Talanta 179 (2018) 575–582

Contents lists available at ScienceDirect

Talanta

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

Fast screening of short-chain chlorinated paraffins in indoor dust samples by graphene-assisted laser desorption/ionization mass spectrometry

Xiu Huang[a,b], Qian Liu[b,c,d,*], Wei Gao[b], Yawei Wang[b], Zhou Nie[a], Shouzhuo Yao[a,*], Guibin Jiang[b,d]

[a] State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China
[b] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[c] Institute of Environment and Health, Jianghan University, Wuhan 430056, China
[d] College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Keywords:
Matrix-assisted laser desorption/ionization
Short-chain chlorinated paraffins
Graphene
Mass spectrometry
Environmental sample

ABSTRACT

As an important class of emerging chemical contaminants, short-chain chlorinated paraffins (SCCPs) are considered as one of the most challenging groups of compounds to analyze. In this paper, we report a new method for fast screening of SCCPs based on matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) with graphene as a matrix and 2,5,6,9-tetrachlorodecane as an internal standard. We found that the use of graphene as MALDI matrix generated high peak intensities for SCCPs while producing few background noises. The ion fragmentation mechanisms of SCCPs in MALDI are discussed in detail. Under the optimized conditions, much lower detection limits of SCCP congeners (0.1–5 ng/mL) than those reported previously were obtained. Other distinct advantages such as short analysis time and simplified sample preparation procedures are also demonstrated. The method was successfully applied in fast screening of SCCPs in indoor dust samples and monitoring of human exposure levels to SCCPs, and the results were verified by gas chromatography coupled to negative chemical ionization quadrupole time-of-flight high-resolution mass spectrometry. This work not only offers a new promising tool for SCCP studies, but also further demonstrates the promise of graphene as a new generation of MALDI matrix.

1. Introduction

Chlorinated paraffins (CPs), also called polychlorinated *n*-alkanes, are widely used as lubricants, plasticizers, and additives in a great variety of industrial and consumer products due to their thermal stability, variable viscosity, flame resistance, and low vapor pressure [1,2]. The production volume of CPs in China was estimated to be 260 kt/year in 2006 [3] and over 1 million t/year in 2013 [4]. CPs are classified into three categories according to the length of the carbon chain: short-chain (SCCPs, C_{10}-C_{13}), medium-chain (MCCPs, C_{14}-C_{17}), and long-chain CPs (LCCPs, C_{17}-C_{30}) [5,6]. Among them, SCCPs are most concerned because of their potential toxicity to human and organisms, long-range migration, and long-term persistence in the environment [7]. SCCPs have been identified as persistent organic pollutants (POPs) by the Persistent Organic Pollutants Review Committee (POPRC) in 2017 [8] and have also been added into the list of toxic chemicals by the U. S. Environmental Protection Agency (USEPA) [9]. However, current understanding of the environmental occurrence and fate of SCCPs is still limited due to the extreme difficulty in the analysis of SCCPs in environmental media.

Due to the presence of thousands of isomers and homologues, SCCPs are regarded as “the most challenging groups of substances to analyze and quantify” [10]. Currently, analysis of SCCPs mainly rely on gas chromatography coupled with electron capture negative ionization low-resolution or high-resolution mass spectrometry (GC-ECNI-LRMS or GC-ECNI-HRMS) [7,11]. However, the GC-MS methods cannot fully separate SCCPs. In fact, due to the extremely complex family of CPs, even by using two-dimensional gas chromatography coupled to electron capture negative ionization high-resolution time-of-flight mass spectrometry (GC × GC-ECNI-HRTOF-MS), complete separation of SCCPs is still impossible [12]. Another disadvantage of GC-ECNI-MS methods is that the instrument response of SCCPs closely depend on their chlorination degree, so adequate reference standards of SCCPs are required to calibrate the analytical results. To achieve congener group-level

* Corresponding author at: State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.
E-mail addresses: qianliu@rcees.ac.cn (Q. Liu), szyao@hnu.edu.cn (S. Yao).

https://doi.org/10.1016/j.talanta.2017.11.055
Received 8 June 2017; Received in revised form 20 November 2017; Accepted 26 November 2017
Available online 28 November 2017
0039-9140/

quantification of SCCPs, mathematical deconvolution methods were developed to resolve congener groups of SCCPs from the mass spectra data [13–16]. To shorten the analysis time, Bogdal et al. recently reported a direct injection atmospheric pressure chemical ionization quadrupole time-of-flight high-resolution mass spectrometry (APCI-qTOF-HRMS) method with deconvolution for analysis of CPs with no chromatographic separation [13]. Gao et al. used a negative chemical ionization quadrupole time-of-flight high-resolution mass spectrometry (GC-NCI-qTOF-HRMS) to extract accurate masses of SCCPs to eliminate interferences from other compounds [17]. However, all currently available methods for analysis of SCCPs require laborious and time-consuming sample clean-up procedures [13]. The low throughput of these methods also limits their application in environmental health or exposomic studies. Therefore, new techniques capable of fast analyzing SCCPs in complex samples are highly desired.

The aim of this study is to develop a fast method for screening of SCCPs. To this end, we used for the first time matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) to analyze SCCPs without any column purification procedures or time-consuming chromatographic separation. MALDI-TOF MS is a simple and high-throughput MS technique that uses a matrix to transfer the laser energy and promote the laser desorption/ionization (LDI) process of analytes. This technique is normally only applicable for qualitative analysis of large molecules due to the strong background noises in low-mass regions caused by organic matrices and poor reproducibility resulting from the inhomogenous co-crystallization process of analytes with the matrix. To overcome these problems, we herein used graphene, a novel two-dimensional carbon nanomaterial [18–20], as a MALDI matrix and 2,5,6,9-tetrachlorodecane as an internal standard (IS). Graphene-based materials have been shown to be useful MALDI matrices due to the exceptional properties of graphene, such as strong optical absorption, efficient energy transfer, and unique two-dimensional structures [21–26]. Here we show that graphene could effectively facilitate the LDI process of SCCPs while producing few background noises in low-mass regions. Furthermore, the use of an IS could greatly improve the accuracy of MALDI analysis. Several selected SCCP congener groups could be well resolved by MALDI-TOF MS with LODs at sub-ppb levels. This method was successfully applied in rapid screening of SCCPs in indoor dust samples and monitoring the exposure levels of SCCPs to human body. The results were verified by GC-NCI-qTOF-HRMS method. Therefore, this method provides a valuable complementary to GC-MS methods for SCCP studies.

2. Experimental section

2.1. Chemicals and materials

Chemically converted graphene (purity > 98 wt%; single layer ratio ~80%; thickness 0.8–1.2 nm; diameter 0.5–2 μm; see Fig. S1) and graphene oxide (GO; purity > 99 wt%; single layer ratio ~ 99%; thickness 0.8–1.2 nm; diameter 0.5–5 μm) were purchased from XFNANO (Nanjing, China). Fluorographite (F% > 56%) was bought from CarFluor Chemicals (Shanghai, China). The standards of individual SCCP congener groups, including 1,1,1,3,8,10,10,10-octachlorodecane ($C_{10}Cl_8$), 1,1,1,3,10,11-hexachloroundecane ($C_{11}Cl_6$), and 1,1,1,3,12,13-hexachlorotridecane ($C_{13}Cl_6$), were bought from Sigma-Aldrich (St. Louis, MO). 2,5,6,9-Tetrachlorodecane ($C_{10}Cl_4$), 1,2,5,6,9-pentachlorodecane ($C_{10}Cl_5$), 1,2,5,6,9,10-hexachlorodecane ($C_{10}Cl_6$'), 1,2,4,5,9,10-hexachlorodecane ($C_{10}Cl_6$''), 1,1,1,3,9,10-hexachlorodecane ($C_{10}Cl_6$'''), and three mixed SCCP standards (C_{10}–C_{13} containing 51%, 55.5%, and 63% chlorine; 100 μg/mL in cyclohexane) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Cyclohexane, *n*-hexane, and isooctane of HPLC grade were from J. T. Baker (Phillipsburg, NJ). α-Cyano-4-hydroxycinnamic acid (CHCA) was from Sigma. Ultrapure water was prepared by using a Millipore Milli-Q system (Billerica, MA, USA). All reagents were of analytical grade unless otherwise noted.

2.2. Sample preparation procedures

For GC-NCI-qTOF-HRMS measurements, the samples were prepared according to the procedures reported previously [17,27]. Briefly, 0.1 g of dust sample was mixed with 15 g of anhydrous sodium sulfate. The mixture was extracted with dichloromethane/hexane 1:1 (v/v) on a Thermo (Dionex) ASE 350 accelerated solvent extractor system. The extract was evaporated to ~ 1 mL and then purified by a 1.5 cm composite column consisting of 3 g of Florisil, 2 g of neutral silica gel, 5 g of acid silica gel, and 4 g of anhydrous sodium sulfate. The column was pre-activated with 50 mL of *n*-hexane, and then eluted with 40 mL of *n*-hexane, 50 mL of dichloromethane, and 50 of mL *n*-hexane in sequence. The fractions of the final dichloromethane and *n*-hexane solution were collected, evaporated to nearly dryness under gentle nitrogen flow, and re-dissolved in 1 mL of cyclohexane. The detailed conditions for GC-NCI-qTOF-HRMS measurements are given in the Section 1.2 in Supporting information.

For MALDI-TOF MS measurements, two sample preparation strategies (i.e., with and without column purification) were compared. Besides the sample preparation procedures described above, we also tested the procedures without column purification as follows: first, 0.1 g of dust sample was extracted by 5 mL of dichloromethane/cyclohexane 1:1 (v/v) for 30 min with the aid of ultrasonication. Then, the mixture was centrifuged at 9000 rpm for 3 min and the supernatant was collected and concentrated to 1 mL under the gentle stream of N_2.

2.3. MALDI-TOF MS

MALDI-TOF MS was performed on a Bruker Daltonics Autoflex III Smartbeam MALDI-TOF mass spectrometer working in reflector mode and controlled by the FlexControl software. The detection was carried out in positive ion mode. 2,5,6,9-Tetrachlorodecane was used as an IS for quantification of SCCPs. The matrix dispersion was prepared by dispersing graphene in water at 1 mg/mL with the aid of ultrasonication. The sample solution, IS solution (10 μg/mL in cyclohexane), and matrix dispersion were mixed at a ratio of 1:1:2 (v/v/v). The mixture was well blended by vortex generator and 2 μL of it was placed on a stainless steel MTP target frame III (Bruker Daltonics) followed by air drying. A Nd:YAG laser with the frequency of 100 Hz was used. The laser power was set to 31%. The spectra were recorded by summing 200 laser shots. The FlexAnalysis 3.4 software was used for data processing.

2.4. Real sample analysis

The indoor dust samples were collected by using a household vacuum cleaner (Puppy D-530, Beijing) in different apartments and offices (n = 20) in Beijing, China. The intake nozzle of the aspirator was covered by a nylon membrane, which was refreshed after each sampling to avoid cross contamination. The samples were sieved by using a 100 mesh sieve, wrapped in aluminum foil, and stored at −20 °C.

3. Results and discussion

3.1. Selection of MALDI matrix

For MALDI-TOF MS, a suitable matrix is critical for obtaining good analytical performance. Generally, a good MALDI matrix should have the following properties: (1) capable of embedding and isolating analytes (e.g. by co-crystallization); (2) soluble in solvents compatible with analytes; (3) stable in vacuum; (4) can adsorb the laser energy; (5) can cause co-desorption of analytes upon laser irradiation; and (6) can promote the analyte ionization. Conventional organic matrices used in MALDI can produce strong background noises in low-mass regions that greatly interfere the detection of small molecules. Recent development