SHIMADZU

Prototype Development of a Digital Linear Ion Trap based Portable GCMS for VOCs Analysis

Chenzhang Zhu; Lin Liu; Hongbing Cheng; Yunlei Hu; Xinfeng Zhou; Wenjian Sun Shimadzu Research Laboratory (Shanghai) Co., Ltd.

1. Overview

With the increasingly stringent environmental protection requirements, the prevention and control of volatile organic compounds (VOCs) pollution has become one of the priorities of China's long-term environmental pollution control project in recent years. We have developed a man-portable GCMS system based on a low thermal mass GC column (LTM) and a digital linear ion trap (DLIT). The man-portable GCMS system using DLIT shows the advantages of small size and higher sensitivity. And the combination of multiple analysis modes givers it a larger dynamic range.

2. Introduction

The man-portable GCMS consists of GC and MS modules with related controlling system. To minimize the size and power consumption, our GC module is LTM based. The MS module consists of Shimadzu commercial EI source, DLIT and a normal sized electron multiplier detector. The DLIT used was driven by a digital square wave, which avoids resonant RF circuit with a huge induction coil. The ion selection is carried out by frequency scanning, and it makes the upper limit of m/z easily extended.

DLIT shows higher dynamic range compared to traditional 3D ion trap. And compared with the quadrupole or TOF used by traditional GCMS, DLIT has a smaller volume and lower vacuum requirement. In our system, DLIT works at a vacuum level maintained by a 30 L/s turbo pump, which ensures higher flow rate of Helium carrier gas and a corresponding higher sensitivity. With those mentioned above, the volume of the man-portable GCMS is only 0.03 m³, 1/2 less than the size of the MS part in the conventional benchtop GCMS system. The weight is 18.5 kg including computer, battery, two gas cylinders.

At present, the power range of the system is 89 – 154 W, with continuous operation time of longer than 2 hours. Two cylinders contain carrier gas and internal standard gas, respectively. Operation time of the carrier gas is more than 2 days.

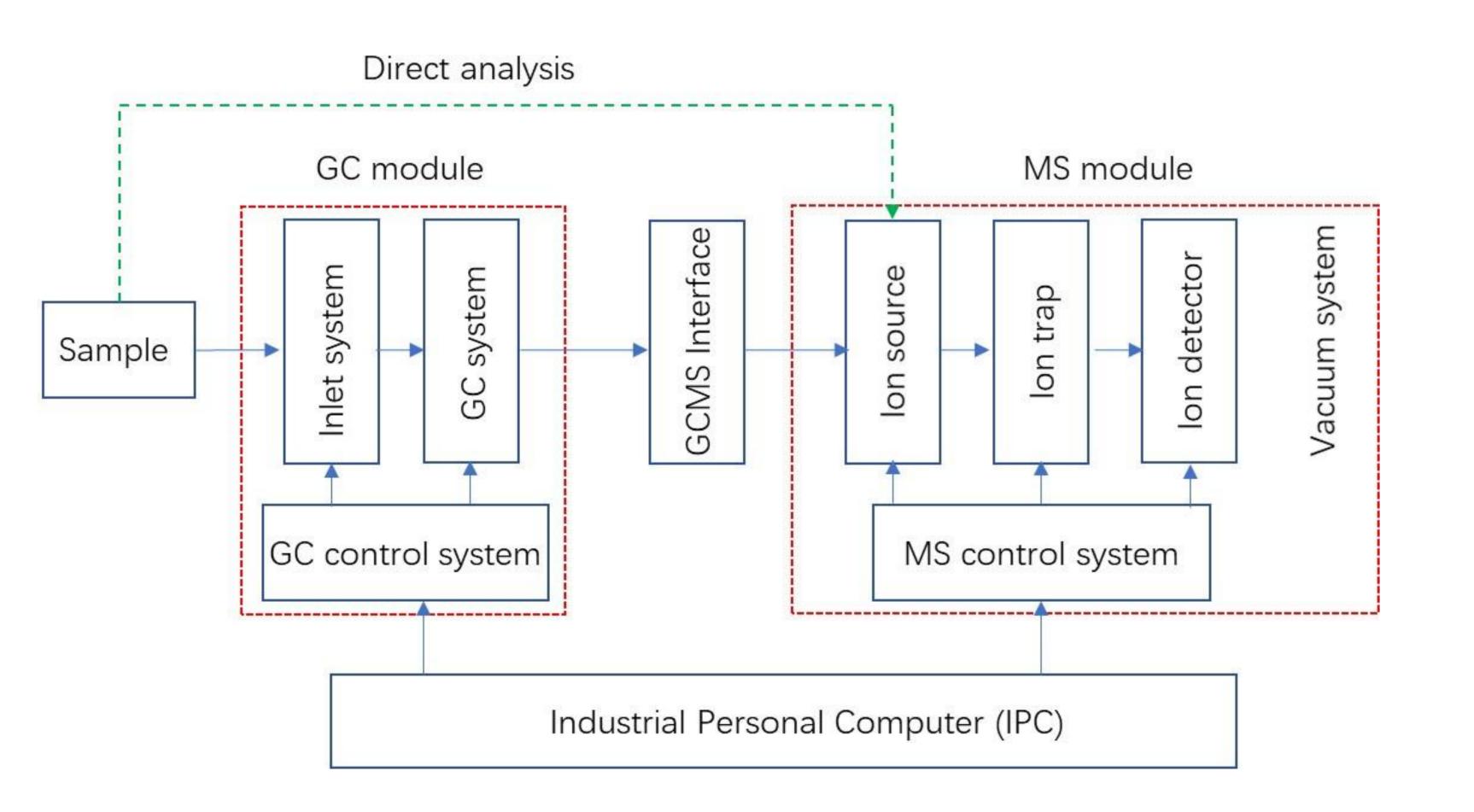
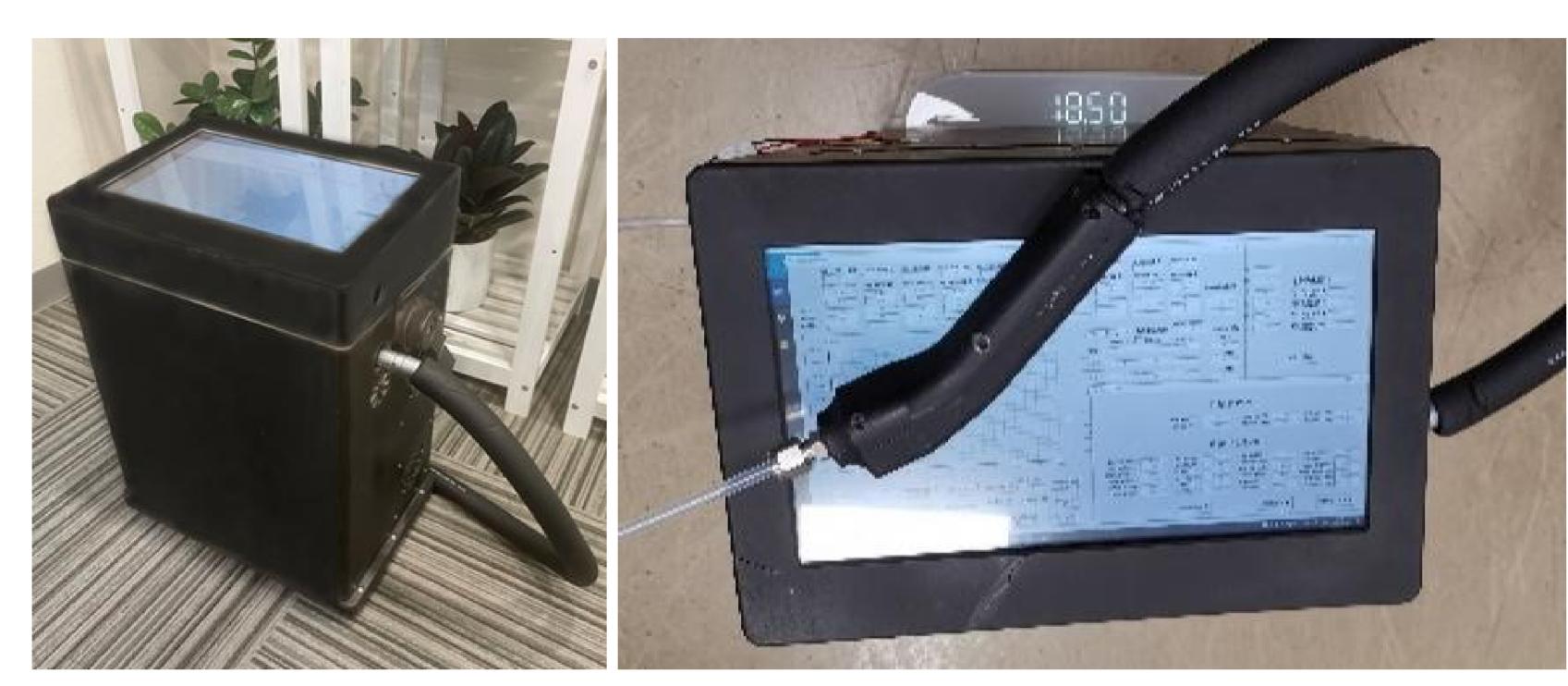


Figure 1 The schematic diagram of portable GCMS.



The portable GCMS supports the modes of gas sampling and liquid injection. For gas sampling, there are modes for direct on-line analysis, high-concentration GC analysis and low-concentration GC analysis. The Liquid injection method was consistent with traditional GCMS.

In on-line analysis mode, gas sample will be directly introduced into MS. This mode was usually used to assess the approximate concentration of VOCs in environmental gas to provide a judgment basis for GC analysis. It is extremely responsive, usually in seconds.

In our system, we used 2 strategies (sample loop injection and post-enrichment injection) to deal with VOCs at different concentrations in gas sample. For high concentration GC analysis, a 100 μ L gas sample is introduced into the GC system through the sample loop, which is used to detect relatively high-concentration sample with good response. For low concentration GC analysis, VOCs in the gas samples collected within a certain time will be enriched in the self-made concentration tube and released into the GC system after rapid heating.

Figure 2 The appearance of portable GCMS

3. Methods

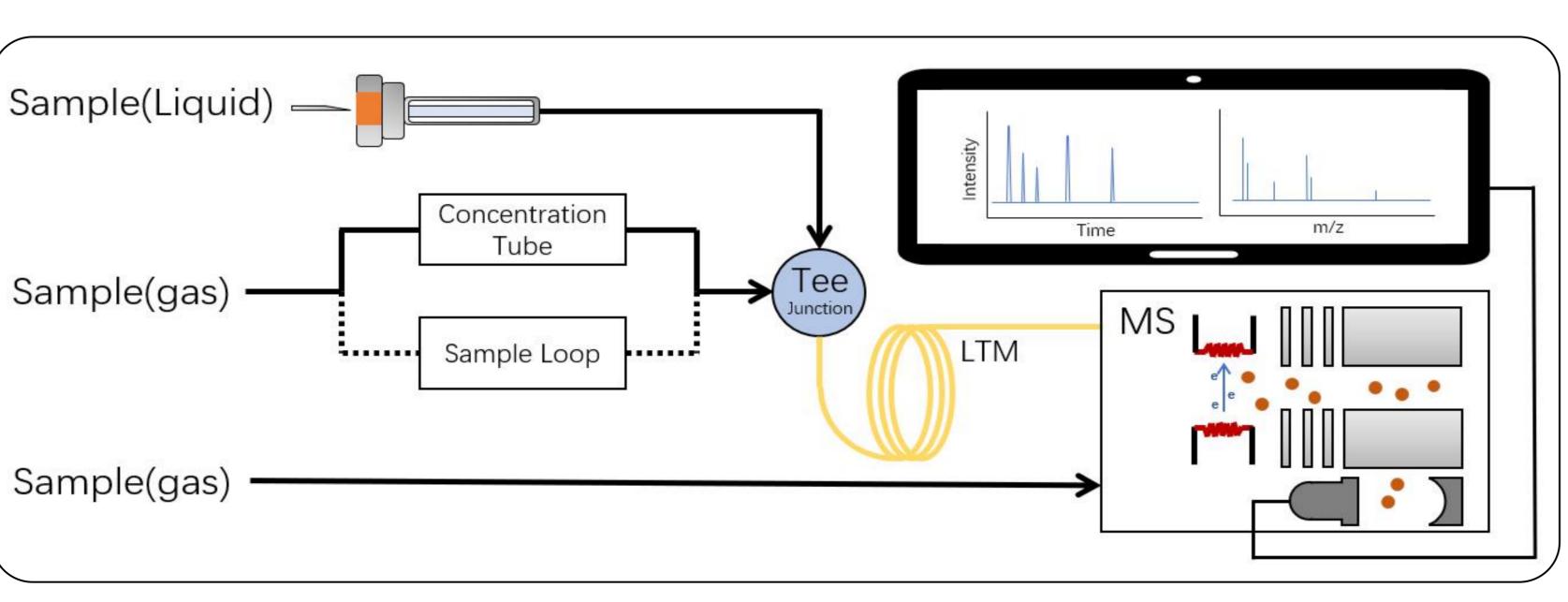
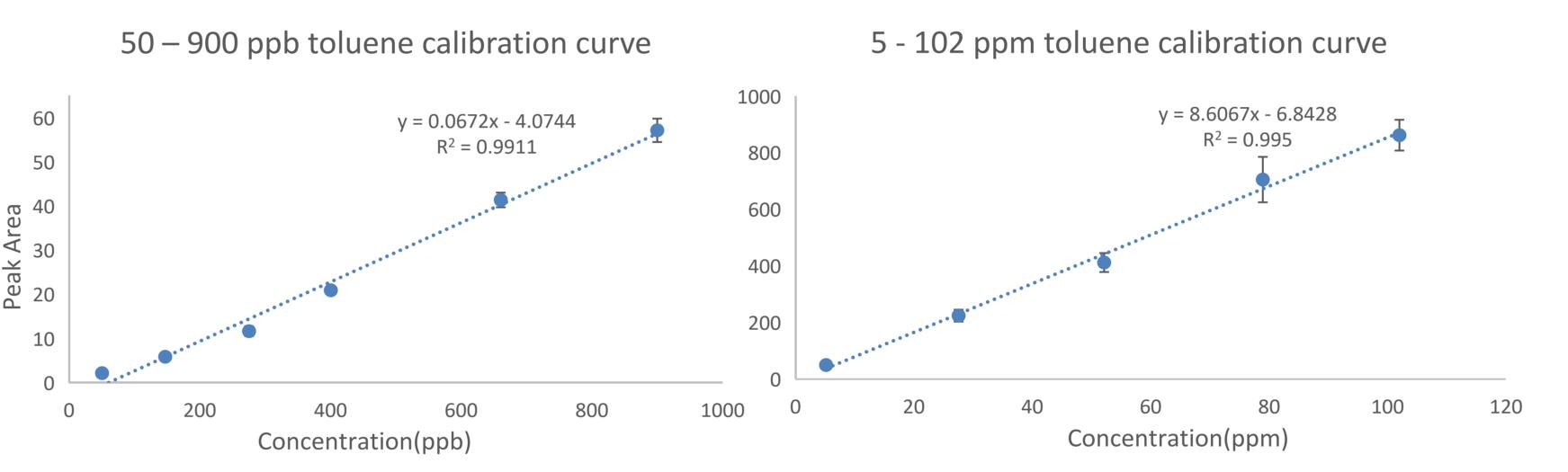


Figure 3 The schematic diagram of sampling mode

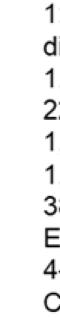
4. Results 4-1. High-concentration GC analysis

Toluene of different concentrations were used to assess quantitative ability (Figure 4). The RSD% of intraday and interday repeatability at different concentrations of toluene is less than 5 %.

1 ppm TO-15 (58 components) were used to assess GC separation (Figure 5). The RSD% of intraday and interday repeatability at 0.2 ppm TO-15 is basically less than 10 %.



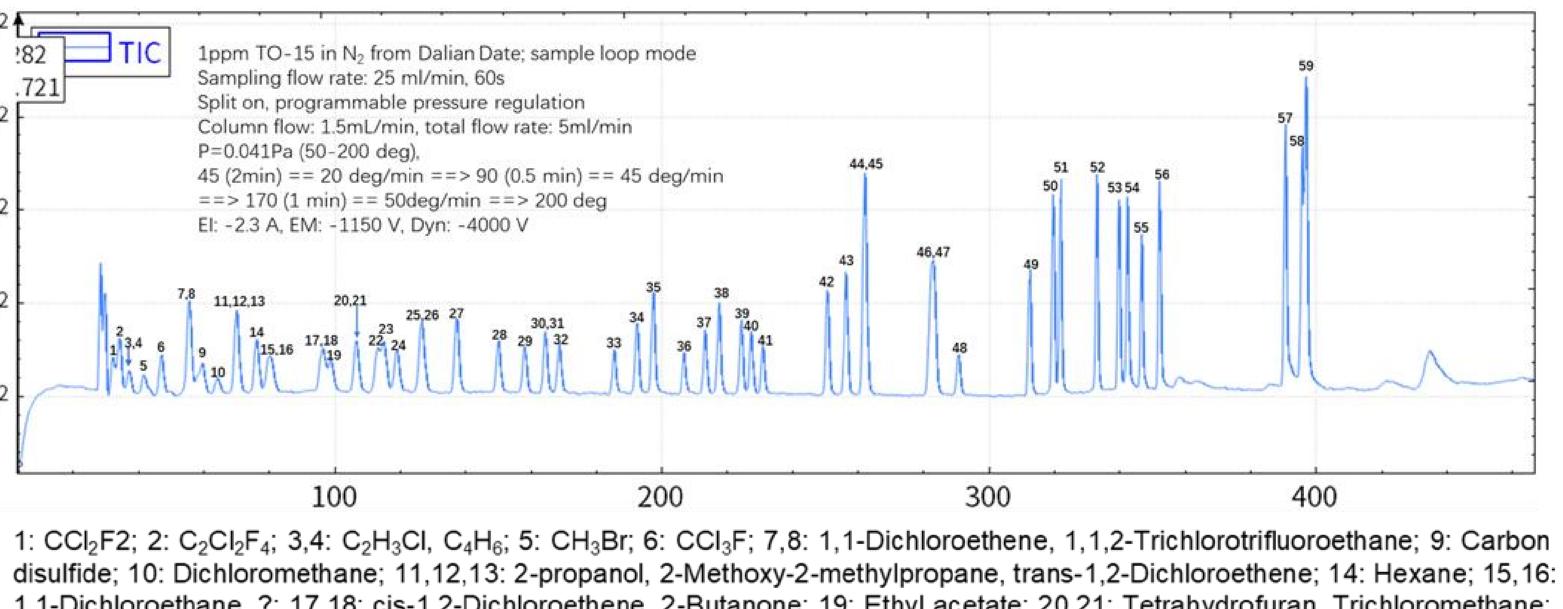
 3.5×10^{2} 3.0×10 2.5×10²





About 100 mL toluene of 0.04 - 4 ppb were used to assess quantitative ability. The RSD of 0.04 ppb toluene is less than 5 %(Figure 6). And the RSD% of intraday and interday repeatability at 0.102 ppb TO-15 is less than 8 %.

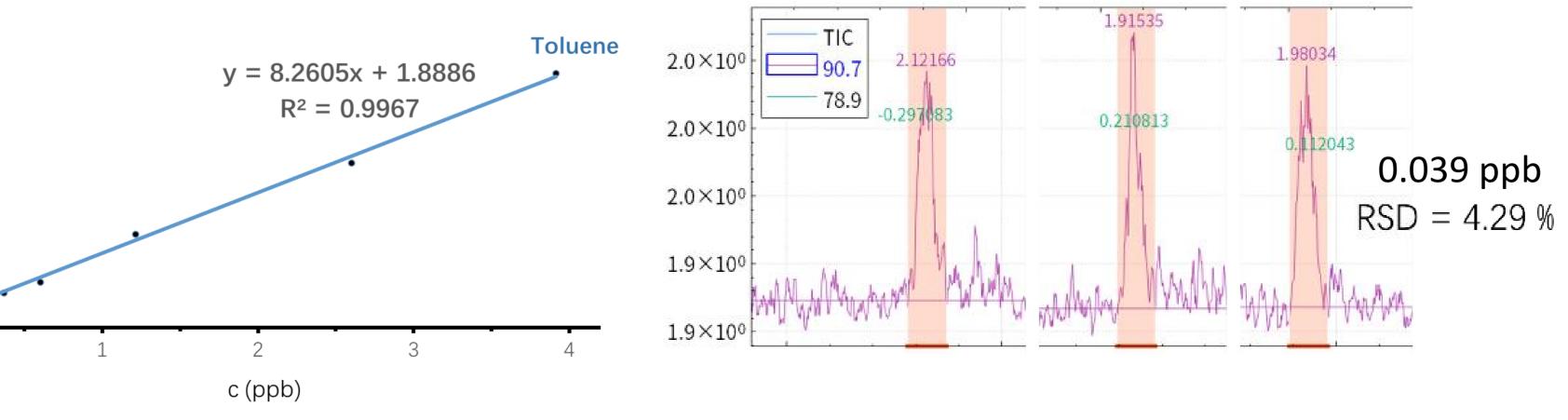
Figure 4 Linearity of toluene with concentration of 0.05-0.9 ppm and 5-102 ppm

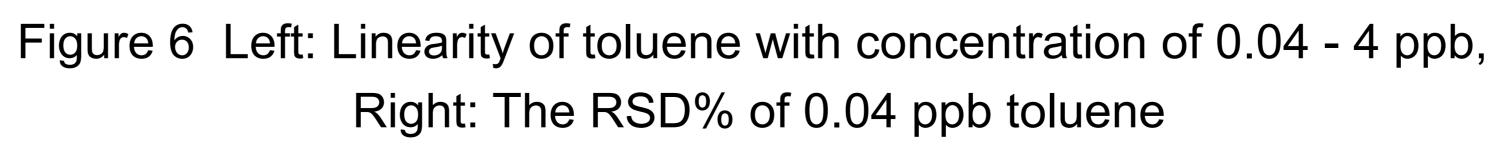


1.1-Dichloroethane, ?: 17,18: cis-1,2-Dichloroethene, 2-Butanone; 19: Ethyl acetate; 20,21: Tetrahydrofuran, Trichloromethane; 2: 1,1,1-Trichloroethane; 23: Cyclohexane; 24: Carbon tetrachloride; 25,26: Benzene, 1,2-Dichloroethane; 27: Heptane; 28 1,1,2-Trichloroethene; 29: 1,2-Dichloropropane; 30,31: 1,4-Dioxane, Methyl methacrylate; 32: Bromodichloromethane; 33: cis-34: 4-Methyl-2-pentanone; 35: Toluene; 36: Trans-1,3-Dichloropropene; 37: 1,1,2-Trichloroethane 38:Tetrachloroethene; 39: 2-Hexanone; 40: Dibromochloromethane; 41: 1,2-Dibromoethane; 42: Chlorobenzene; 43 Ethylbenzene; 44,45: m-Xylene, p-Xylene; 46,47: o-Xylene, Styrene; 48: Tribromomethane; 49: 1,2,2,2-Tetrachloroethane; 5 4-Ethyltoluene; 51: 1,3,5-Trimethylbenzene; 52: 1,2,4-Trimethylbenzene; 53: m-Dichlorobenzene; 54: p-Dichlorobenzene; 52: Chloromethylbenzene; 56: o-Dichlorobenzene; 57: 1,2,4-trichlorobenzene; 58: Hexachlorobutadiene; 59: Naphthalene

Figure 5 Separation of TO-15 sample (1 ppm in N_2)

4-2. Low-concentration GC analysis

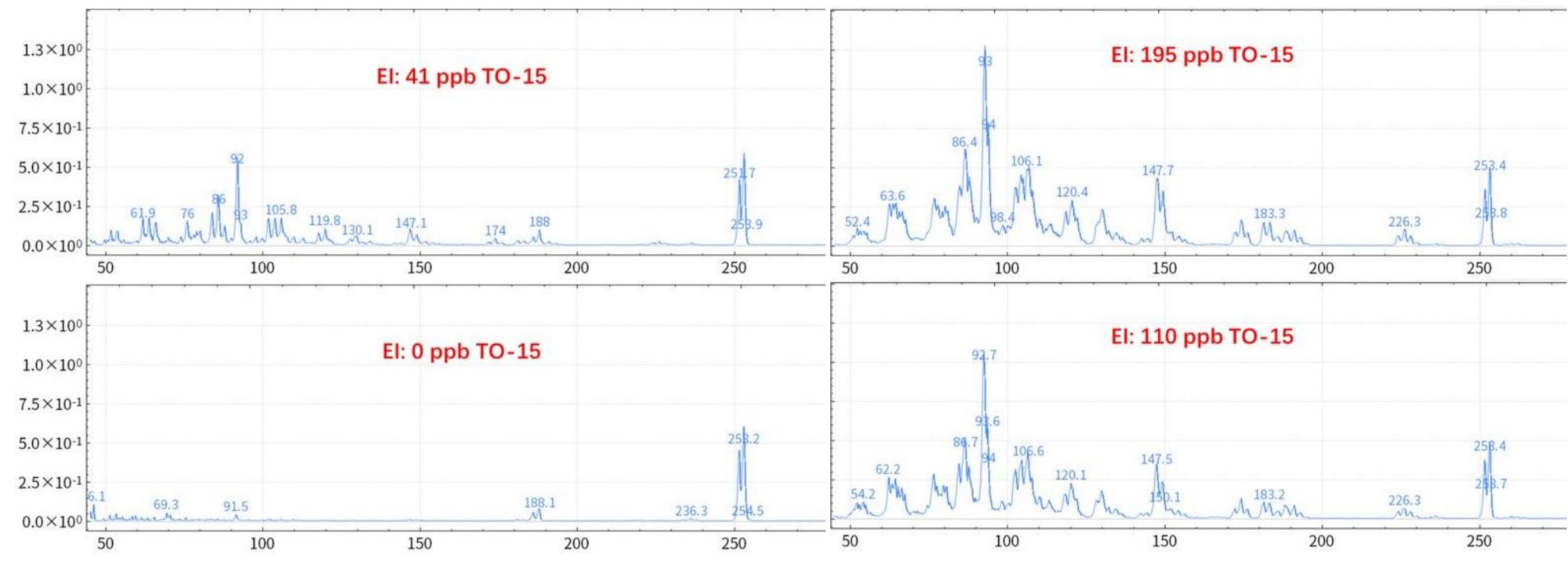




	†
2.1×10)2) .946
2.0×10)2
1.9×10)2
1.8×10)2
1.7×10)2
1.6×10	02
2.1×10)2) ;.11
2.0×10	

2.0×10 ²	
1.9×10 ²	
1.8×10 ²	
1.7×10 ²	
1.6×10^{2}	~





5. Conclusions A DLIT-based portable GCMS has been developed, exhibiting excellent sensitivity, repeatability and wide dynamic range. It is capable of effectively addressing diverse testing scenarios such as routine environmental monitoring, sudden leakage detection, illict drug screening, chemical weapon reagent detection and clinical breath analysis.



The authors wish to thank Shimadzu Cooperation for funding this project.

For low concentration of TO-15 (58 components), RSD% of repeatability of intraday and interday are basically less than 10 %. Figure 7 shows the separation of these low concentration TO-15 samples. The sampled volume of 5 ppb, 25 ppb and 45 ppb TO15 were all about 50 mL.

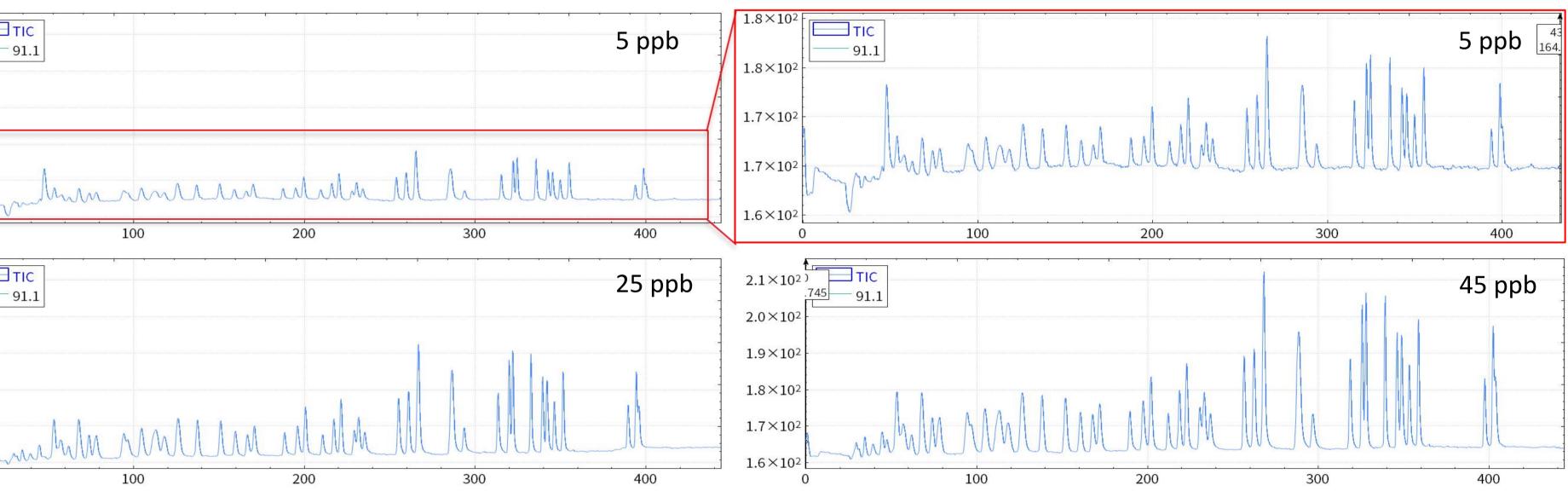


Figure 7 Separation of TO-15 diluted sample (with N_2)

4-3. Direct on-line analysis

In direct on-line analysis mode, the sample will be introduced to EI source. For the VOCs mixture, we tried direct injection of different concentrations of TO-15. For the mass spectra of different concentration of TO-15, the pattern of which are consistent (Figure 8). Although the multi-components and the overlapped fragmented species brought abundant ions, it also caused space charge effect of DLIT. Although this method still cannot accurately judge the concentration of VOCs in gas samples, this result can help identify the choice of chromatographic analysis modes.

Figure 8 Different concentrations of TO15 in directly on-line analysis

Acknowledgement