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Evaluation of gas chromatography–tandem quadrupole mass spectrometry for the determination of organochlorine pesticides in fats and oils

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Abstract

A gas chromatography–tandem quadrupole mass spectrometry multi-residue method for the analysis of 19 organochlorine pesticides in fats and oils has been developed. Gel permeation chromatography was employed to remove lipid material prior to GC–MS/MS analysis. Average recoveries of the pesticides spiked at 10 and 50 $\mu g\,kg^{-1}$ into fish oil, pork fat, olive oil and hydrogenated vegetable oil were typically in the range 70–110% with relative standard deviations generally less than 10%. Calculated limits of detection are between 0.1 and 2.0 $\mu g\,kg^{-1}$ and results obtained for the analysis of proficiency test materials are in good agreement with assigned values. The higher selectivity of the GC–MS/MS compared to electron capture detection and GC–MS in selective ion monitoring mode allowed unambiguous identification and confirmation of all the target pesticides at low $\mu g\,kg^{-1}$ levels in fats and oils in a single analysis.

Keywords: Tandem quadrupole mass spectrometry; Gas chromatography; Organochlorine pesticides; Fats and oils

1. Introduction

Regulations governing permitted levels of persistent organic pollutants such as organochlorine pesticides (OCPs) in food products are becoming increasingly stringent in response to an increased awareness of the toxic hazards they pose to humans [1]. Since these analytes do not readily degrade in the environment and are lipophilic, with a tendency to bioaccumulate, they can be found at high concentrations in fatty foods, especially meats and fish. Current UK maximum residue levels (MRLs) for these analytes in animal products are set between 0.02 and 1 $mg\,kg^{-1}$ on a fat basis [2]. Due to the mounting concerns about the effects of these pollutants an international treaty restricting the use of persistent organic pollutants, including OCPs, came into force on 17 May 2004 [3]. In order to enforce the regulations, improved analytical methodologies with adequate confirmation of identity and limits of quantification need to be available.

Methods of analysis for OCPs in fatty matrices invariably involve a clean-up step, usually gel permeation chromatography (GPC) [4,5] and/or solid-phase extraction (SPE) [6]. GPC is relatively effective at removing fats and oils and is applicable to a wide range of OCPs, but a further SPE clean-up step is often required to remove any remaining lipid and other matrix components. Although the use of a further SPE clean-up step provides cleaner extracts, it can also result in low recoveries for some OCPs and, in addition, the increase in time and solvent usage makes this option less desirable.

The majority of methods for the determination of OCPs involve gas chromatography coupled with either electron-capture detection (ECD) [5,7,8] or mass spectrometry (MS) [8]. The former technique does not provide unequivocal confirmation of identity and is often subject to matrix interferences, thus MS detection, usually in selected ion monitoring (SIM) mode, is the preferred method of choice in

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many monitoring laboratories. Although GC–MS in the SIM mode is necessary to provide adequate quantification at the low levels required, confidence in the confirmation of identity is reduced if one or more of the selected ions are affected by matrix interferences. The use of high-resolution GC–MS can allow better selectivity, but sector instruments are complex and expensive and the accuracy of the measured *m/z* values in time-of-flight MS (TOF-MS) instruments are strongly influenced by the signal intensity and can decrease both at low and at high signal intensities [9]. Alternatively, MS/MS with triple quadrupole or ion trap instruments can also be employed to achieve a high level of selectivity and low detection limits. Garrido Frenich et al. [7] reported that the use of GC ion-trap MS/MS overcame the problems arising from interferences that occurred with GC–ECD and as a consequence showed better sensitivity for the determination of OCPs in serum. Serrano et al. [10] employed ion-trap MS/MS for the analysis of low levels of organochlorine pesticides in fatty materials but a similar evaluation of tandem quadrupole MS/MS for the determination organochlorine pesticides in fatty matrices does not appear to have been previously reported.

The main aim of this work is to evaluate the capability of tandem quadrupole mass spectrometry (GC–MS/MS) for the unequivocal confirmation and accurate quantification of OCPs at low $\mu g\,kg^{-1}$ levels in fatty matrices without the need for a SPE clean-up following GPC.

2. Experimental

2.1. Chemicals and reagents

Pesticide reference standards (purity >98.0%) were purchased from Qm_x (Thaxted, UK) and LGC-Promochem (Teddington, UK). Hexane, ethyl acetate and cyclohexane (analytical reagent grade) were all purchased from Fisher Scientific (Loughborough, UK).

Individual stock standard solutions ($1000\,\mu g\,ml^{-1}$) were prepared in hexane. Working standard mixtures in hexane, containing $1\,\mu g\,ml^{-1}$ of each OCP, were prepared for use as spiking solutions.

2.2. Apparatus

Determination was performed using a Varian GC–MS system comprising of a CP-3800 gas chromatograph with a 1177 injector, a CP8400 autosampler and a 1200 triple quadrupole MS (Varian, Walnut Creek, CA, USA). Data acquisition and processing were performed using a Varian Star workstation, version 6.20. A fused-silica capillary column (VF-5ms phase, 30 m × 0.25 mm I.D., 0.25 μm film thickness; Varian) protected by a CarboFrit insert (Restek, Bellefonte, PA, USA) in the GC liner was used for all analyses.

The GPC system was comprised of a model 307 high-performance liquid chromatography (HPLC) pump connected to a 232 automated sample processor, incorporating a 401 dilutor fitted with a 1 ml sample loop (Gilson, Villiers-le-bel, France). Two Envirosep-ABC columns, 60 mm × 21.2 mm I.D. and 350 mm × 21.2 mm I.D. (Phenomenex, Macclesfield, UK) were connected in series, and cyclohexane–ethyl acetate (1:1, v/v) was used as mobile phase at a flow rate of $5\,ml\,min^{-1}$. A centrifugal evaporator (Jouan, Tring, UK) was used for concentration of GPC extracts.

2.3. GC–MS/MS conditions

Splitless injections (4 μl) were performed with a splitless time of 1.5 min and the injector temperature set at 250 °C. The GC temperature program was 100 °C for 1.5 min followed by a $20\,°C\,min^{-1}$ ramp to 200 °C (held for 6 min), $10\,°C\,min^{-1}$ ramp to 260 °C (held for 1 min) and a final ramp of $10\,°C\,min^{-1}$ to 280 °C (held for 2.5 min). The total GC run time was 24 min, with 3.5 min between injections to allow for cool-down (1.75 min), stabilization (0.5 min), and injection (1.25 min).

The tandem quadrupole instrument was operated in electron ionisation (EI) mode. The MS/MS detector interface temperature was set at 200 °C, source temperature at 300 °C and detector voltage at 1600 V. The filament was switched on after 7.5 min, approximately 1 min before the elution of the first peak of interest. The MS/MS conditions in the multiple reaction monitoring (MRM) mode are given in Table 1. Helium (99.997% purity) at a flow-rate of $1\,ml\,min^{-1}$ was used as carrier and argon (137 kPa) as the collision gas. The GC–MS/MS system was calibrated weekly using perfluorotributylamine.

2.4. Samples

Samples of pork fat, fish oil, hydrogenated vegetable oil and olive oil (organically-produced) were used as blanks and for the preparation of spiked samples and matrix-matched calibration standards.

2.5. Extraction procedure and clean-up

A 1.25 g portion of the sample was weighed into a volumetric flask (10 ml) and adjusted to volume with GPC mobile phase (ethyl acetate–cyclohexane, 1:1, v/v). For estimation of recovery, samples were spiked with 12.5 or 62.5 μl of a standard solution containing $1\,\mu g\,ml^{-1}$ of each OCP, to provide spiked concentrations equivalent to 10 or $50\,\mu g\,kg^{-1}$ for each OCP in the sample. An aliquot of the extract (1 ml) was cleaned-up by GPC, collecting the fraction eluting between 14.5 and 24.5 min. The GPC fraction was concentrated to near dryness using a centrifugal evaporator, and δ-HCH added (equivalent to $50\,ng\,ml^{-1}$ in the final extract) as an internal standard and the extract then solvent exchanged into hexane (1 ml).

Table 1
Summary of MRM transitions selected for analysis of OCPs in EI mode

Pesticide	Peak number	t_R (min)	Time segment (min[a])	First transition *m/z*	CE/V	Second transition *m/z*	CE/V	Quantification ions
α-HCH	1	8.46	7.50–8.70	219 > 147	30	219 > 183	10	183
Hexachlorobenzene	2	8.56		284 > 214	40	284 > 249	30	249
β-HCH	3	9.05	8.71–10.20	181 > 145	30	219 > 183	10	183
γ-HCH	4	9.21		181 > 145	30	219 > 183	10	183
δ-HCH (IS)		9.97		181 > 145	30	219 > 183	10	183
Heptachlor	5	11.31	10.21–11.80	272 > 237	20	274 > 239	40	237
Aldrin	6	12.77	11.81–13.20	263 > 191	40	293 > 257	10	191 + 257
Oxychlordane	7	14.20	13.21–14.65	187 > 123	10	185 > 149	20	123 + 149
Heptachlor epoxide (*trans*)	8	14.36		253 > 217	40	289 > 253	10	217 + 253
Chlordane (*trans*)	9	15.01	14.66–15.20	373 > 264	40	373 > 266	30	266
Chlordane (*cis*)	10	15.41	15.21–15.70	373 > 264	40	373 > 266	30	266
α-Endosulfan	11	15.44		241 > 206	20	195 > 125	20	206
p,p′-DDE	12	16.07	15.71–16.50	246 > 176	40	318 > 246	30	176
Dieldrin	13	16.25		263 > 193	40	277 > 241	10	193 + 241
Endrin	14	16.85	16.51–16.95	263 > 191	40	281 > 245	20	191 + 245
β-Endosulfan	15	17.10	16.96–17.50	241 > 206	20	195 > 160	20	160 + 206
p,p′-TDE	16	17.19		235 > 165	30	235 > 199	30	165
o,p′-DDT	17	17.25		235 > 165	30	235 > 199	30	165
Endosulfan-sulfate	18	18.22		272 > 235	30	272 > 237	40	235
p,p′-DDT	19	18.15	17.51–22.00	235 > 165	30	235 > 199	20	165

IS: internal standard.
[a] A scan time of 0.3 s data point^{-1} was employed for all analysis.

2.6. Method performance

The accuracy and precision of the method were assessed by the analysis of five replicate recoveries at two spiking levels (10 and 50 μg kg^{-1}) for each sample type (2.4). In addition to recovery spikes, 10 proficiency test samples (all hydrogenated vegetable oil) were analysed. Matrix-matched, multi-level calibration curves, which bracketed the samples, were used for quantification and all results were calculated using peak area and δ-HCH internal standard to correct for volumetric errors.

3. Results and discussion

3.1. Optimisation of MS/MS transitions

From full scan spectra, the most intense higher mass precursor ions were selected for the development of the MRM method. For most of the analytes these were the base peak ions in the mass spectra, but in some cases higher mass ions of lower intensity were selected to minimise the possibility of matrix interferences. Fragment ions with *m/z* ratios <150 were generally disregarded if other ions were available. Following the selection of these precursor ions, product ion spectra were acquired by collision induced dissociation with argon gas. Precursor ions were examined at collision energy (CE) voltages of 10, 20, 30 or 40 V (potential on quadrupole 2) and the most intense product ions were selected for each precursor ion. For example, the precursor *m/z* 219 for the OCP α-HCH gave intense transitions for *m/z* 219 > 145 and 219 > 147 at CE 30 V and for *m/z* 219 > 183, at CE 10 V (Fig. 1). In general the CE that gave the most intense response was chosen for each MRM transition; in the above case the transitions *m/z* 219 > 147 (CE 30 V) and *m/z* 219 > 183 (CE 10 V) were selected. In some cases, for example, *cis*-chlordane and *trans*-chlordane, the same precursor ion was selected for both transitions due to the lack of other suitable ions.

3.2. Optimisation of the GC–MRM method

The gas chromatographic conditions were optimised to give adequate separation of *p,p′*-TDE and *o,p′*-DDT

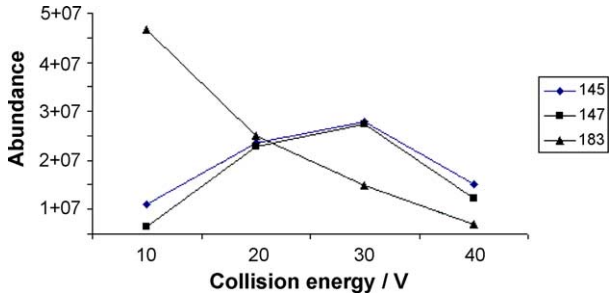

Fig. 1. Plots of abundance vs. collision energy for fragment ions generated from the precursor *m/z* 219 for α-HCH using a 1 μg ml^{-1} OCP standard in hexane ($n = 3$).

(R_s = 0.70). This critical pair produces the same fragment ions, thus necessitating good chromatographic resolution. However, using the same chromatographic conditions the structurally similar chlorinated methanoindene pesticides, *cis*-chlordane and α-endosulfan, co-eluted. It was observed that *cis*-chlordane fragment ions contributed (5–25%) to the response for 13 different MS/MS transitions evaluated for α-endosulfan. No contributions from *cis*-chlordane were observed for five other α-endosulfan MS/MS transitions (all product ions of precursor ion *m*/*z* 339) evaluated but none of these were considered suitable because the abundances were too low. *cis*-Chlordane contributed approximately 10% of the overall response to the 241 > 206 α-endosulfan MS/MS transition selected for this work. The MS/MS transitions selected for *cis*-chlordane were not affected by co-elution with α-endosulfan. Since completing this study, the use of a more polar column, e.g. 50% phenylpolysiloxane was found to improve resolution between *cis*-chlordane and α-endosulfan, as well as *p*,*p*′-TDE and *o*,*p*′-DDT, thus minimising any potential errors.

In EI mode, the HCH and DDT groups of pesticides demonstrated higher signal-to-noise ratios than the endosulfan group, endrin, dieldrin, oxychlordane and heptachlor epoxide. Based on the elution profile, the MRM acquisition method was divided into as many time segments as possible in order to obtain the maximum signal for pesticides that gave the lowest response. The number of transitions (200 transitions allowable per segment) was restricted to maintain adequate sensitivity at the low analyte concentrations of interest. Each segment contained a minimum of two and a maximum of four transitions (i.e. one or two analytes per segment).

The scan time, which can be approximately correlated to dwell time (scan time divided by number of transitions), was varied to determine the relationship between the number of data points and the signal-to-noise ratio. The scan time was set at 1.5–0.2 s data point^{-1} to provide between 4 and 30 data points for analyte peak widths of approximately 6 s. The optimal number of data points for peak area and hence signal-to-noise ratio was found to be between 15 and 20 data points (scan time of 0.3 s data point^{-1} for an analyte peak width of 6 s) as shown in Fig. 2. This equates to dwell time of approximately 75 ms per transition, which is much higher than the minimum of 15 ms permitted by the software. The RSDs for peak area as a function of the number of data points are also plotted in Fig. 2. The results demonstrate that low RSDs and hence acceptable precision in peak area measurements, are also obtained when chromatographic peaks contain between 15 and 20 data points.

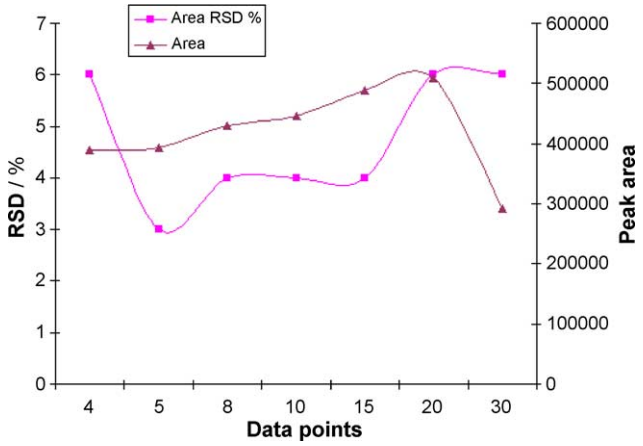

Fig. 2. Response and RSDs for peak area as a function of the number of data points, for endrin using a 50 μg kg^{-1} matrix standard (n = 5 for each data point).

3.3. Calibration

Calibration was evaluated comparing calibration standards prepared in solvent with calibration standards prepared in matrix extracts. Matrix suppression and enhancement effects are well documented in the analysis of pesticides in fruits and vegetables [11] but not for the analysis of OCPs in fatty matrices. This may be because of difficulties in obtaining samples, which do not contain traces of these ubiquitous environmental contaminants. In this work, low levels of *p*,*p*′-DDE and *p*,*p*′-TDE were detected in the fish oil (Fig. 3) and pork fat used as blanks.

The relative response for solvent standards compared to matrix standards was found to be dependent on the priming of the inlet system injections with matrix blank (minimum of five injections). With a CarboFrit insert in the injection liner and no priming, the response for matrix standards was consistently higher than the response for solvent standards. Subsequent priming of the inlet system with blank matrix extracts prior to injection of solvent standards reduced the differences in the relative responses. However, the priming effect was found to be inconsistent for certain analytes, particularly *p*,*p*′-TDE and *o*,*p*′-DDT, thus calibration curves were constructed using matrix matched calibration standards. This observation was assumed to be due to the solvent reactivating of the active sites in the injector rather than matrix enhanced GC degradation of the analytes observed by Foreman [12]. This is supported by the fact that the calibration curves for all analytes were generally linear over the range of interest, 0.75–30 ng ml^{-1} (6–240 μg kg^{-1} equivalent), with correlation coefficients >0.980. The only exceptions were *o*,*p*′-DDT and endosulfan-sulfate, which gave poor calibration in the olive oil matrix probably due to incomplete removal of matrix in the GPC clean-up step (see Section 3.5) and in this instance matrix enhanced GC degradation cannot be ruled out.

3.4. Limits of detection (LODs)

The LOD, defined as the amount injected which gave a signal equivalent to three times the baseline noise, was determined experimentally by combining the averages of duplicate measurements for hydrogenated vegetable oil from two different days. The LODs for the OCPs are in the range

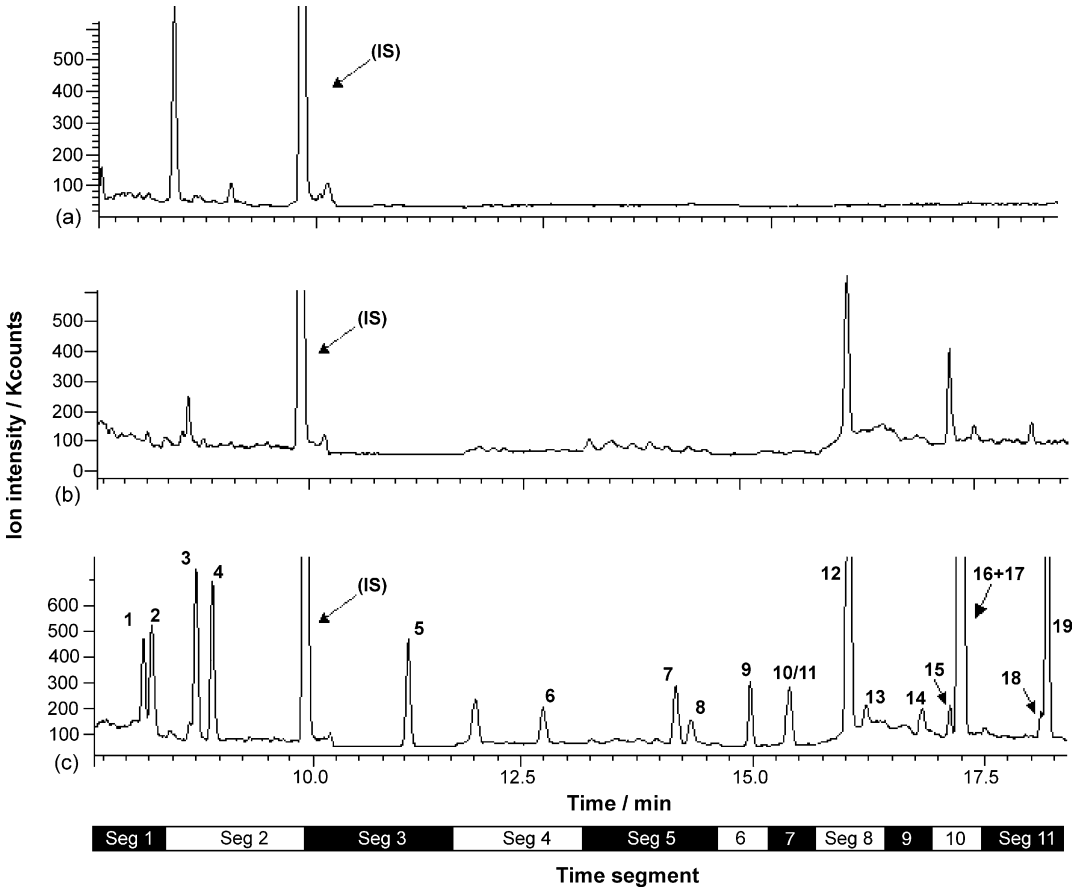

Fig. 3. MRM chromatograms of (a) blank hydrogenated vegetable oil, (b) blank fish oil sample and (c) 6 ng ml^{-1} (50 μg kg^{-1}) OCP fish oil standard. Peak identification numbers are detailed Table 1 (IS refers to the internal standard).

of 0.1–2.0 μg kg^{-1} (Table 2), based on the summed intensities of the two transition ions for each analyte except α-endosulfan which was based on one single transition, *m*/*z* 241 > 206. The limit of quantification of 6 μg kg^{-1} for all analytes was based on a lowest calibrated level of 0.75 ng ml^{-1}. At 6 μg kg^{-1} the response for two individual MS/MS transitions was sufficient for confirmation of identity of all analytes of interest.

3.5. Method recoveries and selectivity

The method was validated for the four representative matrices by analysis of spiked samples at two levels (10 and 50 μg kg^{-1}). The mean recoveries were generally in the range 70–110%, with relative standard deviations (RSDs) between 1 and 18% (Table 2), except HCB, *o*,*p*′-DDT and *p*,*p*′-DDT in olive oil and *p*,*p*′-DDE in pork fat. Thus, the European Union Guidelines [13] for method validation were satisfied for most of the analyte-commodity combinations analysed. The high RSD value (31%) for *p*,*p*′- DDE at 50 μg kg^{-1} in pork fat is difficult to explain since acceptable results were obtained for *p*,*p*′-DDE at 10 μg kg^{-1} in all matrices. The absence of results for HCB (both levels), *o*,*p*′-DDT and endosulfan sulfate (10 μg kg^{-1}) in olive oil was subsequently attributed to a drift in GPC elution times which was caused by fluctuations in the mobile phase flow rate. The low flow rate meant that HCB (the last pesticide to elute) eluted outside of the collection window and was therefore lost to waste. The low flow rate would have also resulted in elution of higher amounts of lipid in the GPC fraction, which appears to have affected the calibration of *o*,*p*′-DDT and endosulfan sulfate. Despite the technical problem with the GPC experienced with the analysis olive oil, the high response and selectivity provided by GC–MS/MS ensured that additional clean-up of GPC extracts was not generally necessary.

The MRM chromatograms for blank hydrogenated vegetable oil and fish oil samples show very few peaks originating from matrix, making the peaks corresponding to target analytes clearly visible (Fig. 3). By contrast, the GC–ECD and GC–MS (operated in SIM) analysis of the same blank fish oil extracts both contained peaks that interfered with the target analytes at the 10 μg kg^{-1} spiking level (Table 3). The same spiked extract analysed by GC–MS/MS showed no matrix interference and permitted quantification of all the OC pesticides at this level. Fig. 4 illustrates specific examples of interferences to the detection of heptachlor by ECD and MS–SIM compared with interference-free chromatogram obtained for MS/MS at the 10 μg kg^{-1} level.

Table 2
Summary of mean recoveries (%), relative standard deviations (RSD, %, in parentheses) and LOD's obtained by GC–MRM analysis of OCPs in samples of oils and fats[a]

OCP	Spiking level ($\mu g\,kg^{-1}$)								LOD[b] ($\mu g\,kg^{-1}$)
	Hydrogenated vegetable oil		Olive oil		Pork fat		Fish oil		
	10	50	10	50	10	50	10	50	
α-HCH	89 (6)	91 (2)	78 (9)	92 (7)	88 (8)	78 (5)	86 (7)	85 (2)	0.5
Hexachlorobenzene	87 (6)	84 (6)	–	–	66 (16)	75 (3)	74 (5)	80 (3)	0.4
β-HCH	89 (7)	102 (4)	84 (9)	98 (3)	92 (8)	86 (1)	85 (10)	90 (2)	0.1
γ-HCH	88 (7)	95 (1)	72 (6)	90 (4)	85 (4)	80 (2)	88 (5)	87 (2)	0.1
Heptachlor	93 (4)	102 (2)	77 (7)	81 (14)	79 (10)	80 (1)	80 (5)	85 (3)	0.5
Aldrin	91 (9)	99 (9)	79 (10)	87 (7)	73 (18)	77 (5)	90 (13)	84 (2)	1.2
Oxychlordane	93 (6)	101 (3)	83 (13)	101 (7)	87 (7)	88 (5)	97 (5)	90 (2)	0.3
Heptachlor epoxide (*trans*)	88 (6)	101 (8)	74 (6)	96 (7)	80 (11)	86 (5)	96 (9)	92 (7)	1.4
Chlordane (*trans*)	93 (5)	103 (3)	88 (12)	102 (6)	89 (4)	86 (4)	93 (10)	93 (2)	0.5
Chlordane (*cis*)	116 (4)	105 (4)	78 (3)	100 (7)	91 (11)	91 (5)	79 (8)	91 (5)	1.8
α-Endosulfan	109 (7)	89 (5)	63 (13)	89 (5)	84 (7)	86 (2)	103 (2)	86 (2)	0.7
p,p′-DDE	84 (6)	101 (3)	80 (4)	105 (4)	79 (5)	70 (31)	80 (6)	93 (4)	0.1
Dieldrin	80 (13)	104 (5)	83 (15)	97 (6)	101 (14)	83 (5)	93 (9)	92 (5)	2.0
Endrin	70 (18)	102 (5)	83 (17)	93 (7)	88 (9)	86 (5)	81 (18)	88 (9)	1.8
β-Endosulfan	94 (7)	100 (5)	65 (12)	97 (8)	88 (12)	86 (3)	94 (12)	89 (9)	1.3
p,p′-TDE	83 (7)	95 (2)	95 (5)	114 (6)	96 (4)	89 (2)	95 (4)	87 (2)	0.1
o,p′-DDT	73 (9)	106 (2)	–	104 (5)	87 (9)	84 (3)	84 (8)	85 (1)	0.1
p,p′-DDT	81 (5)	107 (2)	79 (12)	108 (3)	92 (10)	90 (3)	86 (8)	89 (1)	0.1
Endosulfan-sulfate	94 (7)	96 (4)	–	111 (15)	64 (30)	87 (6)	65 (7)	94 (4)	1.0

[a] Mean of five determinations.
[b] Averages of duplicate measurements on two different days for hydrogenated vegetable oil.

In order to maintain the selectivity and overall integrity of the data, retention times have to be reproducible so that analytes do not elute outside their specified time windows. This is particularly important where analytes elute close to one another but are in separate time windows, e.g. endrin (peak 14, Fig. 3), in segment 9 and β-endosulfan (peak 15), in segment 10. The time between elution of these analytes was approximately 0.167 min. For a typical validation batch consisting of 15 injections of fish oil extracts, retention time repeatability standard deviation was between 0.015 and 0.020 min.

Table 3
Comparison of the capability of MS–SIM and ECD to provide sufficient (+) and insufficient (–) selectivity for the 19 OCPs at the 10 $\mu g\,kg^{-1}$ level

Pesticide	SIM		ECD response
	Ion 1	Ion 2	
Hexachlorobenzene	+	+	+
α-HCH	+	–	+
γ-HCH	–	–	+
β-HCH	+	+	–
Heptachlor	–	–	–
Aldrin	+	–	+
Oxychlordane	–	+	+
Heptachlor epoxide	–	–	+
Chlordane (*trans*)	+	+	–
Chlordane (*cis*)	+	+	+
α-endosulfan	+	–	+
p,p′-DDE	+	+	+
Dieldrin	–	–	+
Endrin	–	–	+
o,p′-DDT	+	+	+
p,p′-TDE	+	+	+
β-Endosulfan	–	+	+
p,p′-DDT	+	+	+
Endosulfan-sulfate	–	–	+

Note: MS/MS provided sufficient selectivity for all OCPs at this level.

3.6. Application

The method developed was applied to 10 food analysis and performance assessment scheme (FAPAS) [14] proficiency test materials of hydrogenated vegetable oil containing known concentrations of OCPs. FAPAS is an interlaboratory comparison as defined by the international organisation for standardisation (ISO Guide 43-1:1997 E). The participating laboratory's reported result for an analyte is assessed with the best estimate of the "true" value of the analyte. Subsequently, the laboratory's performance is compared by generating a z-score, which relates the error associated with a result to a target standard deviation, derived from the proficiency test round. Thus, based on a normal distribution only about 1 in 20 results will be outside two standard deviations from the mean, therefore a z-score of ±2 is considered "satisfactory". The results for the ten samples analysed and the corresponding data as provided by FAPAS show very good agreement for all residues detected (Table 4). In addition, all of the values are well within the specified "satisfactory" range, which are values obtained at ±2 z-scores, including all of the laboratories (>30) taking part for that particular test material.

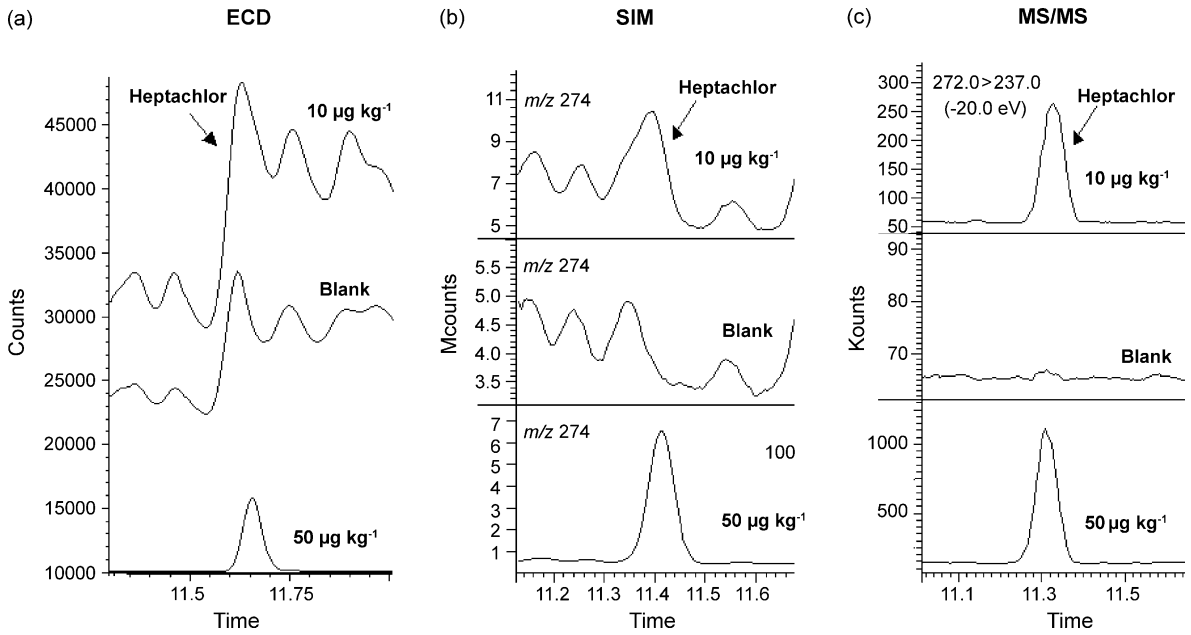

Fig. 4. Comparison of selectivity between (a) ECD, (b) SIM and (c) MS/MS for heptachlor at 10 μg kg^{-1} in fish oil. Chromatograms of the corresponding blank extract and a higher level matrix standard are provided for contrast and identification.

Table 4
GC–MRM results for proficiency test materials with the corresponding assigned values

Test material	Analyte	GC–MS–MS results (μg kg^{-1})	Assigned value (μg kg^{-1})	Satisfactory range (μg kg^{-1})
1	Endrin	31.9	44.8	25.1–64.5
	β-Endosulfan	35.8	37.8	21.2–54.4
	α-Endosulfan	56.6	71.4	40.0–102.8
2	α-HCH	47.8	40.0	22.4–57.6
	p,*p*′-TDE	22.9	34.9	19.5–50.2
3	Heptachlor	23.5	29.3	16.4–42.1
	Heptachlor epoxide (*trans*)	41.2	44.9	25.2–64.7
4	γ-HCH	17.7	24.6	13.8–35.4
	p,*p*′-DDE	59.6	56.6	31.7–81.4
	Dieldrin	23.2	22.8	12.8–32.9
5	γ-HCH	31.4	37.1	20.8–53.5
	Oxychlordane	43.4	42.5	23.8–61.2
	Chlordane (*trans*)	65.5	69.7	39.0–100.4
6	Chlordane (*cis*)	36.5	32.4	18.2–46.7
	α-Endosulfan	25.0	26.0	14.6–37.4
7	β-HCH	19.0	23.9	13.4–34.4
	Heptachlor	71.0	89.3	50.0–128.6
	Endosulfan-sulphate	48.0	48.9	27.4–70.4
8	γ-HCH	53.0	63.4	35.5–91.3
	Chlordane (*trans*)	42.3	43.9	24.6–63.2
	Chlordane (*cis*)	46.3	45.4	25.4–65.4
	p,*p*′-DDT	63.5	90.6	50.7–130.4
9	α-HCH	21.2	27.8	15.6–40.0
	Dieldrin	53.7	54.4	30.5–78.4
10	α-HCH	148.7	161.5	93.5–229.5
	Hexachlorobenzene	73.4	84.1	47.1–121.1
	α-Endosulfan	34.2	45.0	25.2–64.8
	β-Endosulfan	25.0	24.3	13.6–35.0

Note: Assigned values provided by FAPAS.

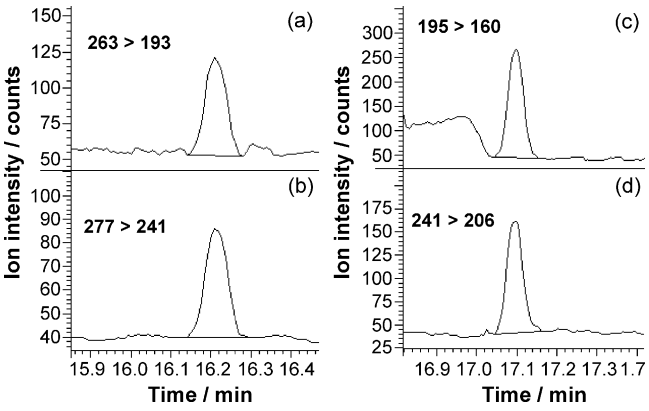

Fig. 5. MRM chromatograms for dieldrin at 23.2 μg kg^{-1} (a and b) in proficiency test material 4, and β-endosulfan at 35.8 μg kg^{-1} (c and d) in proficiency test material 1 (see Table 4). Transitions are given on the chromatogram.

Typical chromatograms obtained using the MS/MS method are illustrated by dieldrin at 23.3 μg kg^{-1} in sample 4 and β-endosulfan at 35.8 μg kg^{-1} in sample 1 (Fig. 5).

4. Conclusion

GC–MS/MS provides excellent selectivity and limits of detection, allowing simultaneous confirmation of identity and quantification of OCPs at low levels in fats and oils. The method is rapid and robust; permitting more than 400 injections of GPC fractionated oil samples, with daily replacement of the liner but without any maintenance of the GC column or ion source. The technique should be applicable to a much larger range of analytes in a range of more complex food commodities and is the subject of ongoing research.

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