

# The Application of Portable GC-MS on the Petrochemical Wharf

Zhao Yun\*

China Waterborne Transport Research Institute, China

## Abstract

It is very important to quickly identify the liquid chemicals in the petrochemical wharf when they volatile in the air. Since most of the liquid chemicals transported in the petrochemical wharf are harmful to people, and they spread very fast in the air. If the exact kind of liquid chemicals is undefined or is wrongly defined, it will lead to a big mistake in detection result. The mass spectrum is very effective in determining the gas kinds, but its big size and complex sampling mode are not convenient for quick detection. To resolve this problem, a method based on portable GC\_MS for VOCs determination is developed. The VOCs are directly extracted by solid phase micro extraction head for 120 seconds. After that, they are analysed on the portable GC-MS, determined by retention time and MS peaks, quantified by external standard method. It only takes 6.4 min from sample extracting to get the result. And its linear correlation is larger than 0.98, and the minimum detectable concentration is lower than half of their occupational exposure limits. In the simulation test, the relative error is lower than 4.4%. This method can directly sample in the air, rarely depends on external conditions. At the same time, it can determine and quantify multiple kinds of VOCs at a time. So, it will be very suitable for the VOCs emergency detection in the leakage scene.

**Keywords:** Portable GC-MS; Volatile organic compounds; Quick detection; Direct sample; Solid phase micro extraction; Petrochemical wharf

## Introduction

There are many kinds of dangerous chemicals in the petrochemical wharf area. And most of them are volatile organic compounds(VOCs). The pollution accidents have occurred many times in the petrochemical wharf area [1,2]. The VOCs diffuses very fast in the air, and would pollute water and soil on a large scale. Also, there are many kinds of VOCs, and their toxicities are very complicated. Once the pollution accidents occurred, the people nearby would be in danger [3,4]. The identification of VOCs is not difficult, but there are few detecting method to quickly quantify the concentration of VOCs when they are identified. So, it is necessary to develop a quick detecting method to identify and quantify the concentration of VOCs in the petrochemical wharf area. The portable gas chromatograph-mass spectrometer (portable GC\_MS) is quite small, and convenient to carry out. So, it is very suitable for quick detection on the scene. When it is used on the scene, the sampling method is very important. Solid phase micro extraction (SPME) is a sampling method without solvents. It can combine the sampling, concentration and injection [5-7]. Especially, the SPME could direct sample in the air, so it will save much time.

## Experimental

### Instruments and reagents

Portable GC\_MS, gas distributing device (MF-3C), bladder tank (5 L), SPME sampling head, micro syringe (10  $\mu$ L, 100  $\mu$ L), standard substance (benzene, toluene, paraxylene, aniline, trichloroethylene, tetrachloroethylene, cyclohexanone).

### Analysis conditions

**chromatographic condition:** Injection temperature: 270°C temperature progress: hold 40°C for 10 s, then heat up at a speed of 2°C/s to 280°C, then hold for 20 s, flow speed: 0.15 mL/min.

**Ionization source:** EI, energy level: 70 eV, scan mode: Full scan, scan range: 45-500 m/z.

### Sampling

The air sample is directly taken by the SPME sampling head for

120 s. Then it is injected into the portable GC\_MS without further treatment.

## Results and Discussion

### The concentrations of standard series of VOCs

The most important purpose of quick detection is to evaluate whether the pollutant concentration will cause health damage and to determine the pollution scope. Here we could refer to the occupational exposure limits of each VOCs, set by national standard. When the pollutant concentrations in the field are higher than their occupational exposure limits, it should be identified as contaminated area. This requires that the minimum detectable concentration of each chemical hazardous agent must be lower than its occupational exposure limit. According to the <Occupational exposure limits for hazardous agents in the work place: Chemical hazardous agents> (GBZ 2.1-2007) [8], the occupational exposure limits of benzene, toluene, paraxylene, aniline, trichloroethylene, tetrachloro ethylene and cyclohexanone are 6, 50, 50, 3, 30, 200 and 50 mg/m<sup>3</sup>, respectively. Based on this, we set the concentrations of standard series gases as 0.5, 1, 2, 4, and 8 times of their occupational exposure limits. The specific concentrations are shown in Table 1.

### The sampling time

The more gases the SPME sample hand collected, the higher precision will be obtained. correspondingly, the sampling time needed will be longer. and if the sampling time is too long, it will not match the demand of the quick detection. So, a balance between the sampling time and detecting precision will be needed, at which, the analysis result could be obtained quickly and the analysis precision is accuracy enough. The analysis precisions at different sampling time are compared

\*Corresponding author: Zhao Yun, China Waterborne Transport Research Institute, China, Tel: 008613810864135; E-mail: [zhaoyun@wti.ac.cn](mailto:zhaoyun@wti.ac.cn)

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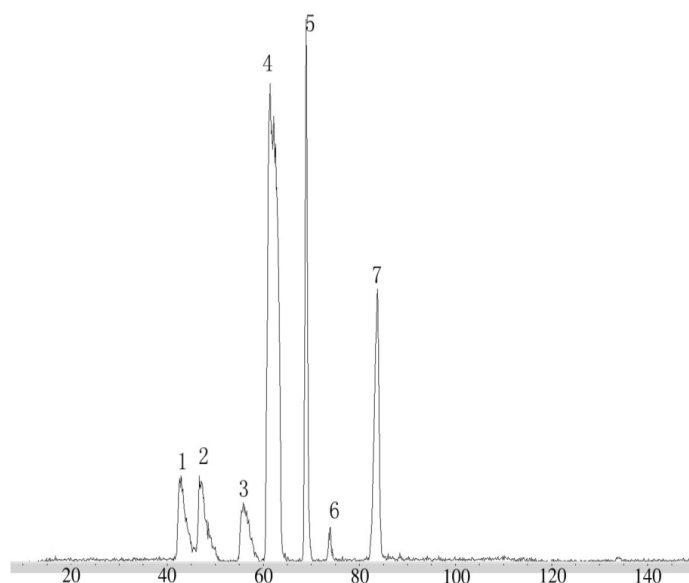


Figure 1: The separation effect of 7 kinds of VOCs (1. Benzene; 2. trichloroethylene; 3. Toluene; 4. Tetrachloroethylene; 5. Paraxylene; 6. Cyclohexanone; 7. Aniline).

Standard series	Benzene (mg/m <sup>3</sup> )	Toluene (mg/m <sup>3</sup> )	Paraxylene (mg/m <sup>3</sup> )	Aniline (mg/m <sup>3</sup> )	Trichloroethylene (mg/m <sup>3</sup> )	Tetrachloroethylene (mg/m <sup>3</sup> )	Cyclohexanone (mg/m <sup>3</sup> )
Series 1	3	25	25	1.5	15	100	25
Series 2	6	50	50	3	30	200	50
Series 3	12	100	100	6	60	400	100
Series 4	24	200	200	12	120	800	200
Series 5	48	400	400	24	240	1600	400

Table 1: The concentration of standard series gases.

Compounds	Retention Time (s)	Mass Peak (m/z)	Linear Equation	Correlation Coefficient	Minimum Detectable Concentration (mg/m <sup>3</sup> )
Benzene	43.0	77	y=4.369x-10.66	0.994	1.1
Toluene	61.4	91	y=0.891x-6.833	0.995	21
Paraxylene	68.9	104	y=2.931x-7.541	0.993	23
Aniline	83.4	91	y=4.513x-1.375	0.986	0.6
Trichloroethylene	46.1	129,131	y=10.86x-10.62	0.996	12
Tetrachloroethylene	61.2	160,162,164	y=0.099x-6.041	0.996	26
Cyclohexanone	74.0	98	y=0.262x+1.375	0.994	20

Table 2: The linear correlations and minimum detection concentrations of 7 kinds of VOCs by portable GC-MS.

using the detection of minimum concentration in the standard series gases. When the sampling time is 120 s, the analysis precision of every gas is good, and 120 s is short enough. So, the sampling time is set as 120 s. The separating effect is shown in Figure 1.

### The standard curve

The standard mix gases of benzene, toluene, paraxylene, aniline, trichloroethylene, tetrachloroethylene and cyclohexanone are prepared with pure air. The concentrations are 48, 400, 400, 24, 240, 1600, 400 mg/m<sup>3</sup> respectively. And it is diluted into the series concentrations shown in Table 1. Then the series gases are analysed on portable GC\_MS. All the gases are determined by the mass spectrum peak and retention time, and the standard curve are plotted through the peak area. Also, the equations of linear regression and correlation coefficients are obtained. The minimum detectable concentrations are calculated through 3 times noise signals. The equations of linear regression, correlation coefficients and the minimum detectable concentrations are shown in Table 2.

### Discussion

A new quick detection method for VOCs based on portable GC\_MS and SPME head was developed. And a mixture of 7 kinds of VOCs was analysed by this method. This detection method took only 6.4 mins to get the analysis result. And the SPME head was used in the sampling process, and it provided convenient sampling procedure. This combination of portable GC\_MS and SPME head would make the detection of VOCs more convenient and fast. So, it would be very suitable for the VOCs quick detection in the petrochemical wharf area. And it is helpful to determine the pollution scope and improve the worker's occupational health for reduce the damage from VOCs [9-13].

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