Rapid Determination of Eight Related Aromatic Acids in the p-Phthalic Acid Mother Liquid Using an Agilent 1260 Infinity LC System and an Agilent Poroshell 120 SB-C18 Column

Application Note

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Abstract

This Application Note describes a method to determine eight aromatic acids simultaneously in *p*-phthalic acid mother liquid using an Agilent 1260 Infinity Quaternary LC system with a diode array detector (DAD). Good resolution was achieved for all eight target analytes on an Agilent Poroshell 120 SB-C18 column without interference from other impurities of the mother liquid. The analysis was completed in 13 minutes. Due to the excellent performance of the 1260 Infinity LC System, good precision was obtained using six sequential injections. The results showed an RSD % ≤ 0.18 % (peak area) and RSD % ≤ 0.05 % (retention time) for eight aromatic acids. This study showed that this method is applicable for the analysis of related aromatic acids in the *p*-phthalic acid mother liquid.

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Introduction

Purified *p*-phthalic acid (PTA) is an important raw material in the production of synthetic resin, polyester fiber, and other chemical products. The content of *p*-toluic acid (TA) and 4-carboxybenzaldehyde (4-CBA) is often used as a critical indicator to control the quality of PTA. This is because both compounds can induce a side chain reaction to terminate the polymerization process, and decrease the molecular weight of the product. However, due to the impurities from *p*-xylene and from the manufacturing process, there can be many other by-products in PTA and its mother liquid. The majority of the by-products are the related aromatic acids, such as TA and 4-CBA. The detection of these aromatic acids in *p*-phthalic acid mother liquid helps determine the real-time oxidation process, and provides data for further purification.

With the growing global demand for PTA, manufacturers are increasingly concerned about the analysis of aromatic acids in mother liquid as it pertains to the quality control of the final product. Monitoring the mother liquid could help to optimize the oxidation process and reduce the manufacturing cost. HPLC is an analytical tool routinely used in modern laboratories to analyze aromatic acids in final PTA, residues from purification, and waste water[2–4]. This Application Note develops a new method for the determination of eight related aromatic acids in *p*-phthalic acid mother liquid by reversed-phase UHPLC with an Agilent Poroshell SB-C18 column. The method has been successfully used for sample analysis by a PTA manufacturer.

Experimental

Instruments

This method was developed on an Agilent 1260 Infinity Quaternary LC System, consisting of a quaternary pump (G1311B, built-in four-channel vacuum degasser), an autosampler (G1329B), a thermostatted column compartment (G1316A), a diode array detector (G4212B), and an OpenLab CDS ChemStation Edition (C.01.03).

Standard solution

Stock solution

Eight aromatic acids: trimellitic acid (TMLA), hydroxymethyl-benzoic acid (HMBA), orthophthalic acid (OA), terephthalic acid (TA), 4-carboxybenzaldehyde (4-CBA), isophthalic acid (IA), benozic acid (BA), and *p*-toluic acid (*p*-TOL) were purchased from Sigma-Aldrich. A 50.0 mg amount of each standard was weighed and put into a 50-mL volumetric flask separately. A 1 mL amount of 1 % (V %) ammonia water was added for solvation and the solution was diluted to 50 mL with MeOH/H_2O (10/90, V/V). The concentration of each standard was 1.0 mg/mL.

UHPLC conditions

Table 1. UHPLC conditions.

Parameter	Value	
Column	Agilent Poroshell 120 SB-C18, 3.0 × 100 mm, 2.7 µm	
Column temperature	40 °C	
Wavelength	240 nm (4 nm)/Ref 360 nm (40 nm)	
Mobile phase A	0.1 % TFA in H_2O	
Mobile phase B	MeOH	
Flow	0.8 mL/min	
Injection volume	2 µL	
Gradient	Time (min)	B %
	0	10
	4	30
	7	60
	10	60
Post time	3 minutes	

Mixed working solution

A 2.5 mL amount of each stock solution was pipetted into a 100-mL volumetric flask and diluted to 100 mL with MeOH/H_2O (10/90, V/V). The concentration of each standard in the mixed working solution was 25 µg/mL.

Sample preparation

Mother liquid was provided by a PTA manufacturer and filtered through a 0.45-µm PTFE membrane before use. A 1 mL solution was pipetted into a 100-mL volumetric flask, followed by the addition of 2 mL of 1 % (V %) ammonia water. It was diluted to 100 mL with MeOH/H_2O (10/90, V/V) and filtered through a 0.22-µm PTFE membrane before UHPLC analysis.

Results and Discussion

Selection of mobile phase

An acidic mobile phase was considered to benefit the retention and resolution for these compounds due to their acidic property. Three common acid additives (formic acid, H_3PO_4, and TFA) were tested at 0.1 % (V %) concentration in the aqueous phase. The pH of 0.1 % H_3PO_4, 0.1 % FA, and 0.1 % TFA was 2.3, 2.7, and 2.0 respectively, as measured by a pH meter. Figure 1 shows that the elution order of eight analytes did not change with the three mobile phases, however, the peak shape and resolution were different from each other. When 0.1 % FA was added in the aqueous phase, TMLA eluted as a shoulder peak, possibly due to the low capability of the mobile phase to suppress the ionization of TMLA. TMLA is a triprotic acid, whose pKa_1 is approximately 2.5. The OA peak tailed under 0.1 % H_3PO_4 and 0.1 % FA, while the 4-CBA peak fronted under 0.1 % FA. Additionally, 0.1 % TFA and 0.1 % H_3PO_4 lead to better resolution for OA and HMBA. Therefore, 0.1 % TFA in aqueous phase was selected as the final mobile phase based on the resolution and peak shape.

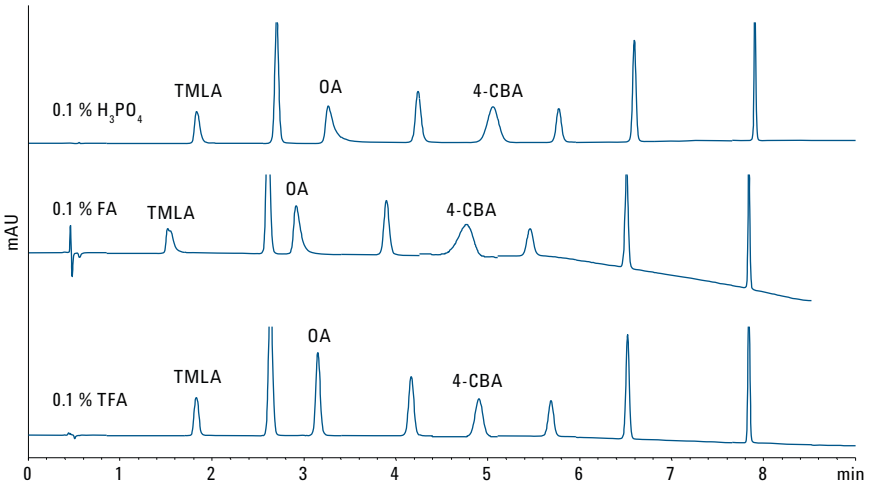

Figure 1. Chromatograms of eight aromatic acids under different acidic mobile phases (Concentration 25 µg/mL of each analyte).

Conditions for Figure 1		
Column	Agilent Poroshell SB-C18 (3.0 × 100 mm, 2.7 µm)	
Flow rate	1.0 mL/min	
Column temperature	50 °C	
Wavelength	230 nm	
Injection volume	1 µL	
Mobile phase A	aqueous phase with different additives (see chromatogram)	
Mobile phase B	MeOH	
Gradient	Time (min)	% B
	0	10
	4	15
	7	60
	9	60
Post time	3 minutes	

Selection of detection wavelength

Due to their chemical structures, the eight aromatic acids have different maximum adsorption wavelengths (Figure 2). To simplify the method, 240 nm was selected as measurement wavelength. The final method parameters are listed in Table 1.

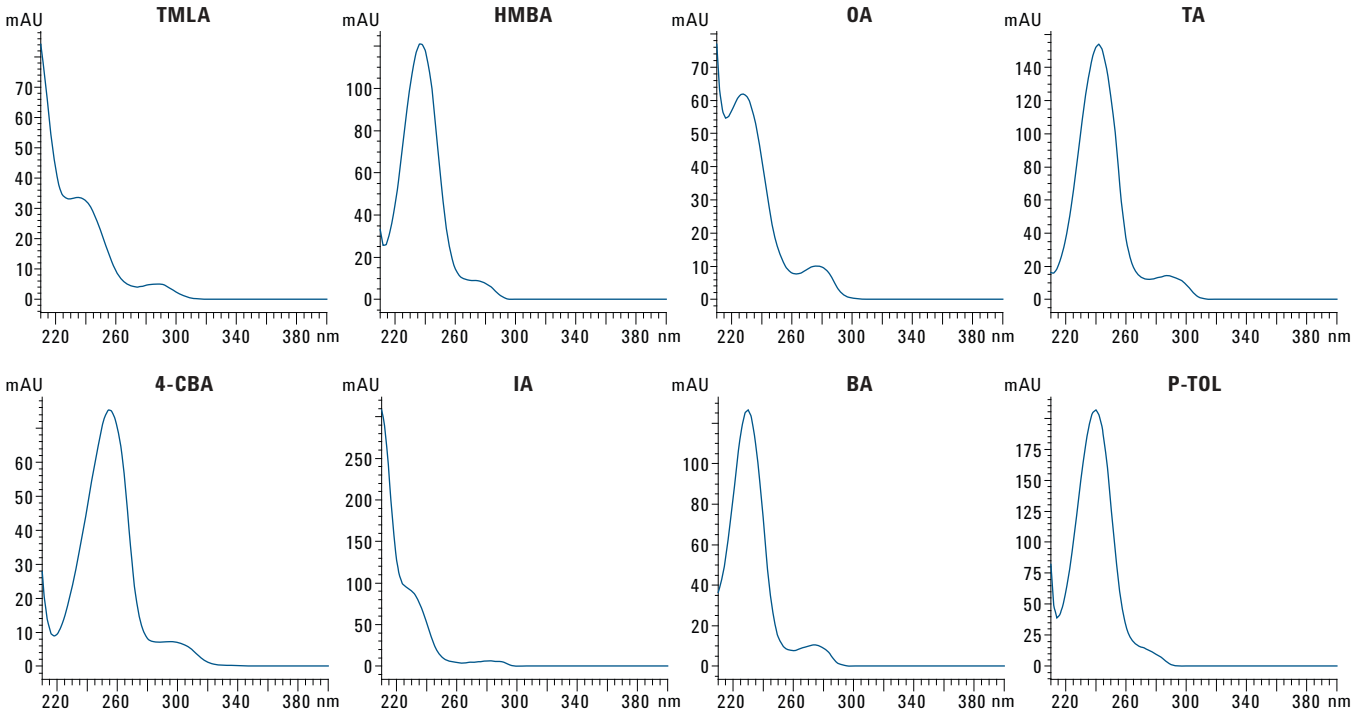

Figure 2. UV spectra of eight aromatic acids.

Reproducibility

Six sequential 25 µg/mL injections of standard solution were used to validate injection reproducibility under the previously discussed optimized method (Table 1). Table 2 shows the retention time and peak RSDs of eight aromatic acids separately. All RSD values were less than 0.05 % for retention time and 0.18 % for peak area, indicating excellent reproducibility.

Sample analysis

The sample was prepared according to the procedure previously outlined, and analyzed under the optimized conditions (Table 1). Figure 3 shows that the impurities from the sample (small peaks eluting between 7 and 10 minutes) do not interfere with the p-TOL (8.05 minutes).

Table 2. RSD values of eight aromatic acids by six sequential injections.

Compounds	TMLA	HMBA	OA	TA	4-CBA	IA	BA	p-TOL
Retention time (RSD, %)	0.05	0.04	0.04	0.04	0.03	0.02	0.02	0.01
Peak area (RSD, %)	0.18	0.16	0.11	0.12	0.13	0.13	0.12	0.09

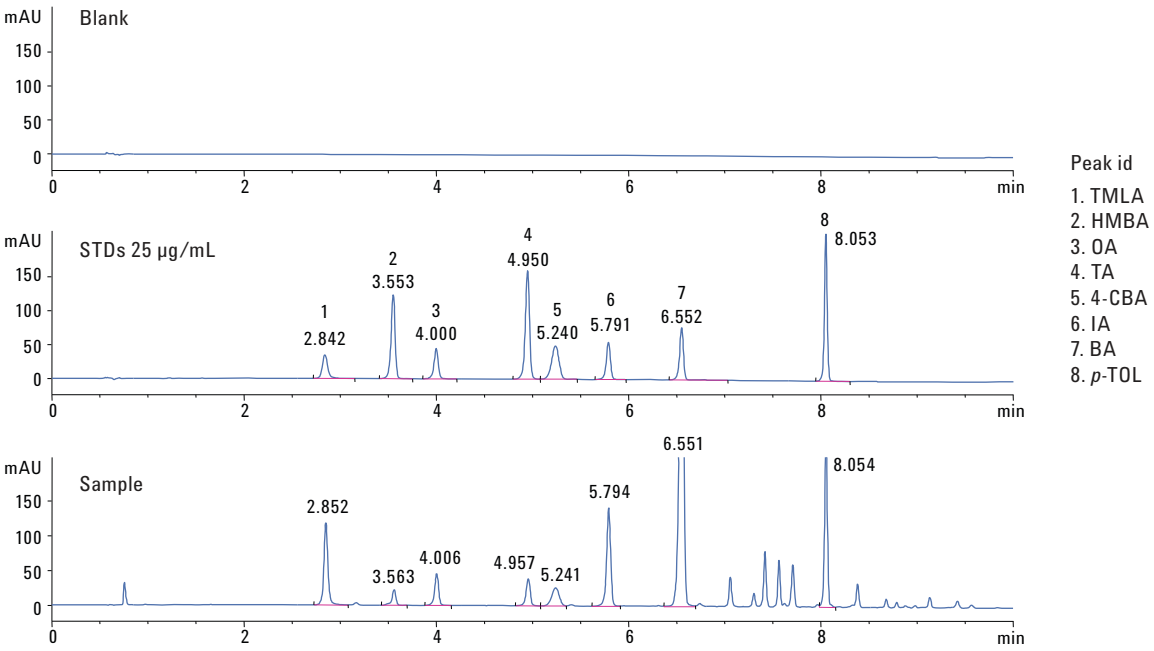

Figure 3. Chromatograms of blank, standard mix, and sample solution.

Conclusion

Aromatic acids are the major components in PTA mother liquid, whose contents could reflect the oxidation process of *p*-xylene directly. This Application Note shows a method to rapidly determine eight aromatic acids using an Agilent Poroshell SB-C18 column without any sample interference. Additionally, aromatic acids, which are difficult to degrade, exist in the wastewater of PTA manufacturers extensively. The level of these compounds can provide some useful data for wastewater treatment. This method may be used for wastewater monitoring in the PTA industry.

Refereneces

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