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A novel analytical method to detect Ozone depleting substances and Fluorine-containing greenhouse gases in the atmosphere

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Abstract: Fluorine-containing greenhouse gases (F-GHGs) and ozone layer substances (ODS) are being monitored without a global commercial monitoring system. In this study, the existing commercial volatile organic compounds (VOCs) monitoring system is modified in hardware and optimized in methodology to provide high-precision monitoring of 33 types of ODS and F-GHGs in the atmosphere. Moreover, the system eliminates the issue of excessive costs and lengthy development cycles associated with special monitoring equipment. Pre-concentration can enhance the enrichment of low boiling point and low concentration components by increasing the injection volume, improving water removal efficiency, and improving adsorption capacity. It is significant to be noted that InertCap 624MS is a one-dimensional column, while GASPRO is a two-dimensional column. It is possible to separate 33 target compounds completely and stably by Heart-cut and TwinLine using dual-column separation and single-detector detection mode. Experimental findings indicate that this monitoring technology has an accuracy of 0.22~3.70%. To accurately observe the changing trend of atmospheric concentration and trace the emission sources over time, a background gas with a known concentration has been used as a standard gas, and background atmospheric samples with unknown concentrations have been quantitatively tested using a single-point external standard method.

Key words: Ozone depleting substances (ODS), Fluorine-containing greenhouse gases (F-GHGs), High-precision monitoring, atmospheric concentration, Emission sources.

1. Introduction

Ozone-depleting substances (ODS) are Ozone-depleting substances are halohydrocarbons produced by human activities that eventually reach the stratosphere and deplete the ozone layer in the atmosphere, causing more ultraviolet radiation to enter the surface biosphere. It has caused widespread concern worldwide since its discovery in the last century (Mario et al., 1975; https://www.britannica.com/science/chlorofluorocarbon, last access: 24 January 2022). It is important to be noted that the Montreal Protocol on ozone-depleting substances successively listed several controlled substances, including chlorofluorocarbons (CFCs), halon, carbon tetrachloride (CTC), methyl bromide (MBr), methyl chloroform (TCA) and hydrochlorofluorocarbons (HCFCs) (https://wenku.so.com/d/f20335e47249c091758302e0db937fdb, last access: 24 January 2022). Alternative products to reduce ODS emissions, such as HFCs, have a second-rank role in the depletion of the ozone layer (https://csl.noaa.gov/assessments/ozone/2014/summary/ch3.html, last access: 24 January 2022), but have thousands of times higher global warming potential (GWP) than CO_2. Therefore, the continuous production and use of HFCs will have a profound greenhouse effect (Stanley et al., 2020). The Kigali Amendment (2016) and Kyoto Protocol (1998) implementation traces greenhouse gases such as perfluorocarbons (PFCs), sulfur hexafluoride, and HFCs, along with ODS, has attracted worldwide attention.

The elimination process and emission assessment of ODS and trace fluorine-containing greenhouse gases (F-GHGs) require accurate concentration monitoring. Using a "top-down" model to simulate emissions based on global observing network data, a 1-2 pmol/mol change in global concentration could calculate millions of tons of illegal ODS emissions (Montzka et al., 2018; Rigby et al., 2019; Fang et al., 2019). The concentration of these substances in the global background atmosphere is about 0.4-500 pmol/mol (http://agage.mit.edu/, last access: 24 January 2022). Therefore, these substances' monitoring technology requires high sensitivity, a large concentration range span, and high detection accurcy.

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The Advanced Global Atmospheric Gas Experiment (AGAGE) Network is the world's most advanced, systematic and contributing observation network for monitoring hydrochlorofluorocarbons using gas chromatography-mass spectrometry (GC-MS) (Prinn et al., 2000; Miller et al., 2008; Montzka et al., 2021; Say et al., 2021).At the same time, they have also been observed in the United States by the NOAA Global Observation Program (NOAA-GMD), the European Caribic Project, and observations organized by scientific research institutions in Japan and other countries (Yokouchi et al., 2006; Maione et al., 2013). Without exception, all the instruments used in the monitoring network are self-integrated, and there is non-commercial equipment. Moreover, the establishment and development of the instrument require high-Tech, time-consuming, and expensive equipment, which is unsuitable for large-scale popularization and use. Especially in developing countries, which are the critical control targets of ODS and F-GHG emissions, it is urgent to introduce monitoring technology for supervision.

This paper aims to establish a high-precision monitoring technology for ODS and F-GHGs that is easy to implement and to promote the its use based on the above monitoring requirements and instrument status. To improve instrument performance, a commercial ambient air volatile organic compounds (VOCs) monitoring system was used (HJ 759-2015, 2015; Zhang et al., 2019; Huang et al., 2021). A comparative test monitoring requirement for VOCs, ODS and F-GHGs is shown in Table 1. It is necessary to increase the system's sensitivity by 10^3 times to detect the background atmospheric concentration. For this purpose, it is possible to increase the sample's volume and enrichment efficiency and the detection's sensitivity. Additionally, the instrument must be improved in terms of its monitoring accuracy. This test's relative standard deviation (RSD) is less than or equal to 5%, ensuring the stability of the injection-dewatering-enrichment-separation-detection cycle At the same time, the monitoring accuracy of the instrument is also required to be higher. In this way, background atmospheric concentrations could be more monitored accurately.

Table 1

Comparison of test requirement

	VOCs	ODS and F-GHGs
Target compounds	Alkane, Alkene, Aldehydes and Ketones, Haloalkane , Benzenes,etc	Haloalkane
Sample concentration level	10^{-9} mol/mol	10^{-12} mol/mol
Accuracy	≤30%	≤5%
Quantitative method	Internal standard	External standard

2. Experiments

2.1 Compounds

The target compounds are summarized in Table 2, including 14 kinds of ODS, 12 kinds of F-GHGs, and 7 kinds of other halogenated hydrocarbons.

Table 2

Information on Target Compounds

	Chemical Name
ODS (14)	Trichloromonofluoromethane (CFC-11), Dichlorodifluoromethane (CFC-12), Trichlorotrifluoromethane (CFC-13), 1,1,2-Trifluorofloroethane (CFC-113), 1,2-Dichlorotetrafluoroethane (CFC-114), Pentfluorofluoroethane (CFC-115), Dichlorodifluorbroomethane (H-1211), 1,2-Dibromotetrafluoroethane (H-2402), Trifluorofromomethane (H-1301), Bromomethane (CH_3Br), Dichlorodifluoromethane (HCFC-22), 1-Fluorine-1,1-Dichloroethane (HCFC-141b), 1-Chlorine-1,1-Difluoroethane (HCFC-142b), , Carbon tetrachloride (CCl_4)
F-GHGs (12)	Trifluoromethane (HFC-23), Difluoromethane (HFC-32), Pentafluoroethane (HFC-125), 1,1,1-Trifluoroet-hane (HFC-143a), 1,1,1,2-Tetrafluoroethane (HFC-134a), Pentafluoropropane (HFC-245fa), 1,1-Difluoro-ethane (HFC-152a), Sevofopropane (HFC-227ea), Pentaflubutane (HFC-365mfc), Hexafluoroethane (PFC-116), Octafluoropropane (PFC-218), Sulfur hexafluoride (SF_6）
other	Iodiomethane (CH_3I), Chloromethane (CH_3Cl), Dichloromethane (CH_2Cl_2), Trichloromethane ($CHCl_3$), 1,1,1-Trichloroethane

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	Chemical Name
halogenated hydrocarbons (7)	($C_2H_3Cl_3$), Tetracloroethylene (PCE), Trichloroethylene (TCE)

2.2 Instruments

ODS and F-GHGs monitoring system is shown in Fig. 1. The part of the dotted line is the hardware modification of the system.

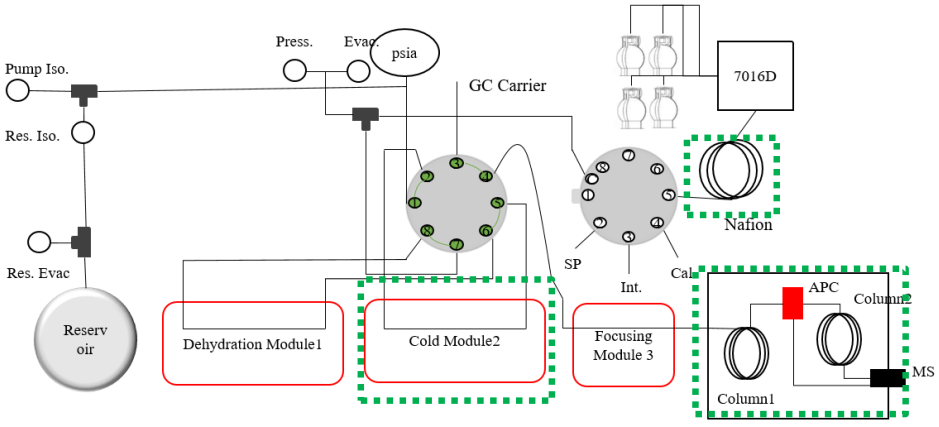

Fig. 1. Flow chart of the monitoring system. The pre-concentration system adopts differential pressure when sampling, firstly the system is pumped to vacuum, after the sample passes through the automatic sampler, water is removed by Nafion, followed by M1 for secondary water removal, M2 for enrichment, M3 for freezing focusing, and finally quickly heated M3 for GC by double column separation, and finally detected by MS.

2.2.1 Pre-concentration System

ENTECH 7200 atmospheric preconcentration sample injection system (ENTECH, USA). It adopts the traditional liquid nitrogen three-stage refrigeration technology to realize the analysis of trace VOCs in the atmosphere (Li et al., 2020; Zhang et al., 2019; Du et al., 2021).

(1) Double dehydration

The initial pre-concentration system used the temperature difference method to remove the water from the sample since the test method contains polar compounds such as OVOCs. Most of the water can be removed, but several factors, such as the accuracy of the temperature control and the difference of samples' humidity, make it impossible to remove completely. The presence of water could affect the system's stability to a certain extent. The test results (Fig. 2) show that ODS and F-GHGS do not meet the requirements for high-precision testing. As described in the Medusa monitoring system method from AGAGE (Miller et al., 2008), the Nafion unit was added before the pre-concentrator sampling was conducted to remove water from the sample. Nafion removes water from the gas by membrane exchange. As a result of two dehydration procedures, the sample's water content was further reduced, and the detection accuracy was increased to 0.97 ~ 7.17%. PFC-218, for example, increased from 17.16% to 5.36%, HFC-227ea increased from 14.32% to 3.41%. The double dehydration method significantly improves the accuracy of the test. To further increase their sensitivity, it is necessary to improve the adsorption efficiency of low-concentration components, such as Halon-2402.

(2) Optimize trap conditions

The enrichment of samples and the elimination of interfering impurities in the pre-concentration process are critical factors in improving the analysis sensitivity. Low temperature assisted absorbents were used to concentrate the sample, as the

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enrichment temperature and the choice of adsorbent were crucial elements of the research.

Tenax TA single filler for VOCs analysis: Tenax TA has weak adsorption capacity for ODS and F-GHGs. Compounds such as hexafluoroethane and sulfur hexafluoride do not adsorb even at low temperatures and, therefore, cannot be detected and analyzed.

Tenax TA + Carbonex 1000, 1/8 tube of about 10 cm: Carbonex 1000 strong adsorbent was added to prepare a composite packing cold trap tube to improve the adsorption efficiency of the cold trap. When the adsorbent content is too high, the adsorption capacity is strong, and hexafluoroethane, sulfur hexafluoride, and other substances will decrease with the reduction of freezing temperature. Excessive adsorbents will absorb more impurities at low temperatures, resulting in considerable background interference of the detector and lifting of the baseline, thus affecting the sensitivity of system detection. The adsorption effect of this filler is the best at -20 ℃. Due to the limitation of the pre-concentration instrument, it cannot remove residual impurities through a back-purge. After long-term use, contaminants will accumulate more and more because of strong adsorption capacity and weak removal capacity, and background interference will gradually increase, which affects the test results.

Tenax TA + Carbonex 1000, 1/8 tubes of about 2-3 cm: Low-temperature enrichment is needed when a small amount of adsorbent is used. The best test effect is at -60 ℃, which can achieve the enrichment of target compounds. The enrichment effect of the temperature-assisted adsorbent was stable, and the test accuracy was further improved (Fig. 2.). RSD of 6 consecutive repetitive tests ranged from 0.22 to 3.70%, which could meet the requirements of high-precision detection of ODS and F-GHGS. In addition, the instrument's baking function can remove impurities due to its moderate adsorption capacity. This cold trap packing is conducive to detecting and analyzing long-time samples.

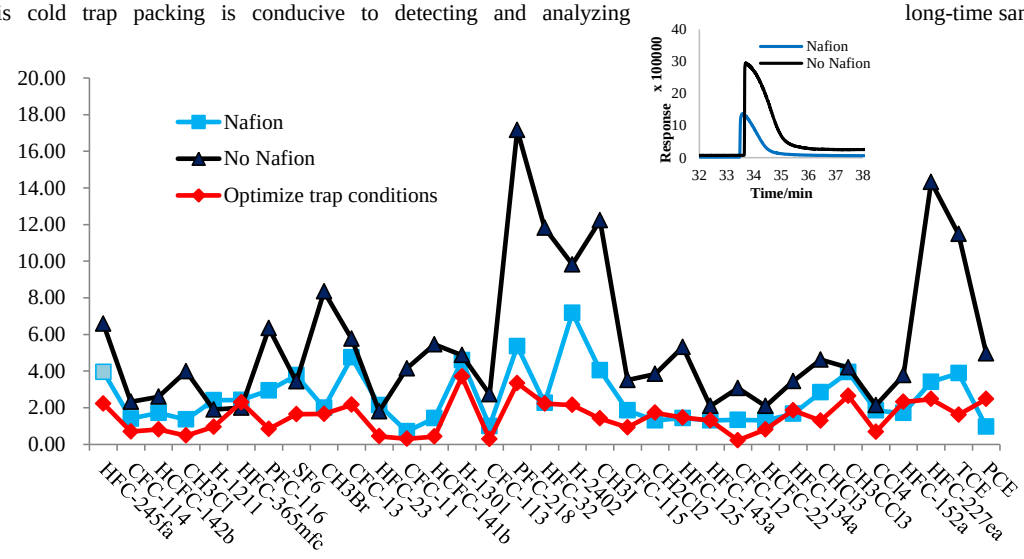

Fig. 2. RSD was obtained by 6 repeated measurements of an 800 mL background atmosphere sample to compare the stability improvement of pre-concentration. The diagram in the upper right shows the difference in water peak with and without Nafion.

The M1 and M2 cold trap enrichment temperatures were 60℃, and the flow rate was 60 mL/min. Then M1 was heated to 10℃ and transferred to M2 at 30 mL/min for 5min. The M2 enriched compounds were desorbed at 220℃, and M3 was focused at -180℃. Finally, M3 was heated at 80℃ for GCMS analysis.

2.2.2 Analytical Instrument

GC-MS QP2020, gas chromatography-single-quadrupole mass spectrometer, equipped with Heart-Cut system (SHIMADZU, Japan). It has a high-performance ion source and high-speed scanning control technology, and is equipped with a new ultra-efficient and large-capacity turbomolecular pump, which further improves the vacuuming rate of the system and enables large flow sampling. GC-MS can provide a mass scan range of mass charge ratio (M/Z) 1.5-1090 (Gong et al., 2021).

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Low boiling point compounds account for a large proportion of target compounds, and the separation of low boiling point compounds is challenging. The separation differences of three different chromatographic columns were compared in this study.

(1) PoraBOND (PLOT, porous layer open tube quartz capillary column)

PoraBOND: PLOT is mainly used to separate C1 ~ C3 substances; as the type of column currently used by international research institutions, it can separate ODS and F-GHGs at room temperature, which can withstand the repeated samples of water-containing samples and maintain a stable peak. However, after experiments, it is found that the peak tailing (Table 3) increases the difficulty of quantification, making the accuracy of test results difficult to control. It may take a lot of time to correct the data results.

(2) GASPRO (bonded silica gel capillary column)

GASPRO: Silica gel column has the advantage of a good separation effect of low boiling point compounds at room temperature and good peak shape, therefore, it is suitable for ODS and F-GHGs separation. However, the performance of the silica gel column is unstable. The actual sample testing may affect its surface acidity and alkalinity, which is not conducive to long-term monitoring. In addition, it was found that the peak sequence of different batches chromatographic columns may change, such as HFC-125, CFC-12 and HFC-143a; H-1211 and HFC-152a, the order of their peak will change. Meanwhile, when the sample volume or water content is high, the high boiling point group will have a bifurcation peak, and baseline uplift and noise will also increase (Table 3). The column is not suitable for testing components with high boiling points

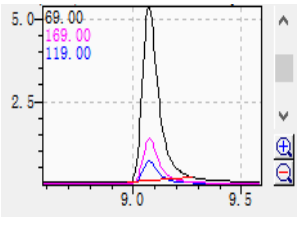
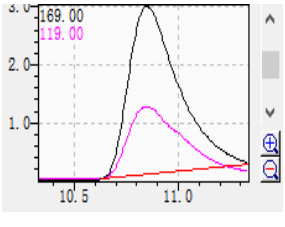
(3) InertCap 624MS (6% cyanopropylbenzene + 94% methylpolysiloxane, medium polar chromatcolumn)

InertCap 624MS: 624MS chromatographic column is a commonly used VOCs detection column with stable performance, low baseline noise, and sharp peak type. However, it was found that the low-boiling multi-component ODS and F-GHGs could not be separated at room temperature or under the condition of refrigeration in the column box. It can only separate the following substances with high boiling points.

We established a two-column single-detector GCMS method. Shimadzu GCMS-QP2020 is equipped with a dual-pump differential exhaust system and a dual-turbo molecular pump, which can maintain a high vacuum under the condition of large-flow sampling without losing the sensitivity of the instrument and can realize double-column injection. Combined with the characteristics of the various column, the separation effect of high boiling point components was the best for InertCap 624MS as a one-dimensional column, while the separation and peak effect of low boiling point components were the best for GASPRO. Firstly, the sample was separated by InertCap 624MS, and the low-boiling point components that could not be separated were cut into GASPRO by Heart-Cut for separation. Then the high-boiling point components were cut back to 624 for further separation. All separated compounds enter MS for detection by TwinLine (transfer nut+double-hole pressure ring) to realize a single detector with double-column analysis and ensure complete separation of 33 target compounds (Fig. 3).

Table 3

Comparison of chromatograms of individual compounds

	InertCap 624MS	GASPRO	PoraBOND
PFC-218	Unable to separate		

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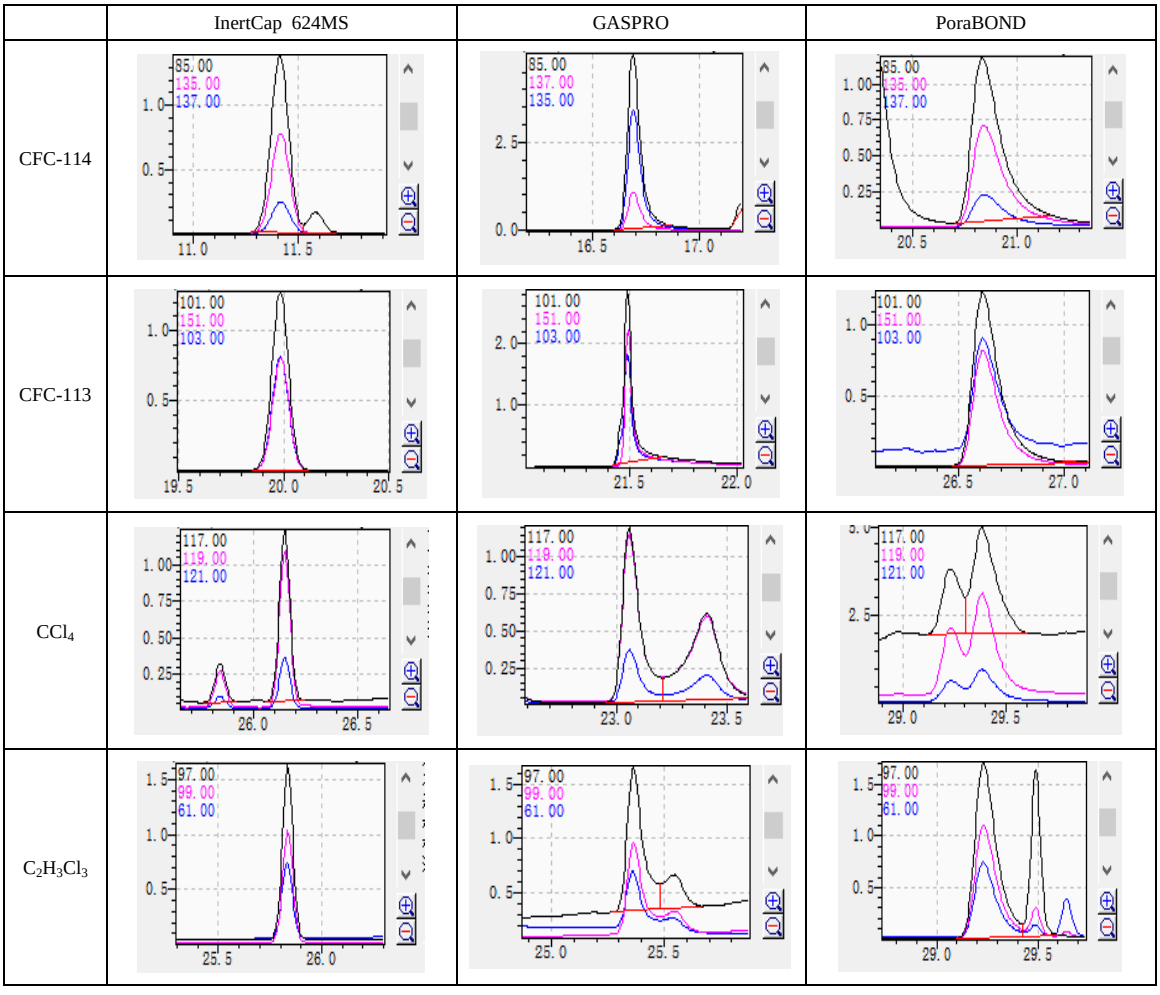

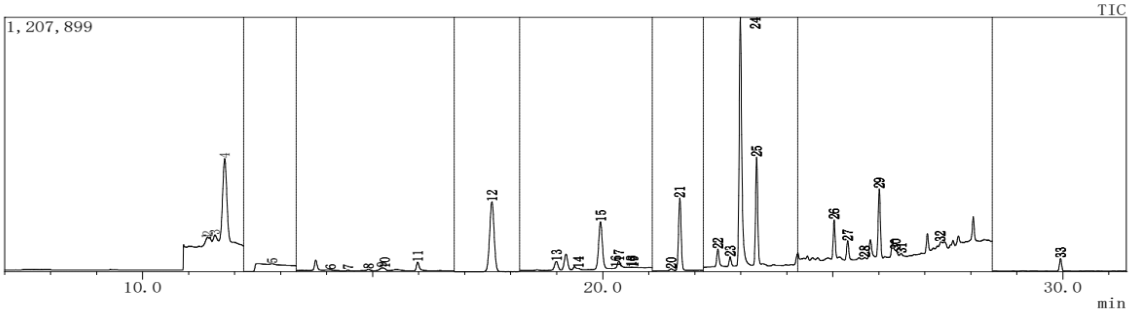

Fig. 3. TIC of target components in the background atmosphere for GCMS analysis. 1—HFC-245fa; 2—CFC-114; 3—HCFC-142b; 4—CH_3Cl; 5—H-1211; 6—HFC-365mfc; 7—PFC-116; 8—SF_6; 9—CH_3Br; 10—CFC-13; 11—HFC-23; 12—CFC-11; 13—HCFC-141b; 14—H-1301; 15—CFC-113; 16—PFC-218; 17—HFC-32; 18—H-2402; 19—CH_3I; 20—CFC-115; 21—CH_2Cl_2; 22—HFC-125; 23—HFC-143a; 24—CFC-12; 25—HCFC-22; 26—HFC-134a; 27—$CHCl_3$; 28—$C_2H_3Cl_3$; 29—CCl_4; 30—HFC-152a; 31—HFC-227ea; 32—TCE; 33—PCE.

The initial temperature of the tank was kept at 35℃ for 15 min, then heated to 50℃ at 5℃/min and 200℃ at 15℃/min for 4 minutes.The column flow rate was 2.36 mL/min. The APC can be used for column switching at 45 kpa. In terms of

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mass spectrometry, the ion source temperature was at 200℃, and the compounds were scanned by selecting ion scanning (SIM) mode.

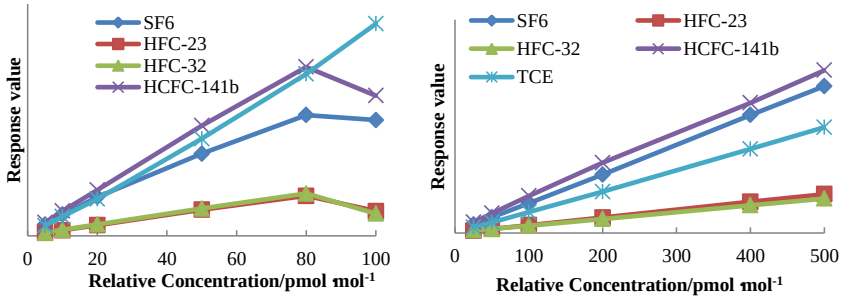
2.3 Standard gas and Sampling gas

A background atmosphere with known concentration was used as the standard gas. Standard gas samples were collected at Beijing Shangdianzi Background Station, with concentrations calibrated by the China Meteorological Administration (AGAGE monitoring network)..

The vacuum Summa tank was brought to the sampling point. The atmospheric sample was pressed into the Summa tank with a positive pressure sampler to prevent contamination caused by the leakage of the sampling tank. Several sampling were taken from various locations, including Changbai Mountain in Jilin, Mount Wuyi in Fujian, Hailuogou in Sichuan, and Wuzhishan Mountain in Hainan.

2.4 Injection volume of the experiment

Increasing sampling volume is the most direct method to improve instrument sensitivity. The VOCs monitoring adopts 400 mL as the sample volume with the injection rate is 60 mL/min. A study was conducted to determine the effect of increasing the sample size on the instrument. As can be seen from the test results (Fig. 4.), when the sample inlet volume was $\leqslant$ 800 mL, the linearity of the two concentrations was $\geqslant$ 0.99. When the sample volume reached 1000 mL, the response values of some compounds decreased, showing penetration of the adsorption tube. Fig. 4. (b) can prove that this phenomenon is not caused by the high concentration of the standard gas. The possible reason is that as the sample volume increases, the amount of impurities will also increase, which may lead to the reduction of the selective adsorption capacity of the cold trap and the loss of the enrichment of some target compounds. Therefore, the injection volume was increased from 400 to 800 mL to improve detection sensitivity and ensure accuracy.



(a) (b)

Fig. 4. Calibration curve of different volume injections of different concentration samples. (a) The test results of partial components of 100 pmol·mol^{-1} standard gas with 1000 mL as the injection standard. 50,100,200,500,800, and 1000 mL were extracted, and the corresponding relative concentrations were 5,10,20,50,80, and 100 pmol·mol^{-1}; (b) When the same component is 500 pmol·mol^{-1} at 800 mL, 40,80,160,320,640, and 800 mL were extracted, and then the corresponding relative concentrations were 25,50,100,200,400, and 500 pmol·mol^{-1}.

2.5 Quantitative method

According to the AGAGE network for ODS and greenhouse gases trace compounds quantification methods (Prinn et al., 2000). Using the sampling mode of "standard gas-sample 1 ⋯ sample *i*-standard gas", taking the average value of the response of the standard gas before and after and establishing a single-point external standard method for quantitative analysis to analyze the change of background atmospheric concentration. The calculation formula is as follows:

$$C_i = \frac{A_i}{\overline{A_{S1} + A_{S2}}} \times C_S$$

C_i——sample *i* concentration, pmol/mol;

A_i——sample *i* peak area;

$\overline{A_{S1} + A_{S2}}$——average peak area of standard gas before and after sampling;

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C_S——calibration concentration of standard gas, pmol/mol.

3. Results and discussion

3.1 Sensitivity and accuracy of the instrument

The monitoring technology uses a continuous injection of 1 pmol/mol sample 7 times over a period, and the detection limit of the calculation method used was 0.051–0.382 pmol/mol. A range of 0.41–531 pmol/mol was measured for 6 consecutive injections of 800 mL of the standard background atmosphere. The RSD of the response value has been estimated at a value as high as 0.22 ~ 3.70%.

Compared with other international monitoring, this method can achieve high-precision monitoring of 33 trace ODS and F-GHGs, mainly when the test stability of essential compounds is less than 1%, such as CFC-11 (Table 4). Despite this, there are still several ultra-low concentration components in the international monitoring network that are not within the scope of this method, and further research and discussions are needed in future research work.

Table 4

Comparison of test accuracy with international monitoring network

NO.	Industrial Name	In the method	Medusa	JESC	NO.	Industrial Name	In the method	Medusa	JESC
1	PFC-116	0.84%	3.0%	1%	28	HCFC-123	/	10.0%	1%
2	PFC-218	3.34%	6.0%	0.9%	29	HCFC-124	/	3.0%	0.4%
3	PFC-318	/	2.0%	1%	30	HCFC-132b	/	5.0%	/
4	C_6F_{14}	/	5.0%	/	31	HCFC-133a	/	4.0%	/
5	SF_6	1.64%	1.0%	0.7%	32	HCFC-141b	0.42%	0.8%	0.9%
6	SO_2F_2	/	3.0%	/	33	HCFC-142b	0.81%	0.5%	1%
7	HFC-23	0.44%	2.0%	4.6%	34	HFC-161	/	3.0%	5%
8	HFC-32	2.23%	2.0%	6.1%	35	HCFC-31	/	10.0%	/
9	HFC-125	1.46%	2.0%	5.5%	36	H-1202	/	15.0%	/
10	HFC-134a	1.85%	0.5%	1%	37	H-1211	0.95%	2.0%	0.7%
11	HFC-143a	1.30%	2.0%	8.9%	38	H-1301	3.70%	3.0%	1%
12	HFC-152a	2.32%	2.0%	11%	39	H-2402	2.15%	3.0%	ECD
13	HFC-227ea	2.47%	3.0%	3.2%	40	CH_3CCl_3	2.64%	3.0%	0.8%
14	HFC-236fa	/	6.0%	2.4%	41	CH_3Cl	0.48%	0.8%	2%
15	HFC-245fa	2.22%	3.0%	8.1%	42	CH_2Cl_2	1.72%	1.0%	/
16	HFC-365mfc	2.30%	3.0%	3.5%	43	$CHCl_3$	1.29%	3.0%	0.7%
17	HFC-4310mee	/	8.0%	3%	44	CCl_4	0.67%	2.0%	0.5%
18	CFC-11	0.31%	0.3%	0.8%	45	CH_3Br	1.66%	0.8%	0.3%
19	CFC-12	0.22%	0.2%	0.5%	46	CH_2Br_2	/	1.5%	/
20	CFC-13	2.16%	1.5%	0.9%	47	$CHBr_3$	/	2.0%	/
21	CFC-112	/	10.0%	/	48	CH_3I	1.41%	2.0%	1%
22	CFC-113	0.28%	0.5%	0.5%	49	COS	/	0.5%	/
23	CFC-114	0.69%	0.5%	0.5%	50	HCFO-1233zdE	/	10.0%	/
24	CFC-115	0.92%	1.5%	2%	51	HFO-1234yf	/	10.0%	/
25	CFC-1113	/	5.0%	/	52	HFO-1234zeE	/	15.0%	/
26	HCFC-21	/	3.0%	/	53	PCE	2.47%	1.5%	2%
27	HCFC-22	0.81%	0.5%	1%	54	TCE	1.62%	5.0%	1%

Note: Medusa-AGAGE online monitoring system; JESC-online monitoring system of Japan Environmental Health Center.

3.2 Quantitative quality control analysis

For quality control purposes, the RSD of standard gas before and after the sample should be consistent with the results of

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continuous injection using the single-point external standard method. The number of samples between the standard gas is according to the instrument's stability to ensure that the accuracy of the results meets the detection requirements.

This study used the "standard gas 2 times-samples-standard gas 2 times" procedure, and the 3-5 samples were imported before and after standard gas. In this experiment, four changes in the standard gas before and after were investigated (if the instrument fluctuated significantly, the sampling frequency of the standard gas should be increased) (Table 5), which could be used to determine whether a normal fluctuation caused the error in the mass spectrum or by an abnormality in the system. For example, the peak areas of CCl_4 before and after injection are 212, 168, and 210, 523, respectively, and 203, 186, and 204, 637, respectively. Taking the average peak area four times to calibrate sample concentration may be due to the mass spectrum response decay. Two continuous samples can be used simultaneously as a quality control measure to reduce the deviation caused by the system's contingency.

Table 5

Changes in standard gas response during actual sample test

NO.	Industrial Name	Before injection 1	Before injection 2	After injection 1	After injection 2	Sample test RSD%	Continuous standard gas test RSD%
1	HFC-245fa	3191	3178	3293	3128	2.16	2.22
2	CFC-114	41114	41124	41050	40979	0.16	0.69
3	HCFC-142b	73630	73141	73478	73325	0.29	0.81
4	CH_3Cl	1015196	1016937	1017654	1004733	0.59	0.48
5	H-1211	12392	11991	12291	12118	1.46	0.95
6	HFC-365mfc	6104	6317	6350	6258	1.74	2.30
7	PFC-116	7356	6887	7019	6998	2.87	0.84
8	SF_6	30785	30613	30539	30395	0.53	1.64
9	CH_3Br	14084	13683	13741	13571	1.61	1.66
10	CFC-13	12483	13394	12527	12558	3.43	2.16
11	HFC-23	30062	30179	29778	29898	0.59	0.44
12	CFC-11	827499	817029	821261	820115	0.54	0.31
13	HCFC-141b	98361	98145	98083	97984	0.16	0.42
14	H-1301	1118	1220	1180	1132	4.01	3.70
15	CFC-113	255622	253430	254154	254476	0.36	0.28
16	PFC-218	927	963	935	984	2.75	3.34
17	HFC-32	30698	30008	31093	31081	1.66	2.23
18	H-2402	1277	1270	1189	1203	3.66	2.15
19	CH_3I	1148	1046	1196	1127	5.54	1.41
20	CFC-115	16329	16320	16648	16156	1.26	0.92
21	CH_2Cl_2	239714	236867	236405	237289	0.62	1.72
22	HFC-125	79030	78329	78780	78704	0.37	1.46
23	HFC-143a	98514	99382	104328	101757	2.58	1.30
24	CFC-12	2081011	2066598	2066260	2066611	0.35	0.22
25	HCFC-22	933353	918581	920858	925190	0.70	0.81
26	HFC-134a	222569	224005	223270	223221	0.26	1.85
27	$CHCl_3$	42926	43073	42420	42884	0.66	1.29
28	CH_3CCl_3	4876	4907	4707	4809	1.83	2.64
29	CCl_4	212168	210523	203186	204637	2.11	0.67
30	HFC-152a	11950	12023	11436	11628	2.34	2.32
31	HFC-227ea	3251	3191	3331	3215	1.88	2.47

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NO.	Industrial Name	Before injection 1	Before injection 2	After injection 1	After injection 2	Sample test RSD%	Continuous standard gas test RSD%
32	TCE	1111	1160	1195	1087	4.26	1.62
33	PCE	8166	8109	8120	8180	0.42	2.47

3.3 Concentration accuracy

Laboratory parallelism can reflect the instrument and method stability. The actual samples were tested for parallelism to verify this method's practical application.

Parallel laboratory tests were conducted on 16 actual samples, deviations between the two tests were calculated, and the statistical deviation results were obtained. Fig. 6 shows that this method can test background atmospheric samples with high precision, and the sample concentration deviation is 0.007-5.299%, which is several times higher than the 30% deviation for VOC tests. Even for substances containing less than 1 pmol/mol, there is a less than 0.01 pmol/mol difference between the two test results, which indicates that each step in the method is critical to capturing global background concentrations better.

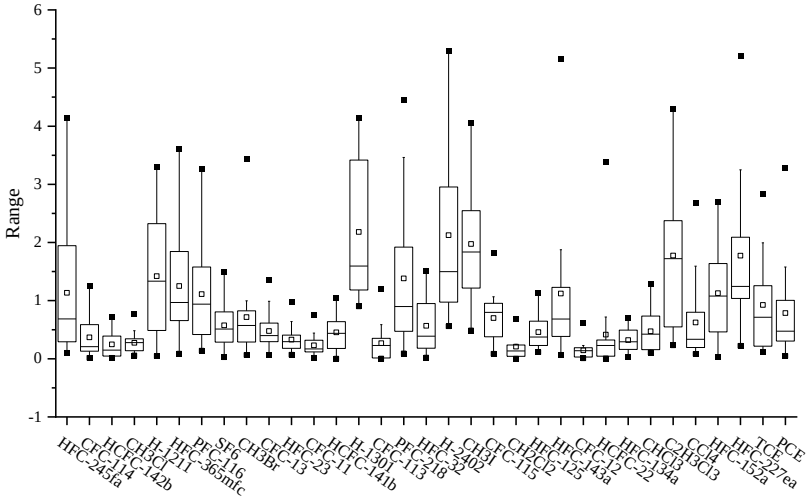

Fig. 5. Accuracy analysis of actual sample test results

3.4 Samples concentration analysis

Since this method has a low systematic error and a stable change of global background concentration, it is well suited for tracking ODS and F-GHGs emissions. Analyses were conducted on background atmospheric samples collected from Jilin, Sichuan, Fujian, and Hainan. Calculate the tested sample's average concentration and plot their differences with the average value. It should be uniformly circular if the concentration does not change significantly. It is evident from Fig. 6 that if there are fluctuations in the concentration of the individual sample. If high values are found in the data, the meteorological conditions at that time of high concentration points can be retrieved from NOAA to analyze the backward trajectory of the emission.

The test results were statistically divided into CFCs, Halon, HCFCs, HFCs, Halo, Hydrocarbon, and other F-GHGS. It is noteworthy that CFCs, and Halon performance controlled substance concentration did not changes within the test accuracy deviation, indicating that there was no additional emissions present; HCFC-22 is an industrial raw material produced and used in China, and the considerable variation in background concentration is consistent with the current environmental conditions. HFC-32 and HFC-125 are easily affected by the sampling environment, the reason is that these substitutes for commonly air-conditioning refrigerants. Since CH_3Cl and CH_2Cl_2 are common organic solvents with widespread use, their concentration in the atmosphere fluctuates wildly. Since SF_6 has a low atmospheric concentration, it has not attracted much

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attention. With the continued development of industrialization, SF_6 may become a more critical insulating gas, and its emissions may continue global warming (Simmonds et al., 2020). A high value was found in the sample test, so the backward trajectory analysis in time should be used to identify the emission source (Fig. 6.).

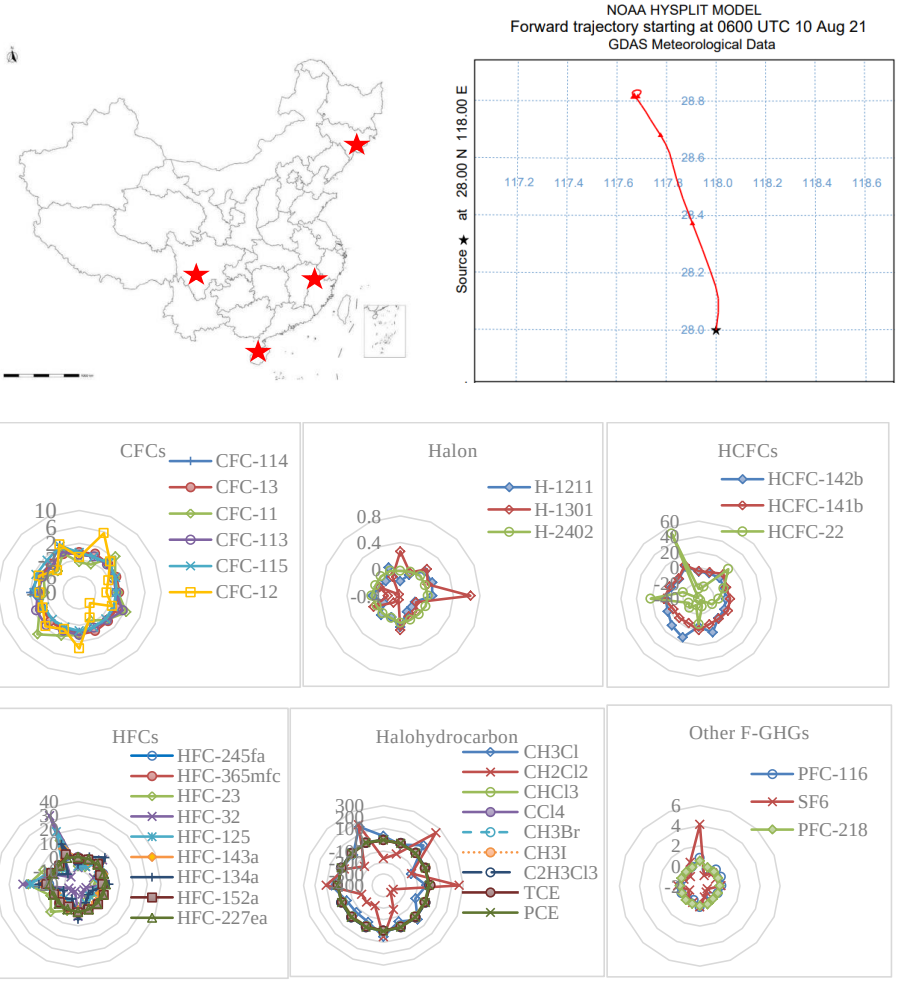

Fig. 6. Analysis of variation of sample concentration (from Baidu Map).

4. Conclusions

Based on the findings of this study, the developed method has excellent maneuverability and popularity, which makes it one of the most promising methods in the field. Using hardware upgrades and method optimization, a liquid nitrogen cryogenic device and GCMS can detect trace amounts of ODS and F-GHGs with low boiling points and concentration. It improved the monitoring sensitivity and precision of 33 target compounds, and the detection limit is 0.051-0.382 pmol/mol, which can be used to detect background atmospheric pollutants. In the case of the gas sample with a concentration of 0.41–531 pmol/mol, the RSD was 0.22-3.70%, which is consistent with the precision of the self-built testing system established by the international monitoring network and research institutions. According to the single-point external standard method, there was a deviation of 0.007–5.299% in the concentration of the actual sample. Compared to multi-million-dollar research and development of new equipment, this method is cost-effective, requires a short reconstruction time, and can be reproduced quickly in the laboratory. The summa tank could be used in future research to collect samples and send them to a la-

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boratory for analysis to track the emission source. This system will also enable government departments to monitor compliance and control emissions levels.

Author contribution

Chen Chunrong and Zhang Ting designed the experiments and Shan Danying carried them out. Cao Guan collected samples. Du Zhenyu and Zhang Xiulan developed the data model. Tang Ka prepared the manuscript with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

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