Short communication

Determination of chlorinated volatile organic compounds in polyamine epichlorohydrin solution by headspace gas chromatography

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A B S T R A C T

This study demonstrated a headspace gas chromatographic (HS-GC) method for the determination of residual epichlorohydrin (ECH) and the by-product 1,3-dichloro-2-propanol (DCP) in polyamine epichlorohydrin (PAE) solution. It was based on the vapor-liquid phase equilibrium of these analytes at 60 °C for 30 min in a closed headspace sample vial before GC measurement. It was found that matrix of the PAE solution had the effect on the headspace equilibrium of these species and therefore a standard addition must be applied in the method validation. The results showed that the present method has a good measurement precision (RSD = 2.90%) and accuracy (recoveries from 93.6 to 105%), and the limit of quantitation (LOQ) is 3.75 mg/L for ECH and 0.8 g/L for DCP. The present method is suitable to be used for analyzing the chlorinated volatile organic compounds in the commercial PAE resin solutions.

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1. Introduction

Attributed to its good performance in the application, polyamide epichlorohydrin (PAE), a kind of water-soluble, cationic and thermosetting resin, is widely used as a wet-strength agent in papermaking process [1–4]. There are three monomers, i.e., adipic acid (AA), diethylenetriamine (DETA), and epichlorohydrin (ECH), involved in the PAE synthetic process [5,6] and the reactions are described below:

\[ \text{AA + DETA} \rightarrow \text{PPC} \]  \hspace{1cm} (1)

\[ \text{PPC + ECH} \rightarrow \text{PAE} \]  \hspace{1cm} (2)

where polyamide polymine (PPC), an intermediate compound from the reaction between AA and DETA, can further react with ECH to form PAE resin. There is also 1,3-dichloro-2-propanol (DCP) presented in the solution due to the acidolysis from the unreacted ECH [7–9]. Because the chlorinated organic compounds are very toxic substances [10,11], e.g., irritating to skin and mucous membrane, they have been strictly regulated by countries and organizations. In the commercial PAE solution, ECH and DCP are the typical chlorinated volatile organic compounds. Due to the nature of easy migration, they are more harmful than the other co-existing organic species. Therefore, an efficient method that can determine ECH and DCP is highly desired to both process control and quality check in the PAE production and its related applications.

Traditionally, the content of chlorinated organic compounds can be determined by the precipitation titration, in which a standard solution of silver nitrate (as titrant) is used [12]. Before the titration, the chlorinated organic compounds need to be extracted with organic solvent followed by an oxidation process in potassium permanganate-sulfuric acid solution to convert the organic chlorine to free chloride ions. The major problem of this method is its non-selective, since it could not determine an individual chlorinated organic compound in the mixtures, e.g., ECH or DCP in the PAE solution. Moreover, the titration method is not suitable to be used for determining chlorinated organic compounds with very low concentration (e.g., ppm level), due to its sensitivity limitation.

There are also several instrumental analysis methods available to determine ECH and other organic chlorides, typically gas chromatography (GC) [13,14] and high performance liquid chromatography (HPLC) [15]. However, because these compounds are presented in polymer containing aqueous solution, the sample pretreatment (to exclude the polymer with large molecular weight or salts), typically solvent-extraction, is required before GC or HPLC measurement. Although GC and HPLC method are selective and have good detection sensitivity, the similar pretreatment proce-

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2.2. Sample preparation and measurement

Pipetted 5 mL of PAE sample solution and added 1.5 g of NaCl into two 20 mL vials, added 10 μL of ECH solution (1%) and 30 μL of pure DCP into one of the vials and then seal the vials immediately with a PTFE/Butyl septum and screw cap. Placed these vials to the headspace sampler for HS-GC measurement. ECH and DCP can be well separated in the GC test [18].

3. Results and discussion

3.1. Conditions for the headspace equilibration

In the conventional headspace analysis for liquid sample, it is essential to achieve the vapor-liquid phase equilibrium (VLE) of analytes before GC measurement. In Fig. 1, it shows the time-dependent DCP and ECH released from a PAE sample at different temperatures. It can be seen from Fig. 1a that the phase equilibrium for DCP can be achieved in 10 min. Surprisingly, it requires a much longer time to achieve the phase equilibrium for ECH if the equilibration is operated at a higher temperature. This abnormal phenomenon is caused by the formation of PAE’s flocculation in the solution [4], which could affect the analyte’s release rate, especially for the species with very low concentration.

To have a good efficiency in the analysis, a shorter phase equilibrium time is desired. Therefore, the phase equilibrium at a lower temperature, according to Fig. 1b, is suggested for the present sample analysis. However, the lower temperature can greatly affect the detection sensitivity in the HS-GC measurement, as shown in Fig. 1. As a compromise, the headspace equilibration at 60 °C for 30 min is suggested if the conventional headspace analysis would be used in this work.

Regarding to the measurement efficiency, full evaporation (FE) based headspace analysis is a good choice [20] since it usually
required a very short time (e.g., ~5 min) for headspace equilibrium (due to a very small sample size, e.g., 10 μL). However, it is mandatory for the FE based headspace analysis to conduct the headspace at high temperature, typically above solvent boiling point. In Fig. 2, it shows both ECH and DCP release during the headspace equilibration. It can be seen that DCP is partly hydrolyzed at such high temperature, and the release of ECH from the medium is still very slow due to the effect of PAE flocculation. Therefore, the FE headspace analysis is not suitable to be applied to the determination of ECH and DCP in the samples.

3.2. Effect of sample matrix

The matrix in the PAE solution is complicated, which includes the PAE resin, the residual chemical compounds initially added for the synthesis, and the species produced by the side-reactions. Therefore, the matrix effect on the analysis of ECH and DCP should be investigated. By spiking 50 μL of ECH solution (1%) and pure DCP in the samples (from different sources) and deionized water, we found that the net GC signals (before and after spiking) for ECH and DCP from the headspace measurements are higher than those of deionized water, especially in the DCP measurement. It confirms that the matrix effect could produce the positive errors in both ECH and DCP analysis if an external calibration method were applied.

Therefore, a standard addition calibration, based on VLE at a mild temperature (60 °C), was introduced in the present HS-GC method in order to minimize the sample matrix effect. The equation used for calculating the analyte content using the standard addition method can be written as below [21], which is based on two HS-GC measurements, i.e., before and after the standard addition.

\[
C_0 = \frac{C_S V_S}{(A_2/A_1 - 1)/V_0}
\]

where \(C_0\) is the solute concentration in the original sample, g/L; \(V_0\) is the volume of the sample solution, mL; \(C_S\) is the known solute concentration added in the system, g/L; \(V_S\) is the volume of the added solution, mL; \(A_1\) is the GC peak area of the species detected.

3.3. Improvement of the detecting sensitivity

As mentioned above, 60 °C is a proper temperature for the headspace equilibration in the present work. However, the lower temperature also sacrifices the detection sensitivity in the headspace analysis, especially for the low content species, i.e., ECH in the PAE samples. It is well known that there is a salting-out effect on the volatility of some organic compounds [22]. In the present study, we found that the addition of salt (i.e., NaCl or Na₂SO₄) in PAE solution can increase the contents of both ECH and DCP in the headspace. As shown in Fig. 3, the addition of both NaCl and Na₂SO₄ can increase the GC signal for the headspace measurement, the salting-out effect of Na₂SO₄ is more significant than that of NaCl. Therefore, it is suggested that to add Na₂SO₄ in the PAE solution to improve the method sensitivity in the ECH measurement.

3.4. Evaluation of the method

3.4.1. Method sensitivity

Based on a set of ECH and DCP solutions and HS-GC measurement, we can obtain two linear equations, i.e.,

\[
A_{ECH} = -48.34(\pm 1.08) + 2.88(\pm 0.016)C_{ECH} \quad (n = 6, \quad R^2 = 0.999)
\]

\[
A_{DCP} = -0.57(\pm 16.39) + 189.38(\pm 1.35)C_{DCP} \quad (n = 6, \quad R^2 = 0.999)
\]

where \(A_{ECH}, A_{DCP}, C_{ECH}, \) and \(C_{DCP}\) represent the GC signal and concentration for ECH (mg/L) and DCP (g/L), respectively.

With the uncertainty of the intercept and slope in Eqs. (4) and (5), the limit of quantitation (LOQ) can be calculated, which is 3.75 mg/L for ECH and 0.8 g/L for DCP.

3.4.2. Method precision and validation

The precision of the present HS-GC method was investigated by conducting a triplicate test on a commercial PAE sample. The results showed that the relative standard deviations (RSD) for ECH and DCP measurement are less than 0.69 and 2.90%, respectively, which included the uncertainty in both sampling and GC detection.

Because there is no any reference method available for analyzing ECH and DCP in PAE aqueous solution, a recovery test approach was used to verify the accuracy of the present method. It was done by accurately spiking different amount of ECH solution (1%) and pure DCP into a set of PAE sample solutions and then conduct the HS-GC measurement with a standard addition method. In Table 1, it shows the comparison between the amounts of ECH and DCP added and measured by the standard addition (using Eq. (3) in the calculation) on a set of commercial PAE samples. The results show that the recoveries in both ECH and DCP are in the range of 93.6–105%, indicating that the present method is suitable to be used for the quantification of ECH and DCP in the commercial PAE samples.
Table 1
The method validation.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>ECH (mg/L)</th>
<th>DCP (g/L)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Added</td>
<td>Measured</td>
<td>Added</td>
</tr>
<tr>
<td>1</td>
<td>71</td>
<td>70.8</td>
<td>6.79</td>
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<tr>
<td>2</td>
<td>94.6</td>
<td>88.5</td>
<td>9.51</td>
</tr>
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<td>118</td>
<td>114</td>
<td>12.2</td>
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<tr>
<td>4</td>
<td>166</td>
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<tr>
<td>5</td>
<td>189</td>
<td>199</td>
<td>21.7</td>
</tr>
</tbody>
</table>

Table 2
Contents of ECH and DCP in the commercial PAE samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Effective solid content, %</th>
<th>pH</th>
<th>Content of analyte</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ECH, mg/L</td>
<td>DCP, g/L</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>13.9</td>
<td>3.41</td>
<td>23.1</td>
</tr>
<tr>
<td>2</td>
<td>11.0</td>
<td>3.89</td>
<td>24.9</td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>3.35</td>
<td>20.7</td>
</tr>
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<td>21.8</td>
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</tr>
<tr>
<td>9</td>
<td>16.9</td>
<td>3.83</td>
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</tr>
<tr>
<td>10</td>
<td>10.4</td>
<td>3.86</td>
<td>24.1</td>
</tr>
</tbody>
</table>

3.5. Applications

In this work, we simultaneously determined 10 different kinds of commercial PAE by HS-GC. The results of ECH and DCP content calculated from Eq. (3) were shown in Table 2. As we can see from it, the general content of DCP (g/L) is much higher than that of ECH (mg/L), and the content of these two species varies in different PAE solutions. It contained excessive levels of ECH and DCP in 2# PAE solution, which far surpassed the stipulated chlorinated volatile organic compounds of 0.7%, thus making it existing high risk to use the final PAE product.

4. Conclusion

A vapor-liquid phase equilibrium based HS-GC technique for the determination of ECH and DCP in the commercial PAE solution has been developed. The results showed that the method has a good measurement precision (RSD < 2.90%) and accuracy (recoveries from 93.6 to 105%), and has the advantage of being rapid, automated and practical. It overcomes the shortness of the traditional method, and needs no pretreatment and calibration, which can greatly improve the work efficiency. Therefore, it is more suitable for research on the synthetic process of PAE.

Notes

The authors declare no competing financial interest.

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References