Journal of Chromatography A, 1394 (2015) 26–35

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Highly sensitive determination of dialkyl phosphinate acids in environmental samples by ion chromatography tandem mass spectrometry

Yu-Min Niu[a], Yong Liang[b,c], Ji-Yan Liu[b], Jing-Fu Liu[a,*]

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, China
[b] School of Medicine, Jianghan University, Hubei Province, Wuhan 430056, China
[c] Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, Jianghan University, Hubei Province, Wuhan 430056, China

ARTICLE INFO

Article history:
Received 29 January 2015
Received in revised form 18 March 2015
Accepted 18 March 2015
Available online 24 March 2015

Keywords:
Dialkyl phosphinate acids
Solid phase extraction
Environmental water sample
Soil and sediment sample
IC–ESI–MS/MS

ABSTRACT

Dialkyl phosphinate acids (DPAs) are the hydrolysates of aluminum dialkyl phosphinates (ADPs), one class of emerging phosphorus flame retardants since brominated flame retardants have been gradually phased out in recent years. It has been found that once dissolved in water, ADPs are completely hydrolyzed and exist as DPAs. However, there is no report on the determination of DPAs in environmental water samples. For the first time, we developed a method for the analysis of trace DPAs and ADPs in different environmental samples, including waters, soils and sediments. In this proposed method, MAX cartridges were employed for the purification, and ion chromatography (IC) tandem mass spectrometry (MS) method with large volume injection (200 μL) and postcolumn addition of methanol and $NH_3{\cdot}H_2O$ were employed for the determination of DPAs and ADPs. The matrix effects were <16% for water samples and <25% for soil/sediment samples, which were greatly improved in comparison to the liquid chromatography (LC) tandem MS determination. Determined at three fortified levels of 0.02 μg/L, 0.2 μg/L and 1.0 μg/L, the mean recoveries were from 75.8% to 110.2%, with an acceptable coefficient of variation (3.3–20%, $n=6$) for water samples. The limits of the method were 3.5–9.3 ng/L for DPAs in environmental water samples, and 0.06–0.09 μg/kg for DPAs and ADPs in soil and sediment samples. For soil and sediment samples, results determined by the present IC–MS method were in good agreement with that determined by LC–MS in our previous study.

1. Introduction

Aluminum dialkyl phosphinates (ADPs, aluminum salts of phosphinic acid having alkyl and/or aryl substitutes) are a class of the most promising flame retardants used as substitute of brominated flame retardants (BFRs) which have been gradually phased out in the United States (US) and European Union (EU) in recent years [1–5]. ADPs have already been widely used in the electrical and electronic equipments, connectors, switches, and encapsulated electronic components in many countries, including China [6]. Due to this activity, it is estimated that up to 165 kg per annum of aluminum salts of diethylphosphinic (ADEP) could be disposed to landfill according to authority statistics [7].

Accompanying with the production and application, ADPs will inevitably be introduced into the human living environments [5], like other organophosphate esters flame retardants. In our previous study, three kinds of ADPs, including aluminum salts of methylethylphosphinic (AMEP) and methylcyclohexyl phosphinic (AMHP) and ADEP have been found in soil and sediment samples. At the same time, the hydrolysates of ADPs (dialkyl phosphinate acids, DPAs) have also been found, and both ADPs and DPAs showed relatively high vertical mobility in soil and sediment [8]. Although it was speculated that ADEP was unlikely leached into the water compartment due to its low solubility [7,9], the high hydrophilicity of DPAs indicating ADPs could potentially contaminate groundwater in the form of DPAs by leaching from soils and sediments [10]. Moreover, we have demonstrated that once dissolved in water, the O-Al covalent bonds in ADPs would be broken, thereafter ADPs hydrolyzed to DPAs [8]. Therefore, it is speculated that ADPs would present in environmental water samples in the form of DPAs. For example, the direct discharge of ADPs in manufacture plant and the

---

[*] Corresponding author. Tel.: +86 10 62849192; fax: +86 10 62849192.
E-mail address: jfliu@rcees.ac.cn (J.-F. Liu).

http://dx.doi.org/10.1016/j.chroma.2015.03.041
0021-9673/

diffusion from the flame retardant products could bring the risk of contamination of wastewater by DPAs. Subsequently, DPAs could be introduced into surface water via waste water treatment plant (WWTP).

As the 72-h no observed effect concentration (NOEC) based on *algae* was 2.2 mg/L for ADEP, a predicted no effect concentration for aquatic organisms of 44 μg/L was given by National Industrial Chemicals Notification and Assessment Scheme (NICNAS) [9]. In addition, Waaijers et al. reported that ADEP could affect the sublethal life cycle parameters of *daphnid* for chronic exposure, such as cumulative reproductive output and population growth rate [11]. Given the fact that ADPs were hydrolyzed to DPAs once dissolved in water [8], the reported negative effects on the aquatics mentioned above should be caused by DPAs.

Considering the potential toxicity of ADPs to aquatic organisms and the possibility of DPAs existing in environmental water samples, an overall investigation on the occurrence and the environmental behavior of ADPs and DPAs is urgently needed. However, a bottleneck of this work is the absence of sufficiently sensitive analytical procedure for the determination of DPAs in environmental water samples at trace levels. ADPE in the exposure solutions has been determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) through determining phosphorus [11], or by measuring Al^{3+} through complexation with Alizarinred [7]. However, these two methods are not appropriate for the determination of ADPs and DPAs in environmental water because of the ingenerate of phosphorus and Al^{3+} in water samples.

In this study, a novel analytical method based on solid phase extraction (SPE) and ion chromatography (IC) tandem mass spectrometry (MS) method was developed. Three DPAs including methylethylphosphinic acid (MEPA), diethylphosphinic acid (DEPA) and methylcyclohexyl phosphinic acid (MHPA) in water samples were extracted by SPE, and injected into the IC–MS system with large volume injection for highly sensitive detection. This method was applied to determine DPAs in four different environmental waters, including tap water, river water, influent and effluent water of WWTP with satisfactory results. In addition, the IC–MS method was also appropriate for the determination of DPAs and ADPs in soil and sediment samples.

2. Materials and methods

2.1. Chemicals and reagents

AMEP, ADEP and AMHP with purity >95% were provided by Jianghan University (Hubei province, China). MEPA and DEPA with the purity >95%, and MHPA with the purity >90% were synthesized from AMEP, ADEP and AMHP individually in our laboratory, according to the reported methods [8]. HPLC grade methanol was supplied by Fisher Scientific (Fair Lawn, NJ). Formic acid with 99% purity was purchased from Acros Organics (Morris Plains, NJ). Ammonium hydroxide ($NH_3{\cdot}H_2O$, 15 M) was obtained from Sinopharm Chemical Reagent Co. (Beijing, China). Ultra-pure water produced with a Milli-Q Gradient system (Millipore, Bedford, USA) was used throughout the experiment.

Individual DPA stock solutions (1000 mg/L) were prepared by dissolving an appropriate amount of each substance in methanol and storing at −20 °C in amber glass vessels. Working standard mixtures were prepared by combining the stock solutions and diluting with ultra-pure water before immediate use.

2.2. Sample preparation

On the arrival in the laboratory, all water samples were filtered through GF/A glass fiber membrane filters (1.2 μm; Whatman, Maidstone, UK) and immediately analyzed. Aliquot of 7 mL water samples with pH 5–9 were applied to a lipophilic exchanger mixed-mode sorbent (MAX) cartridge (6 mL, 500 mg, Waters, Milford, MA, USA). The cartridges were conditioned sequentially with 6 mL of methanol and 6 mL of ultra-pure water prior to use. Water samples were passed through the cartridges under gravity. After samples loading, the SPE cartridges were dried under vacuum aspiration for 2 h. Then the analytes were eluted by 5 mL methanol with 2% formic acid. The eluates were evaporated to dryness by a gentle nitrogen stream under 40 °C and finally made up to 1.0 mL with ultra-pure water for IC–MS/MS analysis.

For soil and sediment samples, the pretreatment procedure was exactly the same as our previous study [8], except for the finally dilution solution. In brief, 0.5 g of samples were weighed in duplicate, and extracted by 2.5 mL aqueous solutions of 75 mM $NH_3{\cdot}H_2O$ and formic acid–water–methanol (5:5:90, v/v/v) respectively. The supernatants were cleaned up by MAX cartridges and eluted by 5 mL 2% formic acid in methanol. The eluates were evaporated to dryness and finally made up to 1.0 mL with ultra-pure water for IC–MS/MS analysis.

2.3. Instrument analysis

The chromatographic separation was carried out on a Dionex ICS-3000 Regent-Free^{TM} Ion Chromatography (Thermofisher, Sunnyvale, CA, USA), consisting of an autosampler (AS), a dual pump unit (DP), an eluent generator unit (EG) and a column and detector compartment (DC). A 2 mm × 250 mm IonPac® AS11-HC weak anion-exchange analytical column protected by its guard column, AG11-HC (2 mm × 50 mm), was employed as the separation column. The injection volume was set at 200 μL and the column temperature was set at 30 °C. Potassium hydroxide solution generated by the EG was used as the eluent. With a flow rate of 0.3 mL/min, the gradient elution was operated with 5 mM potassium hydroxide held for 2 min, followed by a 5-min linear gradient to 10 mM, then a further 8 min to 30 mM, and finally kept for 5 min. The suppression of column effluent was accomplished with an anion self-regenerating suppressor (ASRS ULTRA II, 2 mm) in the external water mode at 30 mA. A T-fitting was inserted between the electrical conductivity detector and MS detector. Through the T-fitting, the eluent and 0.1 mL/min methanol with 45 mM $NH_3{\cdot}H_2O$ delivered with a ACQUITY Waters Pump (Waters, Mildord, MA, USA) were mixed, and then interfaced with an electrospray probe (ESI) of a triple quadrupole MS (TSQ Quantum Access, Thermo Fisher Scientific, San Jose, CA, USA).

MS/MS acquisition was conducted in the negative ion mode, which has been described in our previous study [8], and from which the only difference was that ion sweep gas set at 3 (in arbitrary units) was used to decrease the interference with matrices.

2.4. Method validation

To evaluate the performance of the established method for the analysis of DPAs in environmental water samples, quality parameters such as matrix effects, linearity, sensitivity, accuracy and precision were studied in four different water samples (tap water, river water, influent and effluent water of WWTP). The assessment of matrix effects is critical since isotope labeled standards are unavailable for the target compounds [12]. It was evaluated by preparing a neat standard curve and a matrix-matched standard curve, plotted by using standards spiked in ultra-pure water and in extracts of blank environmental water samples before IC–MS/MS analysis, respectively. The ratio between the slope of matrix-matched standard curve and neat standard curve multiplied and subtracted by 100 was identified as the matrix effects [12]. The sensitivity of the method was evaluated by the limit of determination