Food Chemistry 151 (2014) 47–52

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

A simplified procedure for the determination of organochlorine pesticides and polychlorobiphenyls in edible vegetable oils

Jindong Li, Donghui Liu, Tong Wu, Wenting Zhao, Zhiqiang Zhou, Peng Wang *

Department of Applied Chemistry, China Agricultural University, Beijing 100193, PR China

ARTICLE INFO

Article history:
Received 25 August 2013
Received in revised form 29 October 2013
Accepted 10 November 2013
Available online 19 November 2013

Keywords:
Organochlorine pesticides
Polychlorinated biphenyls
Matrix solid-phase dispersion
Edible vegetable oils

ABSTRACT

A one-step extraction–purification multiresidue method for the determination of 14 organochlorine pesticides (OCPs) and 7 polychlorinated biphenyls (PCBs) in edible vegetable oils based on matrix solid-phase dispersion (MSPD) has been developed. The experimental parameters affecting the recoveries and the efficiency of the cleanup procedure were thoroughly evaluated. Under an optimised condition, 0.5 g of oil sample was blended with 3.5 g of sulfuric acid-impregnated silica and 0.8 g of silica gel was used as co-column absorbent. The PCBs and OCPs were eluted by 10 mL of *n*-hexane/dichloromethane (70:30, v/v) and determined by gas chromatography equipped with an electron capture detector (GC-ECD). Good recoveries were obtained in the range of 69.6–105.3% with relative standard deviations (RSD) values below 15% in most cases. The limits of detection (LOD), based on a signal-to-noise ratio (S/N) of 3, were in the range of 0.04–0.74 ng/g.

1. Introduction

Organochlorine pesticides (OCPs) were widely used for the control of disease vectors and agricultural pests in the 1960s. Polychlorinated biphenyls (PCBs) were extensively used as heat exchange fluids in electric transformers and capacitors and as addition agents in paint, plastics, etc. since 1930. Both of them are chlorinated hydrocarbon chemicals, which break down slowly in the environment and tend to accumulate and biomagnify in higher trophic level organisms, and cause high level exposure for human and other animals because of their chemical stability and lipophilicity. Many OCPs and PCBs are endocrine disrupting chemicals and carcinogens, and have effects on liver function, the nervous system and so on (Kaushik & Kaushik, 2007; Soto & Sonnenschein, 2010; Steinberg, Juenger, & Gore, 2007). Although banned for many years, these compounds still exist in the environment at present (Barakat, Khairy, & Aukaily, 2013; Ben Ameur et al., 2013; Li et al., 2013). More seriously, because of the volatility and long-range transport through the atmosphere, they can be found in the regions where they have never been used or produced, such as Antarctic and Arctic (Baek, Choi, & Chang, 2011; Cabrerizo, Dachs, Barcelo, & Jonest, 2012; Verreault et al., 2005). In other words, they may be detected in any place in the environment.

OCPs and PCBs can be taken up by crops from the contaminated soil (Kacalkova & Tlustos, 2011; Zohair, Salim, Soyibo, & Beek, 2006) or the polluted air (Yang et al., 2007), and transferred into different tissues of the plants. For oil crops, they may accumulate into the oil seeds easily and consequently exist in the oils because of their lipophilicity. Many studies reported the OCPs and PCBs contamination in edible oils (Adenugba, Headley, McMartin, & Beck, 2008; Bajpal, Shukla, Dixit, & Banerji, 2007; Qin, Leung, Leung, Zheng, & Wong, 2011; Skrbic & Predojevic, 2008). As a necessity in daily life, edible vegetable oil is a large part in daily diet, particularly in Asian populations. For example, the consumption of edible vegetable oils in china is 22.35 million tons in 2006–2007 (Hanzhong, 2007). So the determination and monitoring of OCPs and PCBs in edible vegetable oils are significant for the assessment of dietary safety.

The development of methods to extract fat-soluble non-polar compounds (viz., OCPs and PCBs) from the whole fatty matrix (such as edible vegetable oils) is a challenging issue, because it is difficult to avoid the co-extraction of fatty material, which is harmful for columns and detectors, even in small amounts (Gilbert-Lopez, Garcia-Reyes, & Molina-Diaz, 2009). At present, the commonly applied methods for OCPs and PCBs analysis in oils matrices involve liquid partitioning with organic solvents followed by a clean-up with GPC or SPE (Patel, Fussell, Hetmanski, Goodall, & Keely, 2005). Compared with other methods, GPC can be fully automated and relatively effective at removing lipids. But it needs long analysis times, large amounts of solvents and substantial cost to acquire and maintain the instrument, which are important drawbacks of this methodology. As an alternative to GPC, SPE using adsorption columns with different sorbents (e.g., Florisil, alumina, silica gel) is applicable to remove lipids. Besides, freezing (Nguyen, Lee, & Lee, 2010) and oxidation treatment with concentrated

* Corresponding author. Tel.: +86 10 62732937.
E-mail address: wangpeng@cau.edu.cn (P. Wang).

0308-8146/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodchem.2013.11.047

sulfuric acid (Valsamaki, Boti, Sakkas, & Albanis, 2006) are also used to remove lipids.

MSPD, firstly introduced by Barker et al. in 1989 (Barker, 2000), is a relatively recent sample-treatment procedure used for the simultaneous dispersion and extraction of solid and semi-solid samples. MSPD is performed by blending the sample with an appropriate amount of solid support materials (generally Florisil or C18) in a glass mortar with a glass pestle, to generate a chromatographic material suitable for the extraction of compounds from the dispersed sample. Then, the obtained material is packed into a common syringe barrel SPE column, from which target compounds are isolated with a suitable elution solvent. MSPD offers the possibility of performing extraction and clean-up in one step and does not need special instruments. Because of its flexibility, simplification, and high-efficiency, MSPD is becoming more and more useful in analysis area (Barker, 2007; Capriotti et al., 2010).

Sulfuric acid-impregnated silica is an effective medium for the destructive removal of lipids from food samples (Bjorklund, Muller, & von Holst, 2001) which was applied in many methods (Nevado et al., 2010; Surma-Zadora & Grochowalski, 2008). The purpose of this work is to develop and validate a one-step procedure for the simultaneous extraction and cleanup of 21 OCPs and PCBs from edible vegetable oils, based on MSPD using sulfuric acid-impregnated silica as dispersant. To achieve the best performance of the method, the effects of various experimental parameters on the yield of MSPD extraction process and on the cleanup efficiency were investigated. Four kinds of edible vegetable oils were used to evaluate the efficiency of the method.

2. Experimental

2.1. Reagents and materials

Selected OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, quintozene, hexachlorobenzene, heptachlor, trans-chlordane, cis-chlordane, p,p′-DDD, o,p′-DDT, p,p′-DDT ,p,p′-DDE, and mirex) individual standard solutions at a concentration of 100 μg/mL in *n*-hexane and PCBs (PCB28, PCB52, PCB101, PCB118, PCB138, PCB153, PCB180) mixed standard solution with all components at 2 μg/mL in *n*-hexane were obtained from Agricultural Environmental Protection Institution in Tianjin, China. Chemical structures of the analytes were shown in Fig. 1. The working standard solutions were prepared by dilution of the above standard solution in *n*-hexane to appropriate concentration levels. All of the standard solutions were stored in dark at 4 °C and left for 1 h at ambient temperature prior to use.

Chromatography-grade *n*-hexane, dichloromethane, acetone and ethyl acetate were purchased from Merck (Germany). Anhydrous sodium sulfate (analytical grade) and sulfuric acid (98%) were purchased from Beijing Chemical Reagents Company (Beijing, China). Florisil (100–200 mesh), alumina (100–200 mesh) and silica gel (100–200 mesh) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Glass SPE reservoirs (6 mL) and corresponding polypropylene frits were supplied by Bonna-Agela Technologies (Tianjing, China). Sulfuric acid-impregnated silica was prepared in the laboratory mixing neutral silica gel (previously baked at 120 °C) with sulfuric acid (98%).

All of the edible vegetable oils were purchased from supermarkets in Beijin, China. The virgin olive oil was produced in Spain, and the other kinds of edible vegetable oil were produced in China.

2.2. Matrix solid phase dispersion procedure

Accurately 0.5 g of edible vegetable oil was weighed into a glass mortar, after adding 3.5 g of 40% (w:w) sulfuric acid-impregnated silica the mixture was thoroughly ground with a glass pestle until it became dry and homogeneous (ca. 5 min), which was then introduced into a 6-mL glass SPE reservoir with a polypropylene frit and 0.8 g silica gel as co-column packing at the bottom to obtain a further degree of fractionation and sample clean-up. A second frit was added to the top of the column and it was compressed softly to avoid the formation of voids or channels. The dropwise elution with *n*-hexane/dichloromethane (70:30, v/v) was made by applying a slight vacuum. About 10 mL of the eluent was collected into a graduated conical tube and evaporated until dry with a gentle nitrogen flow. The residue was re-dissolved with 1 mL of *n*-hexane and transferred to an auto sampler vial for gas chromatographic analysis.

2.3. GC instrumentation

An Agilent 7890 GC equipped with an HP-5 (30 m × 0.32 mm × 0.25 μm) capillary column and an ECD was utilised in this work. Ultrapure nitrogen was used as carrier gas at a constant flow rate of 1 mL min^{-1}. Injector was operated in splitless mode at 270 °C and the injection volume was 1 μL. GC oven temperature was programmed as follows: initial column temperature 90 °C, held for 2 min, rate 15 °C min^{-1} to 200 °C, held for 10 min, rate 15 °C min^{-1} to 270 °C, held for 10 min. Detector temperature was set at 290 °C. The GC condition was the same for all of the experiments.

3. Result and discussion

3.1. Optimization approach of MSPD conditions

The main factors affecting the extraction and purification in the MSPD procedure were evaluated, such as the type and amount of dispersion sorbent, co-column sorbent and eluting solvent. The optimization process was performed with 0.5 g of sample spiked at 40 ng/g level.

Sulfuric acid-impregnated silica was used as the dispersion sorbent and the effect of the content of the concentrated sulfuric acid (30%, 40%, 50%, w/w) was investigated. The results showed that 40% sulfuric acid-impregnated silica was better than both 30% and 50% sulfuric acid-impregnated silica. For the 50% sulfuric acid-impregnated silica, lots of brown interferences were eluted, maybe due to the insufficient retention of the products of the sulfonation reaction with less silanol. On the other hand, part of the oil couldn't be removed by the 30% sulfuric acid-impregnated silica because of the inadequate sulfonation reaction. Sulfuric acid-impregnated silica (40% concentrated sulfuric acid) proved to be a better dispersant giving effective elimination and purification for oil matrix, and was selected as the dispersion sorbent. The amount of the dispersant (3 g, 3.5 g, 4 g) was evaluated and the results (Fig. 2) showed that there were no significant differences in terms of the recoveries of the analytes except δ-HCH which got better recovery when using less sulfuric acid-impregnated silica. However, there were higher background and interfering peaks in the chromatogram if 3 g of sulfuric acid-impregnated silica was used. So the amount of the dispersant was set as 3.5 g to get satisfactory recoveries for the most of the analytes and better purification.

For the clean-up of the OCPs and PCBs by normal phase sorbent from complex matrix samples, the mixed solvent with low polarity as eluent was a common choice, such as *n*-hexane/ethyl acetate, *n*-hexane/acetone or *n*-hexane/dichloromethane (Muir & Sverko, 2006). In the present study, the first two kinds of the mixed solvent, *n*-hexane/ethyl acetate, *n*-hexane/acetone, were able to elute the brown interference and caused worse purification, while the combination of *n*-hexane and dichloromethane was better and thus was used as the eluting solution. The mixture of *n*-hexane and dichloromethane in different proportion (10/0, 9/1, 8/2, 7/3, v/v) as