Obtaining the accurate NMHC data for ambient air in urban: comparison of NMHC data between indirect and direct methods

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Abstract: Since non-methane hydrocarbons (NMHCs) include numerous species of volatile organic compounds (VOCs), they are the only indicators that can characterize the total amount of VOCs in ambient air. More than 90% of NMHC instruments in the market use the indirect method for NMHC determination, utilizing a gas chromatograph to determine the concentrations of total hydrocarbons (THCs) and methane in air. However, we found indirect NMHC measurements incorrectly characterized the low NMHC concentrations in the urban air. These measurements were hindered by the uncertain changes in the errors associated with low THC concentrations, humidity, and macroscopic substances (oxygen) in the atmosphere. In this study, we conducted intercomparisons between 10 instruments in the market using different operation principles; among these, two used the direct method and eight used the indirect method. For the indirect method, experiments showed that when the NMHC concentration was 50 ppbC, the errors in the measurement results were 32% (CH_4) and 98% (THC) when compared to theoretical values. The oxygen content in the sample gas directly affected the response of the THC. The effect of increased oxygen content on the analysis of oxygen-containing substances was more significant than that of the increase in hydrocarbon substances. The response of dry zero was blank, and the response value increased non-linearly with relative humidity (RH). RH had a great impact on low NMHC concentrations of nearly 50%. For the direct method, although various flow designs were applied for different instruments, the results indicated that they generally showed lower interference and higher accuracy for the ambient NMHC measurements. With the online direct methods, we obtained more reliable data and characteristics for low-concentration NMHCs in downtown Shanghai. The median of hourly data was 163.1 ppbC, and the highest ratio of the maximum and minimum concentrations of NMHCs reached 9.56 in a single day.

Keyword: Non-methane total hydrocarbons; Ambient air; Low-concentration; Oxygen interference; Humidity influence

1. Introduction

High concentrations of methane and non-methane hydrocarbons (NMHCs) in the air affect the atmospheric environment. NMHCs are the sum of all other gaseous organic compounds other than methane that respond to the hydrogen flame ionization detector (FID)Baker et al. (2008), (Wang et al. 2015, Wen-qi 2009). Under sunlight, NMHCs exceed a specific concentration and react to form secondary pollutants (peroxyacetyl nitrate (PAN), secondary organic aerosols (SOA), and O_3), which affects the environment and human health(Huang et al. 2014, Liu et al. 2017, Shen et al. 2013, Ahmed et al. 2015, Thoma et al. 2022). Methane causes environmental problems, such as global warming(Panopoulou et al. 2018, Song et al. 2012). NMHC monitoring needs to be strengthened to improve air quality and reduce ozone pollution, and the volatile organic compound (VOC) emission reduction assessment for cities and industrial parks requires NMHC monitoring data as an important reference. NMHCs have become the most widely used comprehensive evaluation factor for organic pollutants, exhibiting the highest monitoring frequency and emission standards. They are used to macroscopically characterize the VOC pollution status of the air. Over 100 countries have conducted NMHC monitoring worldwide, including the United States, those in the European Union, and Japan. In China, NMHCs were measured in 300 cities that had more than 500 sets of online devices(Coelho et al. 2021, Panopoulou et al. 2018, Fan 2019). Additionally, Shanghai has listed NMHCs as one of the evaluation factors for comprehensive environmental remediation in 2015. Therefore, there is an urgent need to ensure the quality and technical specifications of the NMHC real-time monitoring system and the reliability of NMHC real-time monitoring data. However, we evaluated whether the existing methods used for measuring NMHC were accurate and scientific.

Existing NMHC analysis methods, derived from pollution source monitoring, have proven to be suitable for the measurement of high pollutant concentrations according to many environmental standards. However, studies and data associated with direct NMHC measurements are scarce, especially in urban districts with low levels of NMHCs. The majority of studies are concerned with the NMHC concentration after some regional or industrial park accidents. There are other studies that calculate the sum of each VOCs except methane, which range from 50.23 to 127.35 ppbv; these values are considered as the NMHC concentration(Atkinson 2000, Baker et al. 2008). Thus, we believe that the accurate NMHC value is within this range.

At present, scientific research on the type of instrument mainly focuses on the mutual comparison between improved instruments, the advantages and disadvantages, and the concentration trend characteristics of NMHCs in ambient air over a period of time. Most countries currently use gas chromatography with a double-column dual-hydrogen FID (GC-FID) to determine the NMHC values (NMHC content is equal to the total hydrocarbon content minus methane content)(Panopoulou et al. 2021, Hoerger et al. 2015). To avoid the difference in sensitivity, the GC-FID was improved to a single FID (Bai 2010) proposed that the oxygen peak in the instrument based on subtraction represents the oxygen in the experimental environment, which is different from the oxygen in the actual monitoring environment and can cause a monitoring error(Wang et al. 2009)

found that the GDX-502 packed column could not completely separate the oxygen and methane peaks, and the oxygen component values obtained by integration are quite different in certain situations (Chang et al. 2015) showed that volatile compounds containing Cl, O, and S also have varying degrees of response when measuring NMHCs, which affects the final total hydrocarbon concentration(Li and Pan 2013) discussed the categories of substances that should be included in the measurement of NMHCs. However, measuring low concentrations of atmospheric NMHC with instruments based on subtraction may increase the error. The influence of air humidity in different regions is usually not considered.

The lockdown during the COVID-19 pandemic provided a good opportunity to identify problems with analytical methods and observe the performance of instrumental measurements. There are three stations for environmental air real-time monitoring near Shanghai Chemical Industry Park: Zhelin, Caojing, and Shanyang. The distribution of the three sites is shown in Fig. 1. Among them, the NMHC concentrations at the Zhelin and Caojing sites were measured with instruments using the subtraction method. The NMHC concentrations at the Shanyang site were measured with an instrument using the direct method. The variation trends in the NMHC concentrations exhibited significant fluctuations. At the beginning of 2020, owing to the sudden and severe epidemic situation, there was a complete shutdown of production and human activities. However, we found that the NMHC concentration measured with the instrument using the subtraction method during the Spring Festival period was above 450 ppbC, and sometimes even as high as 800–900 ppbC (shown in Fig. 6 and Fig.7(a-c)). The NMHC concentrations measured with the instrument using the direct method was almost less than 100 ppbC. We aimed to understand why atmospheric NMHC concentrations were so different at nearby locations in such an exceptional period. Therefore, we continued to analyze the sum of concentrations of the real-time VOC-monitoring components and the sum of VOC concentrations converted to carbon based on the number of carbon responses of different functional groups (shown in Fig. 6 and Fig.7 (b-c)). The total VOC (TVOC) concentrations obtained at photochemical assessment monitoring stations (PAMSs; including 56 components) and at facilities with PAMSs and TO15 (including 106 components) were separately measured using online GC-MS and GC-FID and mainly ranged between 10–20 ppb. The calculated total NMHC concentrations (below 100 ppbC) were considerably lower than those calculated with the NMHC instrument using the indirect method (by more than 10-fold). This result was consistent with the concentration trend of the NMHC instrument using the direct method. Such a huge difference caused us to suspect the accuracy of the NMHC instrument using the indirect method. The measured value was clearly on the high side, and we examined the cause of this measurement error.

According to the response principle of the FID, the total NMHC content is the sum of the carbon concentration, which is the product of the VOC species concentration and the corresponding number of carbon responses of different functional groups. The TVOC concentrations of 106 and 56 VOC species ranged between 10–20 ppb approximately, while exhibiting

occasionally high values such as 100 ppb. The total NMHC concentrations calculated using 106 and 56 VOC species were

90   approximately 40 ppbC, which is only one-tenth of the value measured with the instrument using the indirect method. The

following factors need to be considered for determining the actual concentrations of total NMHCs in ambient air: the accuracy

associated with determining the total NMHC concentration sufficient for actual ambient air concentration levels; the ability of

the mainstream indirect method in distinguishing the concentration difference of 10 ppb between two sites.

At present, several international countries and China have issued a series of standards, such as GB 16297, DB31/933, and EPA

95   TO12, that stipulate the emission limit of NMHCs in ambient air. However, there is no mature standard associated with real-

time monitoring technologies used for NMHCs; thus, a standard test for assessing instrument practicability is required. The

detection principles, key component types, and technical parameters of real-time monitoring instruments for NMHCs differ

considerably, which causes specific difficulties in data quality control. As we observed the data during the COVID-19

pandemic, we doubted the accuracy of NMHC data for low-concentration atmospheric measurements using the subtraction

100   method. We studied the accuracy of the instruments using subtraction or direct methods to measure the low-concentration

NMHCs along with the influence of humidification. Therefore, we provided a scientific basis for determining the actual

concentration of total NMHCs in ambient air.

2.   Experiment

For a long time in the past, dry methane and propane standard gas were used in quantitative curves of the NMHC instrument.

105   The atmospheric NMHC concentration was slightly different, although there was a good linearity of NMHCs. Among the

NMHCs, besides propane, there are alkanes with less carbon and lower boiling points and those with more carbon and higher

boiling points. In addition to alkanes, a variety of substances such as oxygen-containing hydrocarbons, chlorinated

hydrocarbons, and benzene series also exist. The adsorption and desorption of these substances and their response values to

FID are different. Moreover, while considering NMHCs except for alkanes, we also tested whether the FID could respond well

110   to the other main components of VOCs (such as benzene, halogenated hydrocarbons, and ethyl acetate). Therefore, we referred

to the method promulgated by Japan, wherein the ratio of the actual value to the theoretical concentration of the three

representative substances should be within a certain range. Additionally, a difference in humidity exists between the actual

ambient air and the dry standard gas. The Humidity may affect the quantitative accuracy. We also considered whether low-

level NMHC concentrations could be measured accurately. Therefore, to ensure qualitative and quantitative accuracy, the

115   simulation must represent the actual air as much as possible. Moisture can also change the column efficiency and affect the

shape of the peak. The following experimental plan was designed based on the aforementioned ideas.

2.1   Instruments

2.1.1 Introduction for principles and differences of direct and indirect methods

Total non-methane hydrocarbons (NMHC) are defined as the sum of all volatile organic compounds that can respond on FID. There are two common measurement methods, direct method and indirect method. The direct method refers to the method of separating non-methane hydrocarbons from total hydrocarbon and directly determining the concentration of NMHC. The indirect method refers to the method of measuring total hydrocarbon and methane respectively, and obtaining non-methane concentration by deducting methane from total hydrocarbon. The indirect method is also known as differential subtraction.

2.1.2 Experimental sites and instruments

To solve the problem of qualitative and quantitative accuracy, we selected some instruments in the market according to market shares and technical principles. In summary, 10 instruments (including domestic and foreign brands) jointly participated in the verification test, among which the first two used the indirect method. Detailed information regarding the instruments is presented in Table 1. The subsequent description was not a one-to-one correspondence but only reflected the overall technique level. The sampling site for P1 was located at No.55 Sanjiang Road, Shanghai Environmental Monitoring Center (SEMC, 121.44° E, 31.1746° N), and was set up at a height of 35 m. Site P2 is Xuhui Shanghai Normal University Station (XSNUS, 121.412° E, 31.1654° N), which is about 2.6 km to the west of SEMC. The two sites are located in the downtown area and are near one another to ensure that the data is correlated.

In addition to the gas required in the experiment, we used two other auxiliary equipment. The dynamic dilution calibrator (D3000) is an online dilution gas device equipped with four flow meters with different ranges and a glass mixing pool. The flow meter and mixing tank are connected by inert pipelines to avoid material absorption. When it is being operated, the mixing tank is heated to promote better mixing and avoid high-carbon precipitation. Therefore, the proper concentration of standard gas can be obtained.

The other instrument was a humidity meter to add different humidities to the dry standard gases, aiming to simulate real ambient air. A moisture-resistant melamine faced chipboard (MFC) was used to control the flow of water vapor, and the added water volume per hour was calculated using the following equation:

$$Q = p * q * 60 \text{ min} \tag{1}$$

Q is the water content added to the dilution gas at a certain temperature and humidity (g/h); p is the moisture content per cubic meter at a certain temperature and relative humidity (g/m^3); and q is the dilution gas flow (mL).

2.2 Laboratory testing

145 Laboratory evaluations were conducted in Shanghai. The concentrations of the target standard gases were controlled and mixed using a dynamic dilution calibrator (D3000). The concentrations involved in the test were converted into the concentration of carbon according to HJ/T38-1999 (stationary source emission – determination of non-methane hydrocarbons – gas chromatography).[16] All devices were warmed-up for 24 h and remained stable before conducting the test.

First, we used an external standard method to quantify methane and NMHCs by diluting the standard gas of methane and
150 propane with highly pure nitrogen. The average of three stable values for each concentration was selected, and the corresponding concentration standard curve was obtained based on the mean value of the peak area (methane: 0.5, 1, 2, 3, and 4 ppm, respectively; propane: 0.05, 0.2, 0.4, 1, and 4 ppmC, respectively). To ensure the qualitative and quantitative accuracy of subsequent experiments, we needed to ensure that R^2 was > 0.999, and the peak was normal. In the second step, we tested the FID with ethyl acetate, trichloroethylene, and toluene (representing different components of VOCs) to determine whether
155 there can be a normal response to FIDs. Third, humidity experiments were conducted to examine whether the instruments could be qualitatively and quantitatively accurate under highly humid conditions. The concentration of the calibration gas was constant, and the measurements were conducted under 40%, 60%, and 80% humidity conditions. Each standard gas was measured thrice, and the peak area and concentration were recorded separately. A humidification blank (zero gas) for each instrument was also measured. As the spectrogram of the indirect instrument contains an oxygen peak, we studied the effect
160 of different oxygen contents (10%, 20%, and 30%) on the accuracy of NMHC concentrations. Finally, all the instruments monitored atmospheric NMHC concentrations for a long time under the same conditions to evaluate the comparability and consistency of the results. The real-time monitoring of NMHC values is considered credible only after the consistency of the measured atmospheric NMHC concentration meets the stipulated requirement.

According to the results of the indirect instruments, their accuracies were improved with the principle of direct measurement.
165 Five low concentrations of gases (methane: 1, 1.5, 2, 3, and 4 ppm, respectively; propane: 0.05, 0.1, 0.2, 0.5, 1 ppmC, respectively) were used to conduct calibrations, which was in line with the characteristics of NMHCs in the ambient air. The same experiments were conducted for the response factor and the impact of humidification.

In light of the laboratory results, four sets of equipment were used for the long-term operation of ambient air through the same glass sampling manifold under the same conditions to check the consistency of the atmospheric NMHC data. The relative
170 standard deviation (RSD) was calculated to compare the data.

$$RSD = \frac{S}{\bar{x}} \times 100\% = \frac{\sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}}{\bar{x}} \times 100\%$$ (2)

S is the standard deviation of the data;$\bar{x}$ is the average of the data.

3. Results and discussion

3.1 Test results of instruments using the subtraction method

175 **3.1.1 Low concentration**

Fig. 2 (a-b) presents the curves of CH_4 and total hydrocarbons (THCs) for A and B. The R^2 of linear regression values were all above 0.999, indicating that the integral areas of the peaks were proportional to the concentrations of the target compounds for A and B. Fig. 2 (c) shows that as the propane concentration increased, the accuracy of NMHCs measured by A and B also increased. When the propane concentration was 50 ppbC, the errors were 32 (A) and 98% (B). The concentration of NMHC

180 in the instrument using the subtraction method was obtained from the measured THC concentration after subtracting the methane concentration. Assuming that there was 1% random error in the 2050 ppbC and 2000 ppb of THC and methane measured using an instrument, respectively, after subtraction, the extreme error of 50 ppbC NMHC was 40 ppbC. The error presented by low NMHC concentrations will inevitably be larger than that presented by high NMHC concentrations based on the principle of subtraction. This indicates that the instrument using the subtraction method is unsuitable for ambient air with

185 low NMHC concentrations and is more suitable for areas with high NMHC concentrations, such as industrial parks.

We selected the stable 7 group data and calculated the mean and RSD. At the beginning of the standard gas, because the gas enters the system to reach the detector for a certain amount of time, the data obtained is unstable and does not represent an accurate test value. For this purpose, we select the stable data at the beginning of the third cycle after passing the standard gas as the basis for statistical calculations. Generally, when the response concentration is close to the standard concentration (such as within the range of 2200±100), 7 consecutive datas are taken for calculation.As presented in Table 2, the repeatability of

190 THC and CH_4 of A and B was approximately 2%. However, the RSD of NMHC was greater than 9.5%, which was caused by the instability of THC and CH_4 and the principle of subtraction error. This is consistent with the results shown in Fig. 2 (c).

3.1.2 Oxygen interference

The concentrations of THC and CH_4 were measured on the THC (with all substances) and the methane columns, and the

195 difference represented the concentration of NMHCs. An oxygen peak appeared when the carrier and diluent gases were nitrogen and air, respectively. Oxygen did not respond to the FID. While the chromatographic column sundered oxygen and

methane from air, oxygen molecules entering the detector destroyed the original balance of the flame, causing an interference peak. Owing to the different carrier gas types, oxygen in the zero and sample gases on the THC column had a response, which could deduce the interference of the oxygen in the sample on determining the THC concentration.

200 We assumed that the measured THC concentration in the zero gas was fixed and used it as the intercept; it was subtracted from the THC concentration sample gas to obtain the accurate THC concentration. We conducted an experiment to investigate the above. For the same concentration of calibration gas, the oxygen content increased, and the response of the instrument using the subtraction method to NMHCs also increased(Wang et al. 2009) found that the area of the oxygen peak is directly proportional to the oxygen content in the gas sample. We found that the increase in oxygen content had a more significant

205 impact on the measurement of oxygen-containing substances than on that of hydrocarbon substances (Fig. 3). The response with 30% oxygen content was as high as 36% compared to that with 10% oxygen content. These results indicate that the THC value in the zero and sample gas was not fixed, causing an error as a fixed intercept in the subtraction method.

In view of the effect of oxygen content in the sample gas on the determination, we carried out the following experiments. For the difference subtraction method and the direct test method, the test was carried out simultaneously. Different oxygen content

210 and the same concentration of 2ppm propane into the instrument, different oxygen content and the same concentration of 2ppm ethyl acetate into the instrument. The results showed that: The direct measurement method is basically not affected by oxygen content, and the difference subtraction method is greatly affected by oxygen content and has poor consistency;With the increase of oxygen content, the recovery rate of the difference subtraction measurement value increased, and the two were not proportional. Some instrument test results have increased more, and the recovery rate exceeds 100% The specific reason is

215 unknown. The preliminary judgment is that after a large amount of oxygen enters the FID, the oxidation of the flame is improved, resulting in more complete combustion of organic matter, improving the response of the assay, and leading to an increase in recovery As presented in Table 3, this table shows the recovery rates for each instrument with different oxygen levels of 2ppm propane and ethyl acetate. With the increase of oxygen content, the results of the two subtractive instruments increased, while the results of the two direct measurement instruments were basically not affected by the change of oxygen

220 content. With the increase of oxygen content, the consistency of the two subtraction instruments decreases, while the data of the two direct measurement instruments are basically consistent. There are many methods for deducting oxygen peaks by subtraction instruments, mainly including: deducting the fixed peak area; Deduct the oxygen peak area on the current circulating methane column; There is also the direct use of zero gas as the carrier gas to eliminate oxygen peaks, etc. At present, there is not much data on the difference subtraction method, in addition, we believe that after a large amount of oxygen enters

225 the FID, the oxidation of the flame is improved, resulting in more complete combustion of organic matter, and it will also

improve the response. Although oxygen levels vary around the world, they are small and stable over a small area, and can be removed as systematic errors as long as they are calibrated.

Oxygen has a significant effect on FID determination. The FID uses air as an auxiliary gas in which oxygen is theoretically unresponsive. The oxygen peak occurs because when the chromatographic column separates the air, oxygen and methane are separated. Oxygen molecules enter the detector before methane, destroying the original balance of the FID flame and producing signals, which is actually an interference peak. In the process of the differential subtraction, the oxygen peak in the sample is included in the peak of the total hydrocarbon. At the same time, the oxygen in the sample formed an oxygen-rich combustion environment in FID, which improved the total hydrocarbon response. Therefore, the value of the oxygen peak must be deducted. In terms of different instrument manufacturers, the differential subtraction method to subtract oxygen peak is inconsistent, which reduces the comparability and accuracy of data. However, the direct measurement method is not interfered by oxygen in the sample gas in principle.

3.1.3 Influence of humidity and response factor

Fig. 4 shows the effects of different water contents in zero, low, and high standard gas on FID. Although instruments A and B did not respond for dry zero gas, instrument A had a response of 90 ppbC of NMHCs when a certain amount of moisture was introduced. The blank value increased simultaneously but not linearly as the RH increased, indicating that humidity could affect the instrument A. For the southern regions, where the air humidity is relatively high, the NMHC concentrations in ambient air measured with instruments using subtraction is't inaccurate. There was a certain difference in the responses of A and B to the high- or low-concentration standard gas containing humidity, indicating that RH had a significant and different influence on the measurement of low-concentration NMHCs for days, up to a response of nearly 50%. This resulted in a huge error. In comparison, RH had a relatively small influence on the measurement of high-concentration NMHCs, mostly within ±8%. Therefore, for ambient air, the RH is another possible cause of error. Additionally, we also analyzed the influence of humidity on the FID response of different kinds of substances. RH had little effect on the measurement of propane and trichloroethylene but a significant effect on that of ethyl acetate, and reduced the response by up to 30%, indicating that oxygen-containing substances would be affected more. Therefore, it had a greater impact on hydrophilic substances rather than hydrophobic substances.

Humidity, the water in the air, also has a great influence on the accuracy of non-methane hydrocarbon determination. Water is the product of FID combustion. Small amounts of water generally do not respond on the FID, but large amounts do. Water also changes column efficiency and the peak shape of other substances, and so on. Due to the existence of moisture in the

actual air, the use of dry standard gas calibration will affect the measurement effect of the actual sample. The accuracy of non-methane determination can be improved by applying humidification standard gas. If only considering the measurement effect, the direct measurement method using low temperature preconcentration is a better solution.

3.1.4 Accuracy analysis and evaluation of the uncertainty of measurements

The total NMHC concentration using the indirect method was obtained by subtracting the methane concentration from the measured THC concentration. The concentrations of THCs and methane were an order of magnitude higher relative to those of NMHCs. Small errors in the determination of THC and methane concentrations had a significant impact on the NMHC concentration. Based on the actual concentration levels in the urban air, assuming a THC concentration of 2.5 ppm, the standard instrumental measurement error was 2%, with an error value of $\pm$ 40 ppb. Additionally, with a methane concentration of 2 ppm, if the measurement error was also 2%, the error value would also be $\pm$ 40 ppb. The two numbers were subtracted, and an error of $\pm$ 80 ppb was obtained, which is approximately at the same level as that in the NMHC concentration in ambient air. Therefore, the method of subtracting "big data" from "big data" does not provide accurate NMHC concentration data. To verify the principal error of the instrument, we evaluated the measurement uncertainty of the calculation model based on some standards. However, the results showed that the relative uncertainty (17.2%, k = 2) of the NMHCs far exceeded 1/3 of the technical requirements for the accuracy of methane measurements (10%). According to the requirements of the measurement technical specifications, the uncertainty of the measurement results should be less than 1/3 of the accuracy of the measuring instrument. This indicates that the indirect measurement method has great uncertainty, and should not be recommended as the optimal method for measuring NMHC concentrations.

3.2   Test results of instruments using the direct method

According to the monitoring demand of low concentrations of NMHC in urban environments, the indirect method is affected by oxygen peaks, water vapor, and calculation rules, and it is not possible to obtain accurate measurements and lower detection limits. For this purpose, technology research and development focus on the direct measurement methods. All instrument manufacturers have carried out the development and upgrading on novel technical routes. Through years of affords, a total of three categories and five technical routes have emerged.

- The first category is based on the NMHC airflow counter blowing technology(Trubyanov et al. 2016, Wang, Xu, and Guan 2002), including two paths: single and multiple column adsorption methods. The system is simple and the analysis speed is fast with single column of the direct method. Because of the presence of the damping column, the chromatogram has no obvious valve switching peak, and the data is accurate and stable. However, the NMHC

components flow forward and then backward in the column, resulting in peak broadening (secondary broadening) affecting the integration. The detection limits of both methods are not low.

- The second category is adsorbent pre-concentration technology(Chowdhury et al. 2022), which meets the needs of progressively decreasing NMHC concentration that can be monitored in ambient air with a lower detection limit. The technical route includes two methods: normal temperature preconcentration and low temperature preconcentration. In terms of the normal temperature preconcentration method, adsorbent containing a thermal desorption device is connected to the FID detector. Methane is not adsorbed during sampling, and the adsorbed NMHC components during desorption are directly burned in FID to form NMHC peaks for measurement. The advantages are that the structure is simple, and no column is required. However, it is necessary to strengthen the study of the influence of adsorbent on the adsorption efficiency, thermal desorption temperature and flow rate of different substances. In order to improve the adsorption of C2, the low temperature preconcentration method adds a cold trap to improve the adsorption effect of the sample gas through the low-temperature adsorbent. The advantage is that the detection limit is lower, and the disadvantage is that the analysis time is longer.

- The third category is in a cryogenic environment(Wang, Chang, and Lee 2012), the atc for preconcentration of direct measurement method is adopted. The enrichment temperature is 130 degrees below zero. The advantages of this method are that adsorption effect and peak shape are ideal, but the disadvantages are that water is easy to freeze, which will block the flow path at low temperatures, and the cutting valve in different states affects the baseline, so it is necessary to optimize the design of the system.

Four different instruments from four manufacturers completed the improvement in time. The four instruments used the first and second categories of methods described above. Through the field test for about two months from October to December 2020 (Fig. 7(e-f)), it shows that the mean values of the four products are basically the same, and the statistical values of the test data are basically similar. The hourly average RSD for the 4 instruments was 0.0199 and the daily average was 0.0313.

3.2.1 Lower concentration, accuracy, and detection limit

Similar to Fig. 2, Fig. 5 shows the curves of CH_4 and NMHCs for C-J. The R^2 values of the linear regression were all above 0.995, providing a good foundation for subsequent quantitative testing. H is based on the principle of catalytic oxidation, which can solve the problem of inconsistent response coefficients of different groups on FID, and is introduced into a low- and high-concentration standard gas to check and standardize the H value of the instrument before the test.

The calculated detection limits are listed in Table 4, where the detection limit of all instruments using the direct method was reduced to 20 ppbC, and some were even lower than 10 ppbC. This indicates that the instruments using the direct method are more suitable for NMHC measurements in ambient air.

3.2.2 Response factor

Fig. 7 shows the response of the zero gas, different concentrations of standard gas with 60% RH, and dry standard gas on FID. Except for instruments G and I, the response of zero gas with 60% RH on other instruments was less than 25 ppbC. The influence of humidity in this instrument was greatly reduced compared with those in instruments A and B. The result of the standard gas was the same and significantly different with those of instruments based on subtraction. For C-J, the response of FID did not change much based on whether the standard gas was humidified or not.

3.3   Analysis of NMHC in the ambient air

Based on a series of problems found in the above experiments, such as "large number minus large number," interference of oxygen determination, and interference of water vapor determination, and to ensure the accuracy of measurement, we excluded the equipment of indirect method at first. Subsequently, due to the catalytic method, the catalyst for the low concentration of the non-methane catalytic efficiency instability was also excluded. The direct method instrument entered our second round of testing and mainly experienced two types of technical optimization. The first was to change the enrichment and limiting holes and improve the determination accuracy. In the second process, the columns are specially designed to meet the needs of low-concentration determination. Through method optimization, the test effect was further improved.

The data for the concentration of NMHC in the Shanghai urban area during the winter of 2020 is shown in Fig. 8, which was measured by the equipment that showed the best performance in our test. The observation equipment used in Shanghai Caojing Station has a time resolution of 1.5 minutes, and the observation equipment used in Shanghai Zhelin Station has a time resolution of 1 minute.The technology used by the equipment is adsorbent pre-concentration technology in low temperature. The average of the hourly data was 163.1 ppbC and the median value was 149.2 ppbC; the average of NMHC every 15 min was 124.3 ppbC and the median value was 102.6 ppbC. Notably, the minimum value of 42.8 ppbC occurred at 12:15:28 on Nov 15th, 2020 when the AQI was 37, which was described as excellent. The maximum value in the entire data was 562.3 ppbC that occurred at 14:20:14 on Nov 23rd, 2020; however, the AQI at that time was 32. The ratio of the maximum and minimum value in one day reached 9.56 on Nov 23rd 2020. On this day, the maximum (562.3 ppbC) and minimum (58.9 ppbC) values occurred at 12:15:28 and 00:40:00, respectively. The absolute value of the difference between the maximum and minimum data was 503.4. Thus, high-precision of NMHC measurements is necessary. According to meteorological data from

national urban air quality real-time release platform, the average value of $PM_{2.5}$, O_3, NO_2, and AQI at the Xuhui Shanghai Normal University Station from 12:00 to 13:00 was 15, 58, 23, and 29 mg/m³, which was basically within the normal range. We considered that the occurrence of nearby short-time emissions at that period of time, such as painting, led to the abnormal fluctuation of NMHC. The majority of results of NMHCs in the ambient air were between 60 and 240 ppbC, and the lowest value that could be recorded by instruments was 42.8 ppbC in the results collected every 15 min. The hourly value above 300 ppbC in the hourly data occurred only 56 times, implying that a daily average concentration over 300 ppbC was rare. This indicates that the direct measurement method is completely suitable for measuring low-concentration atmospheric NMHCs. The NMHC data of several instruments were consistent when the NMHC concentration in the air was relatively high. The statistical analysis of NMHC data during this period shows that the hourly and daily average values of NMHCs were similar.

NMHCs contain a large number of VOCs, and systematically measuring them is difficult. As C2 is difficult to capture, high-carbon substances are easily adsorbed. Further studies are required to evaluate the response of C2 and high-carbon substances on FID based on the principle of the direct method.

4. Conclusion

The definition of NMHCs has been expanded to determine whether the original design of NMHC instruments can be applied to measure the sum of concentrations of more VOC components. The market is dominated by instruments using the indirect method, and we evaluated whether the principle of the indirect method was affected by the quantity of gas. We also found that the dry standard gases were used for all calibrations; these gases differed from the actual air content in the environment, thereby causing quantification errors. Based on the above problems, we tested existing instruments available in the current market.

In summary, 10 real-time monitoring NMHC instruments were tested, and the main problems in the experimental results were carefully analyzed by mainly focusing on the low concentration error, oxygen interference, humidity impact, and response factor. Low concentration error and humidity affected the accuracy of the results, and the response factor could sometimes not meet the theoretical value. Therefore, we optimized and conducted an experimental program for the real-time monitoring of the NMHC instrument using the direct method. Moreover, changing the enrichment and specially designed columns further improved the test effect.

The observation in Shanghai continued for about two months. The average daily NMHC concentration was 162.6 ppbC, and daily NMHC values ranged from 83.8 to 309.9 ppbC. The hourly NMHCs over 300 ppbC only occurred 56 times in a total of 1035 results; meanwhile, lowest and highest NMHC values reached 42.8 and 562.3 ppbC, respectively. The majority of values

ranged from 60 to 300 ppbC when the AQI was excellent. Through lab tests and field observations, we found that the results of all the indicators of instruments using the direct method were better than those using the subtraction method and the instruments using the direct method could obtain scientific data. Therefore, the direct method was proven to be suitable for monitoring NMHCs in the ambient air.

The results of this study correct the measurement errors that have prevailed for many years. It can lay a foundation for the evaluation of VOCs in the regional ambient air, and provide a direction for the measurement of low-concentration ambient air pollutants. Due to many influencing factors, in the case of low concentration of pollution, direct measurement is probably the best way to obtain data on the concentration of many complex pollutants in the ambient air, and not just NMHC.

Data availability

All raw data can be provided by the corresponding authors upon request.

Author contributions

Song Gao performed the conceptualization; Yong Yang, Xiao Tong ,Yusen Duan and Lipeng Liu performed the investigation; Song Gao performed the formal analysis; Song Gao ,Yong Yang ,Xiao Tong and Changqing Lin performed the methodology; Song Gao and Linyuan Zhang wrote original draft; Changqing Lin and Qingyan Fu performed the supervision; Lingning Meng reviewed the manuscript draft. Guigang Tang and Qiang Wang participated in establishing methodology and reviewed the manuscript draft.

Competing interests

The authors declare that they have no conflict of interest.

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Figure 1: Geographical map of the observation site at Shanghai Environmental Monitoring Center (SEMC), Xuhui
475 **Shanghai Normal University Station (XSNUS). All maps are from Google Maps.**

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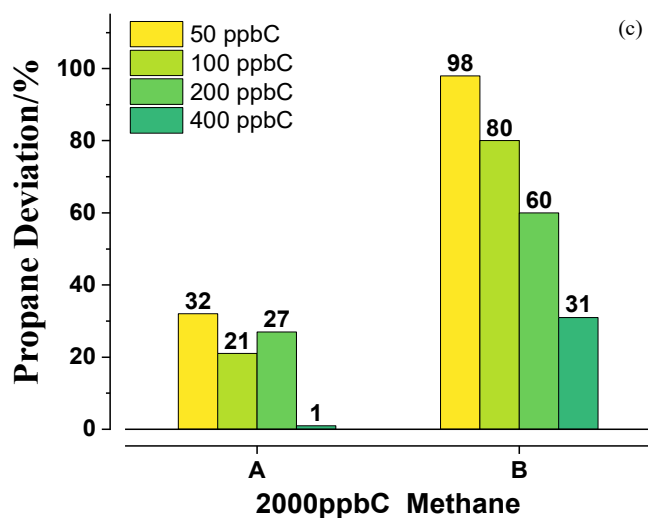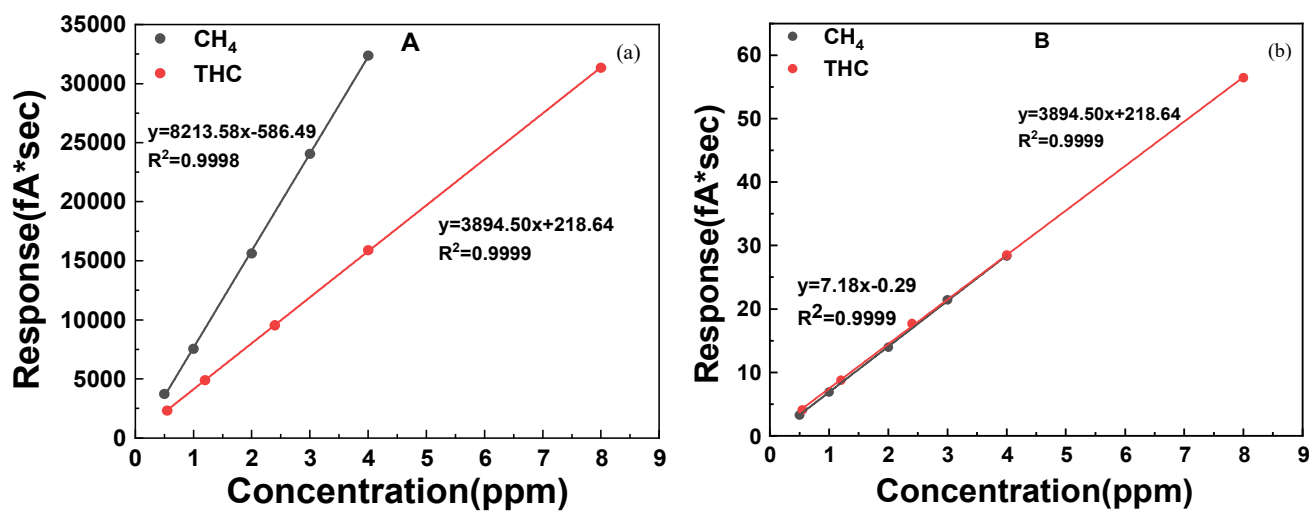
485   Figure 2: (a) Calibration curves of CH4 and (b) THC. (c) Deviation of different concentrations of propane for A and B.
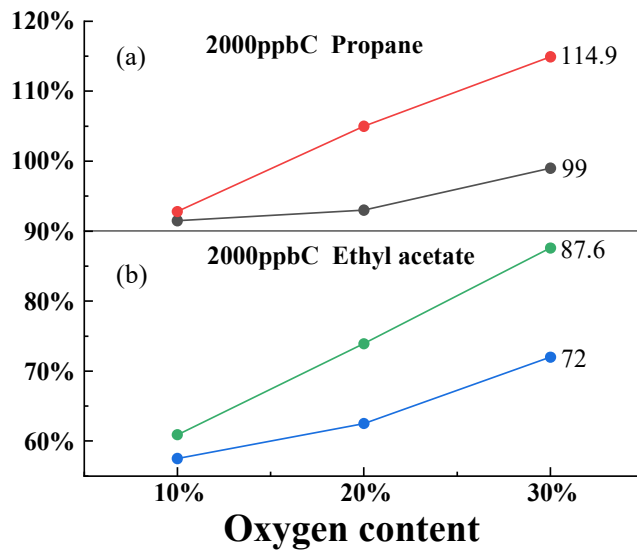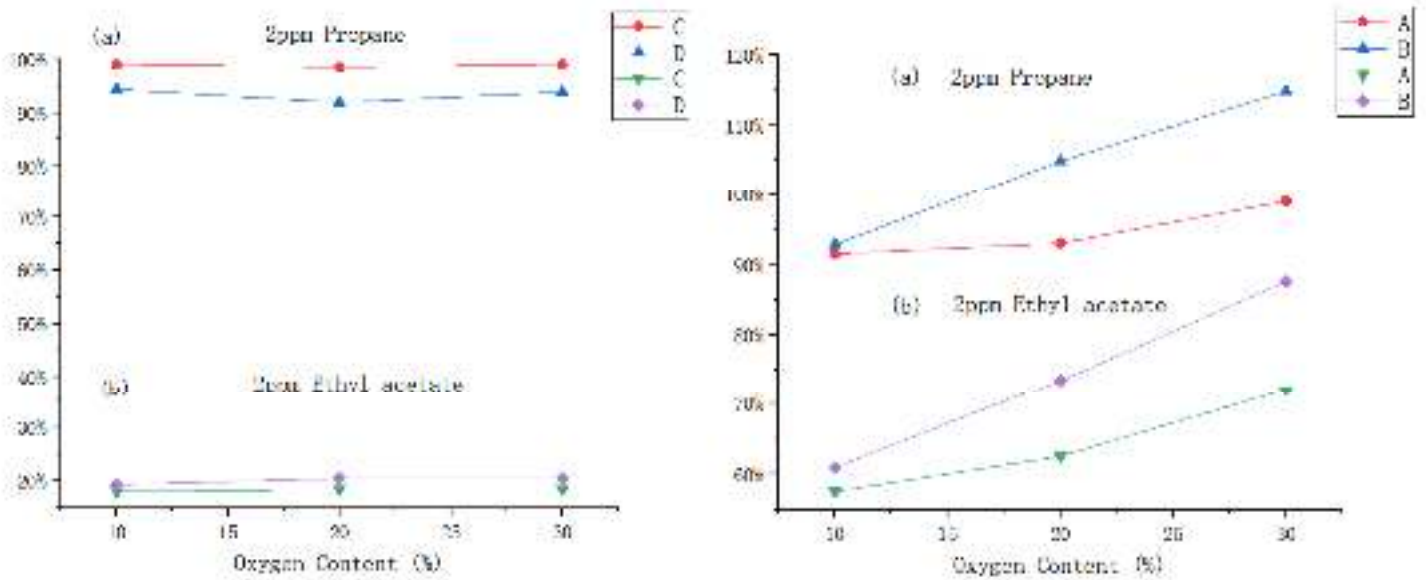
Figure 3: The effect of different oxygen contents on (a) propane and (b) ethyl acetate for A, B,C and D.
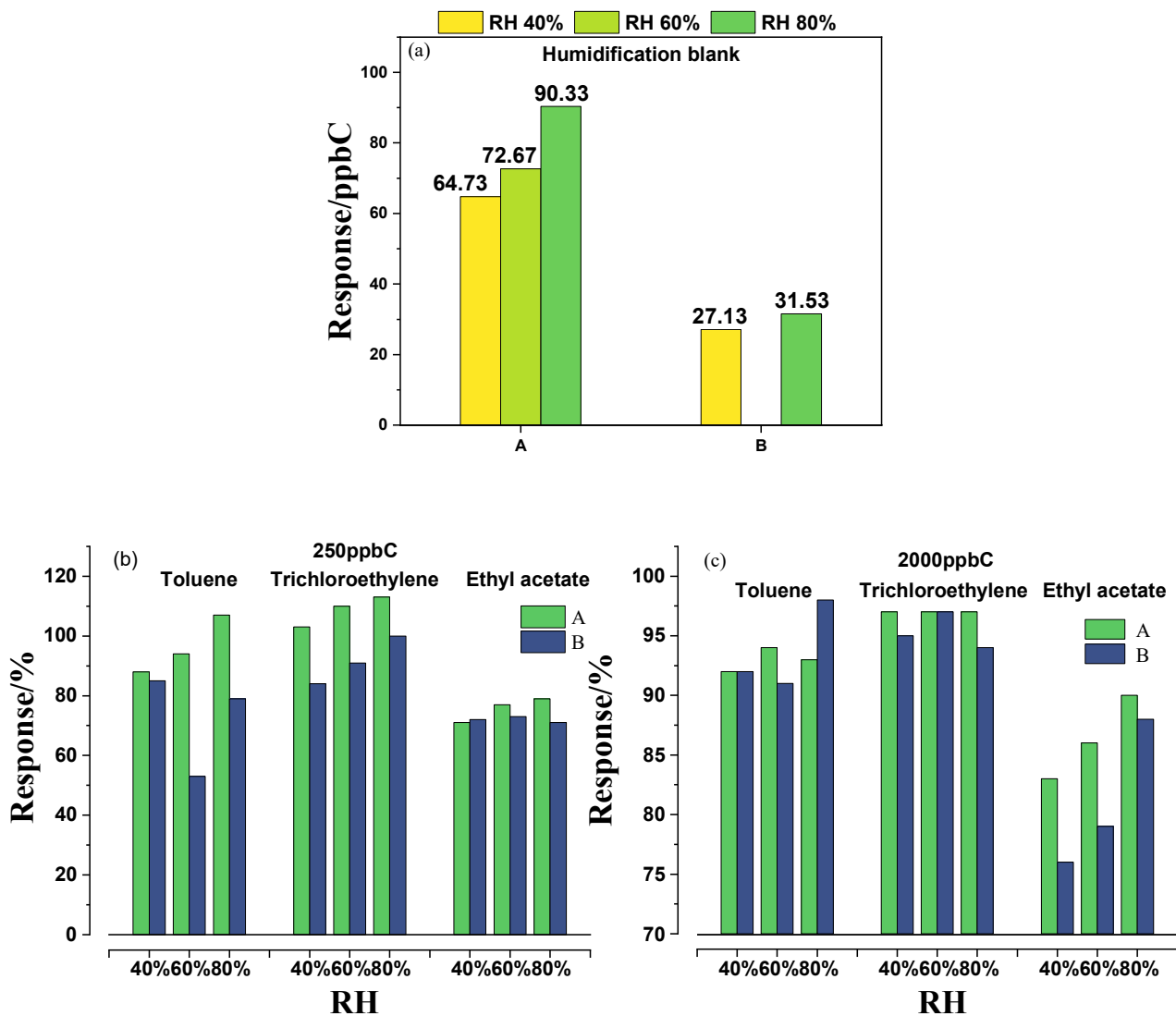
Figure 4: The effect of different RHs on (a) zero gas, (b) 250 ppbC standard gas, and (c) 2000 ppbC standard gas for A and B.
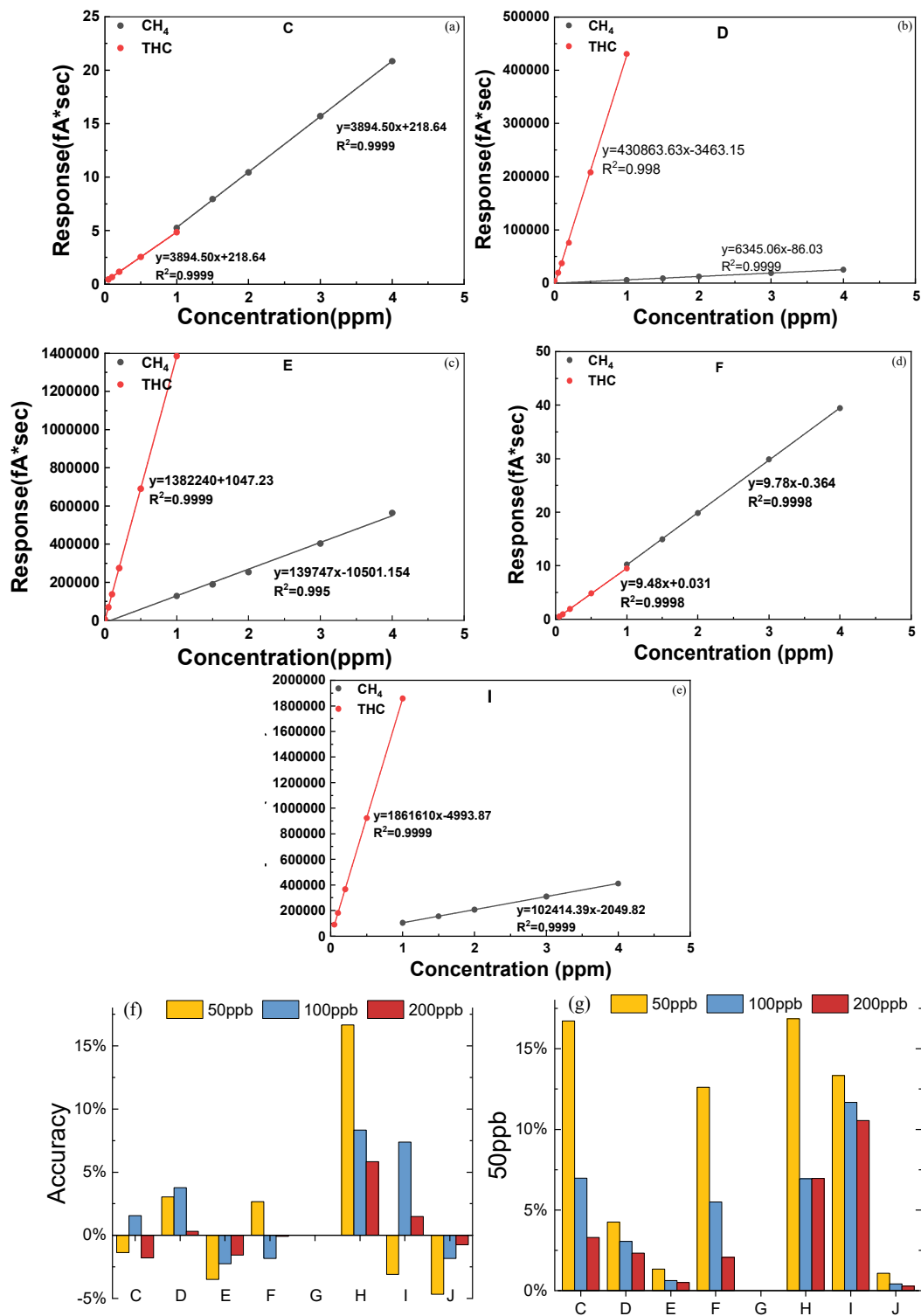
Figure 5: Calibration curves of (a-e) CH4 and (f-g) THC. Accuracy of different concentrations of propane for C-J.

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520   time

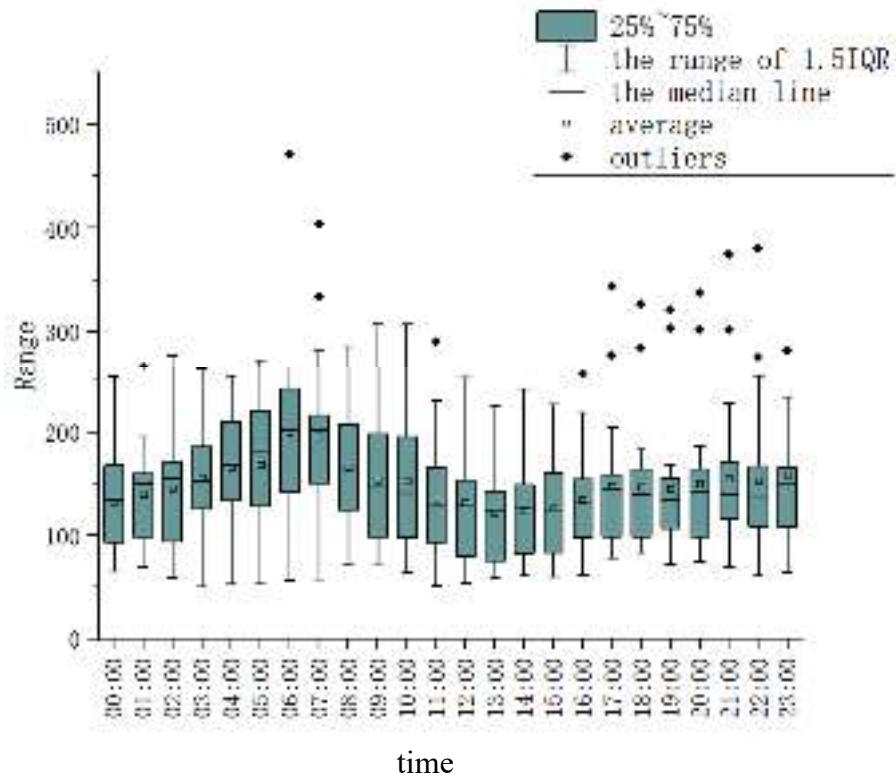



Figure 6:the daily variation of NMHC in the context of meteorological characteristics under normal undisturbed/polluted conditions.

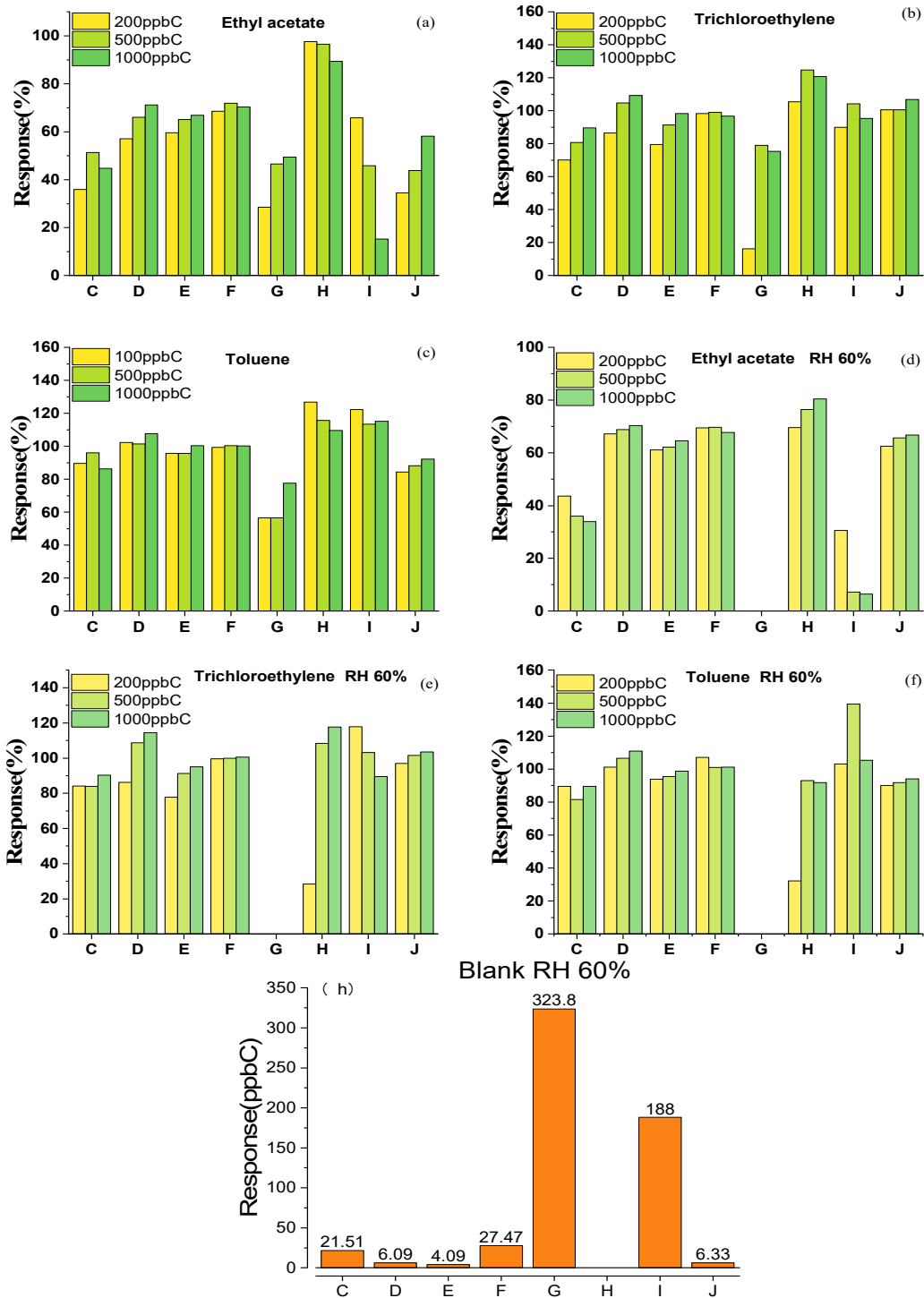



Figure 7: Response of different concentrations of (a-c) dry standard gas, (d-f) wet (RH 60%) standard gas, (h) wet

 blank (RH 60%) for C-J.

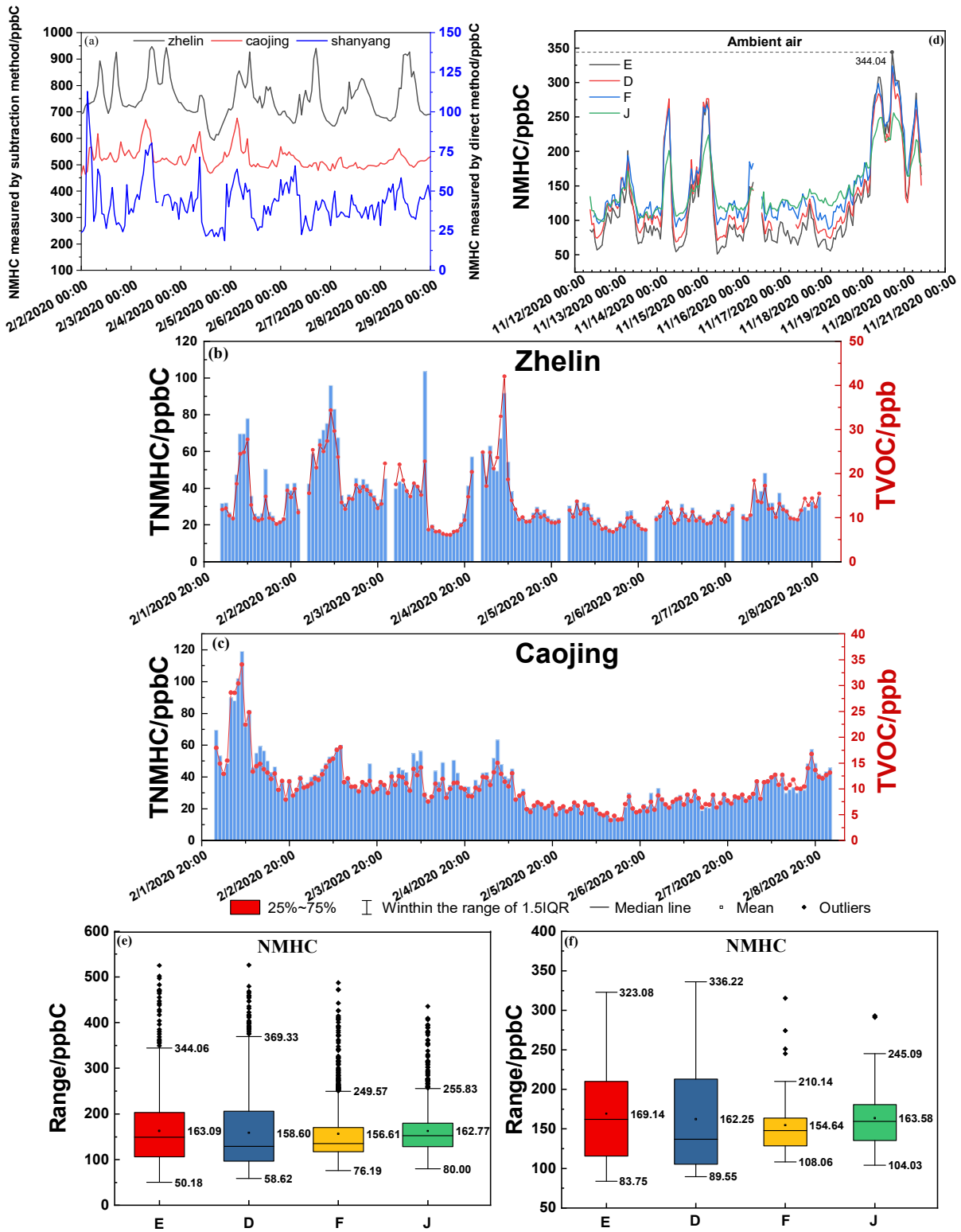



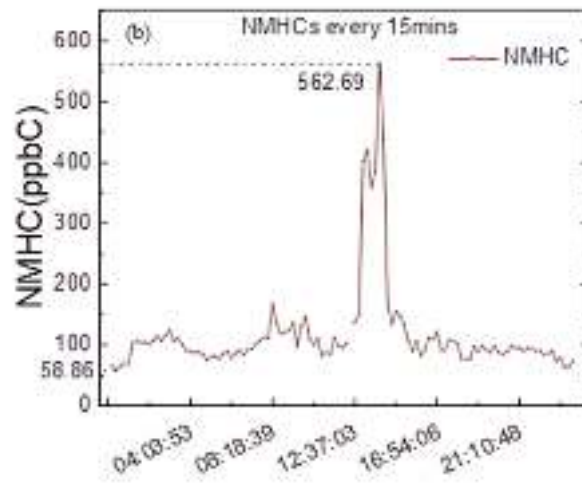
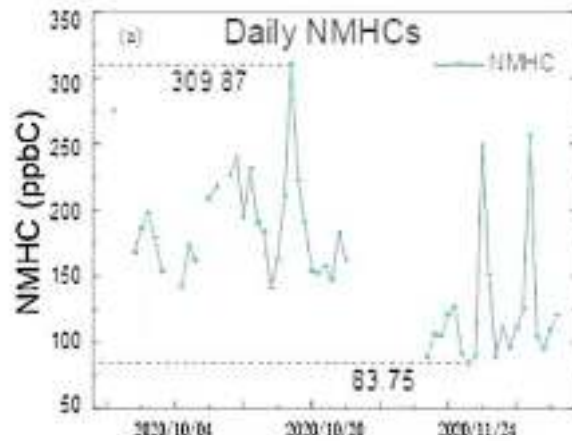
Figure8: Hourly time series diagram of NMHC in the ambient air measured with instruments using (a) the subtraction method at three sites and (d) the direct method during the 2020 Spring Festival. Hourly time series diagram of TVOCs and the total NMHCs calculated by (b) 106 kinds of VOCs and (d) 56 kinds of VOCs (PAMS) in online GC-MS; statistical analysis of the (e) hourly averages and (f) daily averages of NMHCs in the ambient air using the direct method.

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Figure 9: Daily average concentration of NMHCs and that every 15 min on Nov 23rd, 2020 measured using the direct method.

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Table 1 Information about the instruments involved in the test

Instruments	Principle	Sample volume	Analysis cycle time
A	Indirect	Quantitative loop THC 0.5 mL CH$_4$ 1 mL	2 min
B	Indirect	Quantitative loop 0.5 mL	1.5 min
C	Direct	Quantitative loop	15 min
D	Direct	Pre-concentration	10.2 min
E	Direct	Pre-concentration	13 min
F	Direct	Quantitative loop 1 mL	2.5 min
G	Direct	Quantitative loop	6 min
H	Direct	Oxidation	1 min
I	Direct	Quantitative loop	15 min
J	Direct	Pre-concentration	10 min

550 Note: A to J, 10 letters for 10 brands, including Puyu (subtraction method), Thermo Fisher Scientific, XuanYi, Puyu (direct method), Nutech, Lengshan, DKK, Envea, Chromatotec, and Synspec. Among them, B, E, G, H, I, and J are foreign brands.

Table 2 Repeatability results of instruments based on the subtraction method

NO. /ppmC	A			B		
	THC	CH$_4$	NMHC	THC	CH$_4$	NMHC
1	2.223	2.101	0.121	2.224	2.016	0.208
2	2.096	1.979	0.117	2.213	2.060	0.154
3	2.075	1.945	0.131	2.243	2.015	0.228
4	2.077	1.961	0.116	2.182	1.995	0.187
5	2.120	1.996	0.124	2.167	2.035	0.132
6	2.087	1.983	0.105	2.239	2.035	0.204
7	2.132	1.991	0.141	2.137	1.937	0.200
Mean	**2.116**	**1.994**	**0.122**	**2.201**	**2.013**	**0.187**
RSD	**2.44%**	**2.54%**	**9.50%**	**1.82%**	**1.95%**	**17. 88%**

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Table 3 the recovery rates for each instrument with different oxygen levels of 2ppm propane and ethyl acetate

Oxygen content	Propane(2ppm)			Ethyl acetate(2ppm)		
	10%	20%	30%	10%	20%	30%
A	91.5%	93.0%	99.0%	57.5%	62.5%	72.0%
C	99.0%	98.5%	99.0%	18.0%	18.5%	18.5%
B	92.8%	105.0%	114.9%	60.9%	73.9%	87.6%
D	94.4%	91.9%	93.9%	19.3%	20.5%	20.5%

Note: A,B are the subtraction method and C,D are the direct method.

Table 4 Detection limit of the instruments

Brand	C	D	E	F	G	H	I	J
Detection limit/ppbC	25.89	6.89	2.05	20.34	18.91	30.87	20.30	1.62

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Brand	C	D	E	F	G	H	I	J