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Short communication

Determination of isocyanate groups in the organic intermediates by reaction-based headspace gas chromatography

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ABSTRACT

This work reports on a novel method for the determination of isocyanate groups in the related organic intermediates by a reaction-based headspace gas chromatography. The method is based on measuring the CO_2 formed from the reaction between the isocyanate groups in the organic intermediates and water in a closed headspace sample vial at 45 °C for 20 min. The results showed that the method has a good precision and accuracy, in which the relative standard deviation in the repeatability measurement was 5.26%, and the relative differences between the data obtained by the HS-GC method and the reference back-titration method were within 9.42%. The present method is simple and efficient and is particularly suitable to be used for determining the isocyanate groups in the batch sample analysis.

1. Introduction

Isocyanate is an important intermediate for synthesizing many organic chemicals (e.g., pesticides, fungicides, herbicides) [1–4]. It can also be used to synthesize a series of polyurethane (PUR) based materials [5], in which the isocyanate group (—N=C=O) can significantly affect the properties of the products [6]. Clearly, the analytical methods that can efficiently and accurately determine the isocyanate groups in the organic intermediates play an important role for the process control in the related organic synthesis and product quality.

Isocyanate group in the organic intermediates is traditionally determined by the back-titration method [6,7]. In this method, the sample is dissolved in a solvent (e.g., methylbenzene or acetone) followed by adding an excess amount of *n*-butylamine. After the reaction between the isocyanate group and *n*-butylamine (to form substituted ureas, RNHCONHR'), the unreacted *n*-butylamine is titrated with sulfuric acid or hydrochloric acid and thus the isocyanate groups in the intermediates can be determined. The major disadvantages of the method are the time-consuming procedures and inefficiency in the batch sample analysis, which takes more than 20 min to complete a single sample test [7]. Moreover, the method also requires a large amount of methylbenzene and *n*-butylamine in the testing and thus produces more hazardous wastes.

The other methods, mainly based on the separation technique such as gas chromatography (GC) and high-performance liquid chromatographic (HPLC), are available for the determination of isocyanate groups [8–12]. GC method is very suitable to be used for the volatile intermediate compounds [8,9], however it is difficult to be applied to the semi- and non-volatile compounds, e.g., PUR based polymers. Although HPLC method can conduct the measurement for both volatile and non-volatile compounds, there is a difficult to have a good separation for the target intermediate species if there are many coexisting species in the sample matrix. Moreover, the sample pretreatment such as solvent extraction is required before HPLC test, which makes the method not only time-consuming but also subject to large errors.

Headspace gas chromatography (HS-GC) is a powerful tool for analyzing volatile species in samples with complex matrices [13,14]. HS-GC is also able to determine some non-volatile species if they can be quantitatively converted to the related volatile species through some chemical reactions [15]. In a previous study [16], we reported a phase reaction conversion HS-GC technique for the determination of carboxyl acids in pulp fibers. It is based on HS-GC measuring the carbon dioxide released from the reaction between the carboxyl acids in pulps and bicarbonate in a solution. According

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to Wurtz et al. [17,18], the isocyanate groups can react with water to form urea and CO_2, i.e.,

$$2RNCO + H_2O \rightarrow RNHCONHR + CO_2(g) \quad (1)$$

If this reaction can be quantitatively achieved, it is also possible to be determined by measuring the CO_2 formed using the phase conversion based HS-GC technique.

In this work, we proposed a novel method for the determination of the isocyanate groups in the related organic intermediates by HS-GC. The main focuses were to explore the reaction conditions (i.e., the dosage of H_2O, sample size, reaction time and temperature) in order to achieve a complete isocyanate groups conversion and the operation conditions for headspace equilibration in the HS-GC measurement. The precision and accuracy for the present method were also evaluated. Since an automatic headspace sampling mode is available in many commercial headspace samplers, the present method can provide an efficient testing for the batch sample analysis.

2. Experimental

2.1. Chemicals and materials

All chemicals used in this work (i.e., acetone and isocyanate) were analytical grade and purchased from commercial sources without further purification. A set of isocyanate standard solutions (0–0.05 mol/L) was prepared by diluting the original isocyanate with appropriate amount of acetone and then calibrated by titration with hydrochloric acid standard solutions. The organic intermediate samples for the test were obtained from both manufactures and a chemical supplier (Aladdin Reagent Co. Ltd, China).

2.2. Apparatus and operations

The HS-GC measurements were carried out with an automated headspace sampler (Thermo HS TriPlus 300, US) connected to a GC system (Agilent GC 7890A, US) equipped with a thermal conductivity detector (TCD) and a GS-Q capillary column (length = 30 m, inner diameter = 0.32 mm with thickness of stationary phase = 1 μm), operating at a temperature of 105 °C with nitrogen carrier gas (flow rate = 2.7 mL/ min). The headspace operating conditions were as follows: 20 min of strong shaking to allow sample equilibration at 45 °C; sample loop temperature = 55 °C; transfer line temperature = 65 °C; pressurization pressure = 1.00 bar; carrier gas pressure = 1.50 bar; vial pressurization time = 15 s; sample loop fill time = 10 s; and transfer time = 20 s; sample loop volume = 3 mL.

2.3. Procedures for sample preparation and HS-GC measurement

A 25 mg of intermediate was added in 10 mL of acetone. After the intermediate is completely dissolved, 4.0 mL of the acetone solution was pipetted to a headspace sample vial. Then, a 0.2 mL of distilled water was added into the vial, which was immediately sealed by a rubber septum. The reaction/equilibration was conducted at 45 °C for 20 min and measured by GC.

2.4. Determination of isocyanate groups by a reference method [6,7]

A given amount of organic intermediate is first dissolved with a certain amount of methylbenzene solvent, and then an excess of *n*-butylamine is added to the intermediate samples. The excess amount of *n*-butylamine was back-titrated with a standard HCl solution, and then the isocyanate groups in the intermediate samples can be calculated.

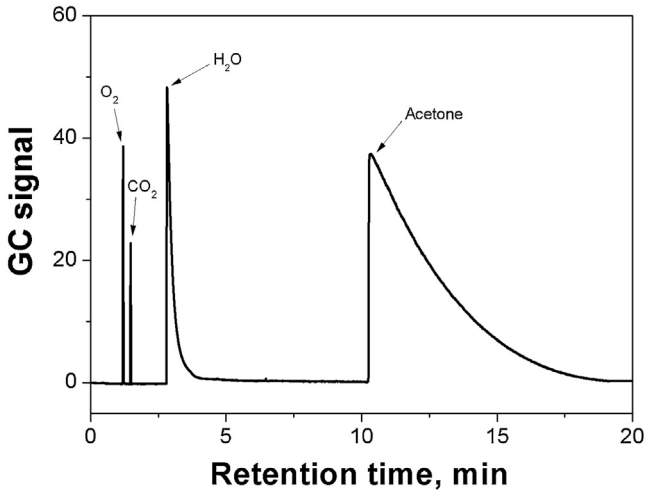

Fig. 1. Chromatogram in HS-GC measurement of an organic intermediate sample.

3. Results and discussion

3.1. Conditions for GC measurement

According to Eq. (1), isocyanate groups in the organic intermediates can be converted into carbon dioxide by reacting with H_2O. Because air was included in the headspace vial, its effect on the GC measurement for the CO_2 formed from the reaction must be considered. In this work, nitrogen and TCD were used as the GC carrier gas and the detector in the GC measurement. As shown in Fig. 1, the oxygen in air, CO_2 released from the reaction, water vapor and acetone vapor are the major detectable species and they are well-separated at the given GC conditions. It should be pointed out that there is small amount of CO_2 in air that could affect the measurement accuracy in the present method. However, such an effect can be simply subtracted by running a blank test.

3.2. Selection of reaction medium

Because the related organic intermediates are insoluble in the aqueous solution, they must be dissolved in an organic solvent. In the traditional method [6,7], methylbenzene is used as solvent for such a purpose. However, water (as the reactant) is not soluble in the methylbenzene medium, which affects its reaction rate with the isocyanate groups. In order to overcome this problem, acetone (a water miscible solvent) is selected as the solvent. The experiment showed that the organic intermediates can be instantly dissolved by acetone and there is no phase layer after the addition of water.

3.3. Selection of reaction temperature and time

In the present method, the reaction is performed in a closed headspace sample vial and the formed CO_2 from the reaction is measured by HS-GC. Therefore, the selection of a suitable temperature is important for both the reaction and the headspace measurement. In general, headspace analysis for a sample solution must be conducted at temperatures below its boiling point. Because acetone was used as the reaction medium, a temperature below its boiling point (56.5 °C) is selected. In general, a higher temperature can promote the chemical reactions and thus improve the method efficiency. As a compromise, we chose 45 °C as the reaction temperature to avoid the effect of higher acetone vapor pressure on the CO_2 measurement in the HS-GC analysis.

In Fig. 2, it shows the time needed for achieving a complete reaction between the isocyanate groups and water at the given reaction

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