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Determination of epichlorohydrin and 1,3-dichloro-2-propanol in synthesis of cationic etherifying reagent by headspace gas chromatography

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ABSTRACT

This study demonstrates a headspace gas chromatographic(HS-GC) technique for the determination of residual epichlorohydrin (ECH) and generated 1,3-dichloro-2-propanol (DCP) in synthesis process of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHTAC). By a weight-based sampling method, coupled with significant dilution in 15.8% sodium sulfate and 0.1% silver nitrate mixed solution rapidly, the sample for HS-GC analysis is prepared. Based on the reaction stoichiometry, the conversion (R) of CHTAC during the synthesis process can be calculated from sampling weight and GC peak area. The results showed that the method has a good measurement precision (RSD < 2.5%) and accuracy (recovery = 101–104%) for the quantification of both ECH and DCP in the process samples. The present method is simple and accurate, which can be used for the efficient determination of the CHTAC conversion in the synthesis research.

1. Introduction

3-Chloro-2-hydroxypropyltrimethylammonium chloride (CHTAC) is a kind of cationic etherifying reagent synthesized by trimethylammonium chloride (TMAC) and epichlorohydrin (ECH) [1], as described by

$$\mathrm{TMAC} + \mathrm{ECH} \rightarrow \mathrm{CHTAC} \quad (1)$$

where ECH is a major volatile analyte.

Because of its active groups, CHTAC reacts with some natural macromolecular compounds such as lignin, cellulose and starch, to endow them with useful properties such as dispersibility and dissolubility in the applications [2–5]. In addition, CHTAC is also an important organic synthetic intermediate for emulsifier, water softener, fabric antistatic agent, phase transfer catalyst, etc. [6,7]. However, an incompletion in the chemical synthesis due to a poor process control causes a significant amount of residual ECH and the by-products, i.e., 1,3-dichloro-2-propanol (DCP), remaining in the CHTAC final product, which will seriously affect the quality of downstream products in the applications. For example, a cross-linking reaction will occur between ECH and starch in alkaline condition, which reduces the solubility and dispersibility of cationic starch in water and makes the addition of starch derivative less effective in the wet part of the papermaking process [8]. Therefore, a well controlled process aiming at minimizing amount of ECH and DCP in the CHTAC final product is desired. Clearly, an effective analytical method that able to quantify these species of interest during synthesis will be helpful to modify or optimize the reaction process in CHTAC synthesis research.

There is no any individual analytical method that is able to quantify all these major components found during CHTAC synthesis, and thus several analytical techniques such as gas chromatography (GC) [9–12], ion chromatography (IC) [13,14], high performance chromatography (HPLC), or titration [8] are usually involved. For instance, the residual ECH is quantified by GC, and the formed CHTAC is determined by titration. Moreover, due to a complex matrix, a direct sample injection in GC analysis will cause contamination and damage the instrument system. Therefore, the sample pretreatment such as solvent extraction is required before the analysis [8,9], which makes the method not only complicated and time-consuming but also subject to large errors.

Headspace based GC method (HS-GC) is an effective technique to minimize the effect from non-volatile species in sample matrix [15]. One of the great advantages in HS-GC analysis is that there is no or less sample pretreatment required, which makes the testing much efficient. In the last decade, a number of methods based on HS-GC have been successfully developed by Chai and his co-authors [16–19] for many difficult process sample analyses. Since ECH and DCP are volatile, HS-GC is suitable technique that can simultaneously quantify these major species, from which the conversion (R) of CHTAC during the synthesis process can be calculated based on the reaction stoichiometry [19].

The objective of the presented work was to develop a HS-GC method for simultaneously determination of ECH and DCP in the

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CHTAC synthesis process samples. The optimal conditions for sample headspace equilibration were established. The precision and accuracy for the species quantification by the proposed method were also evaluated.

2. Experimental

2.1. Chemicals

All chemicals used are analytical grade, in which ECH, TMAC,ethanol, Na_2SO_4 and NaCl were purchased from Sinopharm Chemical Reagent Co. Ltd. (China), DCP was from JingChun Reagent Co. Ltd. (Shanghai, China), and CHTAC was from kasei kogyo Co. Ltd. (Tokyo, Japan).

2.2. Instruments and operations

All measurements were carried out with an automatic headspace sampler (DANI HS 86.50, Italy) and gas chromatograph (GC-2010, Shimadzu, Japan).

The GC employed a DB-5 capillary column (30 m × 0.35 mm, i.d. 0.1 μm film thickness) operating at a temperature of 50 °C with a nitrogen carrier gas flow of 4.3 ml/min. It was equipped with a flame ionization detector, with hydrogen and air flow rates of 40 ml/min and 400 ml/min, respectively. The headspace operating procedure consisted of 10 min of strong shaking at 90 °C to achieve liquid–vapor phase equilibrium and enhance the GC signal of DCP, a vial pressurization time of 0.2 min, a sample loop fill time of 1.0 min, and a loop equilibration time of 0.05 min.

2.3. Synthesis of CHTAC

Considering the solubility of TMAC in ethanol at different temperature, we dissolved TMAC in ethanol (100 ml) completely. This reaction was conducted in a three-neck flask equipped with a graham condenser and a velocity-controlled motor stirrer. After the solution in the flask was heated to a desired temperature in a water bath, the reaction was initiated by adding ECH to TMAC–ethanol solution.

2.4. Sample preparation for HS-GC measurement

About 0.2 g of reaction solution was taken out from the flask at the desired time during the synthesis process, and transferred to a 50-ml volumetric flask placed on a balance. By the weight differences before and after the sample addition, an accurate weight of the sample was determined. The volumetric flask was filled to the mark with a solution containing 15.8% sodium sulfate and 0.1% silver nitrate, and mixed well. A 2-ml above diluted solution was taken by a pipette and added into a 20-ml headspace sample vial. The sealed vial is ready for HS-GC measurement.

3. Results and discussion

The optimal conditions for sample headspace equilibration were established. The precision and accuracy for the species quantification by the proposed method were also evaluated.

3.1. GC separation for ECH and DCP

Fig. 1 shows the chromatogram of a sample from synthesis process conducted by HS-GC measurement. It can be seen that ECH and DCP are well separated from the co-existing species such as ethanol (solvent) and other violate impurities at the given HS-GC conditions. Therefore, ECH and DCP in the process samples from CHTAC synthesis can be quantified when a calibration of these species is established.

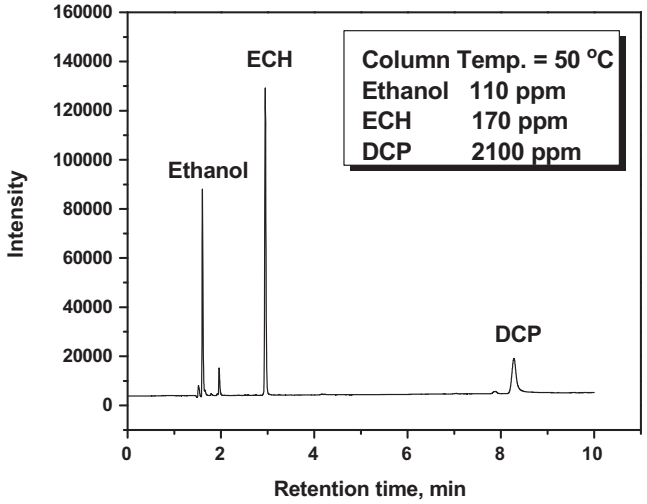


Fig. 1. Chromatogram of HS-GC measurement on a process sample.

3.2. Selection of dilution ratio

The conventional HS-GC method is based on Henry's law, i.e., the analyte of interest in the vapor phase is linearly related to that in its liquid phase at two-phase equilibrium [20]. This can be easily achieved by sample dilution with a large ratio, in which the molecular interaction between the analytes in the liquid phase is not significant. In the initial stage of the synthesis reaction, there are significant amount of ECH (reactant) in the solution, and the amount of DCP generated during the process is very limited. Therefore, the sample dilution is required for ECH analysis. However, this will also reduce the DCP concentration in the testing sample. The larger measurement uncertainties in both ECH and DCP detection will leads to the error in calculating the CHTAC conversion, according to Eq. (2),based on the conservation of ECH's molar mass.

$$N^0_{ECH} = N^t_{ECH} + N^t_{CHTAC} + N^t_{DCP} \quad (2)$$

where N^0_{DCH} is the initial molar mass of ECH in the starting solution ($t = 0$), N^t_{ECH}, N^t_{CHTC} and N^t_{DCP} are the molar mass of the residual ECH, generated CHTAC and DCP at the reaction time t, respectively.

To compromise on these effects, we found that a dilution ratio of 250 is proper in the sample preparation for ECH determination in the initial reaction samples. This ratio also satisfies to the detection sensitivity of the residual ECH in the sample from later stage of synthesis. Good standard curves between the GC peak areas and concentrations of ECH and DCP in the testing solutions in the HS-GC measurement could be obtained, and they could be described as follow

$$A_{ECH} = -5630.38(\pm 2585.88) + 1441.2(\pm 11.66)C_{ECH}$$

with $R^2 = 0.9995$.

$$A_{DCP} = -1647.7(\pm 471.06) + 71.72 \pm (0.97)C_{DCP}$$

with $R^2 = 0.9991$.in which the concentrations of these species are covered the ranges found the CHTAC synthetic process. It can be seen that the slope of GC response to DCP is much smaller than that of ECH. Therefore, a larger measurement error for the generated DCP in the samples from initial reaction is expected.

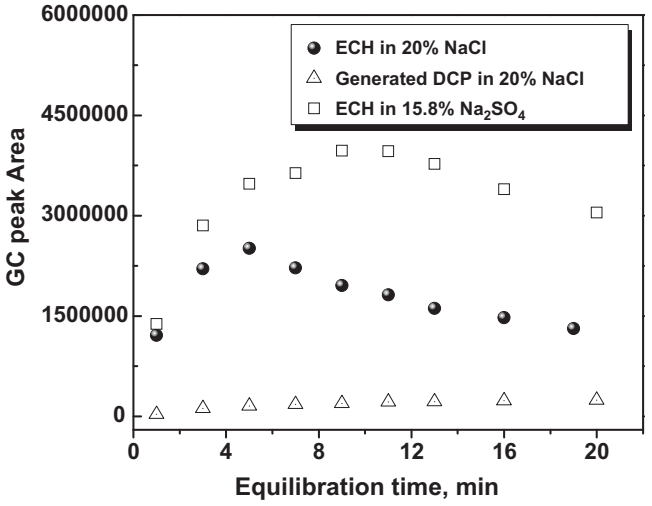


Fig. 2. Further reaction during headspace equilibration.

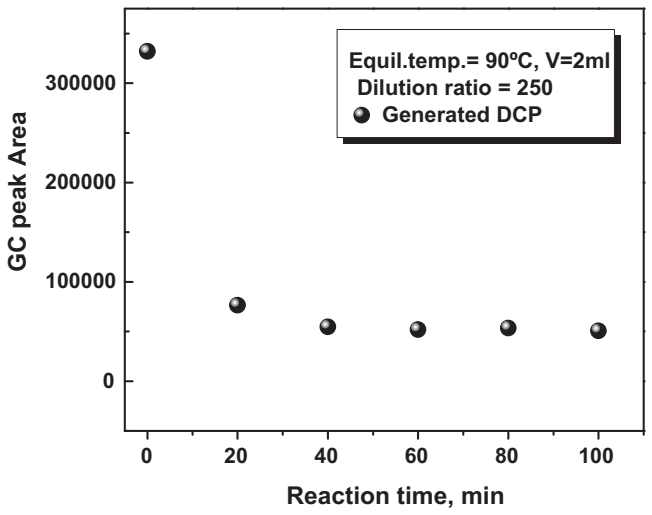


Fig. 3. Time-dependent effect of chloride ions on the DCP formation during the headspace equilibration.

3.3. Addition of sodium sulfate

It was observed in previous work that salting-out effect is helpful to increase the detecting sensitivities of alcohols in HS-GC measurement [21]. In this work, we added 15.8% sodium sulfate (near to its solubility in the room temperature) to maximize the salting-out effect. The equation for new standard calibration curves could be described as follow

$$A_{ECH} = -1107.82(\pm 1447.68) + 1888.84(\pm 6.72)C_{ECH} \quad (3)$$

with $R^2 = 0.9999$. The linear range, limit of detection (LOD), and limit of quantitation (LOQ) in the measurement were 800, 1.7 and 4.1 ppm, respectively.

$$A_{DCP} = 1278.89(\pm 1026.89) + 284.46(\pm 2.55)C_{DCP} \quad (4)$$

with $R^2 = 0.9993$. The linear range, LOD, and LOQ are 1100, 15 and 26 ppm, respectively.

As shown in Eqs. (3) and (4), the detection sensitivity for DCP when the testing solution containing 15.8% of sodium sulfate (near saturation) is 4 times greater than those in the solution without salt addition. It is also noticed that the salting-out effect on ECH in the HS-GC measurement is not significant, in which only 1.3 times greater than the solutions without salt addition.

Table 1
Recovery test.

Component	Content of added (C_a) ppm	Content of measured (C_m) ppm	Recovery[a] %
ECH	82	86	105
	162	165	101
DCP	82	85	104
	174	182	104

[a] Recovery (%) = $(1 + (C_m - C_a)/C_a) \times 100$.

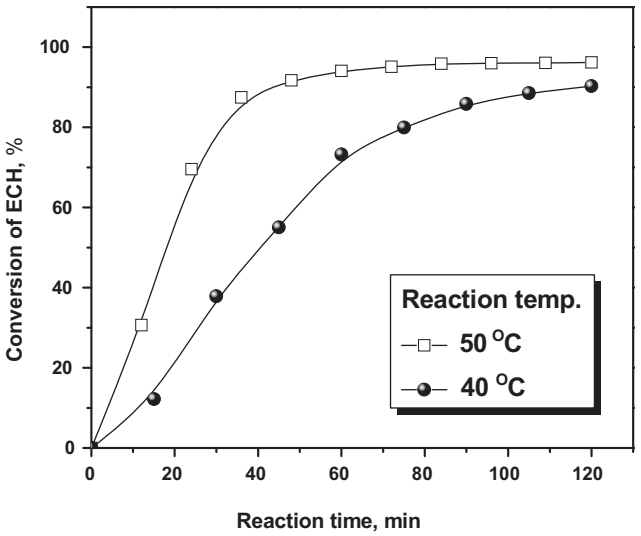
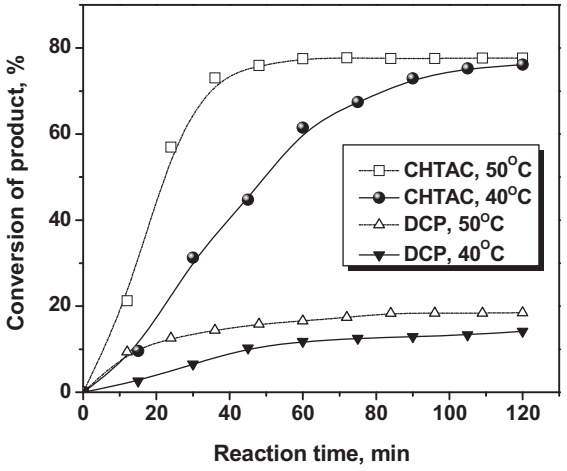


Fig. 4. Conversion of ECH during synthetic process.



(CHTAC is 3-chloro-2-hydroxypropyltrimethylammonium chloride)

Fig. 5. Conversion of CHTAC and DCP during synthetic process.

3.4. Effect of the further reaction during headspace equilibration

Despite it was diluted by 250 times, as the concentration of reactants in the initial sample ($t = 0$) was high, the reaction between the reactants might occur in initial samples during the headspace equilibration, especially when a higher oven temperature (e.g., 90 °C) was selected. Besides the reaction between ECH and TMAC, ECH

would also be hydrolyzed at a high temperature and to form 2,3-epoxy-1-propanol [1], a less volatile compound. Just as shown in Fig. 2, the GC signal of ECH in the diluted sample started to decreased as the equilibration time was longer than 11 min it indicates that a significant hydrolysis of ECH in the solution took place. In our previous work, 12 min was found sufficient to achieve vapor–liquid phase equilibrium of same amount organic volatile species at a lower oven temperature (e.g., 75 °C). Moreover, a good linear relationship (described as above) was also obtained when 10 min was selected at the present headspace equilibration conditions. Thus, an equilibration time of 10 min was selected for the sample headspace equilibration.

3.5. Effect of chloride ion on ECH decomposition

It was noticed that the presence of chloride ions could cause ECH decomposition and to form DCP during headspace equilibration due to a higher temperature (see Fig. 2). In addition, as shown in Fig. 3, a mass of DCP was also detected by GC in initial samples, which was caused by nucleophilic substitution reaction between ECH and chloride ion, as described by

$$\mathrm{ECH} + \mathrm{Cl}^{-}\underset{\rightarrow}{\mathrm{H}^{+}}\mathrm{DCP} \quad (5)$$

where DCP is another major volatile analyte.

As there was vast TMAC dissolving in initial samples, and it dissociated abundant chloride ion which could react with ECH. In order to minimize the effect, we added appropriately excess amount of silver nitrate to precipitate the chloride ion generated from the reaction during the sample preparation. In this way, the decomposition of ECH during the sample headspace equilibration can be minimized. We found that using a 0.1% of silver nitrate solution for the sample preparation was optimal because it just covered the concentration range (molar amount) of the chloride ions produced in the synthesis processes.

3.6. Method evaluation

GC repeatability testing with this method was conducted, the relative standard deviations (RSD) from five measurements for ECH and DCP were within 2.3 and 2.5%, respectively, which included the uncertainty from both sampling and GC detecting. The accuracy of the present method was evaluated based on a set of sample, in which an exact amount of ECH and DCP standard sample was added. In Table 1, it lists the recovery data from these testing and the results show that the present method is justifiable to be used for quantifying the ECH and DCP contents in the process samples.

4. Application: conversion of CHTAC during synthetic process

According to Eq. (2), the conversion (R) of CHTAC during the synthesis process can be calculated by the following equation [19]:

$$R = \left[1 - \frac{m^0}{m^t}\frac{(m^t_{\mathrm{ECH}}/M_{\mathrm{ECH}} + m^t_{\mathrm{DCP}}/M_{\mathrm{DCP}})}{m^0_{\mathrm{ECH}}/M_{\mathrm{ECH}}}\right] \times 100\% \quad (6)$$

where m^0, m^t are the weights of undiluted samples at the reaction time $t = 0$ and $t = t$, respectively. M_{ECH}, M_{DCP} are the molar mass of ECH and DCP; m^0_{ECH} is the weight of ECH in initial sample ($t = 0$), and m^t_{ECH}, m^t_{DCP} are the weights of ECH and DCP in sample at the reaction time ($t = t$), respectively.

Based on the linear relationship between GC signal and species content in the testing sample, the conversion (R) of CHTAC expressed with GC peak area and sample weight can be written as:

$$R = \left[1 - \frac{m^0}{m^t}\frac{\left(A^t_{\mathrm{ECH}} + \varphi A^t_{\mathrm{DCP}}\right)}{A^0_{\mathrm{ECH}}}\right] \times 100\% \quad (7)$$

where φ is equal to ($K_{\mathrm{ECH}}M_{\mathrm{ECH}}/K_{\mathrm{DCP}}M_{\mathrm{DCP}}$), and K_{ECH}, K_{DCP} are the linear coefficient of Eqs. (3) and (4), respectively.

In this work, about 19.54 g TMAC was completely dissolved in ethanol (100 ml) at 40 °C and 50 °C separately, and then 18.53 g ECH(N_{TMAC}:N_{ECH} = 1.02:1) was added in TMAC–ethanol solution. As shown in Figs. 4 and 5, not only the conversion of ECH but also the yield of CHTAC and DCP (main by-product) during synthetic process could be obtained by Eq. (7) simultaneously. Moreover, the differences of this reaction with various temperatures could be distinguished directly. Thus, the present method could be well used for process related analysis and quality control during synthesis of CHTAC.

5. Conclusions

An improved headspace gas chromatographic technique for determination of ECH and DCP during synthesis process of CHTAC has been developed. The results showed that the method has an excellent measurement precision (RSD < 2.5%), much better than that those (>10%) reported in the traditional method [9]. The recoveries of the method, for both ECH and DCP quantification in the process samples, were in the range of 101–104%. The LOQ of the analysis was 4.1 and 26 ppm, for ECH and DCP, respectively. The present method is simple, accurate and practical and quite suitable for research on the synthetic process of CHTAC.

Acknowledgements

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