A Unified Method for the Analysis of Aromatic Solvents Using the Agilent 6820 Gas Chromatography System

Application

Petrochemical

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Abstract

A single method for analyzing aromatic solvent purity is described. This Unified Aromatic Solvent application consolidates ten separated American Society of Testing and Materials methods into an easy-to-use gas chromatography method. An Agilent 6820 gas chromatography system configured with split/splitless inlet and flame ionization detector is used. The successful use of nitrogen as a carrier gas for this application is also demonstrated.

Introduction

Measuring and determining the purity of aromatic hydrocarbons is a critical measurement for many of the QA/QC labs in the chemical and petrochemical industry. In an effort to standardize analysis procedures, the American Society of Testing and Materials (ASTM) has developed and published a number of gas chromatography (GC) methods used to measure the purity of specific aromatic compounds or classes of compounds such as ethylbenzene, styrene, o-Xylene, p-Xylene, etc. These methods also measure key impurities in many of these materials [1].

Most of the China National Criteria in the petrochemical industry comply with these ASTM methods. Many labs need to run several different ASTM methods to ensure the quality of all products. This analysis can be difficult and expensive to perform. One solution to this problem is to develop a single GC method that is the chromatographic equivalent of the separate ASTM methods [2]. A single method would simplify the operation of the lab and offer a number of other advantages. Fewer GCs would replace a large number of instruments previously dedicated to individual methods, and lab space would be reduced. By running one method, any GC could serve as a backup for instruments undergoing maintenance or repair, resulting in shorter down times. A single method would also decrease the need to stock multiple columns and supplies. So, a simplified method with correct measurement performance and an easy-to-use, reliable GC system is necessary for this routine work.

This application describes a GC method that is chromatographically suitable for a wide range of aromatic hydrocarbon samples typically analyzed by 10 ASTM methods (Table 1). Considering that nitrogen (N_2) is the common carrier gas in China, this application employs the method using N_2 as the carrier gas. The advantage for many Chinese customers is reduced cost without the loss of chromatographic performances such as resolution and response. However, there is a somewhat longer analysis time compared to Helium (He) as the carrier gas.

Table 1. Ten ASTM Methods for the GC Analysis of Aromatic Solvents

ASTM Method	Title	Capillary column type
D2306	Standard test for C8 aromatic hydrocarbons	Carbowax 50 m × 0.25 mm × 0.25 µm
D2360	Standard test for trace impurities in monocyclic hydrocarbons	Carbowax 60 m × 0.32 mm × 0.32 µm
D3760	Standard test for cumene	Carbowax 50 m × 0.32 mm × 0.25 µm
D3797	Standard test for o-Xylene	Carbowax 60 m × 0.32 mm × 0.50 µm
D3798	Standard test for p-Xylene	Carbowax 50 m × 0.32 mm × 0.25 µm
D4492	Standard test for benzene	Carbowax 50 m × 0.32 mm × 0.25 µm
D4534	Standard test for benzene in cyclic products	Packed 10% TCEPE on Chromasorb 3.7 m × 3.175 mm
D5060	Standard test for impurities in ethylbenzene	Carbowax 60 m × 0.32 mm × 0.50 µm
D5135	Standard test for styrene	Carbowax 60 m × 0.32 mm × 0.5 µm
D5917	Standard test for trace impurities in monocyclic hydrocarbons	Carbowax 60 m × 0.32 mm × 0.25 µm

Experimental

Experiments were performed on the Agilent 6820 GC equipped with a split/splitless inlet and flame ionization detector (FID). The conditions are shown in Table 2. An Agilent split liner (Agilent part number 19251-60540) and an Agilent advanced green septa (Agilent part number 5183-4759) were used. Manual injections used a 10 µL syringe with N_2 as the carrier gas. The Agilent Cerity Networked Data System for Chemical QA/QC was used for 6820 GC control, data acquisition, and data analysis.

Table 2. Conditions for the Unified Aromatic Solvents Method

GC	Agilent 6820 Gas Chromatograph
Data system	Agilent NDS Cerity for Chemical QA/QC
Inlet	Split/splitess; 250 °C, split mode, with 100:1 split ratio
Injection	1 µL
Carrier	Nitrogen, 7.6 psi at 75 °C
Column	HP-Innowax, 60 m × 0.32 mm × 0.5 µm column (Agilent p/n 19091N-216)
Oven	75 °C (23 min) with 1.3 °C /min to 100 °C (0 min) 4.4 °C /min to 145 °C (0 min) post run 220 °C (5 min)
Detector	FID, 250 °C

A 50 mL n-Hexane solution was prepared containing 0.1 wt% of 24 aromatic solvents as listed in Figure 1. The standard sample for p-Xylene, o-Xylene, ethylene, and styrene were used for injection.

Results and Discussion

Figure 1 shows a chromatogram of the hexane solution containing an aggregate of aromatic solvents and impurities. For most compounds, baseline resolution was achieved with the exception of partially resolved p-Ethyltoluene and m-Ethyltoluene. In the original ASTM method D5060, the components of this pair of ethyltoluene isomers are not resolved either [3]. Using N_2 as the carrier gas shows good resolution and response.

D3797-Standard Test Method for Analysis of o-Xylene

This test method covers the analysis of normally occurring impurities in o-Xylene and the measurement of o-Xylene purity by GC. It is suitable for setting specifications on o-Xylene and for use as an internal quality control tool where o-Xylene is used in a manufacturing process. Figure 2 shows the chromatograms of o-Xylene using N_2 as carrier gas. The injection size was 1 µL and the split ratio was 100:1. The broadening of the cumene peak was due to the reverse solvent effect of the overloaded o-Xylene, as the original ASTM D3797 method observed [4].

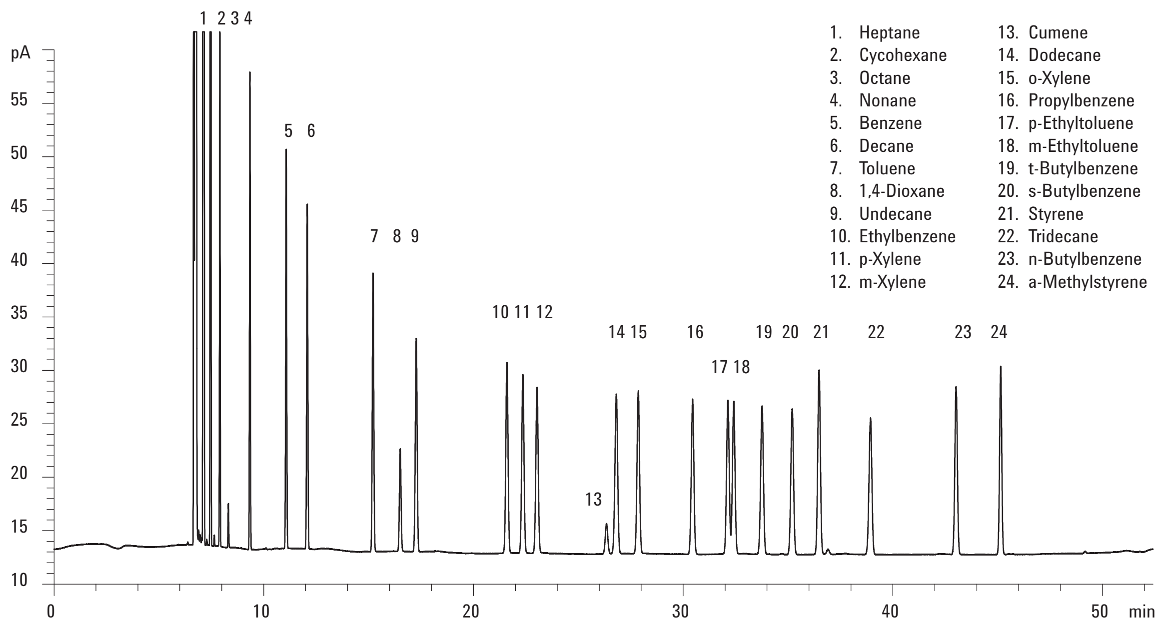

Figure 1. Chromatogram of a unified method to separate 24 compounds with N_2 as carrier gas.

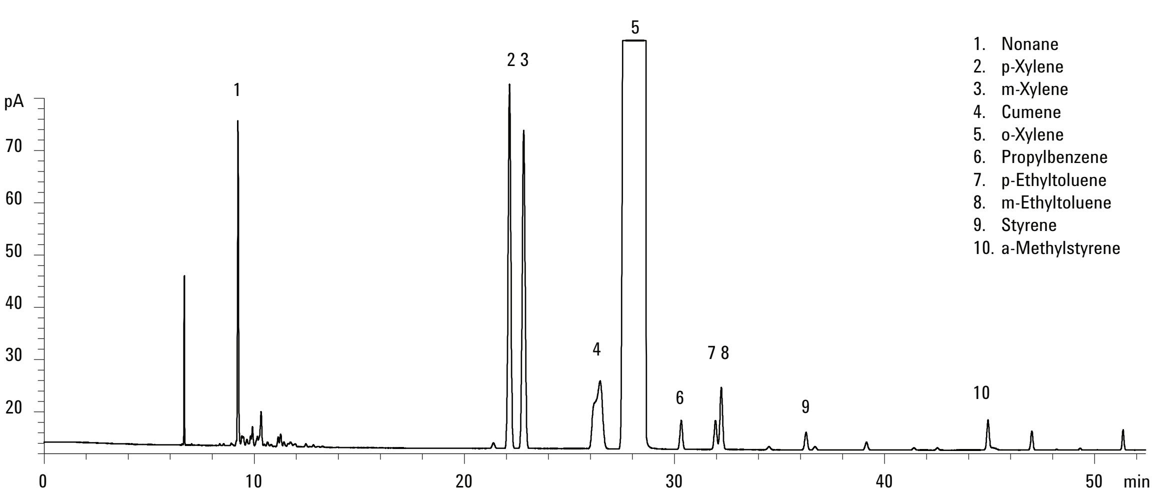

Figure 2. o-Xylene standard run on Agilent 6820 GC using N_2 as carrier gas. The split ratio was 100:1.

D3798-Standard Test Method for Analysis of p-Xylene

This test method covers the determination of known hydrocarbon impurities in p-Xylene and the measurement of p-Xylene purity by GC. It is generally used for the analysis of p-Xylene of 99% or greater purity. It is suitable for setting specifications as an internal quality control tool or development and research work. Figure 3 shows the chromatogram of the p-Xylene standard sample, using N_2 as carrier gas. The injection size was 1.0 µL and the split ratio was 100:1. The original ASTM D3798 method specifies that the valley points between the large p-Xylene peak and the ethylbenzene and m-Xylene contaminants should be less than 50% of the contaminants' peak height [5].

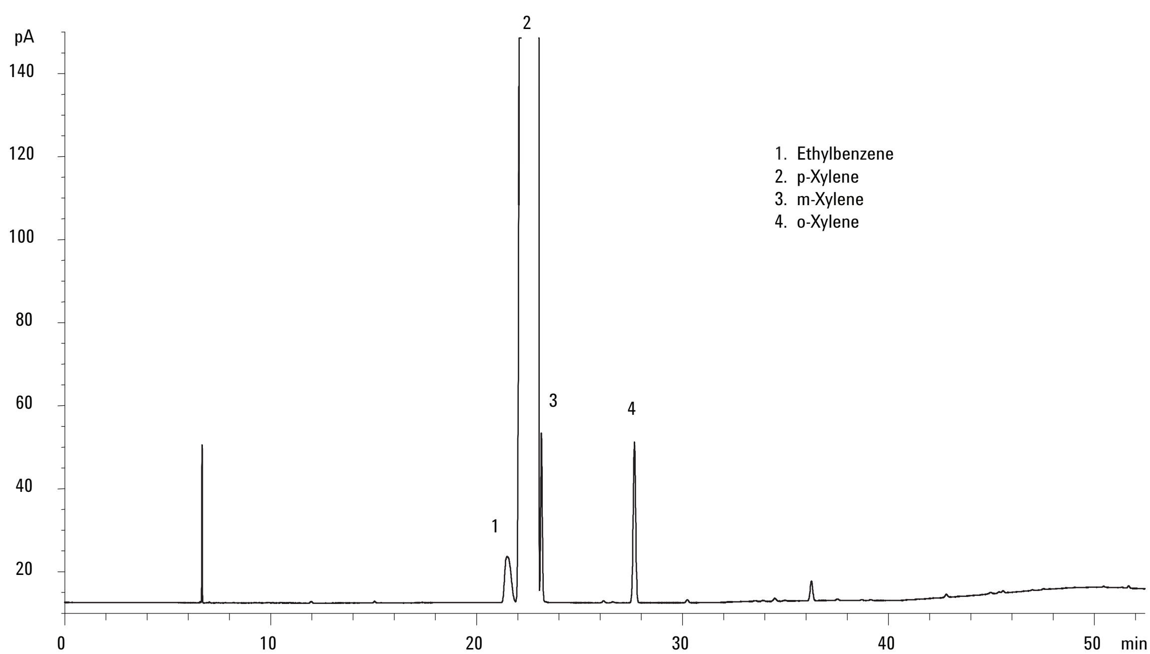

Figure 3. p-Xylene standard run on Agilent 6820 GC using N_2 as carrier gas, split ratio was 100:1.

D5060 Standard Test Method for Determining Impurities in High-Purity Ethylbenzene

The test is suitable for setting specifications on ethylbenzene and for use as an internal quality control tool where ethylbenzene is used in the manufacturing process. It may be used in development or research work involving ethylbenzene. Figure 4 shows the chromatogram of the ethylbenzene standard sample. The injection size was 1.0 µL and the split ratio was 100:1.

D5135 Standard Test Method for Analysis of Styrene

This test method covers the determination of the impurities in styrene and and the measurement of styrene by GC. It is designed to obtain styrene purity on the basis of impurities normally present in styrene and may be used for final product inspections and process control. Figure 5 shows the chromatogram of the styrene standard sample. The injection size was 1.0 µL and the split ratio was 100:1.

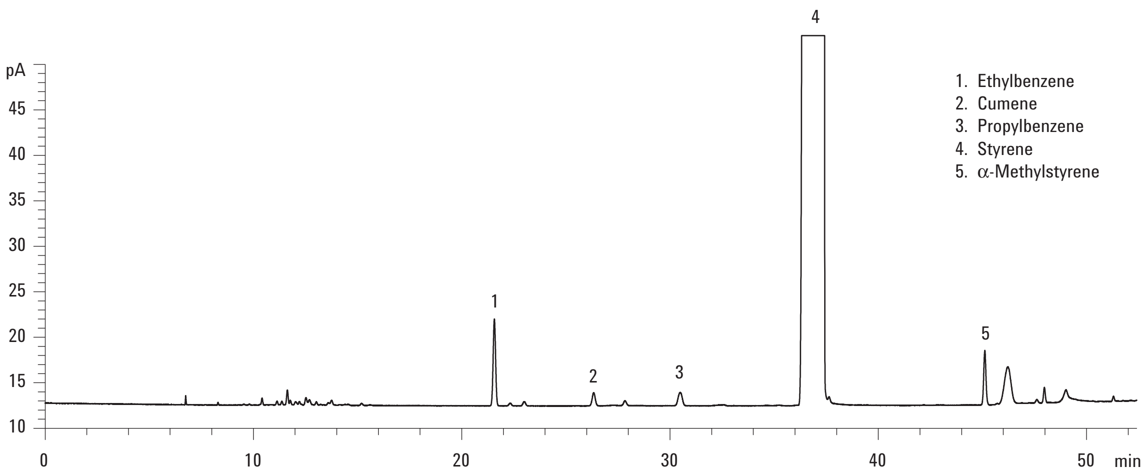

Figure 4. Ethylbenzene standard sample run on Agilent 6820 GC using N_2 as carrier gas. The split ratio was 100:1.

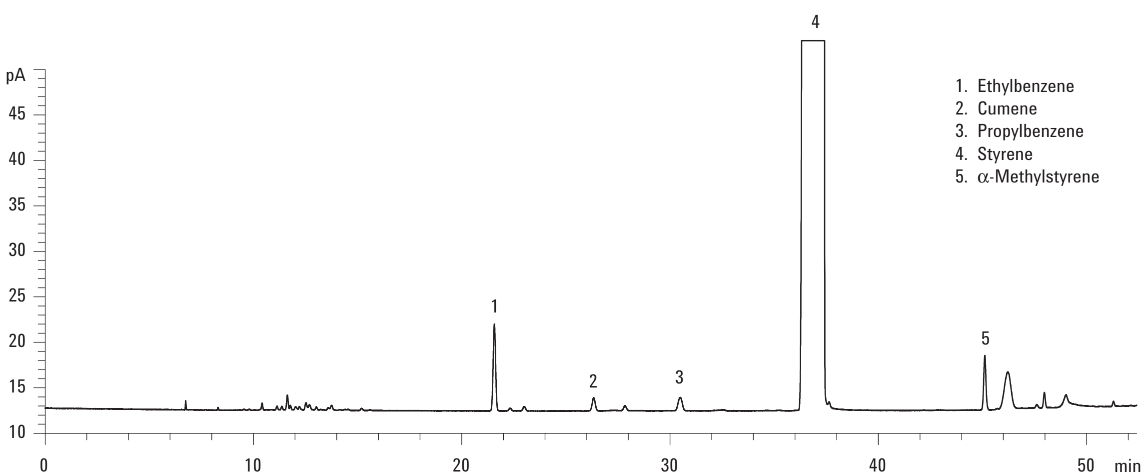

Figure 5. Styrene standard sample run on Agilent 6820 GC using N_2 as carrier gas. The split ratio was 100:1.

Conclusions

A simplified method is described for aromatic solvent purity analysis. The unified method can resolve a number of compounds found in aromatic materials and can successfully run the calibration standards used by each ASTM method to determine solvent purity. The Agilent 6820 GC system shows good applicability by using N_2 as the carrier gas. The single method with the Agilent 6820 GC system is easy to set up for determination of the aromatic solvent purity in the routine lab; it also decreases the need to stock multiple columns and supplies.

Reference

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