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Short communication

Vortex-homogenized matrix solid-phase dispersion for the extraction of short chain chlorinated paraffins from indoor dust samples

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ABSTRACT

A simple and effective method for determining short chain chlorinated paraffins (SCCPs) in indoor dust is presented. The method employed a modified vortex-homogenized matrix solid-phase dispersion (VH-MSPD) prior to its detection by gas chromatography – electron-capture negative-ion mass spectrometry (GC-ECNI-MS) operating in the selected-ion-monitoring (SIM) mode. Under the best extraction conditions, 0.1-g of dust sample was dispersed with 0.1-g of silica gel by using vortex (2 min) instead of using a mortar and pestle (3 min). After that step, the blend was transferred to a glass column containing 3-g acidic silica gel, 2-g basic silica gel, and 2-g of deactivated silica gel, used as clean-up co-sorbents. Then, target analytes were eluted with 5 mL of *n*-hexane/dichloromethane (2:1, v/v) mixture. The extract was evaporated to dryness under a gentle stream of nitrogen. The residue was then re-dissolved in *n*-hexane (10 μL), and subjected to GC-ECNI-MS analysis. The limits of quantitation (LOQs) ranged from 0.06 to 0.25 μg/g for each SCCP congener. Precision was less than 7% for both intra- and inter-day analysis. Trueness was above 89%, which was calculated by mean extraction recovery. The VH-MSPD combined with GC-ECNI-MS was successfully applied to quantitatively detect SCCPs from various indoor dust samples, and the concentrations ranged from 1.2 to 31.2 μg/g.

1. Introduction

Chlorinated paraffins (CPs), with the general chemical formula of $C_nH_{2n+2-z}Cl_z$, are complex mixtures containing thousands of different homologues and isomers. They have been manufactured for more than 80 years, and are used in lubricant additives, cutting fluids, plasticizers, and flame retardants [1–3]. CPs are classified into three categories: short chain (SCCPs, C_{10}–C_{13}), medium chain (MCCPs, C_{14}–C_{17}), and long chain (LCCPs, $C_{>17}$). Among them, SCCPs have received the most attention due to their wide usage in industries, large potential for release into the environment, and high toxicity [1,2,4–7] compared to the other CPs. SCCPs, like other hydrophobic and persistent organic pollutants, have been detected in all compartments of the environment worldwide: for example, in surface water, wastewater, seawater, sewage, sediments/soil, air, indoor dust, and even more worrisome, in human breast milk. These studies have been reviewed by Bayen et al. [1], Feo et al. [2], Muir [8], and van Mourik et al. [9] extensively.

Indoor dust originates from a number of sources and is a sink for various organic compounds. Therefore, the analysis of chemicals in indoor dust is a good indicator of contamination occurring over long periods of time. The potential adverse effects from indoor exposure to SCCPs and increasingly voiced concerns from public health entities prompted our team to develop a simple, yet reliable method of detecting SCCPs in indoor dust samples. Ultrasonic bath extraction (USBE), followed by additional clean-up steps, based on multi-layer silica gels column purification, is commonly used for extraction and isolation of SCCPs in indoor dust samples [10,11]. These methods are not only time consuming, but also generates a large amount of excess organic waste. In comparison, matrix solid-phase dispersion (MSPD), first reported by Barker and his group [12], requires both less time and less special equipment. MSPD is SPE-based, and involves dispersing the sample over a solid adsorbent before eluting the target analytes with comparatively small volumes of the solvent. The primary advantage of MSPD is that extraction, clean-up, and filtration are all performed in one step, so as to not only reduce the volumes of solvent needed, but also simplify the analytical procedure. Furthermore, MSPD produces lipid-free extract, which rids us of the need to obtain special equipment and perform extra steps to clean-up the extract. Already, this technique has been successfully applied to determine various micropollutants in

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Table 1
Quantitation ions of each SCCPs congeners, linear ranges, linearity, limit of detection and quantitation, precision and trueness data.

Quantitation ions (m/z)	Linear range (μg/mL)	r^2	Mandel test F-value[b]	LOD (μg/g)	LOQ (μg/g)	Intra-day (n = 5)	Inter-day (n = 20)
C_{10}: 278 (Cl_5)[a], 312 (Cl_6), 346 (Cl_7), 382 (Cl_8), 416 (Cl_9), 450 (Cl_{10})	0.5–10	0.9998	1.05	0.02	0.06	100[c] (3)[d]	89[c] (5)[d]
C_{11}: 292 (Cl_5), 326 (Cl_6), 360 (Cl_7), 396 (Cl_8), 430 (Cl_9), 464 (Cl_{10})	1.8–35	0.9989	1.09	0.07	0.2	91 (7)	91 (4)
C_{12}: 340 (Cl_6), 374 (Cl_7), 410 (Cl_8), 444 (Cl_9)	2–40	0.9992	0.34	0.08	0.25	90 (5)	92 (7)
C_{13}: 388 (Cl_7), 424 (Cl_8), 458 (Cl_9).	1–20	0.9995	1.30	0.03	0.1	94 (2)	89 (4)

[a] Chlorine number of each congener is given in parentheses.
[b] $F_{\text{critical}} = 10.13$ at the 95% confidence level.
[c] Mean spiked recovery at a final total spiked concentration of 5.0 μg/g.
[d] Relative standard deviation (%RSD) of spiked recovery is given in parentheses.

aquatic biota, animal tissue, soil, indoor dust, and food samples, as extensively reviewed by Capriotti et al. [13,14].

MSPD may often be used as a way to pretreat biota or solid samples, but the technique needs to be fine-tuned for the types of the matrix used and concentrations of analytes. This study demonstrates a modified VH-MSPD method coupled with GC-ECNI-MS-SIM as a simple and effective method to determine SCCPs in indoor dust samples. The parameters affecting VH-MSPD were systematically investigated using an one-factor-at-a-time approach, which has been widely employed by various research groups to optimize MSPD parameters [13,14]. It was determined that VH-MSPD is suitable for detecting SCCPs in indoor dust samples, and this paper also evaluates the trueness and precision of such a method.

2. Experimental

2.1. Chemicals and reagents

A standard solution chloroparaffins (C_{10}-C_{13}, 55.5% Cl, w/w, 100 μg/mL in cyclohexane) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). $^{13}C_6$-hexachlorobenzene (used as an internal standard; purity > 99%) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). n-Hexane was used to prepare working standards with various concentrations. Silica gel 60 (size 0.063-0.200 mm, 70–230 mesh ASTM) was purchased from Merck (Darmstadt, Germany). All other chemicals and solvents were obtained in high purity grade from Mallinckrodt Baker (Phillipsburg, NJ, USA), Sigma-Aldrich (St. Louis, MO, USA) and Merck. Deionized water (Resistivity $\geq$ 18.2 MΩ-cm) was produced using an ultrapure water system from Barnstead Easypure II (Thermo Fisher Scientific, Hudson, NH, USA).

2.2. Sample collection

Two private household dust samples were collected from Taipei, Taiwan. Indoor dust samples from two office rooms and one dorm room were obtained from National Central University in the suburban area of Tao-Yuan County, northern Taiwan. All samples were collected in the dust bag of a household vacuum cleaner (CV-SJ10T, Hitachi, Japan), which is equipped with a paper dust bag and high efficiency particulate air filter.

Recovery experiments and method evaluation were performed using the spiked “dorm-room dust” samples, which were spiked with the standard mixture to give a final total concentrations of 5.0 μg/g. The spiked samples were mixed by tumbling for 2 h, and then stored in a brown glass bottle at room temperature for 24 h to evaporate the solvent before performing the recovery experiments and method evaluation [15].

2.3. Procedure of matrix solid-phase dispersion

A portion of dust sample (0.1-g) was dispersed with 0.1-g of deactivated silica gel by using vortex (2 min) instead of using a mortar and pestle. This blend was then transferred to a glass column, which contains 3-g acidic silica gel (on the top, fortified with 44% conc. sulfuric acid), 2-g basic silica gel (in the middle, fortified with 33% 1.0 M of sodium hydroxide solution), and 2-g of deactivated silica gel (on the bottom, 3% H_2O) as clean-up co-sorbents. A frit was used as cover over the dispersed sample before the sample was slightly compressed. MSPD column was first eluted with 7 mL of n-hexane to remove less polar interfering contaminants. Then, SCCPs were quantitatively recovered using 5 mL of the mixture of n-hexane/dichloromethane (2:1, v/v). Both solutions were passed through the dispersed sample and co-sorbents by gravity (flow rate: 0.7 mL/min), and at the end of the elution, a small vacuum was applied. The second fraction of eluent (5 mL) was collected and evaporated until dryness by a mild flow of nitrogen. The residue was re-dissolved in a solution of n-hexane (10 μL) containing an internal standard of 0.5 ng/μL, and then the mixture was subjected to GC-ECNI-MS analysis.

2.4. GC–ECNI–MS analysis

The GC–MS analysis was performed using a Finnigan Focus gas chromatograph coupled directly to a Focus DSQ quadrupole mass spectrometer (Waltham, MA, USA). Operation was done in the selected ion monitoring (SIM) mode, which was under electron-capture negative ionization (ECNI) for quantitation. The injection volume was 1 μL. The injection-port temperature was set at 250 °C, and was operated in the splitless mode. A DB-5MS capillary column (15 m × 0.25 mm i.d., 0.25 μm film; Agilent, Santa Clara, CA, USA) was employed for the separation. The GC temperature program conditions were as follows: a 100 °C hold for 1 min, followed by a temperature ramp of 10 °C/min up to 260 °C, and holding the temperature at 260 °C for 6 min. Methane (99.995% purity) was used as the reagent gas with a flow rate of 2.5 mL/min. Ion source and transfer line temperature were kept at 200 °C and 260 °C, respectively. The electron energy was 70 eV and the emission current was 100 μA. The dwell time was 75 ms/ion, and the solvent delay was 3 min. Under ECNI conditions, the most abundant isotope ions of $[M-HCl]^-$ for each congener group (C_{10}-C_{13}) were selected for quantitation, as listed in Table 1. The internal standard $^{13}C_6$-hexachlorobenzene was detected by monitoring ions of m/z 288, 290, 292 (at retention time 7.75 min). Quantitation was performed as the sum of each SCCP congener’s area under the curve in the elution profile of SCCPs, as described elsewhere [16,17].