Applikationsbericht

Advanced Polymer Chromatography (APC)™ System Analysis of Polymers in Xylene Tips & Tricks

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Dies ist ein Applikationsbericht, der keinen detaillierten Abschnitt zu Versuchen enthält.

Abstract

Gel permeation chromatography (GPC) analysis of hard to dissolve polymers such as petroleum-based products like tar, bitumen, and asphalt can be challenging, and Xylene is a common mobile phase for these GPC applications. Xylene is often sold as a mixture of the three available conformations: *ortho*, *para,* and *meta*. Each Xylene isomer has unique properties that are not all suited to liquid chromatography (LC). Using Xylene as a

mobile phase in a high-pressure system, such as the Waters™ ACQUITY™ APC System, with a limit of 15,000 psi, will require some method adjustments. This low dispersion system has the unique ability to maintain high resolution of the Waters BEH small particle sized columns. The ACQUITY APC System has been successfully used for polymer size-based separations with an *o*-Xylene mobile phase and an example is included yielding efficient method development and fast analysis times.

Benefits

- *O*-Xylene compatible system for GPC analysis of petroleum-based samples
- Ten-minute analysis time leading to lower hazardous waste and organic solvent consumption GPC option[2]
- APC Isocratic Solvent Manager (ISM) system with successful application use with Xylene

Introduction

The ACQUITY APC System is compatible with *o*-Xylene, and some pre-experimental consideration must be completed before using this mobile phase. A Xylene-soluble polymer, such as a petroleum-based sample, is not usually soluble in typical GPC solvents like THF, and many of the Xylene-soluble polymers usually have a complicated matrix that may need some extra steps to make the sample solution acceptable for LC injection. Before adding a new mobile phase to a system, the previous mobile phase and type of sample used in the previous analysis needs to be removed from the system. Precipitating the previous sample in your LC can lead to backpressure challenges. Just as a mobile phase preparation can affect a chromatographic system performance, so can the quality of sample preparation. The polymer sample needs to be stable in solution within the instrument settings. All these adjustments for Xylene polymer dissolution and GPC are well documented by experts in the analysis of Xylene soluble polymers using APC, and a technology brief reference with some experimental conditions is included. A separate document in the references is available for guidance switching solvents using the APC System.[1] A list of the topics covered includes:

- System solvent compatibility
- Mobile phase considerations
- Instrument setting considerations

- APC application using *o*-Xylene
- Summary and references

Experimental

System Solvent Compatibility

The APC Waters support for the use of o-Xylene in this section is an excerpt from the document link below. For the use of *o*-Xylene in the APC, and the information in this section is an excerpt from the document link below. Isopropanol is used for the seal wash, and *o*-Xylene is used for the needle wash and purge solvent. Additives are never used in the needle wash and purge solvent.

- General Comments: Waters has not tested Xylenes and is not planning to run an evaluation on this solvent. However, we do have customers that have been successfully running this as a solvent on the ACQUITY APC System
- From a material compatibility perspective, Xylene is like toluene and is expected to work with the APC System although we have not conducted extensive life testing
- If you choose to use *o*-Xylene, we suggest isopropanol for the seal wash
- If you choose to use *o*-Xylene, we suggest *o*-Xylene for the needle wash and purge solvent
- Note that *o*-Xylene (0.81 cP at 20 ℃) is a more viscous solvent when compared to other typical GPC solvents like THF (0.48 cP at 25 ℃), but not as viscous as DMSO and IPA (1.9 cP @ 25 ℃)
- *p*-Xylene is believed not to be a good choice due to its melting point (Mp) being close to room temp and may freeze under high pressure
- A mixture of Xylenes should not be used, because it contains *p*-Xylene. This content could have an adverse effect on the overall solvent properties

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Mobile Phase Considerations

There are three different conformations of Xylene: *ortho*, *meta,* and *para* (Figure 1, Table 1). The *ortho*-Xylene is the only one that Waters offers limited support for use with the APC System. The *meta*-Xylene is a good choice too, but the price may be too high for its use. The *para*-Xylene has a melting point near room temperature, so this conformation must be avoided. The mixture of Xylenes has *para*-Xylene content; therefore, mixtures of Xylenes are not supported for APC.[3]

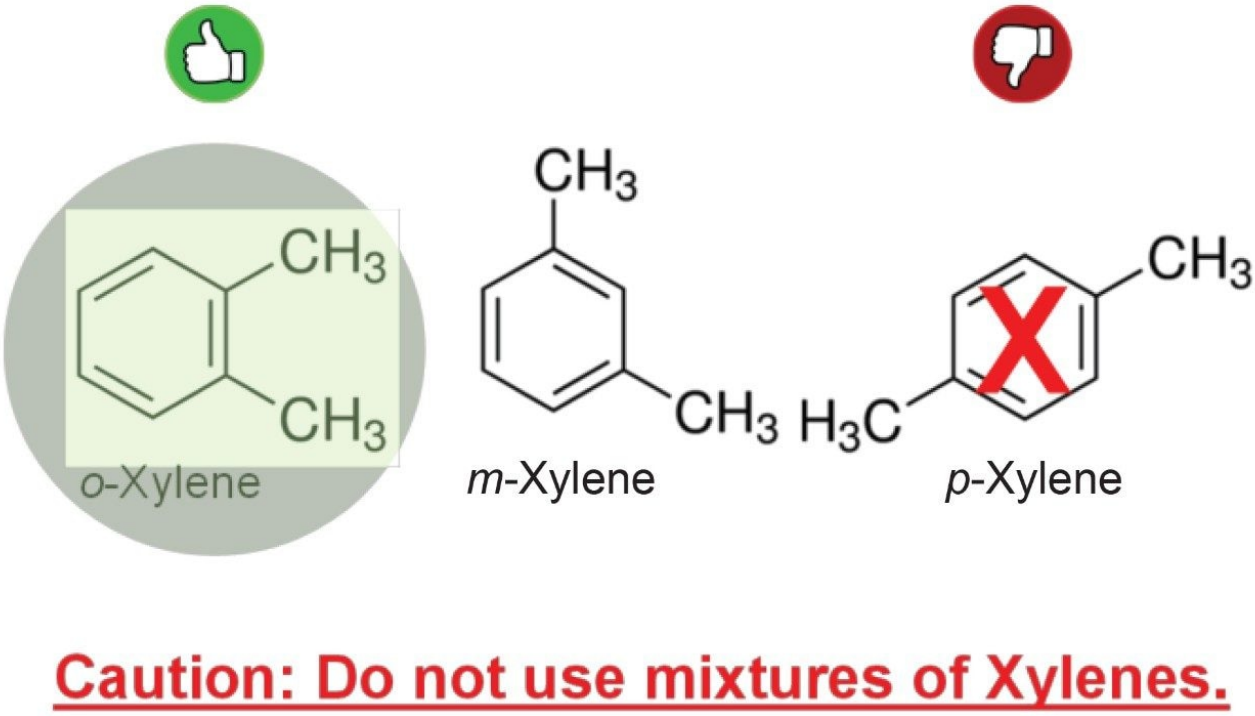

Figure 1. Three isomers of Xylene.

Xylene isomers				
General				
Common name	**Xylene**	***o*-Xylene**	***m*-Xylene**	***p*-Xylene**
Systematic name	Dimethylbenzene	1,2-Dimethylbenzene	1,3-Dimethylbenzene	1, 4-Dimethylbenzene
Other names	Xylol	*o*-Xylol; Orthoxylene	*m*-Xylol; Metaxylene	*p*-Xylol; Paraxylene
Molecular formula		C_8H_{10}		
SMILES		Cc1c(C)cccc1	Cc1cc(C)ccc1	Cc1ccc(C)cc1
Molar mass		106.16 g/mol		
Appearance		Clear, colorless liquid		
CAS number	[1330-20-7]	[95-47-6]	[108-38-3]	[106-42-3]
Properties				
Density and phase	0.864 g/mL, liquid	0.88 g/mL, liquid	0.86 g/mL, liquid	0.86 g/mL, liquid
Solubility in water		Practically insoluble		
Soluble in non-polar solvents such as aromatic hydrocarbons				
Melting point	−47.4 °C (−53.3 °F; 226 K)	−25 °C (−13 °F; 248 K)	−48 °C (−54 °F; 225 K)	13 °C (55 °F; 286 K)
Boiling point	138.5 °C (281.3 °F; 412 K)	144 °C (291 °F; 417 K)	139 °C (282 °F; 412 K)	138 °C (280 °F; 411 K)
Viscosity		0.812 cP at 20 °C (68 °F)	0.62 cP at 20 °C (68 °F)	0.34 cP at 30 °C (86 °F)
Hazards				
SDS	Xylenes[12]	*o*-Xylene	*m*-Xylene	*p*-Xylene
EU classification	Harmful (**Xn**)			
NFPA 704				
Flash point	30 °C (86 °F)	17 °C (63 °F)	25 °C (77 °F)	25 °C (77 °F)

Table 1. Table of Xylene physical properties.

Instrument Setting Considerations

The viscosity of *o*-Xylene is slightly less than the viscosity of water, so the needle draw rate could be left at the automatic setting or be raised to 230 µL per minute. The chromatography may produce an artifact at the beginning of the elution time which can be reduced by adjusting the needle draw rate (Table 2). The temperature setting in the sample manager can affect the viscosity of the mobile phase during sample injection.

Draw rate (µL/min)	Viscosity (cP @ 25 °C)	Recommended for these solvents
120	NA	Automatic
230	1	Water
640	0.48	THF
640	0.441	ACN
100	1.65 (20 °C)	HFIP
100	2.038	IPA
100	1.987	DMSO

Table 2. Table of APC syringe needle draw rates for corresponding solvents.

Results and Discussion

APC Application Using o-Xylene

A collaboration between Waters, the Laboratory of Bioinorganic Analytical and Environmental Chemistry (Pau, France), and TOTAL Refining and Chemicals (Harfleur, France) demonstrated the analysis of petroleum-based samples using APC and Xylene. This application demonstrates the use of *o*-Xylene as a mobile phase for APC analysis. Separations were completed with two ACQUITY APC XT Columns of 125 Å and 450 Å (4.6 x 150 mm, 2.5 µm). 10 µL sample solutions were injected with a dilution factor of 160. Polystyrene (PS) calibration standards were used and the run time was 10 minutes (Figure 2). Sample prep was a simple dilution of 160x with THF, Xylene, or chloroform with a manual dilution.[4]

APC instrument method	
Mobile phase	*o*-Xylene
Wash/purge	*o*-Xylene
Seal wash	Isopropanol
Run time	10 min.
Syringe draw rate	Automatic
Sample conc.	160 dilution factor
Injection vol.	10 µL
Column bank	ACQUITY APC XT (2.5 µm, 4.6 × 150 mm) 450 Å, 125 Å
Detector	ICP-HR-Mass Spectrometer

Table 3. APC instrument method for petroleum-based sample analysis.

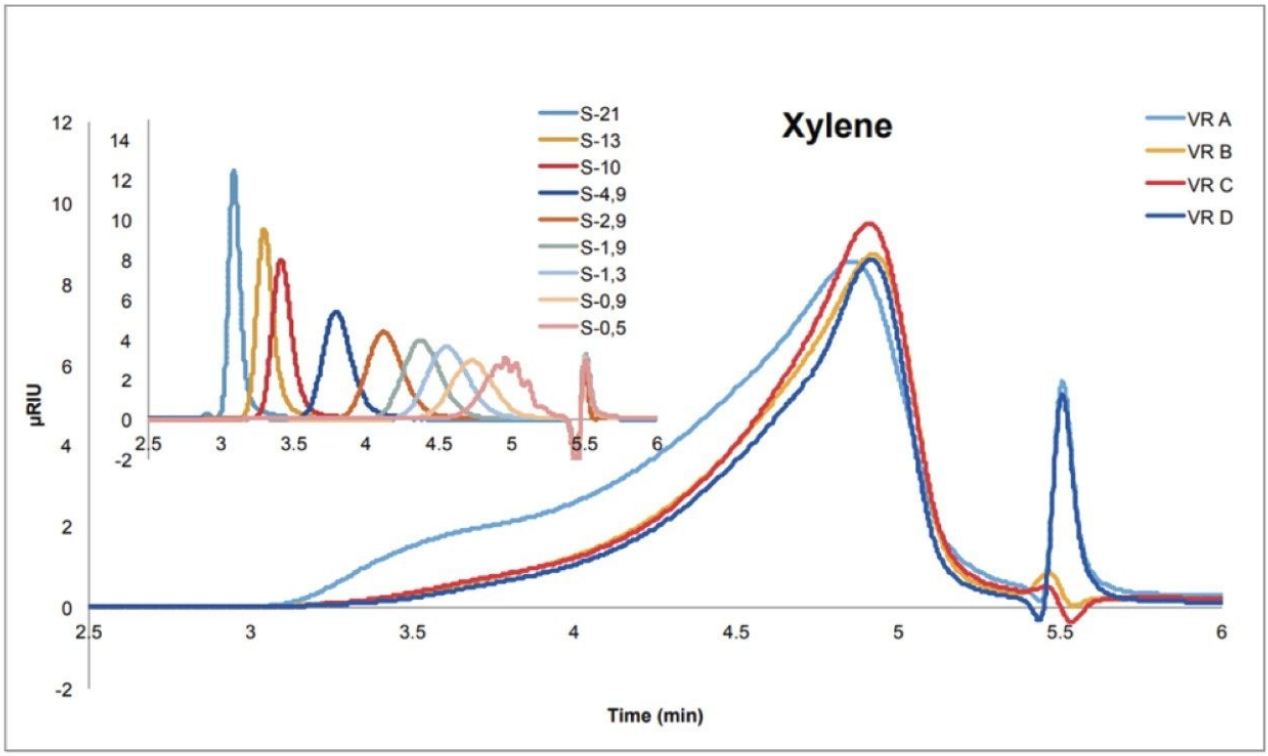

Figure 2. ACQUITY APC system chromatographic data overlay of PS narrow polymer calibration standards (insert) and petroleum-based samples.

Conclusion

- The ACQUITY APC System is supported for the use of *o*-Xylene specifically based on the solvent viscosity and melting point properties, and some key considerations have been addressed in this document.
- An *o*-Xylene-soluble polymer is not usually soluble in typical GPC solvents like THF, and the petroleum-based sample application is a ten-minute analysis example that leads to less hazardous waste and organic solvent use per analysis.
- Adjustments for using APC with *o*-Xylene as a mobile phase are explained in this document, in the reference documents, and through collaborative application.

References

1. ACQUITY APC System Chemical Compatibility Guide, Waters User Manual. USRM135084097 < https://www.waters.com/webassets/cms/support/docs/apc_solvent_compatibilty_consideration_guide_061021.pdf > , 2021.
2. Richard Mendelsohn, Jennifer Gough. Fast, High-Resolution Analysis of Polydimethylsiloxanes in Toluene with Advanced Polymer Chromatography Coupled to Refractive Index Detection, Waters Application Note. 720007658, 2022.
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4. Investigating Metal Containing Aggregates in Crude Oil with ACQUITY APC, Waters Application note. 720005625 <https://www.waters.com/webassets/cms/library/docs/720005625en.pdf> , 2016.

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