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Congener specific determination of toxaphene residues in fish liver oil using gas chromatography coupled to ion trap MS/MS

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Abstract

A new approach to the determination of six toxaphene congeners in edible stuff has been accomplished. The analytical procedure presented in this paper involves a single-step cleanup process prior to the analysis. A solution containing three ^{13}C labelled polychlorinated biphenyls was used as internal standard and tetrachloronaphtalene was used as injection standard.

The analytical technique used was gas chromatography coupled to ion trap mass spectrometry detector in MS/MS mode. The parameters affecting the successive fragmentations were discussed and optimized.

The limits of detection ranged from 2 to 49 pg μl^{-1}.

The toxaphene congeners were determined in two different fish liver oil pills sold in Spain as a supplementary vitamin support.

Keywords: Toxaphene; Ion trap; Fish oil; Edible stuff

1. Introduction

Toxaphene is a complex mixture primarily consisting of chlorinated bornanes (CHBs) with an average elemental composition of $C_{10}H_{10}Cl_8$. Shortly after its introduction in the forties, toxaphene became one of the most heavily used pesticides for several decades. During the eighties, the use of toxaphene was more and more restricted because of residues in the environment, due to its stability, accumulation and long range transport, but it is still widely used in several countries (Saleh, 1991). The total global production is estimated to be 1.3 million tons (Voldner and Li, 1993), which is higher than that of polychlorinated biphenyls (PCBs).

Toxaphene has been detected as a contaminant in several environmental compartments and has a widespread distribution (De Boer and Wester, 1993; Hargrave et al., 1993; Wideqvist et al., 1993; Muir and De Boer, 1995). Due to aerial transport, it has been detected in remote areas (Zell and Ballschmiter, 1980; Bidleman

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et al., 1995), such as polar regions, and it is there that toxaphene is supposed to result in elevated concentrations because of the condensation occurring at low temperatures (Wania and Mackay, 1995).

Different chlorine substitution patterns can theoretically lead to 32768 congeners (Vetter, 1993), most of them having chiral activity. Even though technical toxaphene consists of up to 6840 CHBs, only some hundred were identified in the mixture (Jansson and Wideqvist, 1983; Zhu et al., 1994). Nonetheless, species with highly developed enzyme systems (e.g. marine mammals, birds and some fish) at or near the top marine food webs, are able to metabolize most toxaphene components. As a result, only a few hepta, octa and nonachloro-homologues accumulate in fatty tissues of mammals and fish (Alder and Vieth, 1996; Vetter et al., 1997; Vetter and Oehme, 1999). In contrast to PCBs, the major compounds in the technical toxaphene mixture (Parlar #32 and Parlar #42) do not bioaccumulate (Vetter and Scherer, 1999). On the other hand, two major recalcitrant CHBs in marine mammals have been identified as Parlar #26 and Parlar #50 (Jin and Jury, 1995; Majewski et al., 1995; Yates et al., 1996a,b,c). That is the reason why a congener-specific determination is needed and it also offers the possibility of determining the compounds with a higher toxicological relevance.

In earlier papers (Vetter et al., 2001), eight individual congeners were selected for their determination, including three so-called indicator congeners (Parlar #26, Parlar #50 and Parlar #62) used by German food chemists to control toxaphene levels in fish and fish products.

Since 1997, the Federal Republic of Germany set the allowable limit of toxaphene in fish at 0.1 mg kg^{-1} (Kruse and Geschonke, 1999) and it is known that these congeners represent about 25–50% of the toxaphene residues in fish (Chan and Yeboah, 2000).

Toxaphene was the most commonly used pesticide in the seventies (Saleh, 1991). Because of its persistence, it is still the predominant organochlorine in many ecosystems such as the Great Lakes (Glassmeyer et al., 1997). Elevated levels of toxaphene have also been found in the Arctic environment and toxaphene has become a health hazard to the indigenous peoples (Kinloch et al., 1992). Nonetheless, significant levels have been found in Antarctic fauna as well (Vetter et al., 2001).

Up to now, the two most commonly used detectors for measuring toxaphene in environmental samples have been electron capture negative ionization mass spectrometer (ECNI-MS) and electron capture detector (ECD) (Kinloch et al., 1992; Andrews et al., 1995). Each detector has some advantages but also some remarkable handicaps. ECD enables a similar selectivity for toxaphene compounds and also for other organochlorinated compounds leading to possible overestimated concentrations due to interferences. In contrast, ECNI-MS is based on the mass-to-charge ratios of the compounds, but in this case, the fragmentations of the molecular ions provide major differences in the response factors of the target ion (Alder et al., 1996). In order to overcome these troubles, the high resolution gas chromatography (HRGC) combined with negative ion chemical ionization (NICI) mass spectrometry (MS) is frequently employed, though it does not completely eliminate such disturbances.

Recently, the determination of toxaphene residues using the ion trap tandem mass spectrometry in SIM mode has been reported (Chan et al., 1998; Skopp et al., 2002). This detection mode partially overcomes the EI-LRMS limitations by enhancing sensitivity (increase signal-to-noise (S/N) ratios) and selectivity (fragmentation from isolated parent ion to specific daughter ions when operating the MS/MS mode) and can be an alternative technology to the more expensive high resolution mass spectrometry.

Accordingly, the papers reporting the determination of organochlorinated compounds by using the ion trap detection have increased in the last years.

In this study, the different parameters affecting the MS/MS detection of a variety of toxaphene congeners in an ion trap detector (ITD) have been optimized for each individual congener, whose chemical structures are in Fig. 1. Moreover, these six individual toxaphene congeners in some fish liver oil pills sold in Spain have been determined.

2. Experimental

2.1. Chemicals and standards

Individual standard solutions of toxaphene congeners (Parlar numbers #26, #32, #40, #44, #50 and #62) at 1 ng μl^{-1} were purchased from Dr. Ehrenstorfer, GmbH, (Augsburg, Germany) and kept refrigerated until used.

Likewise, individual standard solutions of the ^{13}C-labelled PCBs #77, #126 and #169 (Dr. Ehrenstorfer, GmbH.) were adequately diluted to prepare a stock solution of them at 2.5 ng μl^{-1}. This solution was kept refrigerated until used as internal standard.

A stock solution of 1,2,3,4-tetrachloronaphtalene (TCN, Dr. Ehrenstorfer, GmbH.) at 10 pg μl^{-1} was prepared in isooctane and kept refrigerated until used as injection standard.

Isooctane was Pestipur quality (SDS, Peypin, France) and hexane was analytical grade (Merck, Darmstadt, Germany). Sulphuric acid was pro analysis quality (Merck). Anhydrous sodium sulphate was obtained from J.T. Baker (Deventer, The Netherlands) and silica gel 60 from Merck.

A set of Hamilton micro-syringes of volumes ranging from 10 to 250 μl were used throughout the work.

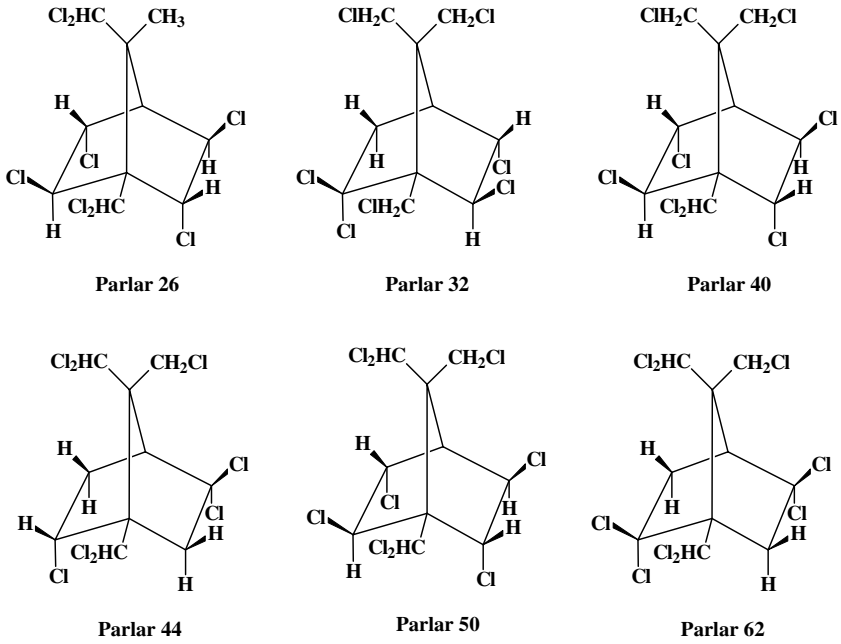

Fig. 1. Chemical structures of the toxaphene congeners studied.

2.2. Sample preparation

Sample preparation for the determination of toxaphene is extremely easy and straightforward. Each sample of fish liver oil, typically 1–2 g, was accurately weighed in a 5 ml glass vial and added 4 μl of the ^{13}C-labelled PCB stock solution containing 2.5 ng μl^{-1}. The sample was then loaded into glass column successively containing two layers of sulphuric acid modified silica at 22% and 44% (w:w) and one layer of neuter silica. The column was topped and bottomed with 1 cm of anhydrous sodium sulphate and was washed with 125 ml of hexane prior to use.

The samples were then eluted with 125 ml of hexane and collected in round bottom flasks. Later on, the samples were rotary evaporated until a volume of about 1 ml was reached. And finally, they were transferred to conical bottom injection vials and evaporated to dryness under a gentle nitrogen stream.

After all this process, the samples were reconstituted with 20 μl of TCN at 10 pg μl^{-1} and analysed by GC coupled to MS-ITD detector.

2.3. Instrumentation

A Varian Gas Chromatograph (CP-3800, Palo Alto, CA, USA) equipped with an ion trap detector Saturn 2000, Varian, was used for MS/MS. Samples were injected in the hot splitless mode (2 μl; 100 °C hold for 2 min, and then to 300 °C at 200 °C min^{-1}; split rate 1:60) in a capillary BPX-5 column (60 m, 0.25 mm i.d., 0.25 μm film thickness) purchased from SGE (Australia). The column temperature was programmed from 60 °C (3 min) to 200 °C (3 min) at a rate of 30 °C min^{-1}, then to 230 °C (15 min) at 3 °C min^{-1} and then to 270 °C (15 min) at 5 °C min^{-1} and finally held for 24 more minutes. Helium was used as the carrier gas at a constant flow rate of 1.0 ml min^{-1}. The temperature of the transfer line and the ion trap were set at 280 °C and 220 °C, respectively.

The ITD was operated in MS/MS mode for toxaphene congeners and internal standards, whereas the SIM mode was used for the injection standard. Further details are provided below.

3. Results and discussion

In 2002, Gouteux et al. (2002) studied the selection of different parent and daughter ions to improve the limits of detection of CHBs in ion trap MS/MS analysis. As a result, an analytical method was optimized including the choice of parent and daughter ions at low mass-to-charge ratios for P#26, P#40/41 and P#44 and at high mass-to-charge ratios for P#50 and P#62.

Although it has been reported in literature that P#32 does not bioaccumulate, this congener has been included in our work because it is one of the major congeners in commercial toxaphene. Thus, it can be considered as an indicator of the presence of toxaphene in environmental

samples and therefore, it is not possible to discard it entering the biotic systems.

3.1. Influence of the voltage for collision induced dissociation

A solution containing six toxaphene congeners P#26, P#32, P#40, P#44, P#50 and P#62 at 0.5 ng μl^{-1} was prepared in isooctane from the stock solutions. This solution, which was called "Z" for labelling purposes, was used for optimizing all the parameters affecting the detection, and it was always chromatographically separated under the GC conditions described earlier.

According to Gouteux et al. (2002), there are two possible dissociation pathways. The first one, the general dissociation, can be observed in all the congeners, and it would be the dissociation of the *m/z* 125 as parent ion (I_p) into the *m/z* 89 as daughter ion (I_d). The second one, the specific dissociation, would involve the dissociation of another different I_p into another I_d, being both different for each congener.

The general dissociation was preliminarily selected in order to study the influence of the voltage applied in collision induced dissociation (CID) mode on the fragmentation of the parent ion. This I_p (*m/z* 125) corresponds to the monochlorotropylium structure, which is an important fragment characteristic of toxaphene congeners (Hainzl et al., 1995) and the resulting I_d (*m/z* 89) corresponds to the full dechlorinated structure of these compounds. The voltage was varied from 0.05 to 0.50 V, applied for 20 ms in the resonant mode, in ten 0.05 V steps in order to obtain the voltages that provide maximum dissociation of I_p into I_d, that is, the highest peaks of I_d for each congener.

Likewise, a similar experience was carried out for the dissociation of the specific ions for each congener. Finally, the general and specific parent and daughter ions as well as the suitable voltages obtained are summarized in Table 1.

The next step was to decide what dissociation of I_p into I_d was best in terms of signal-to-noise ratio, in other words, which daughter ion should be selected for monitoring and quantifying purposes. Thus, the chromatograms monitoring each daughter ion of each congener were overlapped and the peaks were compared in terms of area and height. The peaks obtained monitoring the *m/z* 89 I_d were slightly higher for Parlars #26, #32 and #44 than the ones obtained monitoring the *m/z* 305. On the other hand, the peaks obtained monitoring the characteristic I_d were slightly higher for Parlars #40, #50 and #62 than the ones obtained monitoring the general I_d.

Table 1
Selected voltages for the dissociation of two I_p into I_d for each congener

Congener	I_p (*m/z*)	I_d (*m/z*)	Voltage (V)	I_p (*m/z*)	I_d (*m/z*)	Voltage (V)
P#26	125	89	0.32	305	269	0.48
P#32	125	89	0.30	305	269	0.31
P#40	125	89	0.28	305	269	0.50
P#44	125	89	0.31	305	269	0.38
P#50	125	89	0.31	279	243	0.51
P#62	125	89	0.30	303	267	0.39

3.2. Influence of the CID time on the dissociation of I_p into I_d

Toxaphene congeners are supposed to be labile compounds. This approach means that a key point is how long a precursor ion can take a voltage to produce the expected fragmentation without going further.

For this purpose, a separation of the "Z" sample was run and the selected parent ions for each compound were isolated and stabilized in the resonant waveform mode for 5 ms. Collision induced dissociation by helium gas was made during 5 ms at the voltages selected as suitable and the results were compared with those obtained for a 20 ms CID time. Thus, the CID time that provided the best signal-to-noise ratio was selected as suitable in each case (Table 2).

3.3. Monitoring the internal and injection standards

In earlier papers, the ion monitoring for the compounds that we have used as internal and injection standards have been discussed (Gómara et al., 2002). As a result, the TCN was monitored at *m/z* 264 in SIM mode, whereas the detector was operated in MS/MS for the monitoring of the ^{13}C labelled PCBs used as internal standards (Table 3).

Table 2
Collision induced dissociation times and voltages for the dissociation of the I_p into I_d

Congener	I_p (*m/z*)	I_d (*m/z*)	Voltage (V)	CID time (ms)
P#26	125	89	0.32	20
P#32	125	89	0.30	20
P#40	305	269	0.50	5
P#44	125	89	0.31	20
P#50	279	243	0.51	5
P#62	303	267	0.39	5

Table 3
Selected ions for the monitoring of the internal standards

^{13}C-PCB	I_p (*m/z*)	I_d (*m/z*)
#77*	304	232 + 234
#126*	338	266 + 268
#169*	372	300 + 302

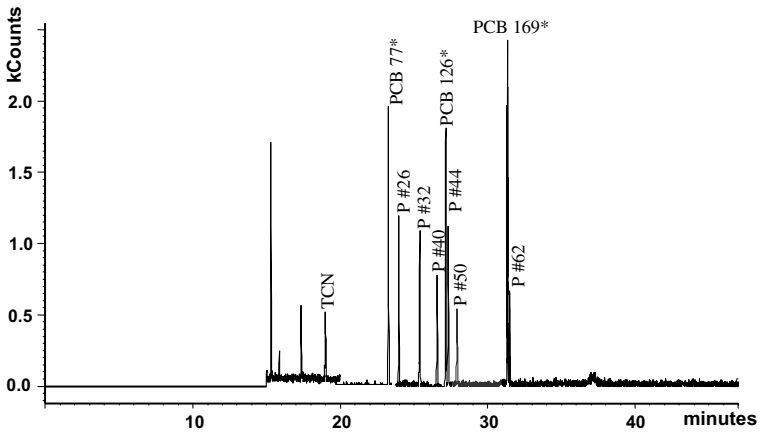

Fig. 2. Chromatogram corresponding to a standard solution containing the toxaphene congeners and the internal and injection standards under the optimized conditions.

Finally, a typical chromatogram of the mixture, recorded under the optimized separating and ion-monitoring conditions, is shown in Fig. 2.

3.4. Quantitative aspects

3.4.1. Limits of detection and quantification

The limit of detection (LOD) was estimated in accordance with the baseline noise. The baseline noise was evaluated by recording the detector response over a period about ten times the peak width. The LOD was obtained as the congener concentration that caused a peak with a height three times the baseline noise level. Likewise, the limit of quantification (LOQ) was obtained as the congener concentration that caused a peak with a height ten times the baseline noise level.

Thus, the LODs ranged from 2 to 49 pg μl^{-1}, whereas the LOQs ranged from 6 to 163 pg μl^{-1}.

3.4.2. Linearity range and calibration curves

The linearity of the assay was checked by duplicate injecting 2 μl of a set of standard solutions containing increasing concentrations of the analytes from the limits of quantification up to 50 ng μl^{-1} following the chromatographic procedure described above. The adequate amount of the internal standard solution was added so that the final concentration of the ^{13}C-PCBs is 0.05 ng μl^{-1}. Each CHB was assigned the ^{13}C-PCB whose retention time was closest. Thus, PCB 77* was assigned to P#26 and P#32, PCB 126* to P#40 and P#44 and PCB 169* to P#50 and P#62.

The calibration curves were obtained by plotting the CHB over internal standard peak area versus the CHB over internal standard concentration.

In all cases, the calibration curves showed an excellent linear relationship between relative concentrations and areas. The equations and determination coefficients are summarized in Table 4. In all cases, the intercepts were considered as negligible according to the Student's test "t" ($\alpha = 0.05$).

3.4.3. Application

The presented analytical procedure was applied to the determination of some toxaphene congeners in fish liver oil commercial pearls.

The reason why a standard reference material (SRM) was not analysed for toxaphene congeners prior to the application to real samples is that there is no SRM certified for these compounds. In spite of it, some authors have used the NIST SRM 1588 for the determination

Table 4
Calibration curves and determination coefficients

	Linear regression equation[a]	r^2
P#26	$A = -1.1\ (\pm 2.2) \times 10^{-2} + 50.7\ (\pm 1.7) \times 10^{-3} \times C$	0.9953
P#32	$A = 3.3\ (\pm 2.9) \times 10^{-2} + 58.9\ (\pm 2.3) \times 10^{-3} \times C$	0.9940
P#40	$A = -2.8\ (\pm 1.2) \times 10^{-2} + 43.1\ (\pm 1.0) \times 10^{-3} \times C$	0.9982
P#44	$A = -1.2\ (\pm 1.0) \times 10^{-2} + 617.0\ (\pm 8.4) \times 10^{-4} \times C$	0.9993
P#50	$A = 5.2\ (\pm 6.9) \times 10^{-3} + 136.6\ (\pm 5.4) \times 10^{-4} \times C$	0.9938
P#62	$A = -15.9\ (\pm 6.3) \times 10^{-3} + 212.5\ (\pm 7.4) \times 10^{-4} \times C$	0.9953

[a] A and C stand for relative area and relative concentration, respectively.

Table 5
Toxaphene congener concentrations in fish liver oil pills (ng g^{-1})

Congeners	Natural Nankervis		Arkofluid	
	Average	Standard deviation	Average	Standard deviation
Parlar 26	48.4	5.0	0.488	0.097
Parlar 32	<LOD	–	<LOD	–
Parlar 40	27.7	5.1	3.09	0.59
Parlar 44	<LOD	–	0.45	0.11
Parlar 50	289	25	7.06	0.45
Parlar 62	47.0	1.2	2.01	0.60

of total toxaphene and/or for some particular congeners (Chan et al., 1998; Skopp et al., 2002) as interlaboratory exercise.

The pearls, mentioned above, are sold without prescription as an extra vitamin support. The samples were analysed as explained in "sample preparation" and the results are summarized in Table 5.

The concentrations of each and every toxaphene congener in the "Natural Nankervis" pills resulted to be slightly higher than in the "Arkofluid" pills.

The resulting toxaphene congener pattern indicated that the P#50 was the most concentrated one and that the concentration of the P#32 congener was found to be under the limit of detection in both samples. This is in agreement with the fact that P#50 is considered as recalcitrant and that P#32 does not bioaccumulate, as explained earlier in the paper.

It is also remarkable that the so-called indicator congeners, P#26, P#50 and P#62 which, according to literature, may represent about 25–50% (w:w) of the full toxaphene content, were found in both samples. Owing to the fact that the dose recommended by the manufacturer ranges from two up to four pills a day, the daily intake of toxaphene for an individual would roughly range from 700 up to 2100 ng a day.

In this way, epidemiology studies on exposure to toxaphene have shown that an adult human being can take up to 75 mg a day (Sherlanski, 1987) of toxaphene with no effect on blood analyses according to environmental health criteria, so the found concentrations are not expected to produce toxic effects if taken as recommended.

Finally, the presented procedure has been proved adequate for the determination of some toxaphene congeners in two kind of fish liver oil pills, both being commercially available in Spain. The concentrations, however, pose a minimum health risk for human consumption.

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