

# Determination of Xylene in Acrylonitrile by High-performance Liquid Chromatography

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## Summary

A method was developed for the separation and determination of trace xylene by high-performance liquid chromatography, using an ODS column and a mobile phase of methanol-water. Conditions necessary to effect baseline separation were demonstrated successfully by employing a methanol-water mixture (100+20) as mobile phase with a flow-rate of 1.0ml/min. The detection limit for xylene was 0.3ppm (signal-to-noise ratio=3) and the coefficient of variation was 1.5% at 17 ppm level. The proposed method was used successfully for the determination of trace amounts of xylene in acrylonitrile samples.

## Introduction

Acrylonitrile is widely used as raw material for synthetic fibers and rubber in a large number of chemical industries. Both acrylonitrile and xylene are also used as solvents in various industrial processes.

A considerable problem has arisen from the contamination of the acrylonitrile with xylene during the transportation by chemical tanker. The contamination may be caused by insufficient washing of the vessel in which xylene had been loaded before acrylonitrile was loaded. The chemical properties of the acrylonitrile is influenced even by trace amounts of xylene, when it is used as raw material for the manufacture of synthetic fiber. The determination of xylene in the acrylonitrile is therefore of great economic significance.

Numerous analytical methods have been developed for the determination of xylene. Among the most common methods of measurement of xylene is gas chromatography. In recent years, high-performance liquid chromatography (HPLC) has become of increasing interest for separation and determination of involatile and thermally unstable compounds in analytical chemistry.

Ogata et al. [1] have recently published a HPLC separation and determination of urinary metabolites of xylenes without solvent extraction technique. However, very little has been reported [2] so far on applications of HPLC for the determination of xylene. It was therefore important to study the liquid

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chromatographic behavior of xylene. Xylene shows strong absorption in the ultraviolet region, and thus may be quite amenable to chromatographic separation and analysis using UV detector. In this paper, the optimum conditions for the separation of xylene by reversed phase HPLC are described and some applications of the method to acrylonitrile samples are reported.

## Experimental

### Reagents and Materials

Methanol and xylene were purchased from Wako Pure Chemical Industries, Ltd. The solvents used as mobile phase were water-methanol mixtures. For the stock xylene solution (1000  $\mu\text{g/ml}$ ), 0.10g xylene was diluted to exactly 100ml with methanol. Standards (up to 70  $\mu\text{g/ml}$ ) were prepared by appropriate dilutions with methanol from 1000  $\mu\text{g/ml}$  xylene stock solution as required. Other chemicals were analytical reagent grade. All acrylonitrile samples analysed were supplied by Central Research Laboratory, Shin Nihon Kentei Kyokai, Yokohama.

### Instrumentation

The analytical HPLC system consisted of an 880-PU pump, and an 875-UV spectrophotometric detector (both from JASCO, Tokyo), a Rheodyne Model 7125 injector with a 20- $\mu\text{l}$  injection loop and a Rikadenki Model R-62M3 Multi-Pen Recorder. A Merck Lichrocart column (125x4.0mm I.D.) filled with Lichrosorb RP-18 (7 $\mu\text{m}$ ) was used.

### Procedure

Chromatographic separation was carried out at room temperature, using methanol-water (100+20) mixture as a mobile phase with a flow-rate of 1.0ml/min. A 20  $\mu\text{l}$  aliquot of the sample solutions was injected into the chromatograph. The concentration of xylene in the sample was determined by measuring the peak height. The wavelength control of the spectrophotometer was set at 265 nm.

The recovery test was conducted as follows: The 1ml and 3ml standard solutions (68.8  $\mu\text{g/ml}$ ) of xylene in methanol were each added to 5ml of acrylonitrile sample solution. The solutions were then injected into the chromatograph.

## Results and Discussion

In the initial studies using pure methanol as a mobile phase, insufficient separation of xylene and acrylonitrile was obtained. Consequently, we investigated the effect of the water content in the mobile phase on the retention of the xylene. The result is shown in Fig.1. The capacity factor  $k'$  is given by  $k' = (t_R - t_0)/t_0$ , where  $t_R$  and  $t_0$  are the retention times of retained and unretained solute, respectively.

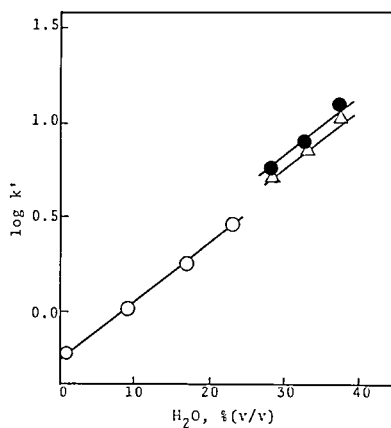


Fig.1 Variation of capacity factor ( $k'$ ) with concentration of water in the mobile phase.

—○— : xylene (mixture of o-, m- and p-xylene);  
 —●— : m- and p-xylene ;    —△— : o-xylene

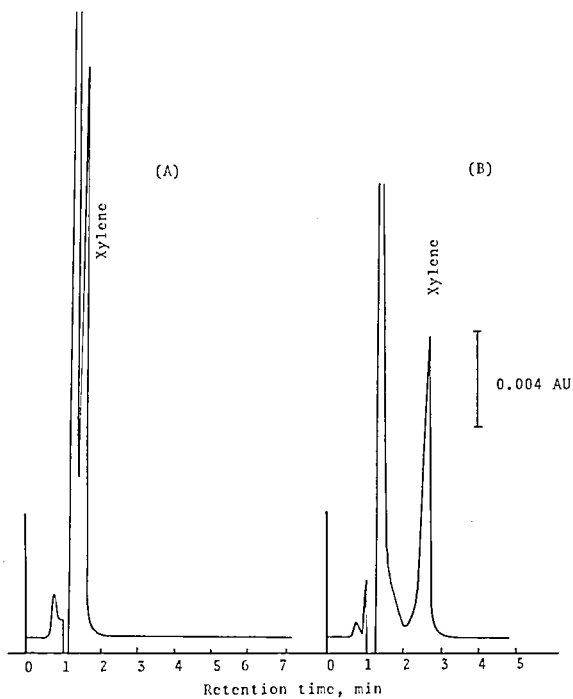


Fig.2 Typical chromatograms of xylene in acrylonitrile  
 Eluent : A) methanol, B) methanol-water (100+20, v/v)  
 flow rate, 1.0 ml/min ; detection at 265 nm ; detection  
 range, 0.04 AUFS ; injection, 20  $\mu$ l ; xylene concentration,  
 42  $\mu$ g/ml

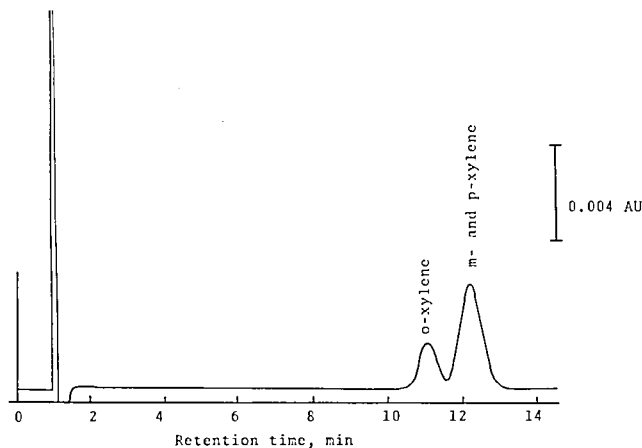


Fig.3 Separation of xylene isomers with methanol-water (100+60, v/v) as mobile phase. Xylene concentration,  $69\mu\text{g/ml}$ ; other conditions were the same as in Fig. 2.

As can be seen from Fig.1, the retention time of the xylene increased with increasing water content. Good separation of the two components was achieved at water contents of more than 15% (v/v), as shown in Fig.2. In this study, the system described above was preferred because of the conveniently short elution times. Furthermore, the overlapped band of three positional isomers of xylene resolved to two peaks of o-xylene and m-, p-xylene at water contents above 30 % (v/v) as shown in Fig.3, and the peaks' shape became broader with increasing water content. The mutual separation of the two isomers of m- and p-xylene could not be performed on the Lichrosorb RP-18 column, even though when the methanol containing approximately 50% (v/v) water was used as the mobile phase.

We did not pursue this point further because the aim of this study is to determine the total amount of xylene in acrylonitrile samples.

Although similar chromatographic behavior of xylene was observed when pure acetonitrile or acetonitrile-water mixture was used as mobile phase, in this study methanol was used because its price cheaper than that of acetonitrile.

The calibration curve (Fig. 4) of peak height versus xylene concentration was linear over the range studied ( $5\text{--}70\mu\text{g/ml}$ ) with  $20\mu\text{l}$  injection, the sensitivity being set at 0.04 absorbance for fullscale detection. Three sample solutions were subjected to the method and then injected directly to the chromatograph. The results are listed in Table I. The detection limit, defined as the concentration where the peak height was three times the background when the sensitivity of the detector was at a maximum, was 0.3ppm for xylene, when the injection volume was  $20\mu\text{l}$ . The results showed that xylene can be sufficiently estimated at the several ppm level by this method. The coefficient of the variation, determined

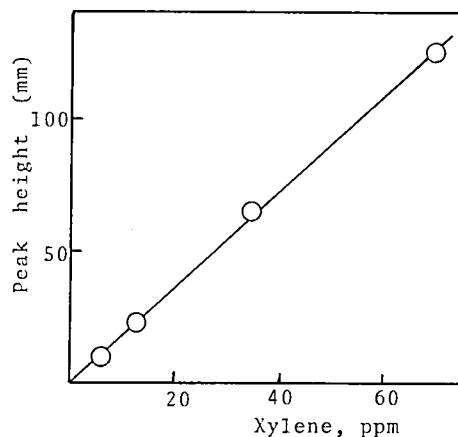


Fig.4 HPLC calibration curve for xylene showing the linear range

at 17ppm by analysing five acrylonitrile samples, was calculated to be 1.5%.

The results were compared with those obtained by the GC method; the agreement is good. The efficiency of recovery of spikes added to the sample is also shown in Table II. Better than 91% recovery was obtained for 17-42ppm levels of the xylene in acrylonitrile.

The optimum concentrations of water and a suitable organic solvent as carrier were evaluated. The analysis was completed within 5min and the precision and sensitivity were high. The method developed in this study may be one of the more suitable methods for determining total xylene in acrylonitrile. However, the mutual separation of m- and p-xylene was not achieved by this method.

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Table I Analytical results for xylene in acrylonitrile samples  
(Results are averages of 5 determinations)

Sample	Proposed method		G. C. method
	$\bar{X}$ ( $\mu\text{g/ml}$ )	R. S. D. (%)	( $\mu\text{g/ml}$ )
1	17	1.5	20
2	42	0.64	45
3	20	0.59	23

Table II Analytical results for xylene spiked samples  
(Results are averages of 5 determinations)

Sample	Aliquot (ml)	Xylene present ( $\mu\text{g}$ )	Xylene added ( $\mu\text{g}$ )	Xylene found ( $\mu\text{g}$ )	Recovery (%)
1	5	85	69	151	95.7
			206	274	91.7
2	5	210	69	273	91.3
			206	402	93.2

#### References

- [1] M. Ogata and T. Taguchi, Int. Arch. Occup. Environ. Health 59, 263 (1987).
- [2] K. Hatada, T. Kitayama, S. Shimizu, H. Yuki, W. Harris and O. Vogl, J. Chromatogr., 248, 63 (1982).