Analysis of Benzoic, *p*-Toluic, and Terephthalic Acids Using Anion-Exchange HPLC

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Key Words
Hypersil GOLD AX, benzoic acid, *p*-toluic acid, terephthalic acid

Abstract
This application note demonstrates the use of the Thermo Scientific™ Hypersil GOLD™ AX HPLC column for the analysis of residual amounts of benzoic acid and *p*-toluic acid in excess terephthalic acid.

Introduction

Terephthalic acid (Figure 1) is predominately used as the starting material in the production of polyethylene terephthalate (PET), which is used in the manufacture of clothes, plastic bottles, and inner coatings of food cans.

Terephthalic acid is produced by the oxidation of p-xylene, where *p*-toluic acid (Figure 2) is the reaction intermediate. Decarboxylation to benzoic acid (Figure 3) is common and responsible for product loss and subsequently lower yields. Therefore, residual quantities of both *p*-toluic and benzoic acid are monitored in terephthalic acid production to check reaction completion and percentage yield.

The retention and separation of benzoic, *p*-toluic, and terephthalic acids using Hypersil GOLD AX HPLC columns is demonstrated in this application.

Based on highly pure silica, Hypersil GOLD columns provide very symmetrical peaks, even when analyzing compounds that give notoriously poor peak shape on traditional silica-based chemistries. Hypersil GOLD AX HPLC columns have a weak anion-exchange phase and feature a novel polymeric amine ligand, which is also suitable for HILIC retention and separation of highly polar molecules.

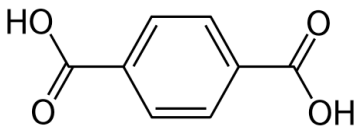

Figure 1: Terephthalic acid

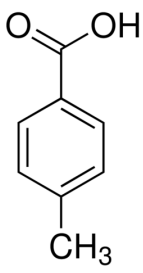

Figure 2: *p*-Toluic acid

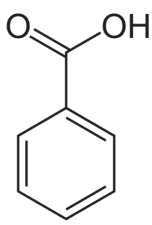

Figure 3: Benzoic acid

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Experimental Details

Consumables	Part Number
Fisher Scientific™ HPLC grade water	W/0106/17
Fisher Scientific HPLC grade acetonitrile	A/0626/17
9 mm Standard Opening Screw Thread Vial Convenience Kit, 2 mL Clear Vial with Patch, Black Polypropylene Closure with Red PTFE/White Silicone Septa	60180-600

Sample Preparation	Part Number
Primary standards of benzoic and *p*-toluic acid were prepared in acetonitrile at 1 mg/mL A solution of 0.8% terephthalic acid was prepared in 1 M NaOH and neutralized to pH 7 with acetic acid	
Working standard contained 25 µg/mL benzoic acid and 150 µg/mL *p*-toluic acid in 0.8% terephthalic acid	

Separation Conditions					Part Number
Instrumentation:	Thermo Scientific™ Dionex™ UltiMate™ 3000 RSLC HPLC system				
Column:	Hypersil GOLD AX 5 µm, 100 × 4.6 mm				26105-104630
Mobile phase A:	5 mM potassium phosphate buffer pH 6.0				
Mobile phase B:	100 mM potassium phosphate buffer pH 6.0				
Mobile phase C:	Acetonitrile				
Gradient:	Time (min)	% A	% B	% C	
	0.0	30	0	70	
	4.0	30	0	70	
	4.1	100	0	0	
	4.5	100	0	0	
	4.6	0	100	0	
	8.0	0	100	0	
	8.1	100	0	0	
	8.5	100	0	0	
	8.6	30	0	70	
	15.0	30	0	70	
Flow rate:	1 mL/min				
Column temperature:	30 °C				
Injection volume:	1 µL				
Injection wash solvent:	90:10 (v/v) water / acetonitrile				

A ternary mobile phase was required for this separation. A low buffer concentration (5 mM phosphate buffer) was initially required to separate benzoic and *p*-toluic acid. To reduce the analysis time, the buffer concentration was then stepped to 100 mM phosphate buffer to reduce the retention of terephthalic acid. However, the solubility of high concentrations of phosphate buffer in acetonitrile needs to be considered. Switching between the two concentrations of the buffered mobile phases in the presence of acetonitrile could cause precipitation and ultimately block the column. To address this, a short flush with 100% of the low buffer concentration was required to bracket the introduction of the high buffer concentration to the column.

Results

Figures 4 and 5 demonstrate the separation of *p*-toluic and benzoic acid. Terephthalic acid is eluted at approximately 8 minutes in the region of the high buffer concentration. The peak shape of terephthalic acid is compromised as overloading the column is required to gain an adequate response from the impurity acids (*p*-toluic and benzoic acid.) A summary of the results obtained from the Hypersil GOLD AX column are shown in Table 1.

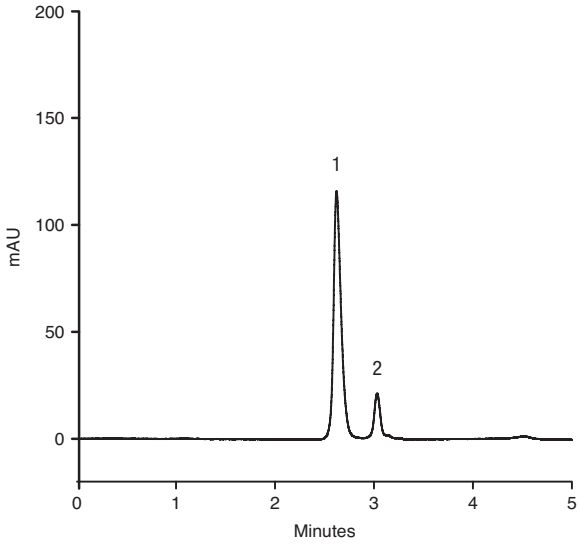

Figure 4: Expanded chromatogram demonstrating the separation of *p*-toluic acid (1) and benzoic acid (2)

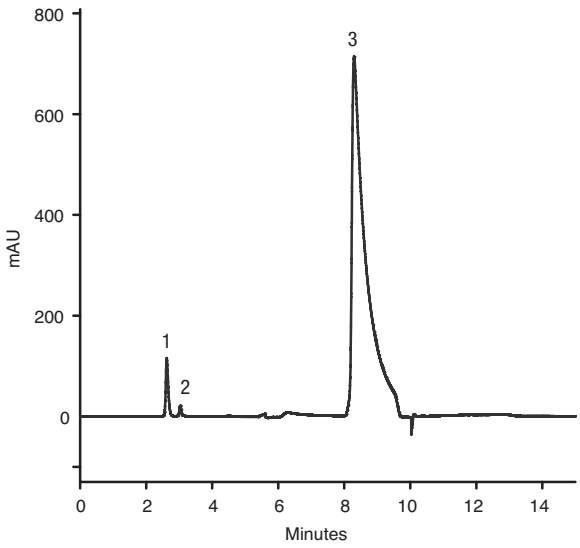

Figure 5: Chromatography for *p*-toluic acid (1), benzoic acid (2), and terephthalic acid (3)

	p-Toluic acid	Benzoic acid
Mean retention time	2.62	3.04
%RSD retention time	0.29	0.18
Mean asymmetry	1.31	1.26
Resolution		3.31

Table 1: Results obtained from Hypersil GOLD AX column based upon data derived from 6 replicate injections

Conclusion

- Benzoic acid, *p*-toluic acid, and terephthalic acid are successfully resolved using a Hypersil GOLD AX column.
- Analysis and re-equilibration time was less than 15 minutes.

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