Abstract
A method based on automated dynamic headspace sampling followed by thermal desorption – capillary GC – MS was developed to monitor ultra-traces of vinyl chloride in water samples. The method shows excellent performance including a limit of quantification (LOQ) below 10 ng/L, good linearity ($r^2 > 0.999$) in the 10 to 200 ng/L concentration range and an RSD below 10% at all calibration levels. The method was applied to study the release of traces of vinyl chloride monomer (VCM) in water from aged polyvinyl chloride (PVC) pipes installed in water supply systems. A solution to avoid this leaching would be the insertion of a polyethylene pipe inside the PVC pipe provided that vinyl chloride does not permeate through polyethylene. Vinyl chloride migration through a high density polyethylene (HDPE) film was therefore studied with the developed sampling method.

Keywords: Vinyl chloride, Dynamic headspace, Capillary GC – MS, Migration, Polyethylene film.
1. Introduction

Whatever its synthesis process, polyvinyl chloride (PVC) intrinsically contains residual vinyl chloride (VCM or vinyl chloride monomer)\(^1\). After confirmation of the toxicity of VCM in 1974, PVC manufacturers optimised their production processes to reduce VCM concentrations in PVC from 200 mg/kg in the early 70’s to less than 1 mg/kg in recently manufactured PVC products.

Through leaching and migration, VCM is a potential contaminant for the environment and water supplies, which might raise health issues since vinyl chloride is classified as a group 1 carcinogen\(^2\). The concentration of vinyl chloride that can potentially migrate out of polyvinyl chloride pipes into water is mainly dependent on the concentration of residual VCM in the used PVC material\(^3,4,5\). Moreover, Al-Malack et al.\(^6,7\) demonstrated that the vinyl chloride release from PVC pipes is also influenced by temperature, pH, total dissolved solids and solar irradiation. An EU Directive specifies that polymers that might come in contact with food products should not contain VCM levels above 1 mg/kg and that the vinyl chloride content in food products should be below 10 µg/kg\(^8\). More recently, the World Health Organization (WHO) set a maximum residue level of 300 ng/L (0.3 ppb) vinyl chloride in drinking water\(^2\).

As vinyl chloride is gaseous at ambient conditions, the analytical technique of choice is gas chromatography (GC). A limit of detection in the order of 1 µg/L could be reached for the determination of vinyl chloride in water samples by static headspace sampling in combination with GC – MS\(^6,7,9,10\). Higher sensitivities were obtained using purge and trap (P&T) sampling\(^11,12\). US-EPA method 524.2 describes the analysis of more than 60 volatile organic compounds (VOCs) including VCM by P&T – GC – MS\(^13\). The detection limit for vinyl chloride in water is 40 ng/L. Other detectors such as electron capture detection (ECD)\(^14\) and electrolytic conductivity detection (ELCD)\(^15\) were used in P&T – GC and detectabilities were in the order of 40-100 ng/L. Direct aqueous injection in combination with GC – MS was also applied to VCM determinations with LODs of 100 ng/L\(^16\). However, the use of cool on-column injection is mandatory making this method not applicable to samples containing high levels of non-volatile material such as salts. Solid phase micro-extraction (SPME)\(^17-19\) and headspace solid-phase dynamic extraction (HS-SPDE)\(^20\) were also applied for VCM determinations but LODs were higher than with P&T.

To our knowledge, the highest analytical sensitivity reported for VCM (LOD of 1.6 ng/L) was obtained by combining off-line P&T followed by derivatization of VCM into 1,2-dibromo-chloroethane and GC – ECD analysis\(^21-23\). This methodology is, however, difficult to apply in routine analysis and the on-line P&T – GC – MS is preferred to monitor VCM according to the WHO guideline.

In our studies on migration kinetics, higher sensitivities were needed and therefore another analytical method was developed. One of the major problems with P&T is the presence of water on the trap. In P&T, an inert gas is bubbled through the aqueous sample and a substantial amount of water is also transferred into the trap and/or analytical system. Increasing sample temperature, extraction time and flow are beneficial for the extraction efficiency of most VOCs, but also increase the amount of “purged” water. Although several water management systems are available for P&T e.g. Nafion dryers\(^11\), water is still interfering with vinyl chloride detection in GC.

For this reason, dynamic headspace sampling (DHS), whereby the water is not purged, but only the gaseous headspace is flushed with an inert gas, was applied as alternative. DHS is performed on a modified XYZ robot developed and commercially available for liquid injection, static headspace sampling and solid phase micro-extraction, resulting in a very flexible multi-purpose sampler. The dynamic headspace adaptor allows to purge the headspace of the sample placed in a 20 mL
vial under controlled temperature and flow conditions. The VOCs are trapped on an exchangeable packed trap (e.g. Tenax, charcoal) at a precise temperature. Finally, the VOCs are thermally desorbed (TD) and analyzed. After optimization of the operational parameters, the dynamic headspace method was applied to evaluate migration of vinyl chloride through a polyethylene thin film.

2. Experimental

2.1. Chemicals and sample preparation

Vinyl chloride monomer (VCM) was obtained as a concentrated solution in methanol (2,000 µg/mL) from Supelco (Sigma-Aldrich, Bellefonte, USA). Dilutions at 0.1 and 1 µg/mL were prepared in methanol (headspace analytical grade, Sigma-Aldrich). Deuterated vinyl chloride (VCM-d3) was obtained from Cambridge Isotope Laboratories (LGC Standards, Molsheim, France) as a 50 µg/mL solution in deuterated methanol. A diluted solution at 0.5 µg/mL in methanol was used as internal standard (IS).

Method validation was done using bottled drinking water (Vittel). Aliquots of 10 mL were spiked with 1, 2 or 5 µL of the 0.1 µg/mL and 1, or 2 µL of the 1 µg/mL VCM standards to obtain calibration samples at 10, 20, 50, 100 and 200 ng/L level. From the IS solution, 4 µL was added, resulting in a 200 ng/L IS level.

2.2. Instrumental conditions

An automated dynamic headspace system (DHS) installed on an MPS2/TDU unit (Gerstel GmbH, Mülheim an der Ruhr, Germany) in combination with a 7890GC – 5975MSD (Agilent Technologies, Wilmington, USA) system was used. The principle of operation is illustrated in Figure 1. During DHS, the sample headspace (10 mL) is purged at 10 °C during 6 min with a flow of 50 mL/min helium (total purge volume = 300 mL) while the vial is agitated. The purged solutes are trapped at 15 °C on a mixed bed composed of Carbotrap B, Carbotrap X and Carbosieve 1000 (B-X-1000 adsorbent from Gerstel GmbH), placed in a TDU (thermal desorption unit) liner.

Separation was done on a 60 m x 0.25 mm x 1.4 µm DB-624 column (Agilent Technologies) using helium as carrier gas at 1.5 mL/min constant flow (160 kPa at 35 °C). The GC oven was programmed from 35 °C (1 min) at 5 °C/min to 60 °C and at 25 °C/min to 250 °C (0.4 min). Mass spectrometric detection was done in SIM mode using ions at 62 and 64 for VCM and ions 65 and 67 for VCM-d3 (IS). Dwell times were 75 ms for each ion. Electron ionization at 230 °C source temperature was used. Quantification was done using the ions at m/z 64 and 67, since they resulted in higher selectivity than the more abundant ions at m/z 62 and 65. The latter ions were used for confirmation.

2.3. Migration study

To evaluate VCM migration through a polyethylene thin film, the experimental set-up shown in Figure 2 was used. Basically, a glass U-tube was designed to place a thin (355 µm) film of high density polyethylene (HDPE) in the middle of the device. The film was tightened between two junctions. On both sides of the U-tube 250 mL water was introduced.
Performance of the DHS method for VCM analysis is dependent on different parameters, including purge conditions (flow × time), sample temperature, solute trapping (adsorbent type and temperature) and desorption conditions. These parameters were varied and their influence on peak shape, peak area (sensitivity) and repeatability was evaluated.

A purge flow of 50 mL/min during 6 min was found to be sufficient for a 10 mL sample volume. A second dynamic headspace extraction performed on the same sample, showed that quantitative extraction was obtained by flushing 30 times the headspace volume (10 mL). Longer purge times and/or higher flow rates resulted in breakthrough of vinyl chloride through the DHS trap. The highest recovery, and thus highest sensitivity, was obtained on a B-X-1000 three bed trap (Carbotrap B, Carbotrap X and Carbosieve 1000). This trap performed much better than a standard Tenax trap. A trap temperature of 15 °C was optimum. Higher trap temperatures resulted in loss by breakthrough of VCM.

An important parameter was the sample temperature (dynamic headspace incubator). Elevated temperatures (up to 70-85 °C) are often used in generic headspace methods, but the best results for vinyl chloride were obtained at low sample equilibrium temperatures. This is commensurate with the observations made by Hino et al.\[24\]. At relatively low sample temperature (10 °C), extraction is complete and apparently it also influences trapping efficiency, desorption and GC – MS analysis, since less water is transferred to the trap and further to the column and detector. Keeping all parameters constant, the peak area of VCM was ca. 2 times higher at 10 °C equilibrium temperature compared to 20 °C. The best peak shape and highest peak area for VCM were obtained when the CIS-4 inlet was placed at -150°C and the liner packed with Tenax. The other desorption conditions listed in the experimental section were found to result in quantitative desorption/injection of VCM. Moreover, no carry-over was noted during a second desorption of the trap. Figure 3 shows the analysis of a water sample spiked with 10 ng/L VCM and 200 ng/L VCM-d3 internal standard.
The results are given in Table 2. First of all, it can be observed that the duplicates give close results illustrating the repeatability of the determination. In addition, it is obvious that the high sensitivity of the method is required to detect VCM migration. Note that at t1 the concentration is close to the LOD value and at t2 close to the LOQ value. The concentration of VCM in the non-spiked side (S₀) increased from 2 to 60 ppt within 7 days. From this experiment, it is clear that vinyl chloride migrates through the HDPE thin film. By plotting the vinyl chloride migration value as a function of time, a linear curve was obtained for the first 3 days (72 h). This curve was used for the determination of the VCM diffusion coefficient.

The diffusion of a solute through a film is described by Fick’s Law:

\[ \text{Fick’s Law} \]

**Table 1.** Figures of merit for VCM determinations using DHS – TD – GC – MS.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration level or range</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linearity</td>
<td>10 – 200 ng/L</td>
<td>R² = 0.9996</td>
</tr>
<tr>
<td>RSD % (n = 6)</td>
<td>10 ng/L</td>
<td>8.2 %</td>
</tr>
<tr>
<td>RSD % (n = 6)</td>
<td>50 ng/L</td>
<td>7.1 %</td>
</tr>
<tr>
<td>RSD % (n = 6)</td>
<td>200 ng/L</td>
<td>9.9 %</td>
</tr>
<tr>
<td>S/N</td>
<td>10 ng/L</td>
<td>13.6</td>
</tr>
<tr>
<td>LOD (S/N = 3)</td>
<td></td>
<td>2.2 ng/L</td>
</tr>
<tr>
<td>LOQ (S/N = 10)</td>
<td></td>
<td>7.3 ng/L</td>
</tr>
</tbody>
</table>

**Table 2.** Measured VCM concentration (ng/L) in S₀ as a function of time for a 6 µg/L level spiking in S₁ (see Figure 2).

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>6 µg/L</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
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<tr>
<td>7</td>
<td>65</td>
<td>55</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Method validation

Some figures of merit are presented in Table 1. The linearity in the concentration range between 10 ng/L and 200 ng/L is excellent with RSDs below 10% at all calibration levels. The signal-to-noise ratio, determined using peak-to-peak noise, on the extracted ion chromatogram for m/z 64 from the analysis of a water sample spiked at 10 ng/L (VCM) and 200 ng/L (IS).

3.3. VCM migration through a thin film of polyethylene

The migration test was performed in duplicate at the concentration level of 6 µg/L in S₁ (Figure 2).
where $\frac{dQ}{dt}$ is the flux of molecules that pass the membrane in function of time (mol/s), $D$ is the diffusion coefficient (cm$^2$/s), $A$ is the membrane area (cm$^2$) and $\frac{dC}{dx}$ is the concentration gradient (with $dC$ in mol/cm$^3$ and $dx$ in cm). By plotting the concentration (in nmol) as a function of time (in hours), the curve concentration (nmol) = 0.0016 time (hours) - 0.0153 ($R^2 = 0.9194$) was obtained by linear regression, using the data points between 0 and 72 h (3 days).

Using the experimental data, the diffusion coefficient $D$ was calculated using:

$$D = \frac{dC}{dt} \cdot \frac{1}{A} \cdot \frac{d}{C_0}$$

in which $\frac{dC}{dt}$ is the slope of experimental curve of concentration (nmol) increase as a function of time (hours), $A$ is 28.27 cm$^2$ (diameter of membrane exposed = 6 cm), $d$ is the film thickness (355 µm or 0.0355 cm) and $C_0$ is the concentration of vinyl chloride at spiked side (80 nmol/L). The calculated diffusion coefficient is 2.51 E-05 cm$^2$/hour.

The experiment was repeated for a 60 µg/L concentration and the diffusion coefficient was 2.06 E-05 cm$^2$/hour. The obtained values are close and the average diffusion coefficient for vinyl chloride migration through a polyethylene film (at room temperature) is thus in the order of 2.3 E-05 cm$^2$/hour or 5.5 E-08 m$^2$/day. The diffusion coefficient is at present refined by additional tests on several HDPE film thicknesses and VCM concentrations. Such data are of great value for engineering purposes of drinking water pipeline networks.

4. Conclusion

Sensitive and reliable determination of vinyl chloride in water samples could be achieved using dynamic headspace combined with thermal desorption – GC – MS. Using a relatively low extraction temperature and optimized DHS and thermal desorption parameters, the limit of quantification is below 10 ng/L. This innovative method has been implemented to assess vinyl chloride migration through polyethylene films.
References