



ELSEVIER

Contents lists available at ScienceDirect

Talanta

journal homepage: [www.elsevier.com/locate/talanta](http://www.elsevier.com/locate/talanta)

# Integrated gas chromatography for ultrafast analysis of volatile organic compounds in air



Yanggang Zhang<sup>a,b</sup>, Dapeng Wu<sup>a,\*</sup>, Xiaohui Yan<sup>a</sup>, Kun Ding<sup>a</sup>, Yafeng Guan<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Separation Science for Analytical Chemistry of CAS, Department of Instrumentation & Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100039, PR China

## ARTICLE INFO

### Article history:

Received 31 December 2015

Received in revised form

31 March 2016

Accepted 3 April 2016

Available online 7 April 2016

### Keywords:

fast gas chromatography (fast GC)

volatile organic compounds (VOCs)

Thermal injection

cryogenic trapping

## ABSTRACT

An integrated instrumentation of a cryogenic microtrap-thermal desorption-low thermal mass (LTM) fast gas chromatographic (GC) system had been designed and evaluated for the ultrafast enrichment and separation of trace amounts of highly volatile organic compounds (VOCs) in air. The LTM fast GC column was wrapped uniformly on outer surface of a thin metal heating cylinder of 65 mm O.D. and 0.5 mm in thickness. Both of microtrap and LTM column could be rapidly cooled by liquid CO<sub>2</sub> down to −35 °C, and heated by resistive heating. A 10 m × 100 μm i.d. micro-bore capillary column was used in the LTM GC column module to provide a high separation speed. Key operational parameters, including adsorbent mass, trapping temperature, thermal desorption temperature and injection time were optimized. Under the optimized condition, the 39 species of TO-14 VOCs were well resolved and quantified in less than 3 min. The detection limits were in the range of 8 ppt–0.22 ppb at sampling volume of 50 mL and trapping temperature of −10 °C. The average peak width was 0.9 s, and the peak capacity of ~150 (at unit resolution) was obtained. The applicability of the setup was evaluated by analyzing three real environmental samples, where some typical VOCs at sub ppb level were detected.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Monitoring of volatile organic compounds (VOCs) in indoor air and atmosphere has received rising attention over the past decades both in China and global scales because of their important roles in atmospheric photochemical reactions [1,2] and toxic or mutagenic effect on human life and organisms [3,4]. Due to the atmospheric circulation and atmospheric chemical reaction, the local concentration and species of VOCs in air can fluctuate in both time and space. In addition, in order to investigate the air pollution state in a city or a region across hundreds of or even thousands of kilometers, an ultra-fast airborne or vehicle-mounted monitoring device for VOCs has to be carried out. In these cases, the total analysis time of VOCs has to be minimized to several minutes or even one minute, and the ultrafast analytical method and corresponding integrated device have to be developed.

Currently, there are at least four major challenges remained for ultrafast analysis of VOCs in air. 1) Sampling and preconcentration process. Standard methodologies, such as TO-14A [5], TO-15 [6], and TO-17 [7], have been developed by using cryogenic or

adsorbent-based focusing combined with GC-FID or GC-MS, their sampling time was usually 30–60 min, which is too long to provide real-time information of VOCs in air. 2) Sample capacity of separation column. Currently, the most widely employed techniques for ultrafast VOCs analysis is the fast GC, which is a compromise between resolution, sample capacity and speed. It is well known that the micro-bore column combined with resistive heating technique is a promising solution to provide a fast speed with high resolution [8]. However, the sample capacity was dramatically reduced by the cubic of the radius of the column, thus the limits of detection were highly restricted [9]. 3) Injection band broadening from the trap to the fast GC. Several techniques for producing narrow injection bandwidths has been developed, such as split injection at high split ratio [10], microloop system [11], high-speed diaphragm valves [12], dual diaphragm synchronized-injection valves systems [13]. Despite the narrow injection bandwidth as low as 20 ms or even 0.5 ms obtained, these methods all suffered from poor detection sensitivity because only a small portion of sample was transferred into the column. An adsorbent trap with cryogenic reinjection is an effective solution to inject total eluent with narrow bandwidth, which has been widely adopted in the literatures and commercial equipment [14,15]. The solvent vent injection mode of a programmable temperature vaporizer (PTV) was also used to provide rapid sample injection in splitless mode;

\* Corresponding authors.

E-mail address: [dpwu@dicp.ac.cn](mailto:dpwu@dicp.ac.cn) (D. Wu).

but the injection time was more than 5 min [16]. Recently, a thermal injection device with injection bandwidth of 10 ms was developed by cryogenic trap and ballistic heat analytes on the head of the metal capillary column [17,18]. However, the sample loadability was still limited due to the small volume of column head. 4) Fast separation. The use of cryogen can improve the separation of analytes with low retention factor [19,20]. Unfortunately, due to the large thermal mass of traditional oven, the consumption of the cryogen is relatively high, and the analysis cycle time also exceeded 30 min. With the development of resistive heating technology in GC, numerous designs of fast GC equipped with low thermal mass column has been reported [21,22] and some have been successfully commercialized [23]. It is very promising to apply the low thermal mass column to the low temperature fast GC, which will benefit both the cryogenic oven-trapping and rapid heating by resistive heating.

In this study, an ultrafast VOC analysis system by using cryogen both for preconcentration and fast temperature programming of separation column was developed. Thus light VOCs can be trapped in the cold microtrap and then quickly thermal desorbed to the cold head of the column, where they were rapidly separated by the resistively heated capillary column. The low initial temperature of the column not only narrowed the injection bandwidth but also increased the sample capacity of the analytes, especially the

volatile VOCs with poor retention in the column. In addition, the equilibration time for the column and the trap to return to initial temperature after analysis was also reduced dramatically due to low thermal mass, so it is possible to achieve near real-time analysis of the VOCs in the air.

## 2. Experimental

### 2.1. Materials and chemicals

Carbon molecular sieves Carboxen-569 (20/45 mesh, specific surface area: 485 m<sup>2</sup>/g) and graphitized carbon black Carboxen B (60/80 mesh, specific surface area: 100–200 m<sup>2</sup>/g) were used as adsorbent materials in this study. Both of them were purchased from Supelco Corporation (Bellefonte, PA, USA). The standard gas containing benzene, toluene and xylene (BTX) with concentration of 5 ppm ea in N<sub>2</sub> were supplied and certified by Dalian Specialty Gas Company (Dalian, China). The standard gaseous mixture containing 39 kinds of VOCs listed in EPA method TO-14 at concentration of 100 ppb ea in N<sub>2</sub> were purchased from Restek Corporation (Bellefonte, PA, USA).

Three environmental air samples, including air in our lab, outdoor air and air in an organic lab were analyzed by the device.

**Table 1**  
Method validation data of 39 species of standard VOCs by fast GC-FID.

peak order	Analytes	Retention time (min)	R <sup>2</sup> <sup>a</sup>	RSD <sup>b</sup> (%)	RSD <sup>c</sup> (%)	LOD <sup>d</sup> (ppbv)
1	Dichlorodifluoromethane	0.386	0.9788	1.5	7.4	0.20
2	Chloromethane	0.386	0.9788	1.5	7.4	0.20
3	Dichlorotetrafluoroethane	0.474	0.9948	2.0	2.6	0.09
4	Vinyl chloride	0.529	0.9759	1.3	8.1	0.19
5	Bromomethane	0.696	0.9903	5.4	7.1	0.06
6	Ethyl chloride	0.821	0.9764	5.6	6.5	0.19
7	Trichlorofluoromethane	0.843	0.9796	2.9	2.9	0.10
8	1,1,2-Trichlorotrifluoroethane	0.899	0.9980	6.8	6.5	0.08
9	1,1-Dichloroethene	0.965	0.9944	4.6	6.2	0.04
10	Dichloromethane	0.974	0.9858	3.4	3.6	0.19
11	Cis-1,2-Dichloroethene	1.013	0.9986	1.8	1.0	0.05
12	1,1-Dichloroethane	1.049	0.9988	1.9	1.5	0.05
13	1,1,1-Trichloroethane	1.124	0.9979	2.9	0.2	0.05
14	Carbon tetrachloride	1.124	0.9979	5.8	0.2	0.05
15	Chloroform	1.154	0.9985	1.5	1.2	0.15
16	Benzene	1.165	0.9983	1.5	1.1	0.02
17	1,2-Dichloroethane	1.209	0.9984	3.3	1.2	0.05
18	Trichloroethene	1.246	0.9982	2.7	0.8	0.05
19	1,2-Dichloropropane	1.274	0.9984	3.5	0.7	0.04
20	cis-1,3-Dichloropropene	1.331	0.9975	6.7	0.9	0.06
21	Toluene	1.415	0.9977	2.4	1.2	0.02
22	Tetrachloroethylene	1.43	0.9984	2.0	1.5	0.05
23	trans-1,3-Dichloropropene	1.475	0.9974	8.6	0.6	0.09
24	1,1,2-Trichloroethane	1.523	0.9982	1.9	1.3	0.06
25	1,2-Dibromoethane	1.588	0.9976	2.0	1.9	0.07
26	Chlorobenzene	1.619	0.9981	0.9	3.8	0.01
27	Ethyl benzene	1.619	0.9981	0.9	3.8	0.01
28	p-Xylene	1.631	0.9974	2.2	3.8	0.01
29	m-Xylene	1.631	0.9974	2.2	3.8	0.01
30	o-Xylene	1.691	0.9924	1.5	4.7	0.02
31	Styrene	1.704	0.9951	5.2	3.8	0.02
32	1,3,5-Trimethylbenzene	1.809	0.9925	7.5	4.1	0.02
33	1,1,2,2-Tetrachloroethane	1.833	0.9940	3.4	7.9	0.08
34	1,2,4-Trimethylbenzene	1.867	0.9954	3.3	6.5	0.02
35	m-Dichlorobenzene	1.929	0.9935	6.7	6.3	0.03
36	p-Dichlorobenzene	1.945	0.9708	5.5	4.5	0.03
37	o-Dichlorobenzene	2.013	0.9774	6.6	2.2	0.03
38	Hexachloro-1,3-butadiene	2.307	0.9935	4.2	5.1	0.24
39	1,2,4-Trichlorobenzene	2.331	0.9916	3.8	5.7	0.07

<sup>a</sup> Number of calibration, n = 5.

<sup>b</sup> Sampling volume of 10 mL.

<sup>c</sup> Sampling volume of 100 mL.

<sup>d</sup> LODs: limits of detection were calculated by S/N=3, based on the sampling volume of 50 mL.

Download English Version:

<https://daneshyari.com/en/article/7678196>

Download Persian Version:

<https://daneshyari.com/article/7678196>

[Daneshyari.com](https://daneshyari.com)