Application Note

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# Determination of Benzene and its Derivatives in Water with the Agilent 8697 Headspace Sampler and 8890 GC


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## Abstract

This application note describes a method for the analysis of benzene and its derivatives using method HJ 1067-2019, a Chinese industrial standard for environmental protection. The Agilent 8697 headspace sampler, coupled with an Agilent 8890 GC with flame ionization detection (FID), is shown to enable reliable, cost-effective analysis of benzene and its analogues in water.

## Introduction

HJ 1067-2019 is a method that describes the determination of benzene and its analogues in water by headspace GC with FID. Sample extraction, analysis, identification, and quantitation are detailed in this method.

This application note demonstrates that the Agilent 8697 headspace sampler, coupled with the Agilent 8890 GC, delivers accurate and reliable analysis of benzene and certain derivatives in water. This system can easily achieve the performance specification for the compounds detailed in method HJ 1067-2019. The calibration curves determined for those target compounds were found to be within method requirements and the correlation coefficients were well above 0.999. The relative standard deviation (RSD) was determined for each compound. The area %RSD was 1.3 to 2.4% and the retention time %RSD was less than 0.045%. For all the compounds, the MDLs were ≤0.2 µg/L. Satisfactory recoveries were achieved at around 99.1 to 101.7%.

## Experimental

### Chemicals and reagents

All reagents and solvents were HPLC or analytical grade. All benzene compounds single standards were purchased from ANPEL Laboratory Technologies (Shanghai) Inc.

### Solutions and standards

Prepare the mixed standard stock solutions by adding defined amounts of each single standard compound. The stock solution of eight compounds at the concentration of 1,000 µg/mL was prepared in methanol solution. The intermediate stock solutions at concentrations of 10 and 100 µg/mL were prepared in methanol.

Six headspace vials were made at each calibration level by filling each vial with 3 g of sodium chloride and 10 mL ultrapure water, and spiking varying amounts of stock solution and intermediate stock solution to achieve the required levels. The calibration standards were prepared at standard concentrations of 10, 20, 50, 200, 500, and 2,000 µg/L. Before putting the samples in the headspace tray, the vials were shaken until sodium chloride was completely dissolved.

### Instrument conditions

Separation was carried out using the Agilent 8697 headspace sampler coupled with an Agilent 8890 GC/FID. Agilent OpenLab CDS 2.5 software was used for data acquisition and analysis. The instrument conditions are shown in Table 1.

**Table 1.** Instrument conditions.

| Parameter | Value |
|---|---|
| **Agilent 8697 Headspace Sampler** | |
| Loop Size | 1 mL |
| Pressurization Gas | Nitrogen |
| Oven Temperature | 80 °C |
| Loop Temperature | 80 °C |
| Transfer Line Temperature | 100 °C |
| Vial Equilibration Time | 40 min |
| Injection Duration | 0.5 min |
| Vial Size | 20 mL |
| Fill Pressure | 15 psi |
| Loop Fill Mode | Default |
| Vial Shaking | Level 8 |
| **Agilent 8890 GC** | |
| Inlet | Split/splitless<br>200 °C, split ratio 10:1<br>Liner: Straight, deactivated, 2 mm id (p/n 5181-8818) |
| Column | Agilent J&W HP-INNOWax, 30 m × 0.32 mm, 0.5 µm (p/n 19091N-213I) |
| Carrier | Nitrogen, 2 mL/min, constant flow |
| Oven | 40 °C (5 min),<br>then 5 °C/min to 80 °C (5 min),<br>then 30 °C/min to 200 °C (5 min) |
| FID | 250 °C, hydrogen: 30 mL/min, air: 300 mL/min |

## Results and discussion

Figure 1 shows a typical chromatogram acquired by the HS/GC/FID system with the eight benzene compounds at a concentration of 200 µg/L. The system shows great resolution and peak shape for all compounds. As shown in Figure 1, ethylbenzene, *p*-xylene, and *m*-xylene were baseline separated on an HP-INNOWax column.

Calibration curves for benzene compounds showed excellent results. Linearity across the range studied gave calibration coefficient ($R^2$) values of 0.9998 or greater for all compounds. Figure 2 displays the calibration curve information of benzene and ethylbenzene obtained on this system. Table 2 lists the $R^2$ value for each of the compounds. Repeatability (n = 8) was tested at concentrations of 20 and 200 µg/L. The area %RSD was 1.3 to 2.4% and the retention time %RSD was less than 0.045%, as shown in Table 3.

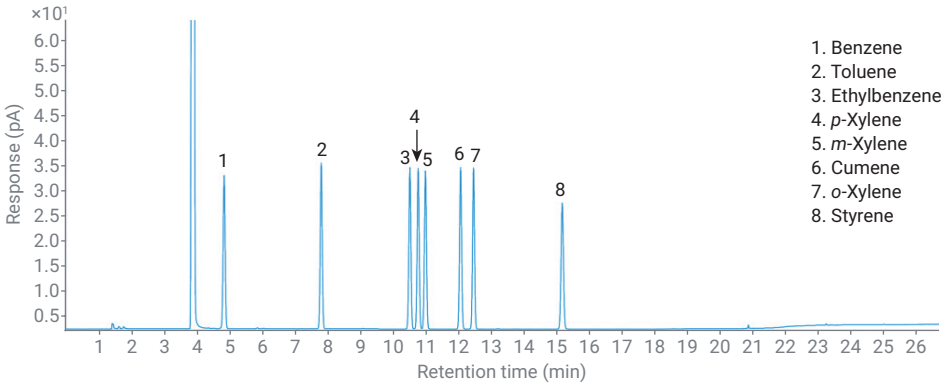


**Figure 1.** Chromatogram of the eight target compounds at a concentration of 200 µg/L.

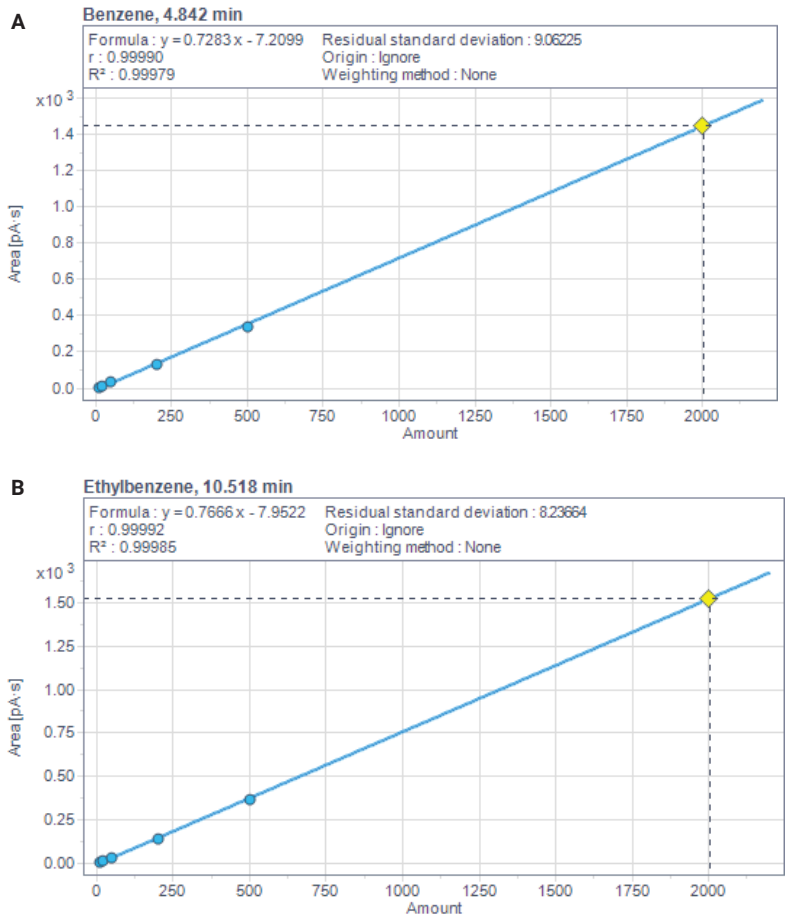


**Figure 2.** (A) Calibration of benzene from 10 to 2,000 µg/L. (B) Calibration of ethylbenzene from 10 to 2,000 µg/L.

Signal-to-noise ratio (S/N) was used for method detection limit (MDL) calculation. A concentration of 2 µg/L standard solution was used to test the MDL, and the values for all compounds are listed in Table 3. For all compounds, the MDLs were ≤0.2 µg/L, which meets the specifications of the HJ 1067-2019 method.

Method recoveries were measured by analyzing unspiked and spiked water samples. Standards containing benzene and its derivatives were spiked into tap water at the concentration of 200 µg/L. Six parallel spiked samples were analyzed by the same method. Recovery was calculated by the Equation 1.

**Conc. of spiked sample:** the calculated concentration of spiked samples based on the calibration curve.

**Conc. of unspiked sample:** the calculated concentration of unspiked samples based on the calibration curve.

**Conc. added:** the concentration of benzene compounds in spiked samples, 200 µg/L.

The recovery data are listed in Table 3, illustrating that the recovery results of 200 µg/L ranged from 99.1 to 101.7%.

**Table 2.** $R^2$ values for benzene and its derivatives in the calibration standard over the 10 to 2,000 µg/L range of this study.

| No. | Name | RT | Formula | $R^2$ |
|---|---|---|---|---|
| 1 | Benzene | 4.839 | y = 0.7283x – 7.2099 | 0.9998 |
| 2 | Toluene | 7.807 | y = 0.7677x – 8.5950 | 0.9998 |
| 3 | Ethylbenzene | 10.519 | y = 0.7666x – 7.9522 | 0.9999 |
| 4 | *p*-Xylene | 10.771 | y = 0.7541x – 7.7485 | 0.9999 |
| 5 | *m*-Xylene | 10.994 | y = 0.7561x – 7.7873 | 0.9999 |
| 6 | Cumene | 12.068 | y = 0.7571x – 5.4705 | 0.9999 |
| 7 | *o*-Xylene | 12.463 | y = 0.7416x – 7.6819 | 0.9998 |
| 8 | Styrene | 15.173 | y = 0.7033x – 7.0938 | 0.9998 |

**Table 3.** RSD, MDL, and recovery percentages for benzene and its derivatives.

| No. | Name | RT %RSD (n = 8) | Area %RSD (n = 8) | | MDL (µg/L) | Average % Recovery (n = 6) 200 µg/L |
|---|---|---|---|---|---|---|
| | | | 20 µg/L | 200 µg/L | | |
| 1 | Benzene | 0.045 | 1.77 | 1.74 | 0.16 | 101.7 |
| 2 | Toluene | 0.034 | 1.66 | 1.71 | 0.14 | 100.5 |
| 3 | Ethylbenzene | 0.022 | 1.69 | 1.62 | 0.16 | 99.9 |
| 4 | *p*-Xylene | 0.030 | 2.13 | 1.92 | 0.16 | 99.1 |
| 5 | *m*-Xylene | 0.026 | 1.82 | 1.73 | 0.17 | 99.7 |
| 6 | Cumene | 0.025 | 1.30 | 1.51 | 0.16 | 100.2 |
| 7 | *o*-Xylene | 0.023 | 1.80 | 1.74 | 0.16 | 100.7 |
| 8 | Styrene | 0.021 | 2.32 | 2.40 | 0.20 | 100.3 |

**Equation 1.**

$$\text{Recovery \%} = \frac{(\text{Conc. of spiked sample} - \text{Conc. of unspiked sample})}{\text{Conc. added}} \times 100$$

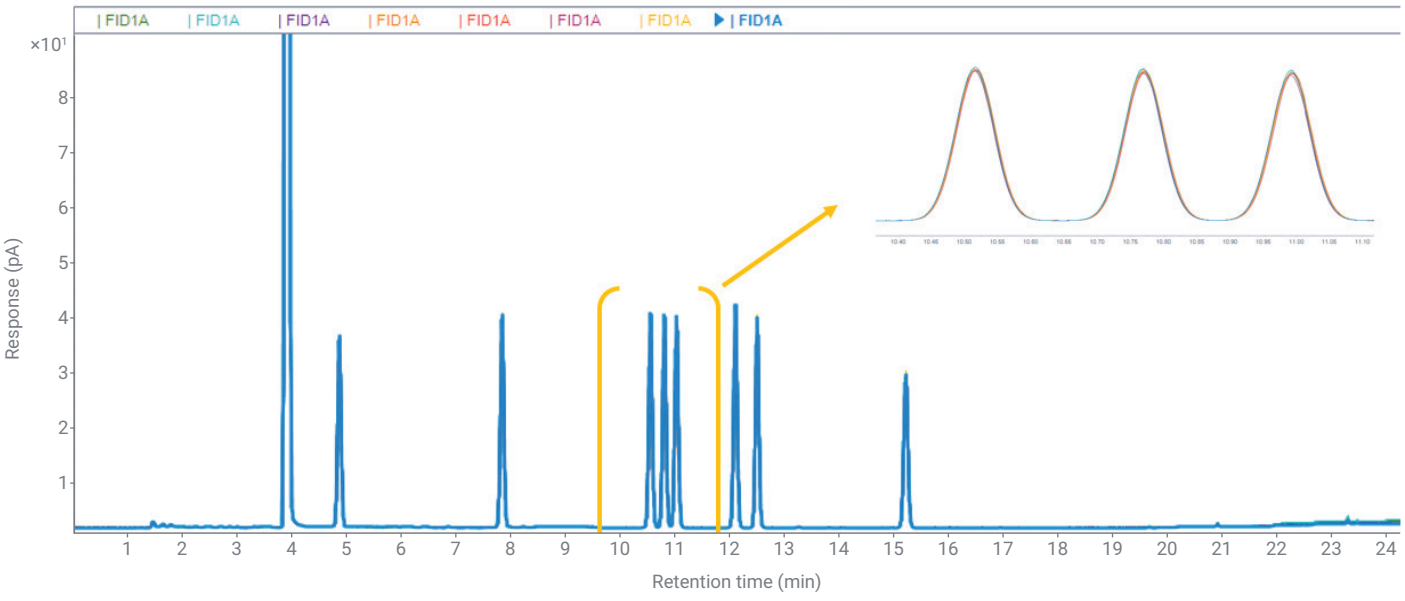


**Figure 3.** Overlaid GC/FID chromatograms of eight repeat injections of 200 µg/L.

## Conclusion

This application note demonstrates that the 8697 headspace sampler configured with an 8890 GC and an FID can provide a reliable and economical solution for the analysis of benzene and its analogues in water. The inert flow path from headspace to detector results in a reliable inertness level that provides excellent peak shape, resolution, and great repeatability.

## Reference


1. HJ 1067-2019. Water Quality—Determination of Benzene and its Analogies—Headspace/Gas Chromatography. China National Environmental Monitoring Station, Chinese Ministry of Ecology and Environment (date of issue: 24 December 2019).



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