Talanta 114 (2013) 176–182

Contents lists available at ScienceDirect

Talanta

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

Determination of chlorophenols in water by headspace solid phase microextraction ion mobility spectrometry (HS-SPME-IMS)

Sanna Holopainen [a,*], Ville Luukkonen [a], Marjaana Nousiainen [b], Mika Sillanpää [a,**]

[a] Lappeenranta University of Technology, LUT School of Technology, Department of Energy and Environmental Technology, Laboratory of Green Chemistry, Sammonkatu 12, 50130 Mikkeli, Finland

[b] Finnish Environment Institute (SYKE), Hakuninmaa Laboratory, P.O. Box 140, 00251 Helsinki, Finland

ARTICLE INFO

Article history:
Received 22 February 2013
Received in revised form
3 April 2013
Accepted 8 April 2013
Available online 15 April 2013

Keywords:
Chlorophenols
Ion mobility spectrometry
Solid phase microextraction
Water quality
Environmental health

ABSTRACT

Chlorophenols (CPs) as persistent toxic compounds are of worldwide environmental concern. Usage of chlorinated phenols, especially pentachlorophenol (PCP), has been restricted or widely banned in many countries due to their possible adverse health effects even at low concentrations. Ion mobility spectrometry (IMS) has received increasing interest in environmental applications due to its unique characteristics, such as portability and speed of analysis. A range of sample introduction methods combined with IMS enable analysis from different environmental matrices. This study utilised headspace solid phase microextraction IMS (HS-SPME-IMS) in the determination of CPs from water samples. The extraction conditions were examined and the method was applied to real water samples. The developed method is suitable to detect CPs at milligram per liter level in water. Based on the results, SPME-IMS setup is feasible as an early warning system for water monitoring of pollutants present in drinking or surface water in case of environmental accidents or leakages.

1. Introduction

Chlorophenols (CPs) are serious environmental concern due to their toxicity and persistence in environmental matrices. These semivolatile organochlorine compounds can be found worldwide in surface and groundwaters, wastewater, bottom sediments, atmospheric air and soils. CPs have been used as antiseptics, insecticides, herbicides, fungicides, wood preservatives, and intermediates in the production of dyes and pharmaceuticals [1–3]. CPs can also be formed as by-products during drinking water chlorination [1,4] and the chlorine bleaching of wood pulp [5]. Chlorinated phenols are also key intermediates in the formation of dioxines in incinerating solid residues [6,7]. Nowadays usage of CPs, especially of pentachlorophenol (PCP), has been restricted or widely banned in many countries due to possible adverse health effects even at low concentrations [3,5]. CP's primary toxic effects are related to the destruction of cellular membranes and inhibition of oxidative phosphorylation [8]. CPs are included in the lists of both US Environmental Protection Agency Priority Pollutants and European Union Priority Substances [9,10].

Although their usage is restricted, CPs still exist in nature due to their persistence in the receiving aquatic environment. In Finland CPs were widely used as a wood preservative, until production was banned in 1984 [11]. For example, up to 190 mg/L of total CP concentration was found in groundwater at Kärkölä in 1987, and probable exposure to CP polluted drinking water was later found to be the cause of increased risk of both soft-tissue cancer and non-Hodgkin lymphoma in the area [12–14]. Studies at Southern Saimaa also indicated the existence of CPs in surface water and sediments in Finland. Up to 47 μg/L of individual CP concentration was measured in pulp mill effluent [15].

The pH of the water, soil or sediment is a major factor affecting the fate and transport of CPs, since increasing pH increases their degree of ionisation [5]. Physico-chemical properties and behaviour in the environment depend on the number of chlorine atoms (Table 1) [16]. Increasing chlorination strengthens the tendency of CPs to partition into sediments and lipids, and increases their bioaccumulation [1,2]. CP toxicity also depends on the degree of chlorination and the position of chlorine atoms in relation to the hydroxyl group [1].

Ion mobility spectrometry (IMS) is a fast, sensitive and portable technique which offers an alternative to conventionally used methods both onsite and laboratory analysis [18,19]. IMS is suitable for

Abbreviations: CAR/PDMS, Carboxen/polydimethylsiloxane; CP, Chlorophenol; CW/TPR, Carbowax/templated resin; GC–MS, Gas chromatography–mass spectrometry; HF-LPME, Hollow fibre liquid phase microextraction; HPLC, High performance liquid chromatography; HS-SPME-IMS, Headspace solid phase microextraction; IMS, Ion mobility spectrometry; LC/ESI-IMS, Liquid chromatography/electrospray ion mobility spectrometry; LOD, Limit of detection; Mfc, Mass flow controller; PA, Polyacrylate; PCP, Pentachlorophenol; PDMS/DVB, Polydimethylsiloxane/divinylbenzene; PTFE, Polytetrafluoroethylene; RIN, Reactant ion negative; SBSE, Stir bar sorptive extraction; SPME, Solid phase microextraction; 2,4,6-TCP, 2,4,6-trichlorophenol; TD, Thermal desorption; UV-Vis, Ultraviolet-visible; 2,3,4, 6-TeCP, 2,3,4,6-tetrachlorophenol.

* Corresponding author. Tel.: +358 406829770.
** Corresponding author. Tel.: +358 400 205 215.
E-mail addresses: sanna.holopainen@lut.fi (S. Holopainen), mika.sillanpaa@lut.fi (M. Sillanpää).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.04.023

Table 1
Physico-chemical properties of chlorophenols [16].

	2,4,6-trichlorophenol (2,4,6-TCP)	2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP)	Pentachlorophenol (PCP)
CAS	88–06–2	58–90–2	87–86–5
Molecular weight [g/mol]	197.45	231.89	266.34
Molecular formula	$C_6H_3Cl_3O$	$C_6H_2Cl_4O$	C_6HCl_5O
Boiling point [°C]	246	150 °C/at 21 hPa [17]	310
Vapour pressure [mmHg]	0.008	4.23×10^{-3}	1.10×10^{-4}
Water solubility [mg/L] at 25 °C	800	1000	14
Henry´s law constant [atm × m^3/mol]	0.008	1.3×10^{-6}	2.45×10^{-8}
Octanol-water partition constant, log $K_{o/w}$	3.69	4.45	5.12
pKa	6.23	5.22	4.70
Taste threshold [μg/L]	2.0	1	30

monitoring gaseous emissions and pollutants [20,21] but also feasible for analysing hazardous chemicals in water matrices [22–26]. IMS is also more easily adapted to real time monitoring than many other analytical instruments [27]. Early ion mobility studies of PCP showed that this wood preservative is directly detectable in waste wood samples [28,29]. In another IMS study various chlorophenols were analysed by liquid chromatography/electrospray ionization-ion mobility spectrometry (LC/ESI-IMS). The obtained limits of detection ranged from 0.135 mg/L for 2,3,5-trichlorophenol and 2.23 mg/L for PCP [30].

Several sample preparation methods including solvent based extraction methods such as hollow fibre liquid phase microextraction (HF-LPME) and sorbent based techniques such as stir bar sorptive extraction (SBSE), and solid phase microextraction (SPME) have been utilised in the determination of CPs in aqueous matrices [31,32]. These sample preparation methods are also applicable to IMS in water analysis [33]. For example SPME has been utilised in several studies with IMS in the water pollutant determination [34–40].

In SPME, both headspace and direct immersion modes have been evaluated for pre-concentration of CPs in water samples. Various fibre materials [41,42] have been utilised in CP analysis and the best results have usually been obtained with semi-polar or polar fibres. Salt addition and pH adjustment have also been commonly used [31,32]. Kim et al. recently determined CPs and related compounds in environmental water samples with SPME combined with high pressure liquid chromatography (HPLC) and UV detection [43]. Analytes were examined without derivatization and carbowax/templated resin (CW/TPR) was the best of the tested fibre materials with 60 min of extraction time. In another recent study Morales et al. evaluated extracting parameters for CP determination with GC–MS without derivatization. It was found that polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibre with 35 min of extraction time was optimal for GC–MS analysis of CPs in water [44]. Simões et al. have determined phenols and chlorophenols in raw and treated water without derivatization with SPME-GC–MS analysis. They utilised polyacrylate (PA) fibre at pH 4, with 10% NaCl addition. Analyses were conducted with direct extraction mode at 35 °C with 40 min of extraction time [45].

Here suitable parameters for HS-SPME extraction procedure were investigated for ion mobility spectrometrical determination. Examination was made without derivatization to obtain a suitable method for detecting CPs in water by IMS. We also discuss the observed ion chemistry of the CPs and the possibilities of the developed method for the environmental monitoring of water samples.

2. Experimental

2.1. Chemicals

The studied CPs, 2,4,6-trichlorophenol (2,4,6-TCP) with a purity of 98% and PCP with a purity of 97% were purchased from Sigma-Aldrich (St.Louis, MO, USA). 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) with a purity of 98.4% was obtained from Supelco (Bellefonte, PA, USA). Stock solutions of 1000 mg/L of each CP were prepared in absolute ethanol obtained from Altia Oyj (Riihimäki, Finland) and sample solutions ranging from 0.5 to 15 mg/L were prepared in ultrapure water. Sample pH was adjusted with 0.5 M HCl and 0.5 M NaOH (pure chemicals obtained from Merck KGaA, Darmstadt, Germany) to 2.2 to ensure that the chlorophenols were in their non-ionised form. In the SPME procedure sodium chloride (99.5% purity, VWR International Ltd., Poole, England) was used to cause salting out. Natural water was collected from Lake Pankalampi, Mikkeli to estimate the matrix effect. Real water samples containing CPs were obtained from Ramboll Finland. Methyl salicylate (extra pure (PhEur), Merck KGaA, Darmstadt, Germany) was used as a calibration reference for the mobility scale [46,47], even though precise information about its mobility is lacking in the literature. Filtered air was used as a carrier gas and nitrogen (99.9990%) was used as a drift gas in ion mobility measurements.

2.2. SPME

SPME fibre assemblies and SPME fibre holders were obtained from Supelco (Bellefonte, PA, USA). The fibre types tested were 100 μm polydimethylsiloxane (PDMS), 85 μm PA, and 75 μm carboxen/polydimethylsiloxane (CAR/PDMS) and two similar fibres of each type were used in the studies. All fibres were conditioned before use (PDMS: 1 h at 250 °C, PA: 30 min at 280 °C, and CAR/PDMS: 1 h at 300 °C) in a custom made thermal desorption (TD) unit, and cooled before use. Sampling was performed in 22 ml glass vials with polytetrafluoroethylene/silicone (PTFE/silicone) septa screw caps (Supelco, Bellefonte, USA). Sample volumes of 10 ml were tempered in a water bath heated by a hot plate stirrer (IKA C-MAG HS7) at least 30 min before analysis. Samples were simultaneously agitated with magnetic stir bars to reach equilibrium between the liquid and the gas phase. Optimizations of fibre parameters (fibre type, fibre depth, extraction time, extraction temperature, addition of salt) were performed with sample concentrations of 10 mg/L.

IMS measurements were performed until analyte signals disappeared (typically 10–20 scans). After measurement the fibre was cleaned at operating temperature and its purity was checked. The calibration reference compound was also measured with PDMS fibre from the headspace of pure methyl salicylate. All the measurements were conducted in triplicate.

2.3. Experimental setup

SPME fibres were exposed to thermal desorption in a custom made TD unit. The experimental setup is presented in Fig. 1. The TD unit consisted of a brass container with height of 75 mm and o.d. of 55 mm, and was heated with a heating rope (Omega Engineering

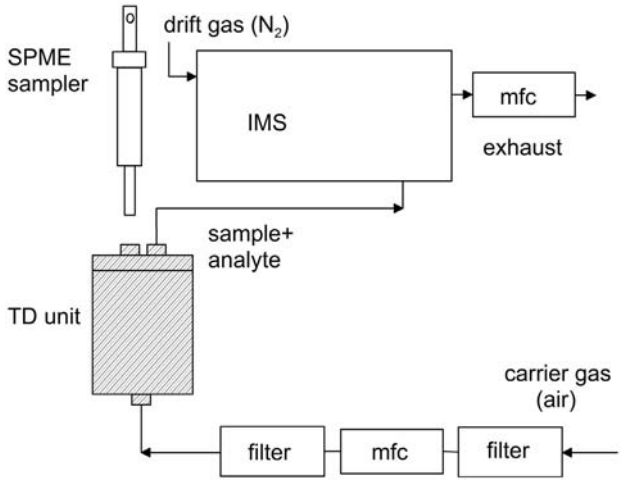

Fig. 1. Experimental setup for chlorophenol IMS measurements. Mfc=mass flow controller.

Inc., Leicestershire, England). Temperature was adjusted to operating temperature with a temperature controller (Omron Corporation, Hoofddorp, The Netherlands). A relatively high desorption temperature was used due to the high boiling points of CPs. The sample was desorbed from SPME fibre at 250 °C with air flow of 0.19 L/min, and drift gas (nitrogen 99.9990%) flow was kept at 0.2 L/min. Gas flows were controlled with mass flow controllers (Bronkhorst High-Tech BV, Ruurlo, The Netherlands). Transfer line between desorber and IMS detector was thermally sealed, and distance between TD unit and IMS was kept as short as possible.

Samples were analysed by a Ni-IMS (G.A.S. GmbH, Dortmund, Germany) with β-ionisation. The drift section length of the device is 6 cm, and the electric field in the drift region is 313.4 V/cm. The IMS detector operates with filtered dry air as a carrier gas and nitrogen as a drift gas. The detector was operated in the negative mode at ambient pressure and at a temperature of 70 °C with drift voltage of −3.5 kV. The shutter grid was open for 100 μs, and samples were collected with a 50 Hz sampling frequency. Ion signals were processed using digital averaging of 128 scans per spectrum with a scan repetition rate of 100 ms. Drift time spectra were registered with the firm software GASpector version 3.99.035 DSP.

2.4. Data processing and calculations

Ion mobilities in the electric field at the ambient pressure can be calculated with the formula:

$$K = \frac{v_d}{E} = \frac{l_d}{t_d E} \quad (1)$$

where K is the ion mobility [cm^2/Vs], v_d is drift velocity [cm/s], l_d is drift length [cm], and E is electric field strength in [V/cm][48]. Furthermore, mobilities are usually normalised to 273 K and 760 Torr, which allows comparison of mobility values between different systems

$$K_0 = K\frac{273}{T}\frac{P}{760} \quad (2)$$

where K_0 is reduced mobility [cm^2/Vs], T is operating temperature in [K], and P is pressure in Torr [48,49]. K_0 of the analyte can also be calculated in comparison to the reference compound

$$K_0 = K_0(ref)\frac{t_d(ref)}{t_d} \quad (3)$$

where $K_0(ref)$ is reduced mobility of the reference compound [cm^2/Vs], $t_d(ref)$ is observed drift time of the reference compound [ms], and t_d is the observed drift time of the analyte [ms] [46,47]. Methyl salicylate was used as a reference compound with reduced mobility of 1.62 cm^2/Vs [46].

For quantitative evaluation data was processed for the reactant ion, monomer, and dimer ions of each compound. Integration was done using a laboratory made Integrator 01 programme which allows the calculation of peak integrals from drift time spectrum [50]. The obtained results are the average of triplicate measurements and the presented values are accurate to ±10%.

Quantitative parameters can be calculated from the obtained results. The limit of detections, i.e. the minimum detectable signals, can be calculated with the equation

$$LOD = \frac{3\sigma}{S} \quad (4)$$

where LOD=limit of detection [ppm], σ= root mean square of the noise (i.e. noise above the background signal) and S=sensitivity [nA/ppm]. Furthermore, $S=R/C_i$; where R=response [nA], C_i=concentration at which detection limit is determined [ppm] [51,52].

Recovery can be calculated by the formula

$$R_A(\%) = \frac{Q_A(\text{yield})}{Q_A(\text{orig})}100 \quad (5)$$

where Q_A(orig) is the known original and Q_A(yield) is the recovered response of the analyte A [52,53].

3. Results and discussion

3.1. Examination of extraction parameters

In theory, there are several parameters affecting the sensitivity of the SPME procedure: coating volume, distribution constant K_{fs} between the fibre and the sample, and extraction variables such as temperature, stirring and possible salt addition [54,55]. Vial size and phase ratio are other variables affecting the SPME response and extraction time [56]. In this work parameters such as fibre type, fibre depth, extraction time, extraction temperature and addition of salt were examined for CP extraction for IMS analysis. Experiments were performed with 100 μm PDMS fibre and 10 ml of sample volume at pH of 2.2 with agitation for 2,3,4-TCP and 2,3,4,6-TeCP. Each experiment was conducted in triplicate at an analyte concentration of 10 mg/L, and in data analysis the average of the product ion areas was calculated. A summary of the parameters used in sample extractions is presented in Table 2.

3.1.1. Extraction time

To study the extraction time of CPs from water, 5, 10, 15, 20, 25, 30, 35 and 40 min were explored. Samples were incubated in a 60 °C water bath for half an hour before extraction with 100 μm PDMS fibre and 3.5 cm fibre depth. There were not significant changes in signal response with different temperatures, thus extraction time of 15 min and 20 min were chosen for 2,3,4,6-TeCP and 2,4,6-TCP respectively to ensure reasonable amount of extracted analytes.

Table 2
Parameters used in sample extractions.

pH	2.20
Fibre type	100 μm PDMS
Fibre depth [cm]	3.0
Extraction time [min]	20
Extraction temperature [°C]	55
Addition of salt	100 g/L of NaCl
Agitation	on

3.1.2. Fibre depth

To examine the effect of fibre depth, 100 μm PDMS fibre was exposed to 2,4,6-TCP for 20 min and to 2,3,4,6-TeCP for 15 min according to extraction time studies. In this procedure 1.5 cm, 2.5 cm, 3.5 cm and 4.0 cm fibre depths were studied at the extraction temperature of 60 °C. A fibre depth of 2.5 cm was chosen for 2,4,6-TCP since it gave the most intensive signal, and 3.5 cm was selected for 2,3,4,6-TeCP because of the most persistent signal. In the determination of real sample a fibre depth of 3 cm was chosen as a compromise between these two values.

3.1.3. Addition of salt

Salt addition can force polar compounds into the vapour phase from the liquid by increasing the partition coefficients of organic compounds, making them less soluble to water [56]. The effect of salt addition was studied for 2,4,6-TCP and 2,3,4,6-TeCP. Studies were performed under the same conditions as in the previous procedures, except that extraction temperatures were 60 °C for 2,4,6-TCP and 70 °C for 2,3,4,6-TeCP. The results of 100 g/L NaCl addition in 10 mg/L of 2,4,6-TCP are presented in Fig. 2. Different increasing salt concentrations were tested in the extraction procedure but salt amounts lower than those presented did not influence on sensitivity significantly. Salt addition of 100 g/L improved 2,4,6-TCP extraction efficiency by 42%. Because a signal improvement of 10% was also observed with 2,3,4,6-TeCP, salt was added in real samples.

3.1.4. Fibre type

Polar fibre coatings such as PA and carbowax (CW) are typically used for CPs on the basis that similar dissolves similar [57]. PCP is rather nonpolar in comparison to other phenols and therefore its distribution constants between fibre material and water are greater for PDMS than for PA coating [58]. Regarding different experimental setups, PDMS, CAR/PDMS [42], CW/TPR [43], PDMS/DVB [41] and PA [45] have given best results for the determination of CPs.

In our current study, the extraction efficiency of CPs in water was tested with 85 μm PA, 100 μm PDMS and 75 μm CAR/PDMS. Both CPs were extracted after 100 g/L of salt addition. 2,4,6-TCP was tested with PA and PDMS fibres with 2.5 cm depth and 20 min of extraction time at a temperature of 60 °C. As a result, PDMS gave about 50% better response for 2,4,6-TCP than PA fibre. PA fibre gave longer lasting response however, but with more interference. To choose the most appropriate fibre material for 2,3,4,6-TeCP, PDMS, PA and CAR/PDMS were tested. The responses of fibre types with 10 mg/l concentration of 2,3,4,6-TeCP are presented in Fig. 3. PDMS was 70% more efficient than PA fibre and 45% more efficient than CAR/PDMS fibre material. Ethanol disturbed the signal more with PA extraction than with the other fibres. Also the rigidness of PA fibre could slow CP adsorption. As a result, 100 μm PDMS fibre was utilised in the determination of real water samples.

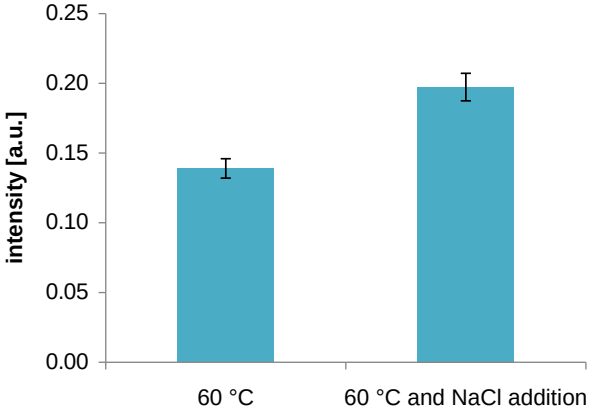

Fig. 2. 2,4,6-TCP signal intensity with and without 100 g/L NaCl addition.

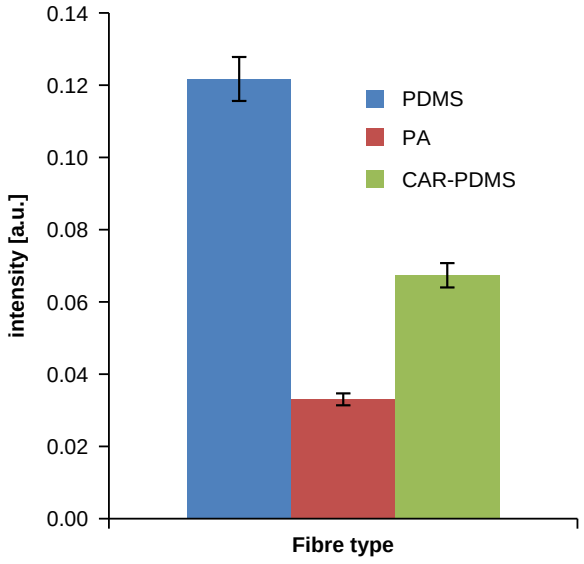

Fig. 3. Effect of fibre type on the signal of 10 mg/L 2,3,4,6-TeCP.

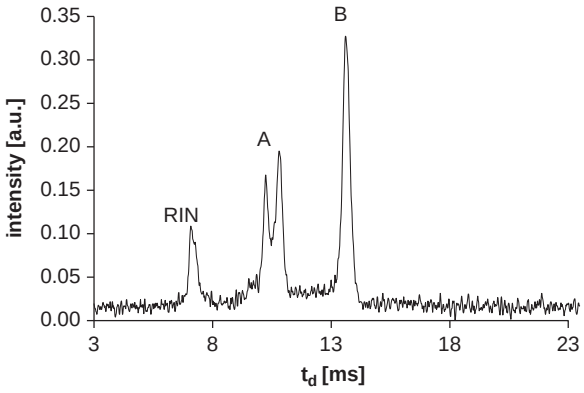

Fig. 4. 2,4,6-TCP at the concentration of 5 mg/L in water.

3.1.5. Extraction temperature

A study of the extraction temperature for 2,4,6-TCP was performed using PDMS fibre with a depth of 2.5 cm at temperatures of 40 °C, 50 °C and 60 °C. For 2,3,4,6-TeCP a fibre depth of 3.5 cm and 15 min of extraction time were used at similar temperatures and at an additional temperature of 70 °C. Temperatures were adjusted with an accuracy of ±2 °C. Higher temperatures were studied to ensure analyte transfer to gas phase. Heating not only drives analytes from liquid into headspace but also alters the partitioning of analytes between headspace and the fibre [56]. Because 50 °C gave the most intensive signal for 2,4,6-TCP extraction and 60 °C for 2,3,4,6-TeCP, 55 °C was used as a compromise in the determination of real samples.

3.2. Calibration curves and reduced mobilities

Calibration curves for analyte CPs were determined with parameters presented in Table 2. Fig. 4 shows the IMS spectrum of 2,4,6-TCP at a concentration of 5 mg/L in water. In the spectrum are visible not only reactant ions (RIN), $O_2^-(H_2O)_n$ [48], but also product ions A and B. Because ions with drift times

9–12 ms (A) were difficult to integrate separately, their total sum was calculated for calibration curves. These ions supposedly have structures with different number of chlorine cleavages. Ions with drift times of 13 to 16 ms (B) are assumed to be dimer ions, because their concentration dependence is similar to positive mode dimer ions observed in our previous studies [22,59]. Also in IMS determination of 2,4,6-trichloroanisole, a fungal metabolite of 2,4,6-TCP, trichlorophenoxide and chloride bridged dimers have been detected in the negative mode IMS [60].

The concentration dependence of studied CPs in the range of 0–15 mg/L is presented in Fig. 5. The results show that formation of PCP product ions is less likely than ionisation of 2,4,6-TCP or 2,3,4,6-TeCP (PCP forms product ions A and B more slowly than the other studied CPs). Thus the sensitivity order of the studied analytes is 2,4,6-TCP > 2,3,4,6-TeCP > PCP. This follows acidity order of analytes: when acidity is increasing, amount of observed ions decreases.

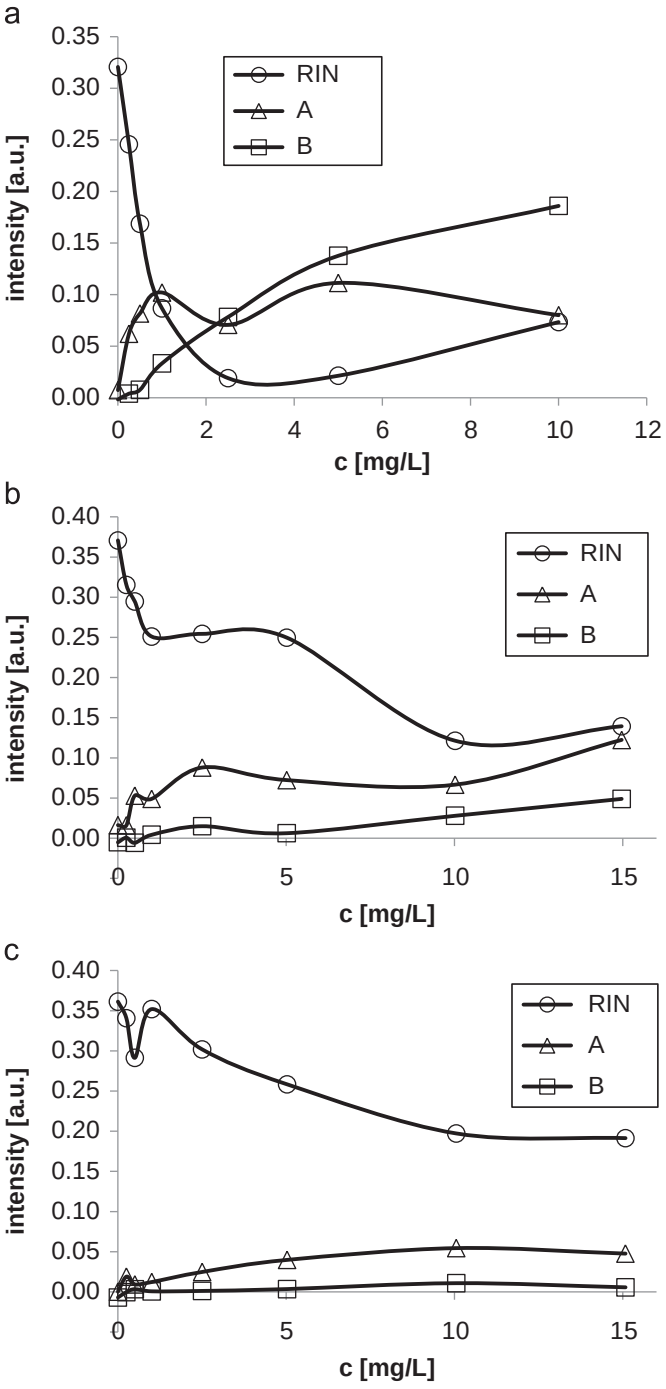

Fig. 5. Concentration dependence of (a) 2,4,6-TCP (b) 2,3,4,6-TCP and (c) PCP signals.

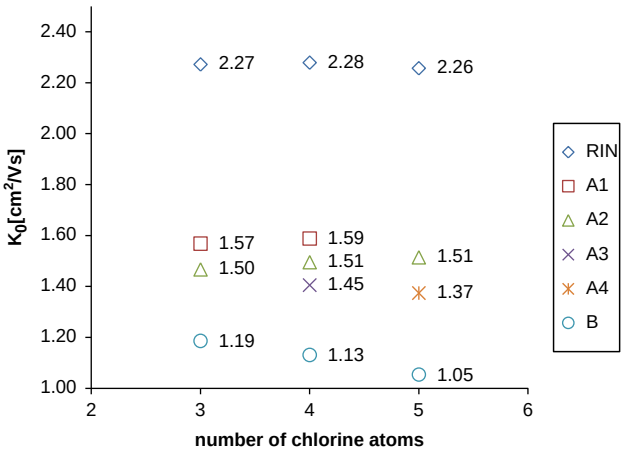

Fig. 6. Observed reduced mobilities for studied chlorophenols.

Table 3
Validation parameters (N = 3).

	LOD [mg/L]	Sensitivity [signal/ppm]
2,4,6-TCP	0.330	0.122
2,3,4,6-TeCP	0.630	0.045
PCP	1.640	0.002

Reduced mobilities of CPs were calculated with Eqs. 1–3. Fig. 6 shows observed reduced mobility values as a function of the number of chlorine atoms in the analyte molecule. For example the reduced mobilities of observed product ions A_1 and A_2 for 2,4,6-TCP were 1.57 ± 0.02 cm^2/Vs, 1.50 ± 0.02 cm^2/Vs, and for supposed dimer ions, B 1.19 ± 0.02 cm^2/Vs. Although CP isomers formed similar product ions A_n, isomers can be distinguished according to product ions B. Typical product ions for halogenated compounds, halide ions, X^- [48,61,62] were not observed in our study. Instead the observed ions are supposedly loss of halogen fragments formed at high desorption temperature. Karasek et al. have also observed thermal decomposition product ions of *p*-nitrophenol in their studies [63].

3.3. Determination of real water samples

To determine the suitability of SPME-IMS for CPs, certain validation parameters were obtained. These were minimum detectable concentration (i.e., limit of detection (LOD)), repeatability, sensitivity and extraction recovery. Sensitivities and limits of detection were determined from linear part of the calibration curve, i.e. concentration range of 0–1 mg/L. The obtained validation values are presented in Table 3.

LODs were determined at a concentration of 10 mg/L of each analyte and values were calculated with Eq. (4). The total responses of each analyte were used in the determination of LODs. Sensitivities were determined from calibration curve slopes and were between 0.12 and 0.002. The repeatability of the measurements was 12.1% (determined from the averages of ten measurements at a concentration of 2.5 mg/L of 2,4,6-TCP). Extraction recoveries from lake water were calculated in comparison to ultrapure laboratory water with Eq. (5). With 0.25 mg/l concentration of 2,4,6-TCP the recovery was 88% and with 0.5 mg/l it was 89%.

Three natural water samples were determined with the developed method. Aliquots of 10 ml of each sample were extracted from the headspace without filtration. Sample 1 and 2 were colourless, but sample 3 contained some brownish precipitates. Samples were stirred because of salt addition and incubated at 55 °C more than an hour before extraction. Otherwise examined parameters (Table 2) were used in the extraction procedure. The SPME-IMS method could detect chlorophenols in sample 3 but the concentrations of analytes in samples 1 and 2 were below detection limits. The results of sample 3 extraction were as follows [SPME-IMS (verified concentration)]: For 2,4,6-TCP: 0.0387 mg/L (0.075 mg/L), for 2,3,4,6-TeCP: 0.449 mg/L (0.470 mg/L) and for PCP:-mg/L, (0.071 mg/L). The verified and measured concentrations of 2,3,4,6-TeCP do not differ remarkably; the difference is only 4.6%. However, in the case of 2,4,6-TCP, the difference is 48.4%. The significant difference in 2,4,6-TCP could be explained by high signal to noise ratio in the concentration range remarkably below LOD. PCP concentration could not be determined from any real sample due to low method sensitivity.

Even though HS-SPME-IMS could not determine the lowest analyte concentrations in real samples, the method is still valid for milligram per liter levels. Because the SPME sampling method would be automated [64], it is suitable for online systems combined with IMS [65] to monitor water quality in the case of environmental leakages or chemical accidents.

4. Conclusions

IMS has received increasing attention as a method of detecting hazardous environmental pollutants from aqueous matrices. In our current study CPs were determined from water samples by HS-SPME as a sample preparation method for ion mobility measurements. Different extraction parameters were examined for 2,4,6-TCP, 2,3,4,6-TeCP and PCP, which were analysed by negative mode IMS. With 100 μm PDMS fibre, 3.0 cm fibre depth, an extraction time of 20 min, extraction temperature of 55 °C and the addition of salt, these semivolatile compounds could be detected at milligram per liter level in water. Ions with similar reduced mobilities were observed for different CPs due to the analytes' similar ion formation pathways. Thus CP isomers could be distinguished according to product ions with lower reduced mobilities. An increasing sensitivity order of PCP < 2,3,4,6-TeCP < 2,4,6-TCP was also observed among the studied CPs. Since no remarkable differences between drinking and surface water matrices were found, the studied method is applicable for different water matrices. As a consequence, IMS combined with SPME is a suitable as an early warning system for water monitoring of pollutants present in drinking or surface water in case of environmental accidents or chemical leakages.

Acknowledgements

The financial support of Tekes (Finnish Funding Agency for Technology and Innovation) Water Safety Management Project is gratefully acknowledged. The authors also thank M.Sc. (Tech.) Iiro Kiukas from Ramboll Finland Oy for providing water samples containing chlorophenols and Dr. Kate Sotejeff-Wilson for language revision.

References

[1] M. Czaplicka, Sci. Total Environ. 322 (2004) 21–39.
[2] A.O. Olaniran, E.O. Igbinosa, Chemosphere 83 (2011) 1297–1306.
[3] W. Zheng, X. Wang, H. Yu, X. Tao, Y. Zhou, W. Qu, Environ. Sci. Technol. 45 (2011) 4668–4675.
[4] World Health Organization (WHO), Chlorophenols in Drinking Water, Geneva, Switzerland, 2003.
[5] U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Chlorophenols, Atlanta, Georgia, USA, 1999.
[6] F.W. Karasek, L.C. Dickson, Science 14 (1987) 754–756.
[7] E.R. Altwicker, M.S. Milligan, Chemosphere 27 (1993) 301–307.
[8] W.E. Pepelko, D.W. Gaylora, D. Mukerjee, Toxicol. Ind. Health 21 (2005) 93–111.
[9] U.S. Environmental Protection Agency (US EPA), Priority Pollutants, ⟨http://water.epa.gov⟩, 2013 (accessed 22.03.13).
[10] Directive 2000/60/EC of the European parliament, ⟨http://ec.europa.eu/environment/water/water-framework/index_en.html⟩, 2013 (accessed 22.03.13).
[11] P. Kalliokoski, T. Kauppinen, in: H. Vainio, M. Sorsa, A.L. McMichael (Eds.), Complex Mixtures and Cancer Risk, World Health Organization International Agency for Research on Cancer, Lyon, France, 1990, pp. 390–396.
[12] P. Lampi, K. Tolonen, T. Vartiainen, J. Tuomisto, Chemosphere 24 (1992) 1805–1824.
[13] P. Lampi, T. Hakulinen, T. Luostarinen, E. Pukkala, L. Teppo, Arch. Environ. Health 47 (1992) 167–175.
[14] International Agency for Research on Cancer (IARC), IARC Monographs 71 (1999) 769–816.
[15] J.V.K. Kukkonen, B.J. Eadie, A. Oikari, B. Holmbom, M.B. Lansing, Sci. Total Environ. 188 (1996) 15–27.
[16] United States National Library of Medicine, TOXNET, Toxicology Data Network, Hazardous Substances Data Bank (HSDB), 2013 (accessed 22.03.2013).
[17] Sigma-Aldrich Co., Safety Data Sheet of 2,3,4,6-Tetrachlorophenol (Version 4.2, Revision Date 18.01.2011).
[18] I. Marquez-Sillero, E. Aguilera-Herrador, S. Cardenas, M. Valcarcel, Trends Anal. Chem 30 (2011) 677–690.
[19] S. Armenta, M. Alcala, M. Blanco, Anal. Chim. Acta. 703 (2011) 114–123.
[20] M. Mäkinen, M. Nousiainen, M. Sillanpää, Mass Spectrom. Rev. 30 (2011) 940–973.
[21] M.A. Mäkinen, O.A. Anttalainen, M.E.T. Sillanpää, Anal. Chem. 82 (2010) 9594–9600.
[22] S. Holopainen, M. Nousiainen, M. Sillanpää, Talanta 106 (2013) 448–453.
[23] Y. Du, W. Zhang, W. Whitten, H. Li, D.B. Watson, J. Xu, Anal. Chem. 82 (2010) 4089–4096.
[24] A.B. Kanu, C.L.P. Thomas, Analyst 131 (2006) 990–999.
[25] H. Borsdorf, A. Rämmler, J. Chromatogr., A 1072 (2005) 45–54.
[26] J.I. Baumbach, S. Sielemann, Z. Xie, H. Schmidt, Anal. Chem. 75 (2003) 1483–1490.
[27] I. Márquez-Sillero, E. Aguilera-Herrador, S. Cárdenas, M. Valcárcel, Trends Anal. Chem 30 (2011) 677–690.
[28] R.K. Ritchie, A. Rudolph, NASA Conference Publication S-799 (1995) pp. 193–208.
[29] W. Schröder, G. Matz, J. Kübler, Field Anal. Chem. Tech 2 (5) (1998) 287–297.
[30] F. Tadjimukhamedov, J. Stone, D. Papanastasiou, J. Rodriguez, W. Mueller, H. Sukumar, G. Eiceman, Int. J. Ion Mobil. Spectrom. 11 (2008) 51–60.
[31] P. de Morais, T. Stoichev, M.C.P. Basto, M.T.S.D. Vasconcelos, Talanta 89 (2012) 1–11.
[32] M.C. Quintana, L. Ramos, Trends Anal. Chem 27 (2008) 418–436.
[33] S. Holopainen, M. Nousiainen, O. Anttalainen, M.E.T. Sillanpää, Trends Anal. Chem 37 (2012) 124–134.
[34] P. Shahdousti, N. Alizadeh, Anal. Chim. Acta 684 (2011) 67–71.
[35] M. Nousiainen, S. Holopainen, J. Puton, M. Sillanpää, Talanta 84 (2011) 738–744.
[36] N. Alizadeh, M. Jafari, A. Mohammadi, J. Hazard. Mater. 169 (2009) 861–867.
[37] A. Mohammadi, A. Ameli, N. Alizadeh, Talanta 78 (2009) 1107–1114.
[38] U. Telgheder, M. Malinowski, M. Jochmann, Int. J. Ion Mobil. Spectrom. 12 (2009) 123–130.
[39] G. Walendzik, J.I. Baumbach, D. Klockow, Anal. Bioanal. Chem. 382 (2005) 1842–1847.
[40] A.B. Kanu, C.L.P. Thomas, Int. J. Ion Mobil. Spectrom. 6 (2003) 15–20.
[41] P. de Morais, T. Stoichev, M. Basto, P. Carvalho, M. Vasconcelos, Anal. Bioanal. Chem. 399 (2011) 2531–2538.
[42] M. Llompart, M. Lourido, P. Landín, C. Garćıa-Jares, R. Cela, J. Chromatogr. A 963 (2002) 137–148.
[43] D. Kim, J. Han, Y. Choi, Anal. Bioanal. Chem. 405 (2013) 377–387.
[44] R. Morales, M. Ortiz, L. Sarabia, Anal. Bioanal. Chem. 403 (2012) 1095–1107.
[45] N.G. Simões, V.V. Cardoso, E. Ferreira, M.J. Benoliel, C.M.M. Almeida, Chemosphere 68 (2007) 501–510.
[46] G. Kaur-Atwal, G. O'Connor, A. Aksenov, V. Bocos-Bintintan, C. Paul Thomas, C. Creaser, Int. J. Ion Mobil. Spectrom. 12 (2009) 1–14.
[47] C.L. Crawford, B.C. Hauck, J.A. Tufariello, C.S. Harden, V. McHugh, W.F. Siems, H.H. Hill Jr., Talanta 101 (2012) 161–170.
[48] G.A. Eiceman, Z. Karpas, Ion Mobility Spectrometry, 2nd Edition, CRC Taylor & Francis Group, Boca Raton, Florida, USA, 2005.
[49] H. Borsdorf, G.A. Eiceman, Appl. Spectrosc. Rev. 41 (2006) 323–375.
[50] W. Dziewiecki, S. Holopainen, A. Knap, M. Nousiainen, B. Siodłowski, M. Sillanpää, J. Puton, Anal. Sci. 26 (2010) 983–988.
[51] A.B. Kanu, H.H. Hill Jr., M.M. Gribb, R.N. Walters, J. Environ. Monit. 9 (2007) 51–60.
[52] D. MacDougall, W.B. Crummett, Anal. Chem. 52 (1980) 2242–2249.
[53] D.T. Burns, K. Danzer, A. Townshend, Pure Appl. Chem. 74 (2002) 2201–2205.

[54] J. Pawliszyn, Handbook of Solid Phase Microextraction, 1st Edition, Elsevier Inc., 2012.
[55] S.A. Scheppers Wercinski, Solid Phase Microextraction—A Practical Guide, 1st Edition, CRC Press, Florida, USA, 1999.
[56] Z. Penton, in: S.A.S. Wercinski (Ed.), Solid Phase Microextraction—A Practical Guide, CRC Press, Florida, 1999, pp. 27–57.
[57] S.A. Scheppers Wercinski, J. Pawliszyn, in: S.A. Scheppers Wercinski (Ed.), Solid Phase Microextraction—A Practical Guide, CRC Press, Florida, 1999, pp. 1–26.
[58] R.E. Shirey, Solid Phase Microextraction —A Practical Guide, in: S.A. Scheppers Wercinski (Ed.), CRC Press, Florida, 1999, pp. 59–110.
[59] J. Puton, S.I. Holopainen, M.A. Mäkinen, M.E.T. Sillanpää, Anal. Chem. 84 (2012) 9131–9138.
[60] Z. Karpas, A.V. Guamán, D. Calvo, A. Pardo, S. Marco, Talanta 93 (2012) 200–205.
[61] H. Borsdorf, T. Mayer, Talanta 83 (2011) 815–822.
[62] I. Márquez-Sillero, Anal. Chim. Acta 702 (2011) 199–204.
[63] F.W. Karasek, S.H. Kim, H.H. Hill, Anal. Chem. 48 (1976) 1133–1137.
[64] J. Pawliszyn, D. Vuckovic, F. Mirnaghi, S. Risticevic, in: Janusz Pawliszyn (Ed.), Handbook of Solid Phase Microextraction, Elsevier, Oxford, 2012, pp. 135–165.
[65] J.I. Baumbach, Anal. Bioanal. Chem. 384 (2006) 1059–1070.