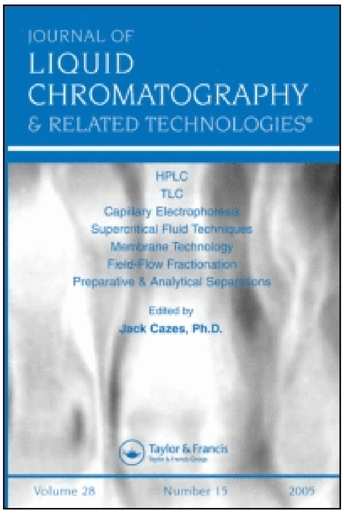

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Abstract: A reversed phase high performance liquid chromatographic method has been developed for the determination of 4-hydroxyanisole in industrial triallyl cyanurate. The separation was accomplished on a C_{18} column by linear gradient elution consisting of methanol, water, and 0.1% perchloric acid, at a flow rate of 1.0 mL/min. The detection was performed by UV absorption at wavelength of 254 nm and 288 nm simultaneously. The response behavior of sample determined was compared between two detection wavelengths. It is found that the use of 288 nm makes the chromatogram simple, so that isocratic elution can be employed instead of gradient elution. The method has been successfully applied for the quantitative analysis of 4-hydroxyanisole as the retarding agent in triallyl cyanurate for industrial purposes in the laboratories of some chemical plants.

Keywords: Cross-linking agent, HPLC, 4-Hydroxyanisole, Retarding agent, Self-polymization, Trially cyanurate

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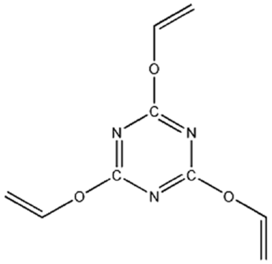
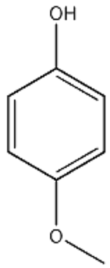
INTRODUCTION

Triallyl cyanurate (2,4,6-tris(2-propenyloxy)-1,3,5-triazine, TAC) is a compound that is very valuable as a solvent, plasticizer, insecticide, bactericide, etc. It is also employed as a cross linking agent for the production of unsaturated polyesters, co-agent for ethylene propylene rubber systems, additive for polyesters, and comonomer in unsaturated polyesters. Various methods have been proposed for TAC manufacturing, most of which is based on the reaction of cyanuric chloride and aqueous allyl alcohol solution.[1–3] TAC normally appears as the glacial crystals of low melting point (m.p. 26–27°C). In addition, TAC is a self-polymerizable compound, and a portion of it forms low polymers during the storage process in spite of good solubility in organic solvents, so 4-hydroxyanisole (4-HA) is applied to TAC as the retardant. The addition amount of 4-HA must be controlled in an appropriate range, because too little could not prevent TAC from polymerizing, whereas too much could affect the quality of TAC product. Thus, the effective monitoring of 4-HA in industrial TAC is necessary. Only a method for high performance liquid chromatographic (HPLC) determination of 4-HA in methacryloyloxyethyl trimethyl ammonium chloride was reported up to now, in which the quarter ammonium ion did not retain on the reversed phase C_{18} column, so the 4-HA separation was very easy and tame, and this method was unsuitable for TAC analysis.[4] In this paper, an HPLC method with UV detection was established for monitoring 4-HA in more complex industrial TAC.



Triallyl cyanurate (TAC)



4-Hydroxyanisole (4-HA)

EXPERIMENTAL

Reagents and Chemicals

The reference substance of 4-hydroxyanisole (99%) and industrial triallyl cyanurate sample were provided by Nanjing Yonghong Chemical Co., Ltd. (Nanjing, China). Methanol (HPLC grade) was purchased from Merck (Darmstadt, Germany). Perchloric acid (70–72%, guaranteed reagent) was obtained from Tianjin Third Reagent Factory (Tianjin, China). Wahaha purified water (Wahaha Group Ltd., Hangzhou, China) was used throughout the experiment.

Apparatus and Chromatographic Conditions

The HPLC system used was a Waters 2695 Alliance separation module consisting of a vacuum degasser, a quaternary pump, and an autosampler, equipped with a Waters 996 UV-Vis photodiode-array detector (PDA) and a Waters Empower chromatography manager system (Milford, MA, USA).

The separation was achieved on a Phenomenex Gemini C_{18} column (150 × 4.6 mm i.d., 5 μm) (Guangzhou FLM Scientific Instrument Co., Ltd, Guangzhou, China). The column temperature was maintained at 30°C. A ternary gradient elution (Gradient 1, see Table 1) with methanol, water, and 0.1% (v%) perchloric acid was employed at a flow rate of 1.0 mL/min. The injection volume was 20 μL. The effluent was monitored by PDA detector set at 288 nm and 254 nm in parallel.

Preparation of Standard and Sample Solutions

The stock solution of 4-HA was prepared by accurately weighing about 25.00 mg reference substance into a 25 mL volumetric flask, then

Table 1. Gradient 1

Time (min)	Methanol	Water (%)	0.1% Perchloric acid
0	15	65	20
30	15	65	20
45	90	0	10
65	90	0	10
70	15	65	20
90	15	65	20

dissolving in methanol and completing the volume with methanol. All other standard solutions were prepared from this stock solution by serial dilution with methanol in the further stages of the experiment. Sample solution was prepared by accurately transferring 1.00 mL of liquid industrial TAC into a 10 mL volumetric flask, and adding methanol to the mark. If TAC crystal exists in the sample, heat it till homogeneous liquid prior to analysis.

RESULTS AND DISCUSSION

Chromatograms

Typical chromatograms of 4-HA standard solution and TAC sample solution, under the given elution condition with two detection wavelengths, are shown in Figure 1. The retention time of 4-HA is 17.5 minutes. There are many other peaks in the chromatogram of TAC sample when detection wavelength was set at 254 nm (Figure 1-a, 1-c), which are likely attributed to reactants and by-products including low polymers of TAC.[5–7] On one hand, TAC was produced using cyanuric chloride and allyl alcohol as the starting materials, so some of them remained in the resultant of reaction. On the other hand, a bit of low polymers existed in the final TAC product, and these polymers were

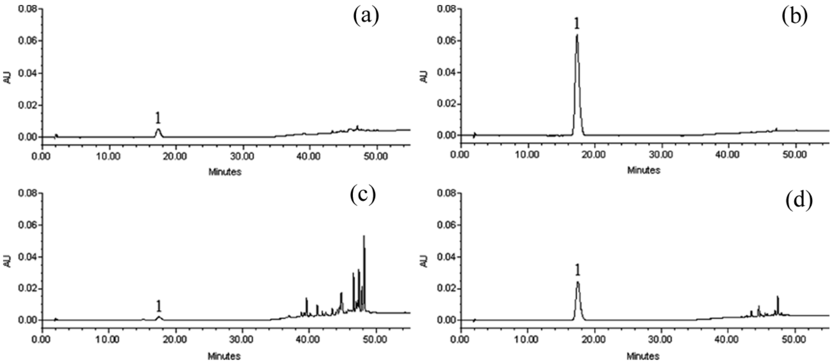


Figure 1. Typical chromatograms of 4-HA standard and TAC sample solutions. Column: Phenomenex Gemini C_{18} column (150 × 4.6 mm i.d., 5 μm). Column temperature: 30°C. Mobile phases: gradient elution of mixture of methanol, water, and 0.1% perchloric acid within 90 min, described in Table 1. Flow rate: 1.0 mL/min. Injection volume: 20 μL. Wavelength used for UV detection: 254 nm (a, c); 288 nm (b, d). a, b. 4-HA standard solution; c, d. TAC sample solution. Peak: 1. 4-HA.

also readily soluble in methanol. Separation time spent for these TAC components and impurities are rather long with isocratic elution of 15% methanol. Therefore, the gradient elution was used to rapidly flush them from the column. By comparison, the absorption of TAC components was much weaker when 288 nm was chosen for detection (Figure 1-b, 1-d). This is because TAC components and impurities have very little absorbance at this wavelength. As both chromatograms show, 4-HA was distinctly separated under the chosen elution conditions in spite of detection wavelength used, which is the basis of quantitative determination.

Calibration Curve and Limit of Detection

The linearity between peak area versus standard concentrations of 4-HA was obtained in the concentration range of 0.005 ~ 0.5 mg/mL at 254 nm and 0.0005 ~ 0.5 mg/mL at 288 nm. The linear equations and correlation coefficients (r), as well as limits of detection (LODs) at signal-to-noise ratio of 3 (S/N= 3), are shown in Table 2.

Result of Sample Analysis

The quantitative analysis of 4-HA in an industrial TAC sample was performed on the basis of standard curve of peak area under two detection wavelengths, 254 nm and 288 nm, respectively. The 4-HA concentration in TAC, together with intra-day and inter-day precisions, shown in Table 3, were obtained from triplicate analyses, respectively. The recovery was evaluated by spiking a known amount of 4-HA standard into the TAC sample and analyzing by the same method as mentioned above. Three replicates were performed for the test. Overall data listed in Table 4 indicates that the recoveries of 4-HA were in the range of 93.0% ~ 96.2% and 94.1% ~ 97.4%, respectively, with 254 nm and 288 nm as the detection wavelengths. The quantitation of 4-HA had little interference, due to the good separation from other components and impurities in the TAC sample.

Table 2. Regression equations and detection limits of 4-HA

Wavelength (nm)	Regression equation	r	LOD (mg/mL)
254	$A = -2598 + 2.11342\text{E}6C$	0.99997	2.00×10^{-3}
288	$A = -13452 + 2.52116\text{E}7C$	0.99997	1.00×10^{-4}

Table 3. Determination of 4-HA in TAC sample ($n = 3$)

	Intra-day			Inter-day		
Wavelength (nm)	Concentration (mg/mL)	Average (mg/mL)	RSD (%)	Concentration (mg/mL)	Average (mg/mL)	RSD (%)
254	0.430	0.428	0.59	0.428	0.426	0.59
	0.425			0.426		
	0.428			0.422		
288	0.425	0.425	0.36	0.427	0.427	0.47
	0.424			0.425		
	0.427			0.428		

Optimization of Chromatographic Conditions

Mobile Phase

Different methanol proportions and perchloric acid concentration in the mobile phase were tested independently to search for optimum elution condition (Figure 2). The retention time of 4-HA increased rapidly with the decrease of methanol proportion from 70% to 10%. When 15% methanol was employed, a satisfactory separation was obtained. On the other hand, although perchloric acid has little influence on retention of 4-HA in the concentration range of 0~0.08%, addition of perchloric acid led to sharper peaks due to the suppression of dissociation of 4-HA containing hydroxy group. Therefore, 15% methanol and 0.02% perchloric acid was selected.

Detection Wavelength

The UV spectrum of 4-HA from PDA detector gives maximum absorption at 221 nm and 288 nm. For the HPLC analysis, the detector

Table 4. Recovery of 4-HA in TAC sample ($n = 4$)

Wavelength (nm)	Original (mg/mL)	Added (mg/mL)	Found (mg/mL)	Recovery (%)	RSD (%)
254	0.427	0.25	0.647	93.0	0.42
		0.50	0.911	96.2	0.05
		1.00	1.362	94.9	1.60
288	0.426	0.25	0.651	94.1	0.29
		0.50	0.915	97.4	0.02
		1.00	1.390	94.5	0.81

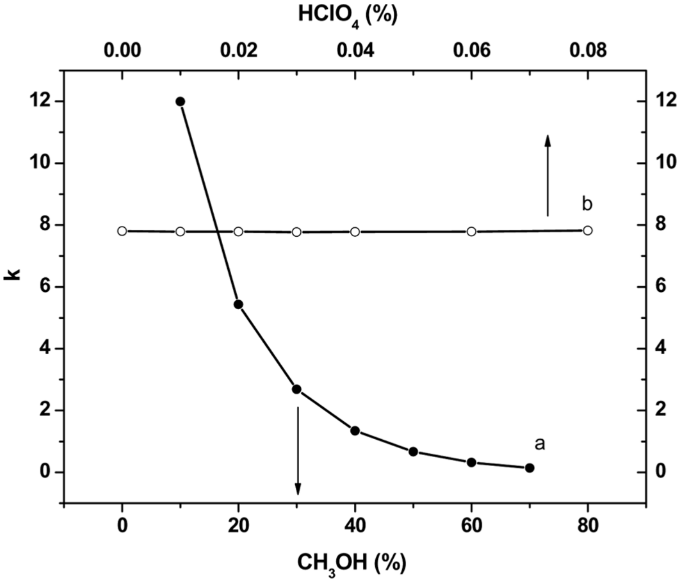


Figure 2. Influence of methanol proportion (a) and perchloric acid concentration (b) in mobile phase on retention of 4-HA. (a) 0.02% perchloric acid; (b) 15% methanol. Other chromatographic conditions as in Figure 1.

was preferentially fixed at 288 nm throughout the work owing to the best signal-to-noise ratio. Another wavelength 221 nm was not selected for the serious baseline drift and noise. A 254 nm was considered because it was commonly used in routine analysis and it can provide rather satisfactory analysis results under the same chromatographic condition as 288 nm. Consequently, the method developed here is also available in the laboratory without a tunable or PDA UV absorbance detector. Moreover, the elution condition was simplified when the detection

Table 5. Gradient 2

Time (min)	Methanol	Water (%)	0.1% Perchloric acid
0	50	30	20
10	50	30	20
18	90	0	10
30	90	0	10
34	50	30	20
40	50	30	20

wavelength was set at 288 nm. As shown in Figure1, the number of peaks was much less at 288 nm than at 254 nm, and 4-HA suffered from much fewer interference from TAC components and impurities even at higher methanol proportion in the mobile phase. Thus, the gradient elution program was modified to start at higher methanol proportion (50%) as described in Table 5. As a result, the analysis time was shortened to 40 min (Figure 3, middle panel). Furthermore, an isocratic elution was applied when detection wavelength fixed at 288 nm. It is found that even isocratic methanol-water-0.1% perchloric acid (70:10:20, v/v/v) was the appropriate elution condition as shown in the right panel of Figure 3, and that the similar accuracy and precision were demonstrated. In fact,

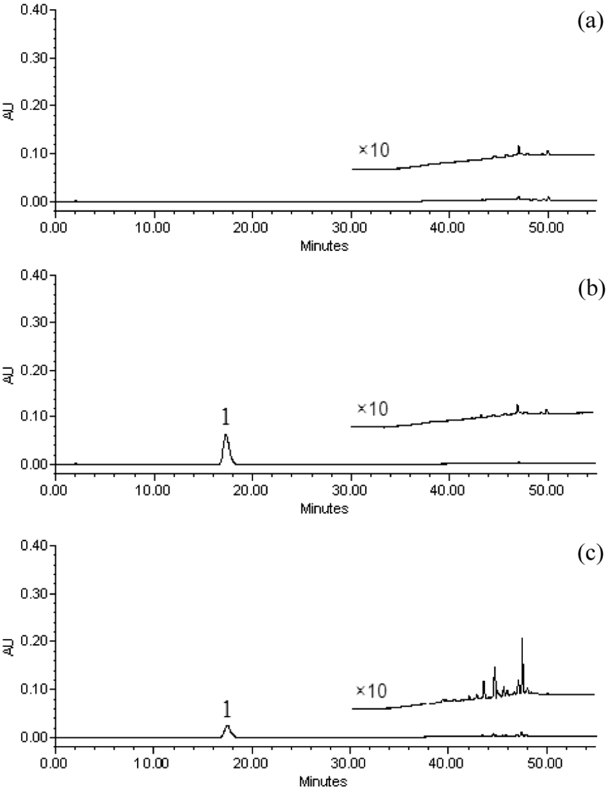


Figure 3. Comparison of chromatograms under different elution conditions. Mobile phase: left panel (a, b, c). gradient 1 as in Table 1; middle panel (d, e, f). gradient 2 as in Table 5; right panel (g, h, i). isocratic, methanol-water-0.1% perchloric acid (70:10:20, v/v/v). Wavelength used for UV detection: 288 nm. a,d,g. Blank solvent; b, e, h. 4-HA standard solution; c, f, i. TAC sample solution. Other chromatographic conditions as in Figure 1.

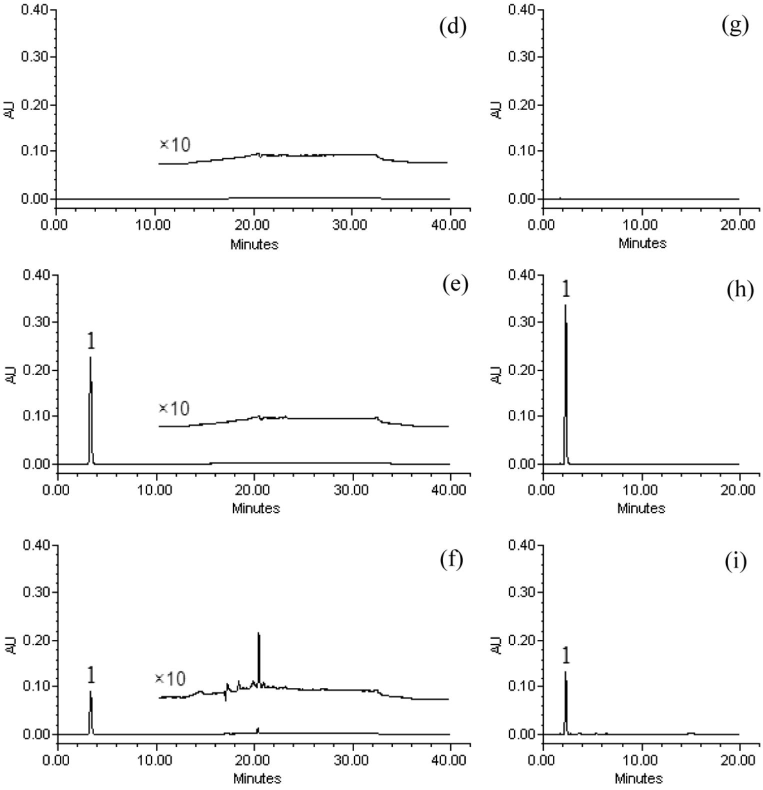


Figure 3. Continued

the main purpose of gradient elution is just to remove TAC components and impurities of stronger retention from the column, and does not contribute to the separation of 4-HA. Thereby, this isocratic elution can be employed when quick quality control analysis is requested in some chemical plants.

CONCLUSION

The concentration of polymerization retarding agent 4-HA in industrial TAC was determined by reversed phase high performance liquid chromatography with two detection wavelength, 254 nm and 288 nm. The results showed that there are lower background absorbance, smoother baseline, lower detection limit, simpler elution condition, and shorter analysis time at 288 nm. However, using 254 nm for detection is indispensable when only a single wavelength UV absorbance detector is available, especially in the laboratories of many small scale chemical plants of China. Consequently, two detection wavelengths combined with three elution conditions were brought forward for different analysis requirements.

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