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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).