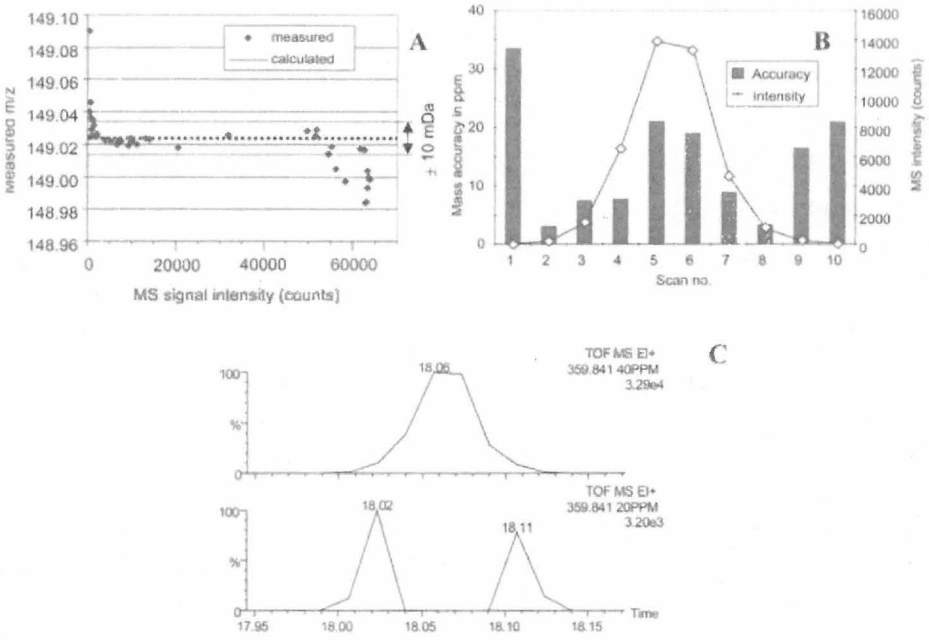

Figure 2.3.2: **(A)** Dependence of measured mass on signal intensity (using *m/z* 149.0239 mass of phthalates as example). **(B)** Mass accuracy across a peak with a high intensity. The bars indicate the mass accuracy, the full-drawn line the MS intensity (*i.e.* the peak profile). The example is for a 620 pg injection of CB 153 in eel extract; *m/z* 357.8444 trace. **(C)** Influence of mass window on peak profile. Extract ion chromatogram of CB 153 (approx. 620 pg, eel extract); upper trace, 40 ppm mass window; lower trace, 20 ppm mass window.

Due to the continuous introduction of a calibration compound during each analysis, its mass spectrum (containing *m/z* 68.9952, 121.0014, 189.9966, 265.9964 and 284.9949) is superimposed on all other mass spectra. These spectra can, therefore, not directly be used

for library searching; a background subtraction has to be performed prior to the search. As an example, Figure 2.3.3A shows the mass spectrum obtained at the peak apex of CB 66 in an eel extract. The mass of the $^{12}C_{12}H_5{}^{35}Cl_5$ isotope peak at *m/z* 323.8817 was measured with a mass error of 5.3 ppm (theoretical value, *m/z* 323.8834). The combination of four spectra across the peak resulted in an improved mass accuracy with an error of only 1.8 ppm (*m/z* 323.8828, Figure 2.3.3B). During this process, a background subtraction was also performed to remove the interfering masses of the calibration compound at *m/z* 265.9946 and 284.9950 providing a much cleaner spectrum. Figure 2.3.3C shows the calculated isotope peaks for $C_{12}H_5Cl_5$.

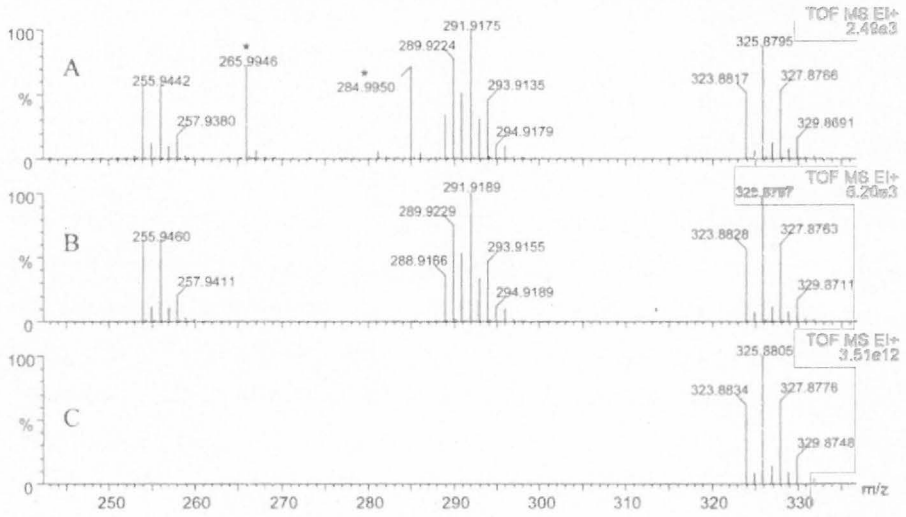

Figure 2.3.3: (A) Part of mass spectrum of CB 66 obtained at peak apex. Peaks indicated with an asterisk (*) are masses of the calibration compound (*m/z* 265.9946 and 284.9950). **(B)** Mass spectrum obtained by averaging four spectra across the peak and subtracting the background. **(C)** Mass spectrum generated for isotope cluster of $C_{12}H_5Cl_5$.

One final remark should be made here. With many complex biological and environmental samples, peak overlap occurs throughout the chromatogram and the recorded mass spectra are, consequently, impure. This causes no insurmountable problems when target analysis performed. If, however, non-target analysis is a relevant aspect of the study, then the automated resolution of the mass spectra of co-eluting compounds, *i.e.* obtaining pure spectra by using a deconvolution algorithm, is extremely powerful – much more than manual subtraction. Unfortunately, this option – which is available on the LECO Pegasus

and the Thermo-Finnigan Tempus – is, as yet, not part of the data-processing software of the GCT.

Table 2.3.1: LODs (pg) of selected analytes using accurate-mass (GCT) or unit-mass (GCT, LECO) resolution*

Compound	Quantification mass (*m/z*)	GCT at 0.05 Da	GCT at 1 Da	LECO at 1 Da
Chlorpyriphos	198.9173	2	10	6
Atrazine	200.0703	1	3	4
Prometryn	241.1361	2	3	4
Trifluralin	306.0702	4	4	5
Metolachlor	162.1283	2	4	2
Chrysene	228.0939	1	2	2
Acenaphthylene	152.0626	1	4	0.5
Benzo[a]pyrene	276.0939	2	5	2.5

*: All experiments at 2 Hz

Detection limits and linearity

Detection limits

The detection limits (LODs) were determined by injecting standard solutions with concentrations of 3 and 10 pg/µl. They were calculated for two different mass windows of 1 Da and 0.05 Da. Data were obtained for 40 pesticides and 16 PAHs; selected data are shown in Table 2.3.1. The results were compared with those from a GC–TOF MS system with a LECO Pegasus II TOF MS, using the same GC column and column dimensions and temperature programme. Both detectors were operated at 2 Hz; however, the LECO Pegasus used a detector (multichannel plate) voltage of 2000 V as against 2500 V for the Micromass GCT. The LECO TOF MS was only used to compare detection limits because the main purpose of the two TOF MS systems used is different (high speed *vs.* high resolution; *cf.* above) and an extended comparison is therefore not appropriate. As for Table 2.3.2, because CB extracts are generally complex mixtures with many closely contiguous or even co-eluting congeners, peak heights are often preferred to peak areas for quantification, and both modes of calculation were used.

When using the GCT TOF MS, the LODs for the pesticides, PAHs and CBs were in the order of 1–14 pg when using a 1 Da mass window. In most cases, a narrower mass window of 0.05 Da provided better detectability since noise was reduced, resulting in an up to 5-fold improved result. In some cases, however, where very selective quantification masses were used (*e.g. m/z* 306.0702 for trifluralin), no improvement could be achieved.

For the CBs, there was no essential difference between peak-height and peak-area based LODs.

Table 2.3.2 : LODs (pg) of selected CBs, peak heights (H) or areas (A) for GCT TOF MS using accurate-mass (at 0.05 Da) or unit-mass (1 Da) resolution.

CB congener	Quantification mass (*m/z*)	LODs at 0.05 Da		LODs at 1 Da	
		H	A	H	A
CB 28	255.9613	1	1	3	7
CB 52	289.9224	1	1	4	6
CB 77	289.9224	1	1	4	3
CB 101	323.8834	1	1	4	6
CB 105	323.8834	1	1	4	4
CB 118	323.8834	1	1	4	3
CB 126	323.8834	1	1	4	3
CB 138	357.8444	1	1	5	4
CB 153	357.8444	1	1	4	4
CB 180	391.8054	1	1	5	9
CB 209	493.6885	4	3	14	25

In summary, with GCT TOF MS, and especially with a 0.05 Da window, analyte detectability is excellent for a wide range of a microcontaminants. As for the CBs, the LODs were at least an order of magnitude better than those found with conventional quadrupole systems operated in the full-scan mode [11]. Of course, for this class of compounds, the ECD still is the most sensitive detector but, in most instances, the much improved selectivity of the GCT TOF MS will far outweigh the loss of sensitivity.

Linearity

The linearity was tested over two or three orders of magnitude in the pg range (injected mass). Representative results for some selected analytes are presented in Table 2.3.3. With the PAHs, linear calibration plots were invariably found, but the plots for the pesticides and CBs were best described by second-order polynomes. Neither we nor the GCT's manufacturers can explain the latter somewhat unexpected result.

The quantification masses for the calibration plots for pesticides and CBs were chosen in such a way that no mass error occurred at the highest concentration level (*cf.* Section 3.1). With the PAHs this was impossible since their mass spectra show only little fragmentation and the (intense) molecular ion had to be used for quantification. A mass error was indicated at the highest injected-mass level of the PAHs (300 pg), indicating that the peaks were too intense to reliably calculate an accurate mass. Naphthalene is

included as an example in Table 2.3.3. However, the data for pyrene and chrysene were kept included in the calibration plot, because in both cases mass accuracy was still better than 10 ppm (at intensities of 6000–9000 counts). Generally speaking, the mass error at higher analyte concentrations limited the linearity to about two orders of magnitude.

Table 3.2.3: Correlation coefficients and calibration equations for selected analytes

Analyte	Quantification mass (*m/z*)	R^2	Calibration equation (y: area, x: concentration)	Concentration range (ng/µl)*
Chlorpyriphos	198.9173	0.9996	$y = 4.4127*10^{-5} x^2 + 0.06204 x$	3–1000
Atrazine	215.0938	0.9954	$y = 5.6522*10^{-5} x^2 + 0.07665 x$	10–1000
Prometryn	199.0984	0.9987	$y = 3.7864*10^{-5} x^2 + 0.04429 x$	10–1000
Trifluralin	306.0702	0.9958	$y = 2.9070*10^{-5} x^2 + 0.03167 x$	10–1000
Metolachlor	238.0999	0.9958	$y = 6.4350*10^{-5} x^2 + 0.06157 x$	3–1000
Naphthalene	128.0626	0.9998	$y = 1.2618 x + 3.115$	3 – 100
Pyrene	202.0783	0.9960	$y = 1.1135 x + 7.0067$	3 – 300
Chrysene	228.0939	0.9982	$y = 1.1196 x - 4.2563$	3 – 300
CB 28	255.9613	0.9991	$y = -0.240559 * x^2 + 90.0592 * x - 94.4804$	2 – 200
CB 52	289.9224	0.9953	$y = -0.27345 * x^2 + 75.4055 * x - 158.665$	2 – 200
CB 101	323.8834	0.9995	$y = -0.122038 * x^2 + 36.3936 * x - 29.7716$	2 – 200
CB 118	323.8834	0.9988	$y = -0.137872 * x^2 + 39.6264 * x - 66.7305$	2 – 200
CB 153	357.8444	0.9975	$y = -0.123917 * x^2 + 33.2781 * x - 65.2652$	2 – 200
CB 180	391.8054	0.9991	$y = -0.0959157 * x^2 + 27.1354 * x - 60.1815$	2 – 200
CB 209	493.6885	0.9960	$y = -0.0552169 * x^2 + 14.0631 * x - 31.7155$	2 – 200

*: 5 or 6 data points

Applications

The high mass accuracy is clearly the main advantage of the GCT TOF MS and will be especially useful when analyzing complex samples. Narrower mass windows will provide a better separation of the analytes from co-eluting compounds and will improve the detectability [12]. The two examples of Figure 2.3.4 should serve to illustrate this, with wastewater as the sample type. The spiking level of the extract was 50 pg/µl.

The example of Figures 2.3.4A and B shows that when a mass window of 1 Da (*m/z* 215) was used, atrazine could not be completely separated from a co-eluting compound (Figure 2.3.4A, peak at 10.02 min) and, overall, the baseline was very noisy. However, when a mass window of 0.02 Da was used, the atrazine peak stood out very clearly and most of the noise had disappeared (Figure 2.3.4B); this resulted in a 3-fold improved LOD. The second example is shown in Figure 2.3.4C where the quantification mass, *m/z* 198.9173, of chlorpyriphos in a 1 Da mass window was not selective at all: many peaks show up in the chromatogram and several of these are at least as prominent as chlorpyriphos itself

(eluting at 10.92 min). Narrowing the mass window to 0.02 Da had an effect which is even more dramatic than with the earlier example: in Figure 2.3.4D a prominent analyte peak stands out against an empty background. In this case, the LOD was improved 15–20-fold.

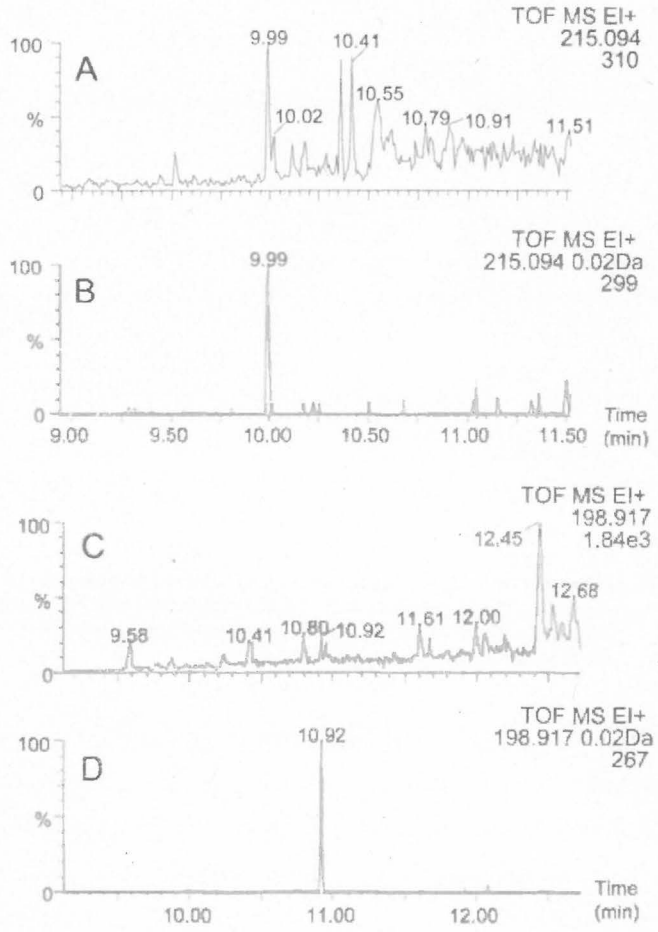

Figure 2.3.4: GCT–TOF MS chromatograms of a wastewater extract (spiked at 50 pg/µl). Extracted ion chromatograms are shown for atrazine (windows A and B; *m/z* 215.0938) and chlorpyriphos (windows C and D; *m/z* 198.9173). The upper chromatograms (A, C) were extracted using a window of 1 Da, the lower chromatograms (B, D) using a mass window of 0.02 Da.

Two further remarks should be made. For the two examples shown, a reduction of the mass window to 0.004 Da did not further improve the S/N ratios because the edges of the chromatographic peaks now were cut off (*cf.* Section 3.1). Secondly, as was earlier observed for trifluralin, using a narrower mass window did not always enhance the

detectability. When, for example, metolachlor was added to the same wastewater sample, the LODs were the same, *viz.* 15 pg, with a 1 Da and a 0.02 Da window. This can be explained by the high selectivity of the *m/z* 162 quantification mass.

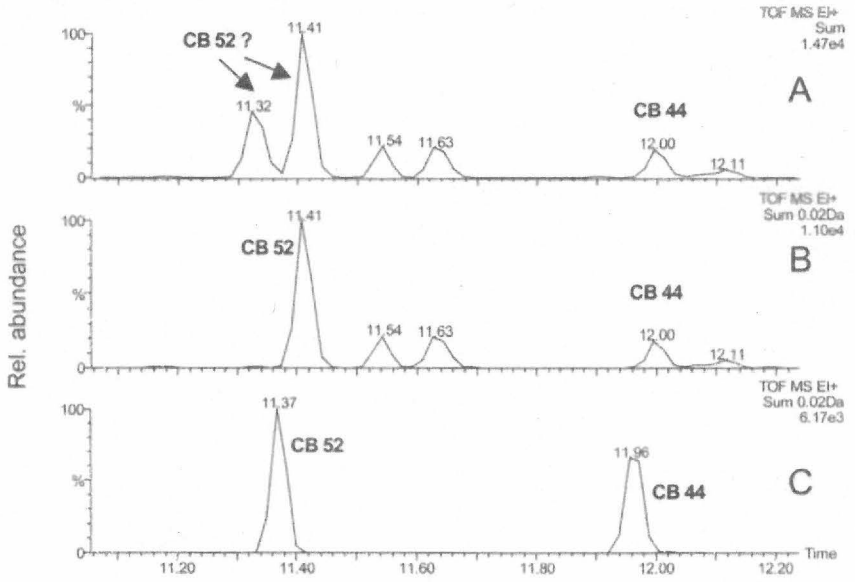

Figure 2.3.5: Influence of the size of the mass windows on the quality of ion chromatograms for an eel sample with high concentrations of CBs. Chromatogram **A** (eel extract) was extracted using a mass window of 1 Da, chromatograms **B** (eel extract) and **C** (standard solution) using 0.02 Da. All chromatograms were extracted using the sum of 10 quantification masses.

LOD calculations for CB in environmental samples were performed with an eel extract that contained only trace levels of these microcontaminants. Even though the general conclusions regarding the GCT were found to hold also in this case, the results differed from those found above for the wastewater in several respects. To quote an example, using a narrower mass window caused only little improvement in analyte detectability, and the LODs (individual data not shown) were 1–2 pg for essentially all CBs, *i.e.* the same as found for standard solutions. Still, the merit of narrow-mass-window recording was clearly shown for contaminants such as, *e.g.*, CB 52, which was present in another eel sample. At nominal mass resolution, no peak was found at the retention time of CB 52 (due to an, initially non-recognized, 0.04-min retention time shift; see Figure 2.3.5C); however, two peaks were found in close proximity (Figure 2.3.5A). Only a narrower mass window revealed that the peak at 11.41 min indeed was CB 52 (Figure 2.3.5B). A similar, but more serious, problem is shown in Figure 2.3.6. In the extracted ion chromatogram of

another extract recorded at a 1 Da window, the fairly large peak eluting at the same time as does CB 118 could easily be mistaken for that compound (Figures 2.3.6A and B, respectively). However, when using an appropriately narrow mass window of 0.02 Da (Figure 2.3.6C), no peak was found at this retention time at all, which means that CB 118 is present in the extract below the LOD of 1 pg injected mass. In this case, a false-positive identification was prevented.

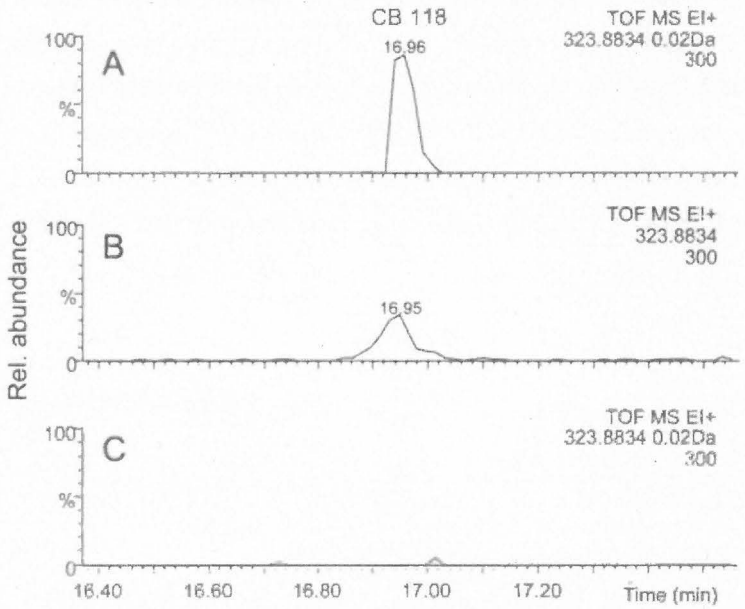

Figure 2.3.6: GCT–TOF MS chromatograms of the *m/z* 323.8834 ion traces of **(A)** a CB standard (10 pg) and **(B, C)** an eel extract. Traces **A** and **C** were extracted by using a window of 0.02 Da, and trace **B** by using a mass window of 1 Da. Signal intensities are the same in all three frames.

2.3.4 Conclusions

The GCT is the first benchtop TOF MS that offers high resolution. The 1 GHz instrument which was tested, achieved a mass accuracy of better than 10 ppm (0.002 Da); at higher analyte amounts or when combining spectra, a mass accuracy of better than 5 ppm was often obtained. The detection limits for pesticides, PAHs and CBs were in the low-pg range. The high mass accuracy allowed the use of narrow mass windows of, typically, 0.02 Da, which substantially improved the identification and quantification of target analytes. However, the accuracy of the measured *m/z* values is

strongly influenced by the signal intensity. It decreases at both too low and too high signal intensities, which is an aspect that has to be considered when selecting the width of the mass windows. This also causes the practically useful ranges of calibration plots to be rather limited.

The high mass resolution of the GCT TOF MS provided excellent selectivity for many of the analytes that were investigated in this study. This selectivity provided improved sensitivity and better identification/confirmation of target compounds in complex matrices. In contrast to sector instruments, the GCT always operates in the scan mode (as do all TOF MS instruments), providing full mass spectra for identification of non-target analytes. One may therefore conclude that the high-resolution GCT instrument (especially once deconvolution software has been developed) can have a role complementary to that of high-speed TOF MS instruments which are to be preferred for fast GC and GCxGC operation.

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