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Identification of impurities affecting commercial ethylene glycol UV transmittance

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Abstract

As a raw material for making polyesters, ethylene glycol has a special specification of UV transmittance. At present, ethylene glycol produced by some plants still has low UV transmittance rendering it unsuitable for use in polyester production. In this paper, a method was developed for the identification of the impurities that cause commercial ethylene glycol to have low UV transmittance, using solid-phase extraction (SPE) and some analytical techniques such as high-performance liquid chromatography, gas chromatography–mass spectrometry and gas chromatography–Fourier transform infrared spectroscopy. The major UV-absorbing impurities were identified as some alkyl homologues of 2-hydroxycyclopent-2-en-1-one, including 2-hydroxy-3,5-dimethylcyclopent-2-en-1-one, 2-hydroxy-3-methylcyclopent-2-en-1-one, 2-hydroxy-3,4-dimethylcyclopent-2-en-1-one, 2-hydroxy-3-ethyl-4-methylcyclopent-2-en-1-one and 2-hydroxy-3-ethylcyclopent-2-en-1-one. Their concentrations were estimated to be less than 2 $\mu g\ ml^{-1}$. It is believed that with the above results, ethylene glycol-producing plants might make process improvements to remove these impurities more effectively and more easily.

Keywords: Ethylene glycol

1. Introduction

Ethylene glycol is an important chemical product. It has many applications [1–3], including as antifreeze, and as a raw material for making polyesters. In recent years due to the rapidly increasing demands for polyester products in the world market, world ethylene glycol production has been increased greatly. It was estimated that the worldwide ethylene glycol production capacity was about $1.25 \cdot 10^{10}$ kg by 1999. The method that currently is mainly used for industrial production of ethylene glycol is based on the hydrolysis of ethylene oxide obtained by direct reaction of ethylene with air or oxygen [1]. Ethylene glycol that is used to make polyesters should be of exceptionally high purity and must meet a special UV transmittance specification, requiring that ethylene glycol have UV transmittances of at least 75%, 95%, 100% at 220, 275 and 350 nm, respectively [4]. It is believed that low UV transmittance at these wavelengths indicates the presence of undesirable impurities that reduce the resulting polyester quality. Some methods have been reported for improving ethylene glycol UV transmittance, including passing ethylene glycol through activated carbon [5] or an ion-exchange resin [6], or exposing ethyl-

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ene glycol to UV radiation [7], and so on. However, up to now, in some ethylene glycol-producing plants, ethylene glycol still has low UV transmittance. Thus, more process improvements are needed to improve ethylene glycol quality.

One way for raising ethylene glycol UV transmittance is to find better technological conditions so that less UV-absorbing impurities or their precursors can be formed during the ethylene glycol production process. In this case, the understanding of the exact structures of these impurities and the mechanism by which they are formed is of essential importance, and a simple method for tracing them or their precursors in various glycol plants needs to be developed. So far the published literature relating to the identification of these impurities is quite limited, let alone reports on the mechanism. A US Patent [5] had reported that two compounds, mexityl oxide and ethylene carbonate, were detected in ethylene glycol–water stream and the former was supposed to be the UV impurity. Another patent [7] reported that crotonaldehyde and 2,4-hexadienal were formed during the ethylene glycol production process (at stripper bottom). However it is not clear if these impurities are the same ones existing in the final ethylene glycol product. Direct analysis of commercial ethylene glycol with low UV transmittance was also performed with gas chromatography–mass spectrometry (GC–MS) [8]. Unfortunately, no convincing result was obtained due to the severe interference of the ethylene glycol matrix.

The aim of this paper is to identify the impurities causing ethylene glycol to have low UV transmittance. In the study, we developed a rapid and simple method of solid-phase extraction (SPE) for sample preparation. Several analytical techniques, such as high-performance liquid chromatography (HPLC) coupled with diode array detection (DAD), GC–MS, GC–Fourier transform infrared spectroscopy (FTIR), were applied together for the structure analyses.

2. Experimental

2.1. Materials

The standards of 2-hydroxy-3,5-dimethylcyclopent-2-en-1-one (A), 2-hydroxy-3-methylcyclopent-2-en-1-one (B) and 2-hydroxy-3,4-dimethylcyclopent-2-en-1-one (C) were obtained from Acros Organics (NJ, USA). Methanol and acetonitrile were of HPLC grade; diethyl ether was of analytical-reagent grade and was purified by distillation before used. Individual stock standard solutions of A, B and C (10 mg ml^{-1}) were prepared in methanol. Working standard solutions were prepared by diluting the stock standard solutions with methanol to obtain final concentrations of 20 $\mu g\ ml^{-1}$ of each compound and used for HPLC analysis. A working standard mixture containing A, B and C at 170 $\mu g\ ml^{-1}$ each were also prepared in methanol and used for GC–MS and GC–FT-IR analyses. All the solutions were stored in brown bottles at 4°C.

Amberlite XAD-4 resin was obtained from Rohm & Hass (Philadelphia, PA, USA). Before used, it was purified with diethyl ether, acetonitrile and methanol, successively, in a Soxhlet apparatus for 8 h each to remove the remaining impurities, especially trace UV-absorbing impurities. Then it was soaked in fresh methanol until use. The purity test was performed by soaking 1 g of XAD-4 resin in 25 ml of methanol overnight. The UV spectrum of the methanol showed an absorbance of 0.10 or less near 260 nm, indicating that the resin was suitable for the SPE process [9].

An ethylene glycol sample with low UV transmittances of 77.0%, 87.0%, 100.0% at 220, 275 and 350 nm, respectively was collected from a petrochemical plant. The sample was stored in a brown bottle at 4°C.

2.2. Sample pretreatment

A glass column (200 mm×15 mm I.D.) was packed with 3 g of purified XAD-4 resin and rinsed with ca. 100 ml of doubly distilled water. Then ethylene glycol–doubly distilled water (1:2, v/v) was passed through the column at a flow-rate of 2 ml min^{-1} by gravity until the UV transmittance of the eluted solution at the maximum wavelength (about 260 nm) was near that before extraction, indicating the absorbents were saturated. The amount of ethylene glycol–water solution passing through the resin was about 750 ml. After washed with about 150 ml of doubly distilled water to remove the residual ethylene glycol almost completely, the column was dried with nitrogen for about 2 min and further

eluted with 3×10 ml of methanol. The methanol eluate was split into two equal portions and concentrated under nitrogen to a final volume of 2 ml for HPLC analysis and 0.2 ml for GC–MS and GC–FT-IR analyses. All solutions were stored in brown bottles at 4°C.

2.3. Structural identification of UV-absorbing impurities in methanol extracts

The HPLC analysis was performed on a HP 1090 HPLC system comprising a quaternary pump, an autosampler and a diode array detector (Hewlett-Packard, Avondale, PA, USA). A Hypersil ODS column (100 mm×4.6 mm I.D. with 5 μm particles) was used for separation. The injection volume of the methanol extracts is 2 μl. The mobile phase consisted of methanol–water (30:70, v/v) at a flow-rate of 0.4 ml min^{-1}. The detector was set at 254 nm.

GC–MS analysis was carried out on a Finnigan Voyager GC–MS system consisting of a 8000 Top gas chromatograph and a MD 800 mass spectrometer (San Jose, CA, USA). A GC DB-Wax capillary column (30 m×0.25 mm I.D. with a film thickness of 0.25 μm) was used for separation. The carrier gas was helium (99.999%) at a flow-rate of 1.0 ml min^{-1}. Splitless injection of 1 μl of the extracts was performed with the exit valve closed for 1 min. The starting temperature of the column oven was 60°C for 3 min and the temperature was programmed at 4°C min^{-1} to a final temperature of 200°C for 1 min.

The MS operating parameters were as follows: electron energy was 70 eV, detector voltage 400 V, source and interface temperatures 200°C and 230°C, respectively. Mass spectra were obtained from m/z 40 to 500 in the full scan mode. For sample analysis, the filament and detector were not turned on until 10 min into the run.

GC–FT-IR analysis was carried out on a Hewlett-Packard (Palo Alto, CA, USA) GC–FT-IR system comprising a HP 5890 II series gas chromatograph and a HP 5965A FT-IR detector. A Carbowax 20M-2-Nitroterephthalic acid (FFAP) capillary column (30 m×0.32 mm I.D. with a film thickness of 0.25 μm) was used for separation. The carrier gas was helium (99.999%) at a flow-rate of 1.25 ml min^{-1}. On column injection of 1.0 μl of the extracts was performed. The injection temperature was 60°C. The starting temperature of the column oven was 60°C and the temperature was programmed at 4°C min^{-1} to a final temperature of 200°C for 4 min.

The FT-IR spectroscopy was performed as follows: the interface temperature was 230°C and the light pipe (120 mm×1.0 mm I.D.) temperature was 250°C, helium (99.999%) was used as make-up gas at a flow-rate of 0.2 ml min^{-1}. The detector was mercury–cadmium–telluride (MCT). The FT-IR spectra were collected by scanning in the range 4000–750 cm^{-1} at a resolution of 8 cm^{-1}.

3. Results and discussion

3.1. Sample pretreatment

Trace analytes in an organic matrix are often analyzed with chromatographic techniques such as GC, HPLC, or coupling techniques such as GC–MS, GC–FT-IR and LC–MS [10–12]. However it is very difficult to detect the UV-absorbing impurities by direct injection of the ethylene glycol sample into the GC–MS system, since ethylene glycol tends to produce a strong and broad peak that might hide the small peaks produced by the UV-absorbing impurities. The separation difficulty may be caused by the following factors: ethylene glycol and the UV-absorbing impurities are polar compounds, and the former is a dominant component (>99.8%) [1] with a high boiling point (196–199°C), while the concentrations of the latter are quite low (at μg ml^{-1} levels, see below). In this case, to find appropriate GC conditions for the separation of the unknown UV-absorbing impurities from the ethylene glycol matrix seems to be a very difficult and time-consuming task.

In order to overcome this limitation, sample pretreatment is required. In this study, SPE [13–15] was used to concentrate the UV-absorbing impurities and isolate them from the ethylene glycol matrix. In the optimized procedure, 750 ml of ethylene glycol–water solution could be passed through the column before the absorbents became saturated. After extraction, the remaining ethylene glycol on the column could be removed almost completely by water and did not interfere with the analysis of the UV-absorbing impurities any further (see Section 3.2.2

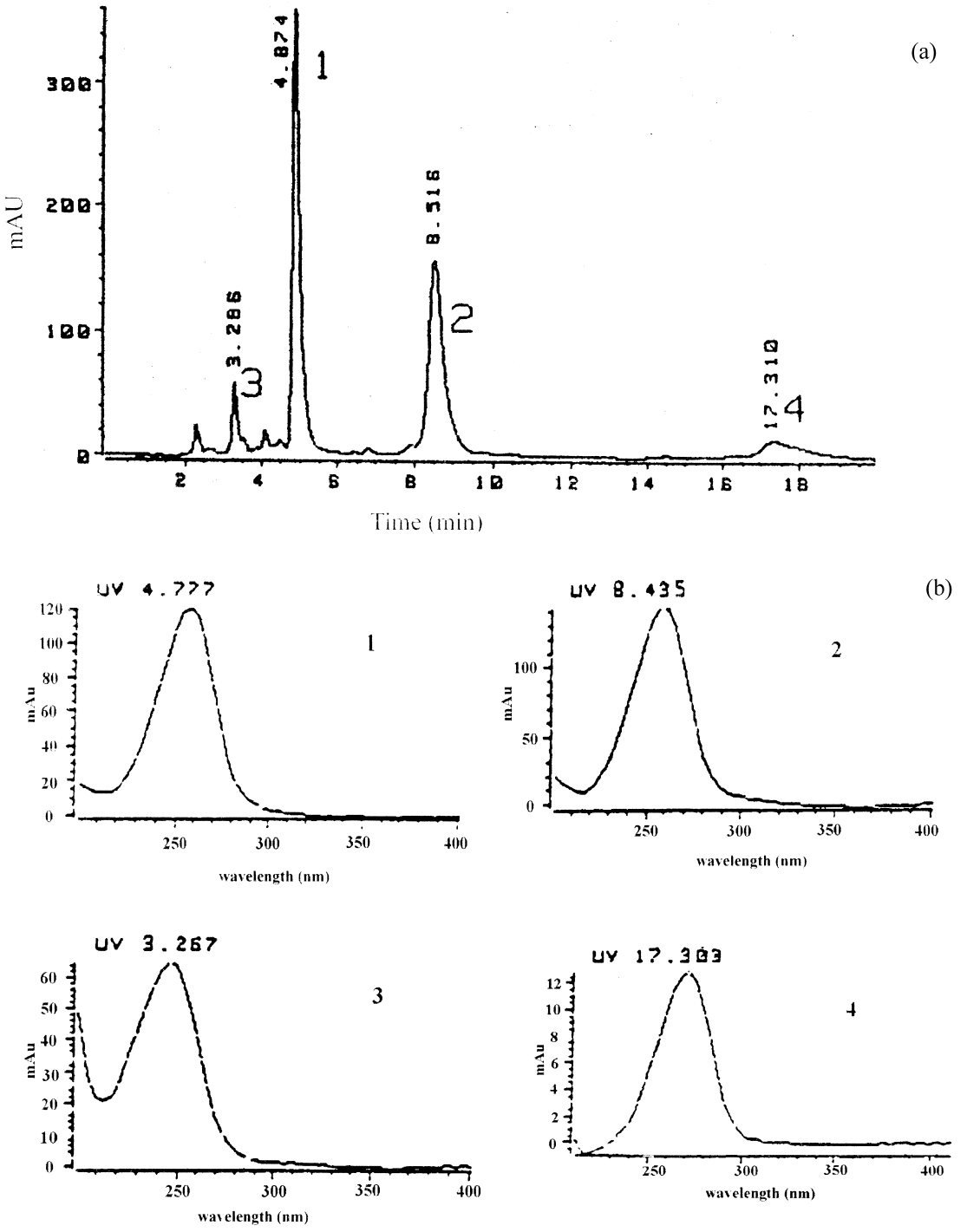

Fig. 1. HPLC–DAD analysis of ethylene glycol sample obtained by the proposed process. (a) Chromatogram detected at 254 nm, (b) UV spectra of peaks 1–4.

later), and the elution of these impurities with methanol took place efficiently. It was worth mentioning that among the main factors relating to the extraction efficiency, the sample matrix (ethylene glycol) was found to be a particular important one. Compared with the original ethylene glycol sample, the dilution of the same volume of ethylene glycol with water (1:2, v/v) led to the extraction efficiency being improved 2.3 times. In this case, we chose ethylene glycol–water (1:2, v/v) rather than original ethylene glycol sample to pass through the XAD-4 resin. In general, under the present conditions, although the extraction efficiency of UV-absorbing impurities on XAD-4 resin was not very high, SPE proved to be effective in the isolation and concentration of these impurities from the ethylene glycol sample.

3.2. Structural characterization of UV-absorbing impurities

3.2.1. HPLC analysis

In order to know generally the number of major UV-absorbing impurities in an unqualified ethylene glycol sample as well as their structural characteristics, HPLC analysis of the methanol extracts was performed. The chromatogram (Fig. 1a) shows two major peaks, peaks 1 and 2, which are symmetric and well separated. Another two smaller peaks (3 and 4) are also observed. The similarity of their corresponding UV spectra (Fig. 1b) indicates that these impurities might belong to a homologous series of compounds. These spectra are in accordance with that of the test ethylene glycol sample that has a strong absorption band with the maximum absor-

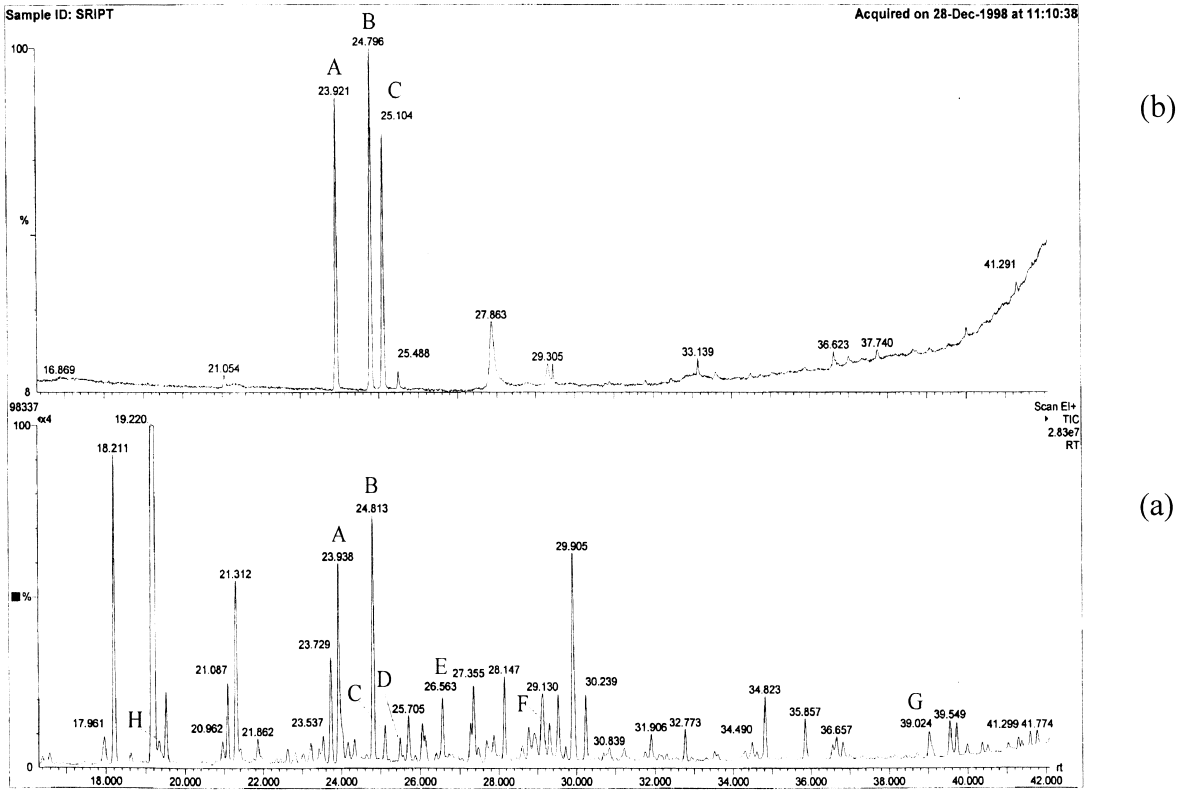

Fig. 2. GC–MS analysis. (a) TIC of ethylene glycol sample obtained by the proposed process. (b) TIC of standards A, B and C at 170 μg ml^{-1}. Peaks: A=2-hydroxy-3,5-dimethylcyclopent-2-en-1-one, B=2-hydroxy-3-methylcyclopent-2-en-1-one, C=2-hydroxy-3,4-dimethylcyclopent-2-en-1-one, D=2-hydroxy-3-ethyl-4-methylcyclopent-2-en-1-one, E=2-hydroxy-3-ethylcyclopent-2-en-1-one.

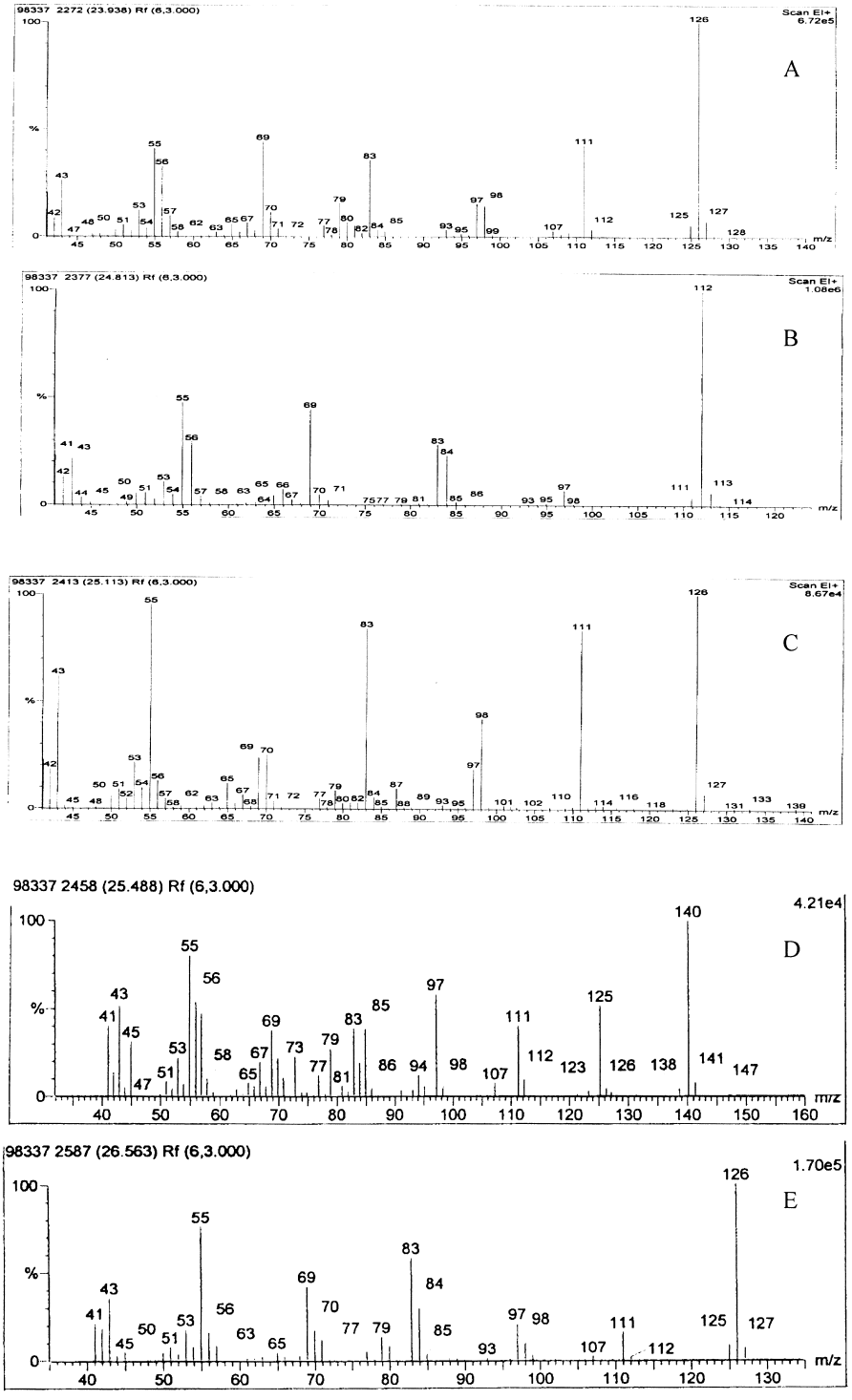

Fig. 3. Mass spectra of peaks A–E from the GC–MS analysis shown in Fig. 2a.

bance wavelength near 260 nm. It was reported that the UV-absorbing impurities in the unqualified ethylene glycol product appeared to have the strongest absorption characteristics in the range 240–280 nm [7].

3.2.2. GC–MS analysis

The methanol extract was analyzed with GC–MS in order to identify the UV-absorbing impurities from their MS spectra. Fig. 2a is the total ion chromatogram (TIC). As can be seen, major peaks are generally separated. The mass spectra of these peaks were searched against the National Institute of Standards and Technology (NIST) library. Five peaks were identified as the alkyl homologues of 2-hydroxycyclopent-2-en-1-one (their tautomers are 1,2-cyclopentanediones). In particular, peaks A, B, C, D and E were identified as 2-hydroxy-3,5-dimethylcyclopent-2-en-1-one, 2-hydroxy-3-methylcyclopent-2-en-1-one, 2-hydroxy-3,4-dimethylcyclopent-2-en-1-one, 2-hydroxy-3-ethyl-4-methylcyclopent-2-en-1-one and 2-hydroxy-3-ethylcyclopent-2-en-1-one, respectively. Their corresponding mass spectra are shown in Fig. 3, in which the molecular ion peaks are base peaks, and a series of ions $(14n-1)$, 41, 55, 69, 83, 97, are present in all spectra although the relative abundance of these ions vary for different compounds. Fig. 4 shows the structures of these compounds. As is known, the 2-hydroxylcyclopent-2-en-1-ones usually have strong molar absorptivities at UV wavelengths [16] due to the conjugated structures of the C=C and C=O double bonds in the molecules. Accordingly these five compounds detected with MS are supposed to be the UV-absorbing impurities in the unqualified ethylene glycol sample. The library search also indicated there were a few of aromatic compounds in the extracts, such as phenol, benzoic acid, corresponding to the small peaks F at 29.31 min and G at 39.02 min in Fig. 2a, respectively. Since these aromatic compounds cannot be formed during the whole ethylene glycol producing process, they cannot be the impurities of interest. They might be the residuals remaining in the XAD-4 resin. A great number of saturated ethers, ethanols and their derivatives were also identified in the extracts by GC–MS. Due to the lack of unsaturated structures in the molecules, they also cannot be the UV-absorbing impurities. It should be noted that the small peak H at 19.34 min was identified as ethylene glycol which was clearly separated from the UV-absorbing impurities and thus did not interfere with the identification of these impurities anymore.

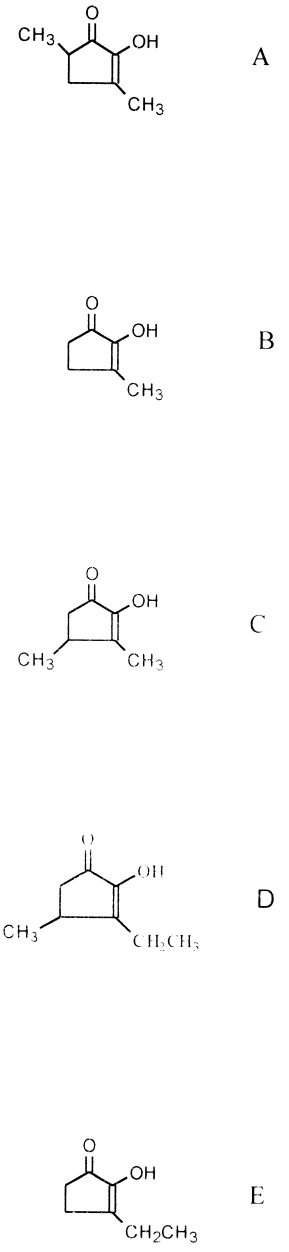

Fig. 4. Chemical structures of identified UV-absorbing impurities A–E (for names, see peak identification in caption to Fig. 2).

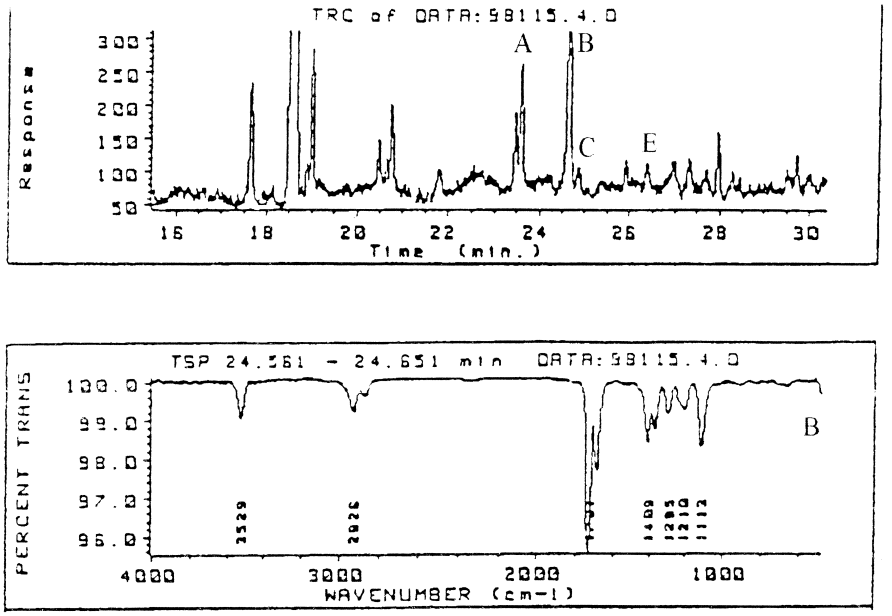

Fig. 5. GC–FT-IR analysis. (a) Gram–Schmidt reconstructed chromatogram of ethylene glycol sample obtained by the proposed process, (b) FT-IR spectra of peak B.

3.2.3. GC–FT-IR analysis

The presence of several 2-hydroxycyclopent-2-en-1-ones in the investigated sample was confirmed by injection of the same extracts into the GC–FT-IR system. Fig. 5a is the Gram–Schmidt reconstructed chromatogram in which peaks A, B, C and E correspond to those peaks in the GC–MS analysis (Fig. 2a). The IR spectra for the four peaks (Table 1) are quite similar and all possess the following absorptive characteristics: there is a weak absorbance band near 3530 cm^{-1}, corresponding to OH stretching vibration in the vapor phase; in the range 1680–1735 cm^{-1}, there are two important and distinctive absorbance bands, one is a strong-intensity band near 1730 cm^{-1}, indicating the simple C=O stretching vibration, another is a medium-intensity one near 1680 cm^{-1}, which is probably related to the C=O stretching vibration involving the strong interaction between the C=O and the enolic structure; finally there are a group of medium-to-weak bands near 1409, 1296, 1210 and 1114 cm^{-1}, probably related to the CH_2, CH_3 and OH bending vibration and C–O stretching vibration. Fig. 5b shows the IR spectrum of peak B.

Table 1
Characteristic IR absorbance bands of UV-absorbing impurities identified in unqualified ethylene glycol product

No.	Compound	IR band positions (cm^{-1})[a]
A	2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one	3535(w), 2978(w), 2922(w), 1728(s), 1686(m), 1407(m), 1366(m), 1296(w), 1203(w), 1119(w)
B	2-Hydroxy-3-methylcyclopent-2-en-1-one	3527(w), 2927(w), 1731(s), 1689(m), 1409(m), 1365(m), 1296(w), 1212(w), 1114(m)
C	2-Hydroxy-3,4-dimethylcyclopent-2-en-1-one	3527(w), 2965(w), 1731(s), 1686(m), 1407(w), 1361(w), 1293(w), 1118(m)
E	2-Hydroxy-3-ethylcyclopent-2-en-1-one	3530(w), 2960(w), 1729(s), 1680(m), 1396(w), 1288(w), 1112(w)

[a] w=Weak; m=medium; s=strong.

The characteristic IR data mentioned above are in accordance with those of 2-hydroxy-3-methylcyclopent-2-en-1-one reported in the Sadtler standard infrared vapor phase spectra [17]. Since the IR spectra reflect the structural characteristics of functional groups, it can be concluded that peaks A, B, C and E correspond to a homologous series of 2-hydroxy-3-methylcyclopent-2-en-1-ones. Peak D which appeared in Fig. 2a was not detected clearly in Fig. 5a due to the lower detection sensitivity of the FT-IR detector compared to that of the MS detector.

3.2.4. Standard verification

Both the GC–MS and GC–FT-IR studies indicated that the UV-absorbing impurities in unqualified ethylene glycol were alkyl derivatives of 2-hydroxycyclopent-2-en-1-one, however the exact structures of these impurities have not been identified definitely. In this case, three standards available were analyzed with GC–MS under the same experimental conditions mentioned earlier. Fig. 2b is the TIC. As can be seen, the three standards possessed retention times similar to those of the three peaks from the testing sample (peaks A, B and C in Fig. 2a). The MS spectra (not shown) for standards A, B and C are also identical to those of peaks A, B and C in Fig. 2a. This is also the case when the standard solutions were studied with GC–FT-IR. The HPLC study of the standards under the reported conditions also confirmed our findings, in which standard B eluted at 4.8 min corresponding to peak 1 in the sample analysis (Fig. 1a); while standards C and A eluted at 8.29 min and 8.51 min, respectively, corresponding to peak 2 in Fig. 1a. Their UV spectra obtained with DAD are shown in Fig. 6. Consequently the three UV-absorbing components in ethylene glycol were identified unambiguously as follows: 2-hydroxy-3,5-dimethylcyclopent-2-en-1-one (A), 2-hydroxy-3-methylcyclopent-2-en-1-one (B), and 2-hydroxy-3,4-dimethylcyclopent-2-en-1-one (C).

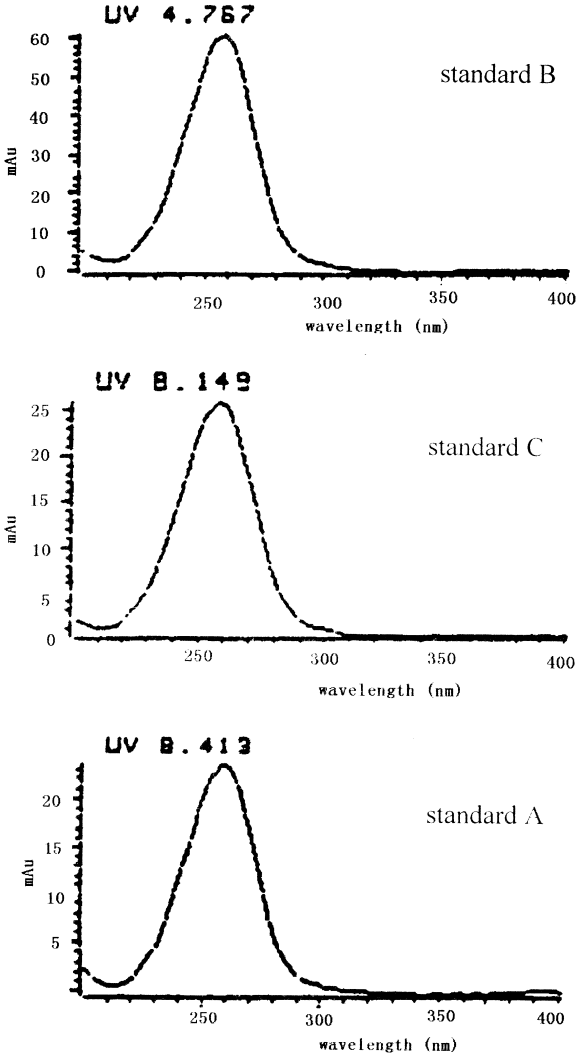

Fig. 6. UV spectra of standards B, C and A obtained with DAD in HPLC analysis.

3.3. Estimation of the amounts of UV-absorbing impurities in the ethylene glycol sample

The GC–MS results (Fig. 2) indicated that among the five impurities detected in the extracts, 2-hydroxy-3,5-dimethylcyclopent-2-en-1-one (A) and 2-hydroxy-3-methylcyclopent-2-en-1-one (B) had relatively high concentrations (by comparing the height of each peak) and their amounts were more or less equal. In order to get a general idea of the levels of these impurities in commercial ethylene glycol, a purified ethylene glycol sample (a) was prepared by passing commercial ethylene glycol sample (b) through enough amounts of XAD-4 resin and then fortified with standards A and B to obtain a final solution (c) containing standards A and B at 2 μg ml^{-1}. Fig. 7 shows the UV spectra of solutions a, b and c. Since the UV transmittance of the fortified

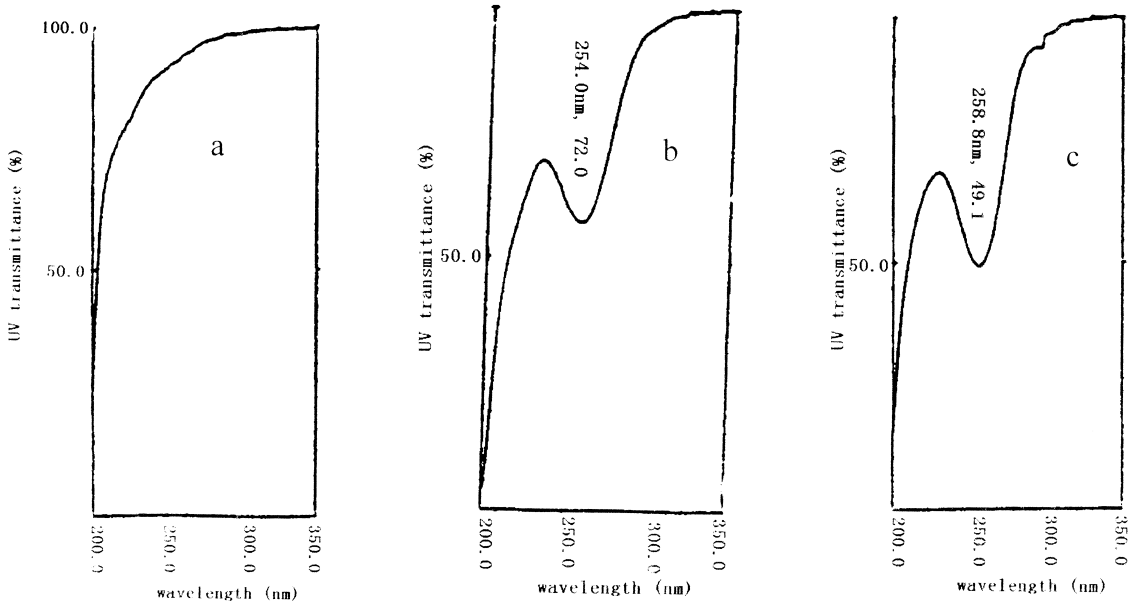

Fig. 7. UV spectra analysis. (a) Purified ethylene glycol sample, (b) commercial ethylene glycol sample, (c) fortified ethylene glycol sample containing standards A and B at the 2 μg ml^{-1} level.

sample (49.1% at 258.8 nm) was still lower than that of the commercial sample (72.0% at 254.0 nm), we assumed that the amounts of UV-absorbing impurities present in the ethylene glycol product, including A and B, were less than 2 μg ml^{-1} each.

4. Conclusion

In this paper, five alkyl homologues of 2-hydroxycyclopent-2-en-1-one were identified as the major impurities causing commercial ethylene glycol to have low UV transmittance, and a method involving SPE was developed for identification of these impurities in ethylene glycol. Up to now, since there is no other simple and practical technique for identifying the impurities in commercial ethylene glycol, and the compounds causing ethylene glycol to have low transmittance are not specifically known, this work should be of value. It is believed that with the above research results, ethylene glycol plants might make process improvements to remove these impurities more effectively and more easily. In addition, our recent work has proved that the reported method and a new improved one can be applied successfully to a media product of the ethylene glycol process as well as to an unqualified ethylene product collected from another plant, and the results are in accordance with those reported in this paper. Further study will be carried out in order to find out the mechanism by which the UV-absorbing impurities are formed.

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References

[1] W. Gerhartz, Y.S. Yamamoto, L. Kaudy, J.F. Ronnsaville, G. Schulz, in: 5th ed., Ullmann's Encyclopedia of Industry Chemistry: Ethylene Glycol, Vol. A10, VCH, New York, 1987, p. 101.
[2] C.J. Worth, R.B. Claude, Eur. Pat. 0 310 189 A2 (1989).
[3] J.I. Kroschwitz, M. Howe-Grant, in: 4th ed., Kirk-Othmer, Encyclopedia of Chemical Technology: Glycols (Ethylene Glycol and Oligomers), Vol. 12, Wiley, New York, 1992, p. 695.
[4] GOST 19710-83, Ethylene Glycol Specifications, Moscow, 1983.

[5] C.R. Reiche, J.A. Heckman, US Pat., 3 970 711 (1976).
[6] S.T. Martin, A.G. Mark, D. Pauls, Can. Pat., 1 330 350 (1994).
[7] R.G. Brildy, F.M. Cummings, US Pat., 4 289 593 (1981).
[8] L.N. Shen, Sepu (Chinese) 12 (5) (1994) 330.
[9] J.L. Robinson, W.J. Robinson, M.A. Marshall, A.D. Barnes, K.J. Johnson, D.S. Dalas, J. Chromatogr. 189 (1980) 145.
[10] T.A. Sasaki, C.L. Wilkins, J. Chromatogr. A 842 (1999) 341.
[11] N. Ragunathan, K.A. Krock, C. Klawun, T.A. Sasaki, C.L. Wilkins, J. Chromatogr. A 856 (1999) 349.
[12] W.J. Blanchflower, P.J. Hughes, A. Cannavan, M.A. McCoy, D.G. Kennedy, Analyst 122 (1997) 967.
[13] M.C. Hennion, J. Chromatogr. A 856 (1999) 3.
[14] M. Moors, D.L. Massart, R.D. McDowall, Pure Appl. Chem. 66 (2) (1994) 277.
[15] C.A. Berruet, B. Gallo, F. Vicente, Chromatographia 40 (1995) 474.
[16] R.M. Silverstein, G.C. Bassler, T.C. Morrill, in: Spectrometric Identification of Organic Compounds, 3rd ed., Wiley, New York, 1974, p. 245.
[17] Sadtler Standard Infrared Vapor Phase Spectra, Vol. 13, Division of Bio-Rad Laboratories, Philadelphia, PA, 1980, 5622V.