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Journal of Chromatography A, 982 (2002) 255–260
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Improvement in the detection of impurities affecting ethylene glycol UV transmittance by gas chromatography–mass spectrometry

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Received 14 May 2002; received in revised form 23 September 2002; accepted 23 September 2002

Abstract

A method was developed for the detection of trace impurities affecting ethylene glycol UV transmittance, using gas chromatography–mass spectrometry in the selective ion monitoring mode. Four 1,2-cyclopentanediones were identified in commercial ethylene glycol as well as in several ethylene glycol plant streams, including 3-methyl-1,2-cyclopentanedione, 3,5-dimethyl-1,2-cyclopentanedione, 3,4-dimethyl-1,2-cyclopentanedione and 3-ethyl-1,2-cyclopentanedione. Quantification of the first three compounds was achieved by monitoring the molecular ion. This method requires no sample preparation and can detect the compounds of interest as low as 0.1 μg ml^{-1}. As a simple and rapid method, it can be used in tracing these 1,2-cyclopentanediones in glycol plants.

Keywords: Ethylene glycol; Cyclopentanediones

1. Introduction

Ethylene glycol is a major chemical product. It has many applications [1,2], including as antifreeze and as a raw material for making polyesters. Ethylene glycol that is used to make polyesters should be of high purity and has to meet a rigid UV-transmittance specification, which is often tested at 220, 275 and 350 nm, respectively [3]. Low UV transmittance of ethylene glycol often indicates the presence of certain impurities, which will reduce polyester quality. Various methods have been reported for improving ethylene glycol UV transmittance, for example passing unqualified ethylene glycol product through activated carbon [4], charcoal [5], or ion-exchange resin [6] to remove the impurities. However, these methods are generally either expensive or tend to introduce unwanted impurities into the final products. Recently, the methods devised for improving ethylene glycol producing process, particularly ethylene glycol distillation process [7–9], have gained much interest. However, more efforts are needed before practical and economic procedures can be applied to real glycol plants. For this reason, a good understanding of these special impurities, such as their chemical compositions, their quantities and distributions in whole plant, is important and desirable.

Recently, we had identified the impurities, which

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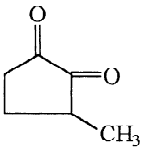
0021-9673/02/$ – see front matter
PII: S0021-9673(02)01595-9

were largely responsible for the low UV transmittance at 275 nm in commercial ethylene glycol [10]. These impurities were cyclic 1,2-diones, including 3-methyl-1,2-cyclopentanedione (A), 3,5-dimethyl-1,2-cyclopentanedione (B), 3,4-dimethyl-1,2-cyclopentanedione (C), 3-ethyl-1,2-cyclopentanedione (D) and 3-ethyl-4-methyl-1,2-cyclopentanedione (E). Their enol tautomers are 2-hydroxycyclopent-2-en-1-ones. The presence of compounds A and B was confirmed by literatures [11,12]. However, up to now, there has been no simple and relatively complete method for tracing these compounds in plant streams, and people still lack sufficient information about their amounts and distributions in whole plants. The method we used in our previous study [10] involved solid-phase extraction (SPE) and several analytical techniques, such as gas chromatography–mass spectrometry (GC–MS), gas chromatography-Fourier transform infrared spectroscopy (GC–FT-IR) and high-performance liquid chromatography (HPLC). However, it was time-consuming and therefore not applicable for routine sample analysis. A direct HPLC method [11] with diode-array detection (DAD) was also reported for ethylene glycol impurity studies. But under the conditions used, only two 1,2-cyclopentanediones, compounds A and B, could be detected in poor quality ethylene glycol. A USA patent [12] described the use of a UV spectrometer for detecting the cyclic 1,2-diones in glycol solutions. It was based on the fact that a solvent (e.g. ethylene glycol) containing cyclic 1,2-diones (>0.1 μg ml^{-1}) alters its UV maximum absorbance wavelength from about 260 nm to 290 nm when the pH of the solvent changes from acidic to basic. However, for some actual plant streams, the UV measurement might be interfered due to the presence of other UV absorbers.

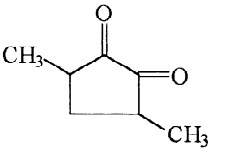
The aim of this study is to develop a simple and practical method for the detection of the target 1,2-cyclopentanediones in glycol plants. In this present paper, the testing samples were analyzed directly by GC–MS in the selective ion monitoring (SIM) mode. The identification of the target compounds was based on the chromatographic retention times and the SIM mass spectra of the reference standards. The quantification was obtained using five point standard calibration curves.

2. Experimental

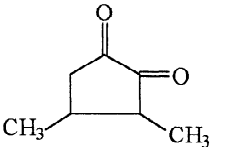
Reference standards of 3-methyl-1,2-cyclopentanedione (A), 3,5-dimethyl-1,2-cyclopentanedione (B) and 3,4-dimethyl-1,2-cyclopentanedione (C) were obtained from Acros Organics (NJ, USA). The chemical structures and relative molecular masses of these standards are shown in Fig. 1. Standards mixtures containing A, B and C at levels of 0.1, 0.5, 1.0, 5.0 and 10.0 μg ml^{-1} were prepared in ethanol. 1,2-cyclohexanedione (also obtained from Acros Organics) at a constant concentration of 10.0 μg ml^{-1} was used as an internal standard in the quantitative analyses.



A. 3-methyl-1, 2-cyclopentanedione
Mr = 112.13



B. 3,5-dimethyl-1, 2-cyclopentanedione
Mr = 126.15



C. 3,4-dimethyl-1, 2-cyclopentanedione
Mr = 126.15

Fig. 1. Structures and relative molecular masses of the 1,2-cyclopentanediones studied in the study.

The GC–MS system consisted of a Hewlett-Packard 6890 gas chromatograph and a 5973 mass-selective detector (Palo Alto, CA, USA). A Stabilwax DA fused capillary column (60 m×0.25 mm I.D. with a thickness of 0.5 μm) was used. The carrier gas was helium (99.999%) at a flow-rate of 0.8 ml min^{-1}. The oven temperature was held at 200 °C. For each analysis, on column injection of 0.2 μl was performed.

The samples were ionized in electron impact (EI) mode with electron energy of 70 eV. The ion source temperature was set at 230 °C and the interface temperature was 210 °C. The detector voltage was 1370 V. Full scan mass spectra were acquired over the range m/z 15~150. In the SIM mode, several ions including the molecular ion of each analyte (see Section 3) were monitored. For sample analyses, the filament and the detector were not turned on until 8 min into the run.

The testing samples comprised a commercial ethylene glycol of low UV transmittance and more than ten plant streams, which were collected at a time from various units of a local glycol plant. All these samples were kept at 4 °C before analyzed.

3. Results and discussions

3.1. Qualitative analyses

Initially, GC–MS in full scan mode was used to analyze the testing samples. However, the target cyclic 1,2-diones could not be detected clearly. This is probably due to the low levels of these compounds in real samples (usually <1 μg ml^{-1}, see Section 3.2) as well as the matrix interference. Therefore, the SIM mode was employed to improve the sensitivity and selectivity of this study.

The SIM method was developed based on the full scan mass spectra (Fig. 2) of the reference standards A, B and C. As seen, the three compounds were ionized in the same pattern. The base peak in each mass spectrum is the molecular ion (M^+ 112 or 126), indicating the high structural stabilities of these compounds. A series of fragment ions with a difference of 14 mass units are also present in all mass

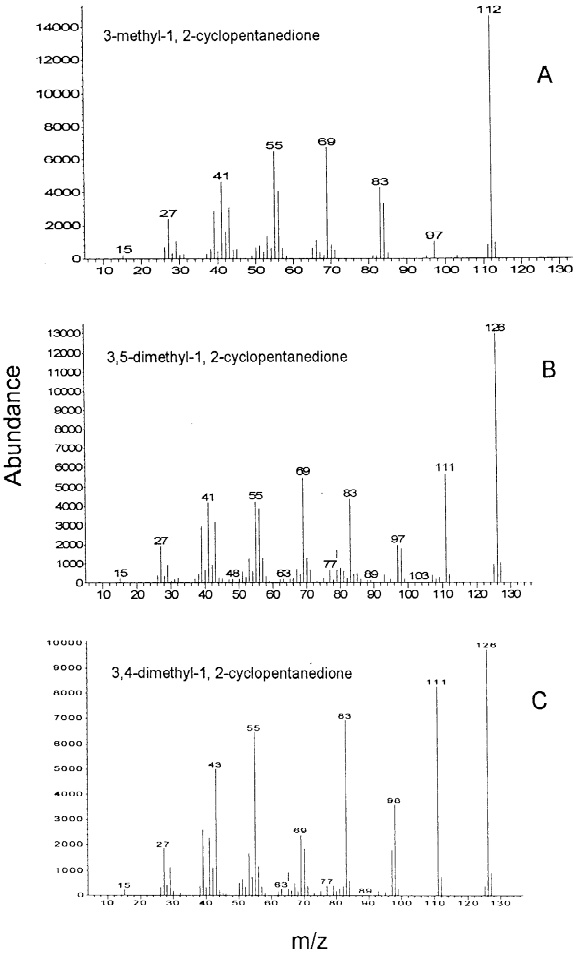


Fig. 2. Full scan mass spectra of the standards A, B and C at 10 μg ml^{-1}.

spectra. For compounds B and C (M^+ 126), these fragments include m/z 111, 97, 83, 69 and 55. The first two ions m/z 111 and 97 might be formed by the loss of CH_3 and CHO from the molecule ion, respectively, and ion m/z 83 might be formed by the elimination of CH_3 and then CO from the molecular ion. The corresponding fragment ions for compound A include m/z 97, 83, 69, 55 and 41. As known, lower mass fragment ions, such as m/z 69, 55 and 41, despite of their intensities, are not specific enough for detecting the analytes of interest in complex matrix. Therefore three higher mass fragments m/z 111, 97 and 83, as well as the molecular

ion (M^+ 126 or 112), were used as confirming ions for the subsequent qualitative analysis.

Fig. 3a shows the extracted SIM chromatograms of a commercial ethylene glycol with UV transmittance of 78, 88 and 100% at 220, 275 and 350 nm, respectively. As seen, during the 15-min analysis, four peaks, a, b, c and d, were well separated and detected, and little interference from sample matrix was observed. Under the same conditions, the standard mixture containing compounds A, B and C at 10 μg ml^{-1} in ethanol was analyzed. The resulting extracted SIM chromatograms are shown in Fig. 3b. As seen, the retention times of peaks a, b and c in Fig. 3a agreed within 2% with those for standards A, B and C, respectively. In addition, the SIM mass spectra (Fig. 4) of peaks a, b and c were identical to those of the standards (not shown). Therefore, peaks a, b and c in the ethylene glycol testing sample were identified as 3-methyl-1,2-cyclopentanedione, 3,5-dimethyl-1,2-cyclopentanedione and 3,4-dimethyl-1,2-cyclopentanedione, respectively. Peak d might be 3-ethyl-1,2-cyclopentanedione, one of the impurities detected in commercial ethylene glycol by our earlier study [10]. Its SIM mass spectrum (Fig. 4d) is seen to be in good agreement with the EI mass spectrum of 3-ethyl-1,2-cyclopentanedione from the NIST library [13]. However, this identification was not confirmed due to the lack of the corresponding standard. The presence of the target compounds in the plant streams was determined in the same way. Detailed results are presented in Section 3.2.

It is worthy noting that the retention times of the target compounds in the ethylene glycol sample were slightly longer than their standard values (Fig. 3). This shift of the retention time was found to result from ethanol, the solvent for preparing the standards.

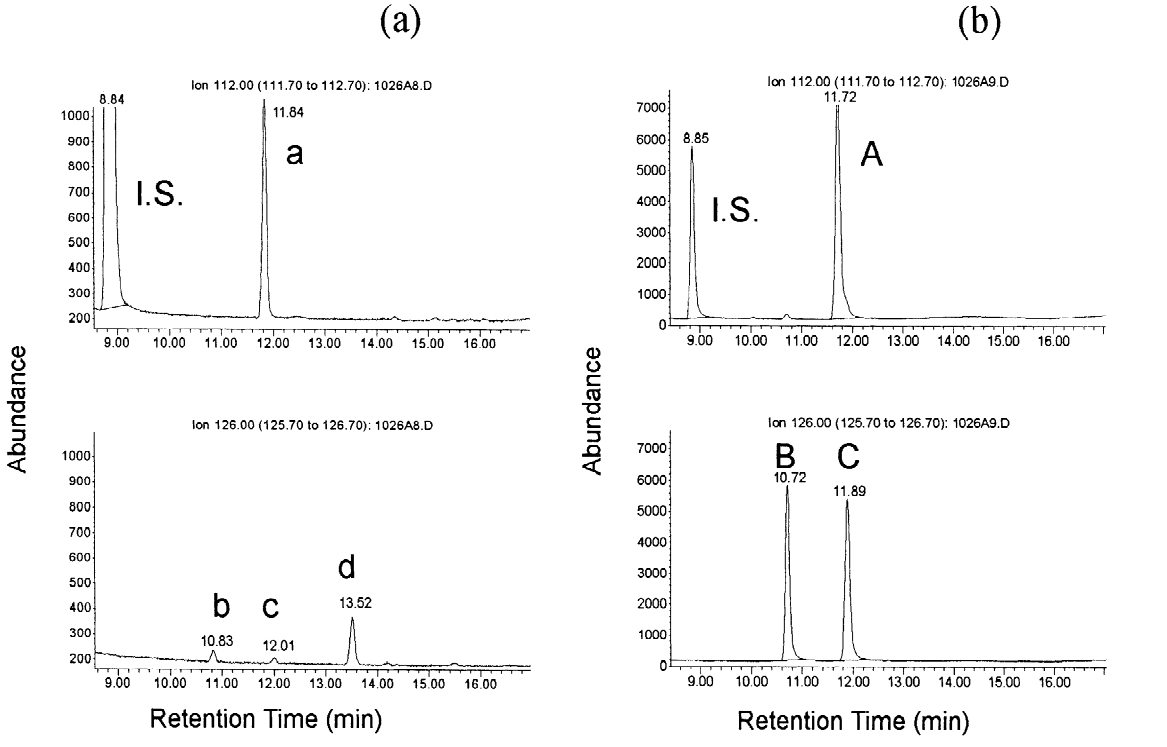


Fig. 3. Extracted SIM chromatograms of (a) commercial ethylene glycol of low UV transmittance (b) the standard mixture containing compounds A, B and C at 10 μg ml^{-1} in ethanol (peak I.S.: the internal standard).

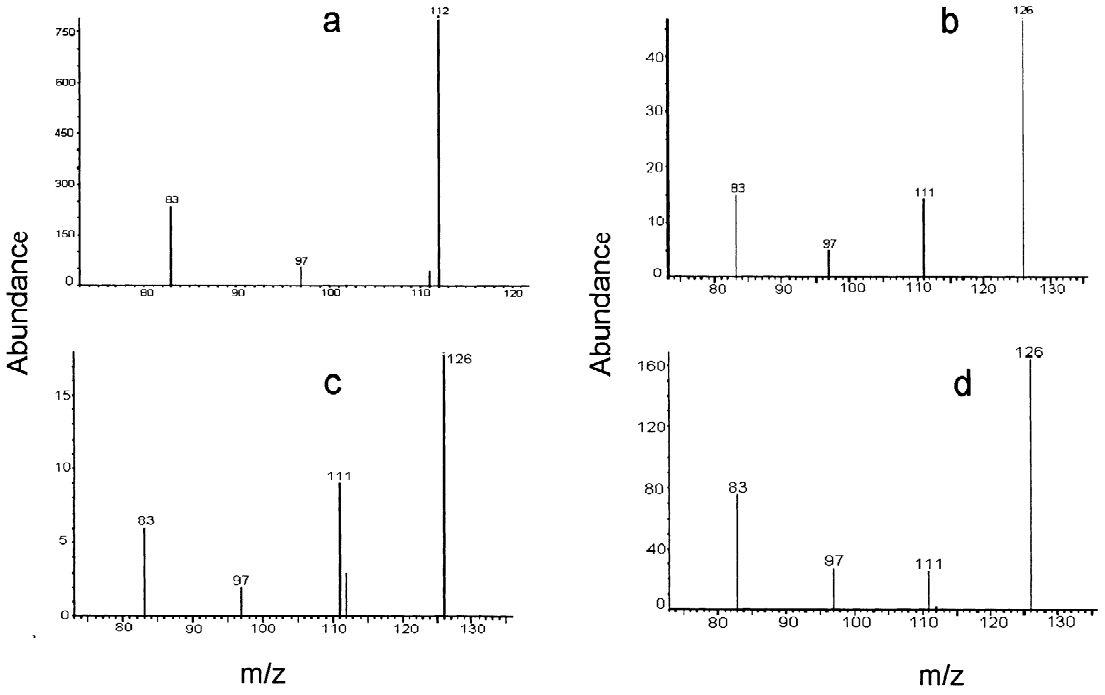


Fig. 4. SIM mass spectra of four peaks a, b, c and d in Fig. 3a.

Therefore, for more accurate analysis of such samples, blank ethylene glycol should be used for preparation of the standards.

3.2. Quantitative analyses

Both internal standard and external standard calibration methods were employed for quantification. The calibration standards were used in the range 0.1~10.0 μg ml^{-1}, corresponding to the concentration ranges of the analytes usually present in glycol plants. The molecular ion (M^+ 112 or 126) was chosen for quantitation, since it is the base ion for each target compound as well as for the internal standard, 1,2-cyclohexanedione. For calibration with internal standard, the calibration curves were built by regression of nominal concentrations against peak area ratio of reference standards to internal standard. The linear regression equations for compounds A, B and C were as follows:

$$y_A = 0.1604x - 0.0099 \quad R^2 = 0.9994$$

$$y_B = 0.0997x - 0.0022 \quad R^2 = 0.9999$$

$$y_C = 0.113x - 0.0062 \quad R^2 = 0.9998$$

External standard calibration curves were built by regression of nominal concentrations against peak area of reference standards. The correlation coefficients for all calibration curves were over 0.99, indicating the robustness of the external standard method.

The instrumental detection limits, defined as twice the noise, were determined to be about 0.005, 0.007 and 0.007 ng for compounds A, B and C, respectively.

The quantities of the target 1,2-cyclopentanediones in real samples were then determined. Each sample was run in triplicate. In the ethylene glycol sample, compounds A, B and c were found at 0.76, 0.11 and 0.13 μg ml^{-1}, respectively. The

analyses of the plant streams showed these compounds mainly occurred in the ethylene glycol purification section of the plant, and compound A was always at the highest concentration compared to compounds B and C. In this section, a top reflux stream from the ethylene glycol column contained the highest levels (2.5, 1.5 and 1.6 μg ml^{-1}, respectively) of compounds A, B and C. A side stream from the ethylene glycol recycle column contained these analytes at less high levels (1.7, 1.0 and 0.8 μg ml^{-1} for compounds A, B and C, respectively). Also in this section, small amounts of these three compounds were detected in two bottom streams as well as in a condensed water vapor stream from the ethylene glycol drying column (for compound A, the concentration was less than 0.8 μg ml^{-1}). The levels of these analytes in other sections of the plant were generally rather low (<0.1 μg ml^{-1}). Taken together, the results of GC–MS analyses of the plant streams provided information on the distribution of the target 1,2-cyclopentanediones in the glycol plant, indicating the key units where these compounds were mainly formed.

4. Conclusion

The GC–MS–SIM method provided a highly sensitive and selective means for determining the target 1,2-cyclopentanediones in ethylene glycol plants. It needs no sample preparation, and can detect these compounds less than 0.1 μg ml^{-1}. With this method, tracing the target compounds in glycol plants and making process improvements to remove them might be easy.

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