Determination of Monochloroacetic Acid and Dichloroacetic Acid for Quality Control of Acetic Acid Chlorination Industry by Ion Chromatography

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An ion chromatographic method is described for the purpose of quality control in the process of monochloroacetic acid production. Using 2.5 mM NaOH–10% methanol as eluent, the simultaneous determination of acetic acid, monochloroacetic acid, dichloroacetic acid, and Cl^- was obtained in a single run. Monochloroacetic acid and dichloroacetic acid showed good linearity in the range 0.1–20 and 0.15–20 $\mu\text{g/ml}$ and correlation coefficients were 0.9999 and 0.9998, respectively. The detection limits (signal-to-noise ratio 3:1) of monochloroacetic acid and dichloroacetic acid were 17 and 25 ng/ml . This simple, sensitive, and time-saving method can be applied for composition analysis in acetic acid chlorination production. © 1999 Academic Press

Key Words: monochloroacetic acid; dichloroacetic acid; ion chromatography.

INTRODUCTION

The chloroacetic acid is an important industrial and commercial solvent. Acetic acid chlorination is the commonly used method for producing monochloroacetic acid (MCA). The reaction of acetic acid chlorination is

During the chlorinating process, the formation of dichloroacetic acid (DCA), the main by-product, not only increases the consumption of raw material but also lowers the quality and purity of MCA product. Moreover, DCA is restricted because of its toxic effect. The objective of acetic acid chlorination is to keep the highest purity of MCA by controlling nonconsumed acetic acid to less than 0.2% and minimizing the formation of DCA.

According to Eqs. (1) and (2), MCA, nonconsumed acetic acid, by-product DCA, and HCl should exist in the productive process. So, we aimed at getting a simple method to determine all the possible compositions simultaneously.

There is a considerable amount of literature investigation of the genotoxic characteristics of chlorinated acetic acids (1–4). Most performed the analysis of MCA and DCA by (a) gas chromatography with a microwave plasma emission detector as the selective determination of chlorine (5–8), (b) gas chromatography equipped with an electron capture detector (9, 10), and (c) gas chromatography using electrospray ionization-tandem

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mass spectrometry as detector after converting them to their benzyl esters (11, 12). To our knowledge, no high performance liquid chromatography methods have been reported.

Ion chromatography offers an attractive method to short chain organic acid analysis (13). The dissociation constant pK_a of acetic acid, MCA, and DCA are 4.76, 2.86, and 1.26, respectively. They all exist in anion form when basic eluent is used. Therefore, they can be separated by anion-exchange chromatography. Compared to the method of gas chromatography, which needs to convert organic acids to their ester form, ion chromatographic procedure is simpler and just requires minimal sample preparation.

In this paper, the method for simultaneous determination of acetic acid, MCA, DCA, and Cl^- by ion chromatography is reported.

MATERIALS AND METHODS

Apparatus

A Dionex Model DX-100 ion chromatography equipped with a 25 μ l sample loop was used along with a conductivity detector. The chromatographic separation was achieved by Dionex IonPac AS11 analytical and AG11 guard columns. Suppression was performed by a Dionex anion micro-membrane suppressor AMMS-I.

Reagents

All chemicals, NaOH, H_2SO_4 , methanol, and NaCl, were of analytical reagent grade. Eluent (NaOH-methanol), regenerant (H_2SO_4), and stand solution were prepared using deionized water. Monochloroacetic acid (MCA, 99+%) and dichloroacetic acid (DCA, 99+%) were obtained from Aldrich Chemical Co. (Milwaukee, WI).

RESULTS AND DISCUSSION

Choice of Eluent

Compared to the results of using Na_2CO_3 or $NaHCO_3$ as eluent, NaOH was chosen as eluent since it gave the best selectivity and sensitivity for determination of acetic acid, MCA, DCA, and Cl^- . The effect of the NaOH concentration on their retention time is

FIG. 1. The effect of NaOH concentration on retention time of acetic acid (HAc), MCA, Cl^- , and DCA.

FIG. 2. The effect of methanol concentration on retention time of acetic acid (HAc), MCA, Cl^- , and DCA.

shown in Fig. 1. The increase of NaOH concentration exerted a greater influence on the retention of DCA than others. To get good separation of the four in a short time, 2.5 mM NaOH was selected.

FIG. 3. Chromatogram of separation of 10 $\mu\text{g/ml}$ HAc, MCA, Cl^- , DCA, and NO_3^- . Peak 1, HAc, 2: MCA, 3: Cl^- , 4: DCA, 5: NO_3^- . Eluent, 2.5 mM NaOH–10% Methanol, flow-rate 0.5 ml/min; regenerant, 25 mM H_2SO_4 , flow-rate 1.0 ml/min; conductivity detection; inject volume, 25 μl .

FIG. 4. Chromatograms of samples (diluted 1:10000). (A) sample 1, Peak 1: MCA 25.08 $\mu\text{g/ml}$, 2: Cl^- 22.28 $\mu\text{g/ml}$, 3: DCA 3.59 $\mu\text{g/ml}$. (B) sample 2, Peak 1: MCA 0.91 $\mu\text{g/ml}$, 2: Cl^- 16.73 $\mu\text{g/ml}$, 3: DCA < 0.1 $\mu\text{g/ml}$. Chromatographic condition is the same as in Fig. 3.

By adding methanol in NaOH eluent, retention time of DCA was further shortened and the resolution of MCA and Cl^- became better (See Fig. 2). The optimum eluent selected was a mixture of 2.5 mM NaOH and 10% methanol. Figure 3 shows the good resolution of acetic acid, MCA, Cl^- , and DCA. They were well separated within 12 min.

Interference

Since Cl^- is eluted after MCA, it does not interfere with the determination of MCA even though Cl^- concentration is 15 times greater than that of MCA. Moreover, during the productive process, most Cl^- will volatilize in the form of HCl while Cl_2 gas is passed through reaction solution, so Cl^- concentration in real samples is not high enough to disturb the determination of MCA.

Interference probably coming from common anions was investigated also. NO_3^- did not disturb the determination of MCA and DCA (see Fig. 3). SO_4^{2-} and PO_4^{3-} were not eluted out within 25 min, but acetic acid was co-eluted with F^- under this experimental condition.

Accuracy and Detection Limit

MCA and DCA showed good linearity in the range 0.1–20 and 0.15–20 $\mu\text{g/ml}$ and the correlation coefficients were 0.9999 and 0.9998, respectively. The detection limits (signal-to-noise ratio 3:1) of MCA and DCA were 17 and 25 ng/ml.

Sample Analysis

Liquid sample 1 and sample 2 were obtained from different reaction steps. The determination results showed the difference between them (See Fig. 4A and 4B). After technological improvement, which converted DCA to MCA by taking oxidative reaction, no DCA was found in sample 2 (Fig. 4B). Solid MCA product (0.018 g) was dissolved directly in 50 ml deionized water and then diluted 25 times before injection. The result obtained showed that MCA content of this product reached 94.7%.

Spike recovery studies were carried out by adding 5 $\mu\text{g/ml}$ MCA and DCA standard solution in diluted sample 1 and 2. The recoveries of MCA and DCA were 98–108% and 94.6–99.6%, respectively.

Conclusion

Separation and determination of acetic acid, MCA, DCA, and Cl^- is achieved by ion chromatography using the mixture of 2.5 mM NaOH and 10% methanol as eluent. The method is simple, sensitive, and time-saving. It has been applied for the analysis of composition produced in the process of acetic acid chlorination production.

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