Establishment and Evaluation of a Method for Analyzing Atmospheric Volatile Organic Compounds

SUN Yang (孙 扬), WANG Yuesi* (王跃思), XIU Tianyang (修天阳),

WANG Yinghong (王迎红), and XU Xin (徐 新)

Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029

ABSTRACT

An automated cumulative sampling system and a method that combines a two-step cryo-concentrated system and gas chromatography/mass spectrometry (CCS-GC/MS) are introduced. The method is evaluated by a set of special experiments and the results are presented. The lowest measurement detection limit was expanded from 10^{-6} nmol mol^{-1} to 10^{-12} nmol mol^{-1} by using CCS-GC/MS instead of the simpler method of gas chromatography/mass spectrometry (GC/MS), with the average responsible factor of 39 object compounds being 2.9×10^{-12}. When the volume of air sample reached 1000 cm^3, the lowest detection limit reached up to 7×10^{-12}–40×10^{-12} nmol mol^{-1}. The CCS-GC/MS method can potentially identify all objective chemical species in an atmospheric sample, with an average 2.5 s bias error of retention time for 39 gas chromatography (GC) peaks. Within the range 0–400×10^{-9} nmol mol^{-1}, the concentration of 39 kinds of objective compounds can be individually calculated very accurately by a standard curve [average r^2 (coefficient of determination) value of above 0.99]. The recovery efficiency was 88%–111%, with an average of 100.8% ±5.6%. The bias error of precision was 2%–14%, with an average of 6.6%.

Key words: atmosphere, cryo-concentration, volatile organic compounds (VOCs), evaluation, bias error

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1. Introduction

Volatile Organic Compounds (VOCs) are the most important pollutants in the aerosphere. In the air, VOCs have a low concentration, but their reactions are strong and can seriously harm human health (Ivan and Sollars, 1998). With the exception of methane, the average volume concentration of VOCs in the atmosphere is generally lower than 1×10^{-9} nmol mol^{-1}, however for some components this figure may reach 100 nmol mol^{-1} or higher in seriously polluted areas, such as in big cities (Derek, 1996). As a VOC molecule generally includes a C-H chemical bond, it can easily react with OH free radicals and can be oxidated and degraded under light. Through complex atmospheric photochemical reactions in sunlight, the secondary pollutant ozone, produced in air, can be formed (Christebsen et al., 1999), and part of a VOC can be oxidated to aldehyde acid [RC(O) OO] compounds, which are harmful to human health (Christophe et al., 1998) RC(O) OO compounds can then further re-

act with inorganic oxides, such as NO$_x$, that originate from automobile exhaust fumes, as well as SO$_2$ from the burning of coal. This reaction can produce tiny particles, such as over-oxidation organic acid esters [RC(O)-OONO$_2$] and sulfonic organisms [RC(O) OOSO$_3$] (Wang et al., 2000). Not only are ozone and tiny particles the main air pollutants in most megacities at present, but they also directly and indirectly affect the balance of radiates in the atmosphere, which in turn will influence climate change (Seinfeld and Pandis, 1997). Through the increased exploitation of coal, oil and natural gas, emissions of VOCs into the aerosphere have multiplied, meaning the atmospheric degradation component has become more and more complex and the effect upon climate and the environment has gained in prominence (Wang et al., 2001) Therefore, effective and systemic monitoring and research of VOCs in the aerosphere is urgently needed (Chen et al., 2001). A number of recommended methods developed outside of China currently exist for analyzing and detecting VOCs, such as (from Amer-

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ica) the EPA TO-1, TO-2 and TO-14 (Environmental Protection Agency measure Method for Toxic Organic Compounds) methods (Wang et al., 1996), but there are three problems with using these methods in China:

(1) The apparatus required is very expensive and not easily obtainable.

(2) VOCs in different cities each have different characteristics, i.e., American and Chinese cities are not necessarily comparable.

(3) No existing approach is suitable as a practical and standard method for analyzing the effect that VOCs have on climate and the environment.

Since 1993, we have been making use of a two-step cryo-concentrated system to monitor and research various kinds of VOCs in the atmosphere of Beijing. A set of analytic methods for tracing VOCs in the atmosphere has gradually been established, and the system has also been used to monitor and study alkenes, alkanes, BTXEs, and CFCs in the atmosphere of Beijing. The results have been fruitful: see Chen et al. (2002), Xu et al. (2004), Xiu et al. (2005).

This paper expatiates the principle of the method and the instrumental structure. Performance of the method is evaluated through actual usage.

2. Instruments and methods

2.1 *Equipment*

The main part of the analytical system comprised a gas chromatogram (5890 II, HP, USA) and a mass spectrum system (5972, HP, USA). The automated sampling and concentrated injection system included a two way solenoid valve, a three way solenoid valve (VERSA, Holland), a six way solenoid valve (VICI, USA), and a dividing vapor pipe and air pump (Du Pont, GAST, USA). All the pressure adjective valves and flow adjective valves were made by NUPRO, USA.

2.2 *Automated cumulative sampling system*

To acquire accurate average concentrations of VOCs in the atmosphere over a period of time, a cumulative sampling system was adopted. Figure 1 shows the arrangement of the sampling system, and the basic principle is as follows:

A large capacity air flow pump (0.025 m^3 min^{-1}) took the air from outdoors, 32 m high (third storey of the 325-m weather tower of Beijing (39°58′27″N, 116°22′19″E), into a constant temperature gas mix chamber (Hong, 1983) in the lab. An indoors sampling pump then contained the air samples into steel bottles from the gas mix chamber one by one. Over a period of time, such as two hours, air samples were then cumulatively collected by a stable gas flow, and were considered as an even air mix sample of that place

at that time.

After washing the sampling airway and tube line, the electron flow adjustable valve was adjusted to the invariable sampling flow calculated according to the following formula:

$$F = \frac{p \times V}{T \times 60} , \qquad (1)$$

where F is the sampling flow (cm^3 min^{-1}) set through the flow controller, p is the ultimate pressure of the sampling steel bottle (kPa), V is the volume of the sampling steel bottle (cm^3), and T the time of collecting a single sample (h). This method collected a single sample in two hours, the ultimate pressure of the sampling steel bottle was 303.9 kPa, and the volume of the steel bottle was 1000 cm^3. According to the calculation, we collected samples with a flow of 25 cm^3 min^{-1} for two hours that made the ultimate pressure of the steel bottle 303.9 kPa.

2.3 *Two-step cryo-concentrated system*

Figure 2 shows a flow chart of the two-step cryo-concentrated system (CCS), and can be summarized as follows:

Air samples were collected by the automated cumulative sampling system and ducted into the CCS in turn. First, they were concentrated in a cold trap (Tr) to catch the VOCs, and the atmospheric main components, including N$_2$, O$_2$, Ar, and CO$_2$, were wiped off during this stage. Next, VOCs concentrated during the first step were ducted into a deep cold focusing adjoining port [cryo-focus intelligent interface (CFII)], where they were collected gradually in the thin top (5 cm in length) of the GC capillary column for further decreasing the dead volume of the system. The CFII was rapidly heated up to 220°C after completing the deep freezing, causing VOCs in the top of the GC capillary column to quickly boil away, after which they were pushed by a carrier gas (highly purified He) into the GC capillary column to be separated. The other end of the GC capillary column was connected to a mass spectrum detector (MSD). After separation by the GC, VOCs were pushed into the MSD.

The entire separation and detection process lasted 36 minutes. When one sample had been separated and detected, the next sample would begin. When running automatically, the system washes itself after analyzing a sample. One sample is collected and analyzed per hour and no personnel are required to tend to the system.

2.4 *GC/MS parameters*

2.4.1 *GC parameters*

A PONA (Polymethyl hydrosiloxane) GC capillary column was used in this method. The column
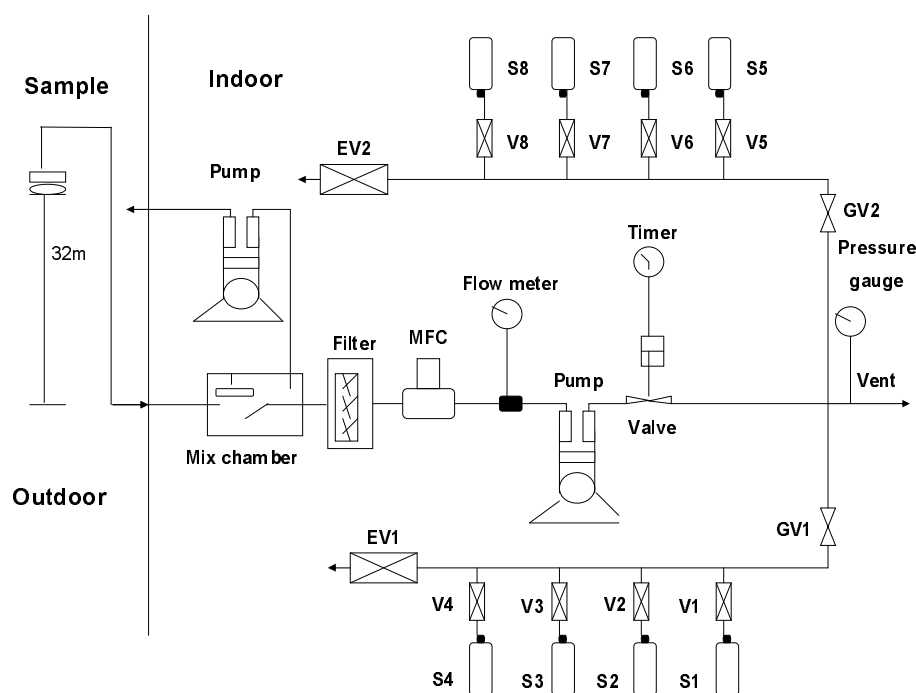
Fig. 1. Automated cumulative sampling system. V1−V8=switch solenoid valves of the bottle sampling; S1−S8=sampling bottles; GV1=first bench sampling solenoid valve; GV2=second bench sampling solenoid valve; EV1=first bench venting solenoid valve; EV2=second bench venting solenoid valve.

(50 m×0.2 mm×0.5 μm) is applicable to analyzing all kinds of non-polar or mildly polar VOCs. The carrier gas is highly purified He that is filtered by a HP-220 purification strainer produced by VICI (Valco Instruments Co. Inc.); the purity exceeds 99.9999%. The carrier gas linear velocity was established as 29 cm s^{-1}, the front press of the column was stabilized at 241 kPa (35 psi), and the carrier gas flow was roughly 1.4 cm^3 min^{-1} at 0°C and 0.7 cm^3 min^{-1} at 280°C. The GC column chamber was heated according to the following procedure:

First, the GC column chamber was kept for 1 min at 0°C (Liquid nitrogen is cooling), before being heated at a speed of 10°C min^{-1} to 100°C; second, it was kept for 1 min at 100°C min^{-1}, before being heated at a speed of 5°C min^{-1} to 150°C; and finally, it was heated at a speed of 12°C min^{-1} from 150°C to 280°C, before being kept for 1 min at 280°C. The procedure runs for around 34 min, and the targeted compound can be separated from other substances well. The MSD transmission line temperature was controlled by the GC and was generally established at 290°C.

2.4.2 *MSD (Mass Spectrometry Detect) parameters*

EI (Electron Impact) ionization, ionization energy was 70 eV, electric current emanation was 10–12 μA, and the ion source temperature was controlled at 180°C via a transmission line that diffused the heat. Adopting a full quantity range scan in this experiment, sweeping mass and scope was 35–250 (lu=1.66054×10^{-27} kg), and the RF (Radio Frequency) voltage was 1671 V after the highest sensibility tune value.

3. Application and evolution of the method

The CCS-GC/MS method has successfully been used in previous studies of Beijing atmospheric alkenes (Chen et al., 2002), BTXEs (Xu et al., 2004), chlorofluorocarbons (Xiu et al., 2005) and alkanes. also obtained some good results by using the CCS-GC/MS method to measure VOCs in the exhaust gas produced by burning coal (Luo et al., 2003).

3.1 *Qualitative analysis*

Through making use of the dual conditions of the standard mass spectrum database (NIST98) and the retention time of the standard component, VOCs were qualitatively analyzed.

First, a computer was used to search for the same charts as for the samples in the NIST98 database (about 130000 sheets of standard substances' mass spectrum charts): if the degree of matching was grea-

Table 1. Evaluation of qualitative and quantitative parameters, and detection method for the goal analysis compound.

Number of peak	Compound name	Characteristic ion (I+)	Molecular weight	Retention time (min) Mean (n=5)	Anomaly (±min)	Linear regression equation $y = ax + b$ $a \times 10^4$	$b \times 10^5$	r^2	Rf ($\times 10^{-12}$)	Recovery rate (%)	Applicable concentration scope ($\times 10^{-9}$)	Lowest detection limit ($\times 10^{-12}$)	Precision (n=5)
1	Froen-12	85,87	120	2.66	0.17	-	-	-	14.10	92	-	31	12%
2	Chloromethane	50,52	50	2.86	0.16	1.27	−1.87	0.993	5.33	93	0-400	21	4%
3	Froen-14	85,87	170	3.05	0.15	3.32	−0.65	0.993	1.64	103	0-400	9	13%
4	Vinyl chloride	62,64	62	3.16	0.15	1.19	−0.9	0.982	9.23	108	0-200	12	12%
5	Bromomethane	94,96	94	3.63	0.14	0.38	0.72	0.987	8.08	103	0-400	7	13%
6	Ethyl chloride	64,66	64	3.87	0.13	0.21	0.28	0.989	11.70	93	0-400	7	9%
7	Freon-11	101,103	136	4.73	0.10	2.73	2.39	0.998	1.76	94	0-400	8	1%
8	1,1-Dichloroethene	61,63	96	5.36	0.09	1.76	0.29	0.999	2.29	93	0-400	10	3%
9	Methylene chloride	49,51	84	5.52	0.08	1.08	1.19	0.99	2.50	96	0-400	8	3%
10	Froen-113	117,119	186	5.80	0.07	2.39	1.84	0.996	1.35	101	0-400	7	2%
11	1,1-Dichloroethane	63,65	98	6.56	0.06	2.29	−0.63	0.998	2.29	95	0-400	12	8%
12	1,2-Dichloroethane	61,63	96	7.31	0.05	1.76	−0.68	0.997	1.90	103	0-400	12	7%
13	Chlorform	83,85	118	7.56	0.04	2.55	−0.48	0.997	1.69	100	0-400	23	7%
14	1,2-Dichloroethane	62,64,49	98	8.18	0.03	1.77	−1.43	0.997	2.55	105	0-400	19	10%
15	1,1,1-Trichloroethane	97,99,61	132	8.39	0.03	2.5	1.95	0.994	1.39	98	0-400	7	11%
16	Benzene	78	78	8.78	0.03	4.01	−1.21	0.999	1.26	99	0-400	13	11%
17	Carbon thtrachloroide	117,119,121	152	8.91	0.03	2.53	1.26	0.992	1.48	97	0-400	15	14%
18	1,2-Dichloropropane	61,63,41,39	112	9.50	0.02	1.52	−0.4	0.999	1.67	103	0-400	21	3%
19	Trichloropropene	130,132,95	130	9.72	0.02	1.96	−2.38	0.995	1.12	103	0-400	31	3%
20	1,3-Dichloropropene	75,77,39	110	10.50	0.01	2.28	−3.51	0.993	2.24	111	0-400	40	3%
21	1,3-Dichloropropene	75,77,39	110	10.98	0.01	1.95	−4.58	0.985	3.26	110	0-400	40	4%
22	1,1,2-Trichloroethane	97,99,83	132	11.13	0.01	1.68	−2.83	0.994	1.26	104	0-400	34	3%
23	Toluene	91,92	92	11.40	0.01	5.14	−7.66	0.994	9.83	104	0-400	33	3%
24	1,2-Dibromoethane	107,109	186	12.06	0.01	2.67	−7.3	0.982	2.16	108	0-400	40	3%
25	Tetrachloroethene	129,131,133	164	12.60	0.01	1.93	−3.93	0.986	1.43	103	0-400	27	3%
26	Chlorobenzene	112,114,77	112	13.40	0.008	4.14	−1.17	0.981	1.04	105	0-400	24	4%
27	Ethylbenzene	91,105	106	13.91	0.007	6.92	−17.82	0.983	0.81	103	0-400	29	3%

Table 1. (Continued.)

Number of peak	Compound name	Characteristic ion (I+)	Molecular weight	Retention time (min)		Linear regression equation $y = ax + b$			Rf ($\times 10^{-12}$)	Recovery rate (%)	Applicable concentration scope ($\times 10^{-9}$)	Lowest detection limit ($\times 10^{-12}$)	Precision ($n = 5$)
				Mean ($n = 5$)	Anomaly ($\pm$min)	$a \times 10^4$	$b \times 10^5$	r^2					
28	Meta-xylenes	91,105	106	14.17	0.007	10.52	−28.73	0.983	0.44	107	0–400	30	4%
29	para-xylenes	91,105	106	14.17	0.007	10.52	−28.73	0.983	0.44	107	0–400	30	4%
30	Styrene	104,78	104	14.65	0.007	0.93 / 4.49	−0.29 / −24.00	0.987 / 0.993	1.04	106	0–70 / 50–400	40	5%
31	1,1,2,2-Tetrachloroethane	83,85	170	14.80	0.006	3.66	−17.64	0.994	0.51	106	50–400	40	5%
32	Ortho-xylene	91,105	106	14.88	0.007	5.37	−14.58	0.98	0.32	98	0–400	37	5%
33	1,3,5-Trimethylbenzene	105,120	120	17.03	0.006	7.08	−39.64	0.988	0.85	102	50–400	31	6%
34	1,2,4-Trimethylbenzene	105,120	120	17.81	0.006	0.86 / 6.91	−0.27 / −40.10	0.983 / 0.987	0.87	99	0–70 / 50–400	33	6%
35	1,3-Dichlorobenzene	146,148	146	18.04	0.004	0.3 / 4.58	−0.12 / −29.73	0.981 / 0.989	1.16	98	0–70 / 50–400	25	7%
36	1,4-Dichlorobenzene	146,148	146	18.19	0.005	0.31 / 4.35	−0.06 / −28.38	0.993 / 0.989	1.30	96	0–70 / 50–400	39	8%
37	1,2-Dichlorobenzene	146,148	146	18.9	0.004	0.32 / 4.05	−0.11 / −26.12	0.982 / 0.989	1.28	94	0–70 / 50–400	35	9%
38	1,2,4-Tichlorobenzene	180,182,145	180	23.29	0.002	0.16 / 1.49	−0.13 / −10.70	0.994 / 0.985	5.02	109	0–70 / 50–400	40	9%
39	Hexachlorobutadiene	190,192,188	225	24.57	0.002	1.22	−9.21	0.992	2.20	88	70–400	14	13%

Peak number as in Fig. 3. NO. 28 peak and NO. 29 peak were inseparable and treated as a kind of substance. Characteristic ion(+): 1–3 positive ions that had the largest abundance in the molecule fragmentations. Molecular weight: sum of the atomic weights of all the atoms in a molecule. Retention time (RT): The mean ($n = 5$) is the average RT value of five repetitions of parallel sampling; unit=minutes; the anomaly ($\pm$min) is the largest scope of the drift of RT. Linear regression equation is made according to mensurating the result of the 3–7 seriate concentration standard gas. Because the freon-12 (NO. 1 peak) is not an obvious linearity, the standard gas, which has a concentration similar to the air sample, was used to quantify this. The NO. 28 peak and NO. 29 peak were inseparable, and so the same standard curve was used to quantify these. The NO. 30 peak and NO. 39 peak had different linearity rules at $0-70 \times 10^{-9}$ and $70 \times 10^{-9} - 400 \times 10^{-9}$, and therefore two different standard curves were used. Applicable concentration scope ($\times 10^{-9}$): valid range of the linear regression equation.
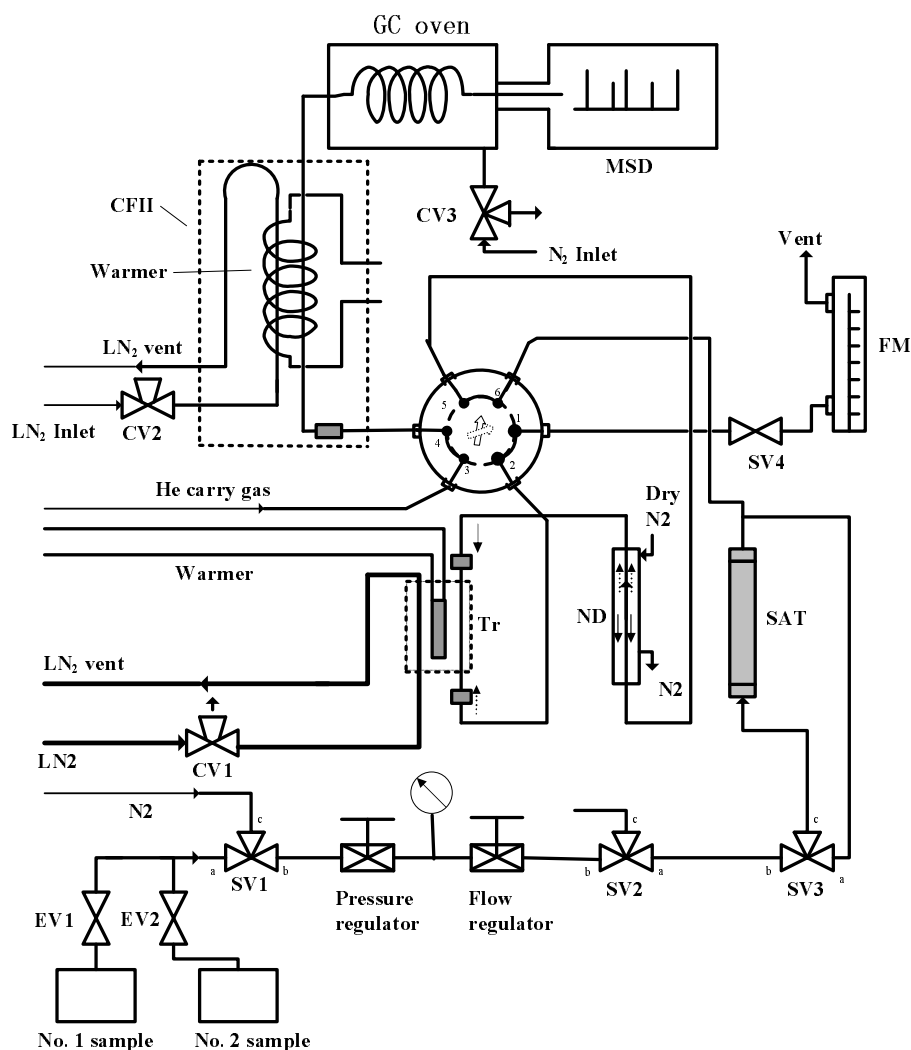
Fig. 2. Two-step cryo-concentration GC/MS system flow chart. CV=cryo-value; CV1−CV3=solenoid valves for control of liquid nitrogen; →=gas running direction; EV1−EV3 and SV1−SV4=three way solenoid valves; $b{\to}c$=often open; $b{\to}a$=often closed; CFII=cryo-focus intelligent interface; Tr=refrigeration trap; ND=diffuse dividing vapor pipe; GC oven=gas chromatogram column box; MSD=mass spectrum detector.

ter than 90%, the reliability of qualitative analysis was higher; and if the degree of matching was less than 60%, then the reliability was lower. Next, the retention times of the standard gas were compared with that of the air sample; because they come from the same experimental conditions, the contrast between the certain target components and the unknown components made the qualitative analysis more certain.

In this system, the degree of matching for spectrum charts was greater than 90% and the difference in the retention time was less than 30 s between the air sample and the standard gas. The accuracy rate of

qualitative analysis was close to 100%. Figure 3 shows a typical total ion current chart for the standard gas; the number of peaks in this chart correspond to the serial number in Table 1. Table 1 shows the name and qualitative parameters of the 39 kinds of compounds in the standard gas. Characteristically, one to three positive ions were in the largest abundance among the ion fragmentation peaks. The retention time is the average value when the measure of the standard gas was repeated five times. It can be seen that the entire target compounds were separated well from the chart.
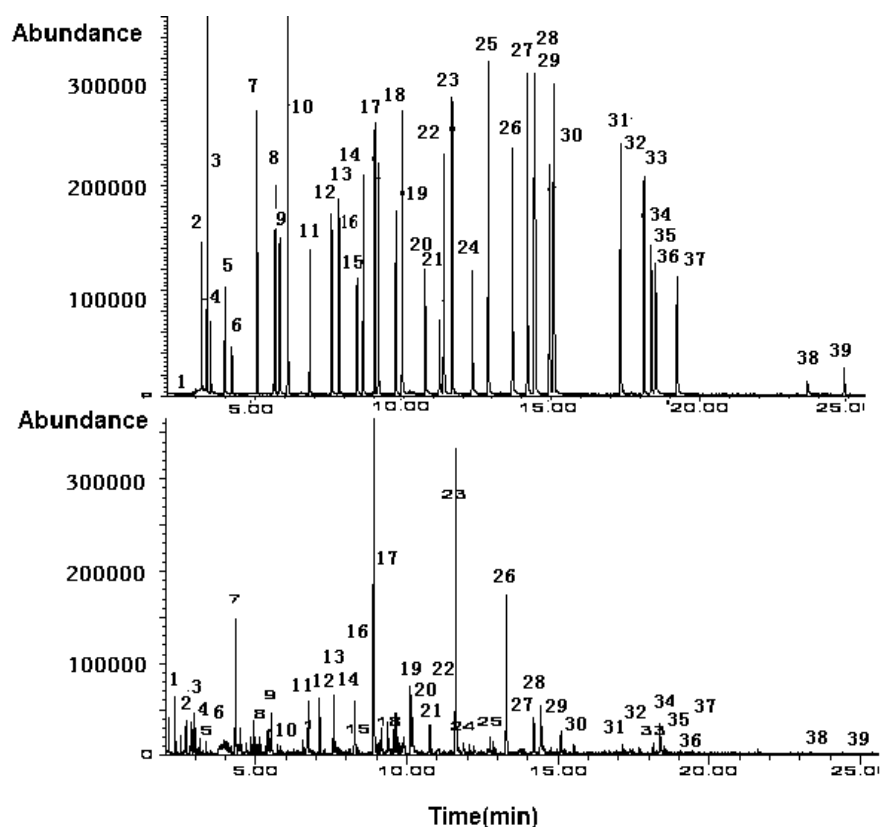
Fig. 3. Chromatogram of a sample of ambient air and standard gas

3.2 *Quantitative analysis*

Quantitative analysis of GC/MS usually adopts the internal standard calibration method or the outside standard calibration method. The internal standard calibration method is considered more accurate than the outside standard calibration method because the former is not affected by the drift error of apparatus or by small amounts of turbulence. However, in the system, the impurity of internal standard menstruum, or of other diluters usually affects analytical results. For this method to be used in analyzing trace VOCs in the atmosphere, there were some obvious interferences to the analytical results of a sample, due to the existence of certain impurities in the internal standard menstruum and diluters sold in the markets of Beijing. Therefore, the outside standard calibration method was adopted for quantitative analysis.

Using the TO–14 standard gas according to EPA criterion, we made use of static gas dilution to produce six different concentration levels. Respectively, their concentrations were $20 \times 10^{-9}, 50 \times 10^{-9}, 70 \times 10^{-9}, 100 \times 10^{-9}, 200 \times 10^{-9}$, and 400×10^{-9} nmol mol^{-1}; the dilutent gas was a highly purified nitrogen gas and its concentration was zero. The volume of standard gas sampling for each concentration was,

without exception, 1000 cm^3. The linear equation between the concentration value (y) and the response to signal (peak area x) can be expressed as $y = ax + b$; the value of "a", "b" and r^2 corresponding to each of the compounds listed in Table 1. The majority of compounds of the TO-14 standard gas had a linear response, or a linear response by stages, when their concentration was within 0–400×10^{-9} nmol mol^{-1}. Within the scope of suitable concentration, the concentration of the compounds can be calculated by putting the measured response peak area into the linear regression equation. The freon-12 showed a nonlinear response in this CCS-GC/MS system, so we had to use the single point outside standard calibration quantitative analysis method with a standard gas which has a concentration close to the samples in this system, or the other measurement methods developed by the authors (Sun et al., 2004). The concentration scope of trace VOCs is generally 0–100×10^{-9} nmol mol^{-1} in a polluted urban atmosphere; even in automobile exhaust emissions, single pollutant concentration will not be higher than 400×10^{-9} nmol mol^{-1}. Therefore, the calibration quantitative curve established by this method is basically applicable to the demands of daily monitoring.

3.3 *Everyday correction*

The method adopts a large sampling volume (1000 cm^3) and aims to measure a batch of samples as quickly as possible in order to reduce the determination error caused by the drifting of apparatus. In addition, for ensuring the usefulness of quantitative computing with the curve during operation, everyday—before the sample is analyzed—the curve was evaluated through comparing the calculated concentrations of the standard gas, which represents the middle concentration level in the curve. With the true concentration, if the scope of deviation between the calculated result and the true value was under 30%, the operating curve could be considered available; otherwise, the standard gas had to be mixed again. The following formula can be used for calculating the everyday percentage error:

$$D = \frac{\sum\limits_{i=1}^{n} [(C_i - C_s)/C_s]}{n} \times 100\% \qquad (2)$$

where D is the standard deviation, C_i the measured concentration of the target compound; C_s the concentration of standard gas, and n is the number of target compounds.

After completing five air sample measurements, a standard gas with a concentration close to that of the air sample was measured in order to continuously correct the operating curve.

3.4 *Method evaluation*

3.4.1 *Response factor(RF)*

As a measurement for system sensitivity, RF is the symbol of the concentration of the targeted compound that corresponds with a unit of integral peak area. If the RF value is low, this indicates a strong response of the system method to the targeted compound, and the system sensitivity is higher. Furthermore, any change made to the system, and the aging of parts, will make the RF change, meaning the RF values must be contrasted and the standard curve must be corrected for reducing error in the analytical data during long-term running.

The RF values of 39 kinds of target compounds (listed in Table 1) in this experiment system were analyzed. It can be seen that the CCS-GC/MS system responds to all targeted compounds very well, except freon-12 and ethyl-chloride.

3.4.2 *Recovery rate*

The recovery rate (R) is a measurement that indicates whether the targeted compounds have any loss, or whether pollutants remain in the system during the whole analytical treatment process. The recovery rates (R_{1000})—that is, the interrelated value between a 1000-cm^3 atmospheric sample and a 100-cm^3 TO-14 standard gas sample—are listed in Table 1.

The ideal recovery rate is 100%. If the recovery rate is less than 100% then that means the sample has had some losses during the inspissation process, and if the recovery rate is more than 100% then that means that the diluting gas contains few target compounds, or some previous samples from the last run remain in the system.

Table 1 shows that the R_{1000} values of 39 kinds of target compounds are mostly greater than 100%, with the average value being 100.8%±5.6%. This means that the amount lost and the amount remaining were basically equal during the CCS-GC/MS concentrating and analytical process, with a 1000-cm^3 sampling volume. The remaining amount of most target compounds was slightly more than those lost.

3.4.3 *Lowest detection limit*

The lowest detection limit represents the lowest concentration that can be measured by the system. The method for ascertaining the lowest detection limit was to measure a standard gas sample five times which had a concentration close to the detection limit. Analyzing the results, and calculating the standard deviation of five results, the lowest detection limit was three times the standard deviation value. Measuring and calculating according to this method, the lowest detection limit of the CCS-GC/MS system for 39 kinds of VOCs was very low with a 1000-cm^3 sampling volume. The values range from 7×10^{-12}–40×10^{-12} (see Table 1).

3.4.4 *Precision*

The system precision represents directly the magnitude of stochastic error of the analytical method. Table 1 lists the precision values of 39 kinds of targeted compounds obtained after five continuous experiment repetitions. As can be seen from this data, the design target of this experiment was achieved so far as the majority of precision values were less than 15%, apart from those of some volatile chloro-fluorocarbons, and benzene, which were more than those of others compounds in the atmosphere.

4. **Conclusions**

(1) This system adopts cumulative automated equipment for sampling and injecting samples. It can avoid importing individual error that may occur during operation and eliminates the instantaneous concentration diversification caused by weather conditions. It also makes samples more uniform and more representative.

(2) The two-step cryo-concentration sampling system that was designed and produced independently by current authors was used to measure atmospheric samples. It allowed the sampling volume of the GC/MS to increase greatly and the sensibility to increase 106 times than before. All parts of the sampling system modularized in design, which is beneficial to the popularization or commercial production of the system.

(3) The test data of the system, which indicated the sensibility, the recovery rate, the linear scope, the detection limit, and the precision of the CCS-GC/MS system was excellent. It was competent for observation of atmospheric trace VOCs, and was accurate in terms of qualitative and quantitative analysis. The system is operated completely automatically.

(4) The system is widely applicable and has a better response to most organic pollutants in the city. Because the adopted calibration method is recognized internationally, it is widely comparable. The system is applicable to the continuous monitoring of atmospheric trace VOCs in an urban area or in a regional atmospheric background observation station.

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