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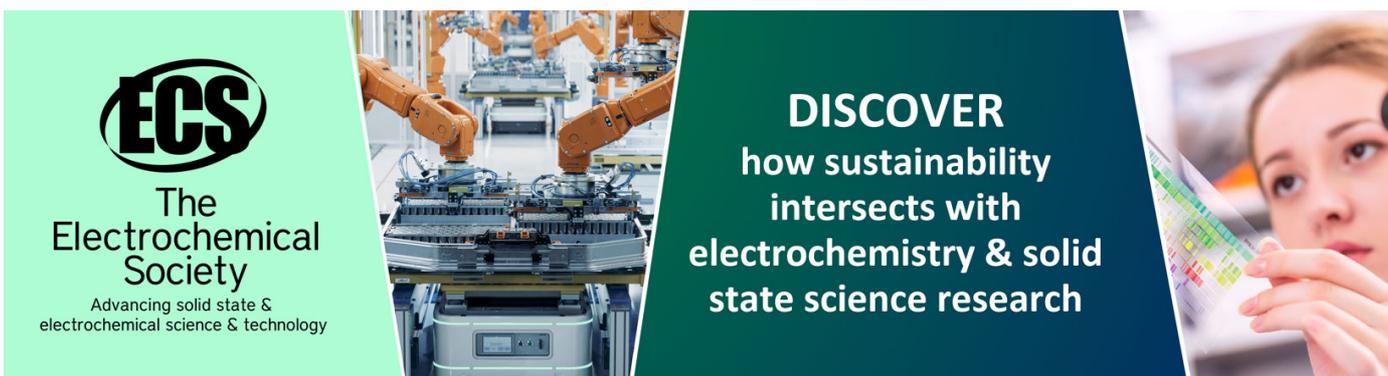
## Establishment of Pollutant Component Spectrum of Atmospheric Emission Sources in Typical Petrochemical Enterprises in Hainan Province

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# Establishment of Pollutant Component Spectrum of Atmospheric Emission Sources in Typical Petrochemical Enterprises in Hainan Province

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**Abstract:** On the basis of investigating the production process of petrochemical enterprises, The components of non-methane volatile organic compounds (NMVOCs) of each emission link in two typical petrochemical enterprises in Hainan Province using adsorption tube adsorption-thermal desorption/gas chromatography were measured and studied. The sampling analysis was conducted on the wastewater treatment and organic waste gas collection device, isomerization device, product refining deodorization device, desulfurization and denitrification device, as well as the unorganized (ambient) air around the factory. Based on this, the NMVOCs component emission inventory and ozone formation potential were studied. The results show that the emission mass concentration of NMVOCs from the above-mentioned petrochemical enterprises in Hainan Province was rather high, at 33-627.9 mg/m<sup>3</sup>. A total of 21 types of NMVOCs were quantified, of which acetaldehyde, methanol and acetone were the three dominant substances. In addition, as major categories of photochemical pollutants in petrochemical enterprises, aromatic hydrocarbons and olefins were mainly shown as xylene, propylene and butane.

## 1. Introduction

As the pillar industry in China, petrochemical industry plays a decisive role in the development of national economy <sup>[1]</sup>. Petrochemical industry has a long production line, covers a wide range, and is the key one to discharge non-methane volatile organic compounds (NMVOCs), particulate matter, SO<sub>2</sub> and NO<sub>x</sub> <sup>[2, 3]</sup>. The production process equipment of petrochemical enterprises is complex, with multiple discharge modes such as process device discharge, equipment pipeline leakage, wastewater leakage, storage tank volatilization. The component characteristics of NMVOCs discharged by different processes vary greatly, and the emission components are complicated, which makes treatment difficult. The current research of pollutants in petrochemical industry mainly focuses on the concentration variation and component characteristics of volatile organic compounds in the ambient air inside and outside the factory <sup>[4-5]</sup>, and has quite limited cognition of the pollutant emission characteristics of various processing installations, which is to the disadvantage of controlling the pollution emissions of petrochemical enterprises. Therefore, it is necessary to collect samples for varied processes and build emission characteristic spectrums of petrochemical process sources based on different technical processes.



Emission source component spectrum is the important basic data for pollution source identification of regional volatile organic compounds and particulate matters, air quality model simulation and the formulation of pollutant control countermeasures<sup>[6-7]</sup>, and the basic information to identify the pollutant emission characteristics. The study on the emission characteristics of different processes in petrochemical industry is of great significance to carry out the composite study of air pollution and formulate control strategy in China's petrochemical industry. At present, the data survey and field measurement method are mainly used to study the component spectrum of pollution sources. The data survey method is mainly in the way of component spectrum in the American SPECIATE database, but the data survey method lacks study on localization of emission source component spectrum, which is not conducive to the accurate formulation of control measures and management policies. The emissions information obtained by the field measurement method can reflect the actual emissions of pollution sources in a more authentic way. In the process of emissions estimation, the assumptions on the applicability of emission source data, fuel characteristics and effectiveness of control measures can be reduced, so as to obtain a more accurate emission source inventory<sup>[8-9]</sup>.

Hainan Province is located at the southern tip of China, as the largest and only provincial special economic zone. According to the statistical data of Hainan Statistical Yearbook 2017<sup>[10]</sup> released by Hainan Provincial Bureau of Statistics, the total output value in petroleum refining accounted for about 27.6% of the total industrial output value of Hainan Province. However, there are rare studies on VOCs emissions and component spectrum of the petrochemical industry in Hainan Province. Therefore, in this study NMVOCs field sampling and laboratory analysis were combined, accurately obtained the NMVOCs concentrations of different processes in typical petrochemical enterprises in Hainan Province, set up NMVOCs emission source characteristics of 2017 petrochemical industry in Hainan Province, and determined the component that contributed the most to the ozone formation potential (OFP) in petrochemical enterprises, providing scientific reference and theoretical support for the precise pollution control in Hainan petrochemical enterprises.

## 2. Sample collection and analysis

### 2.1 Setting of sampling points

After on-site exploration, two representative enterprises (A and B) were selected from Hainan petrochemical enterprises according to their scale, process installations, product type, output and production status, and field research was conducted. These two enterprises mainly process crude oil and manufacture petroleum products. The sample collection of organized pollutant emissions and unorganized (ambient) samples was conducted for 8 days in total from November 14, 2017 to November 17, 2017 and from November 20, 2017 to November 23, 2017, in Enterprise A and Enterprise B, respectively. The sampling points of both organized and unorganized samples in two enterprises are arranged as shown in Fig. 1. The sample collection points in Enterprise A included 2 points of process heating furnace (DA003/DA004), acidic gas recovery device (DA005), wastewater treatment and organic waste gas collection device (DA009) and isomerization device (DA006). There were also 5 sample collection points in Enterprise B, including 2 points of process heating furnace, wastewater treatment and organic waste gas collection device, product refining deodorization facility, as well as desulfurization and denitration device. In the unorganized sampling points, sampling was conducted in the upper and lower wind directions within the factory bound of Enterprise A and Enterprise B respectively. Each process device in the sampling points was sampled 3 times, with the sampling frequency of 1 time/half a day and sampling time of 1 hour. Finally, a total of 70 samples were collected from the two enterprises.

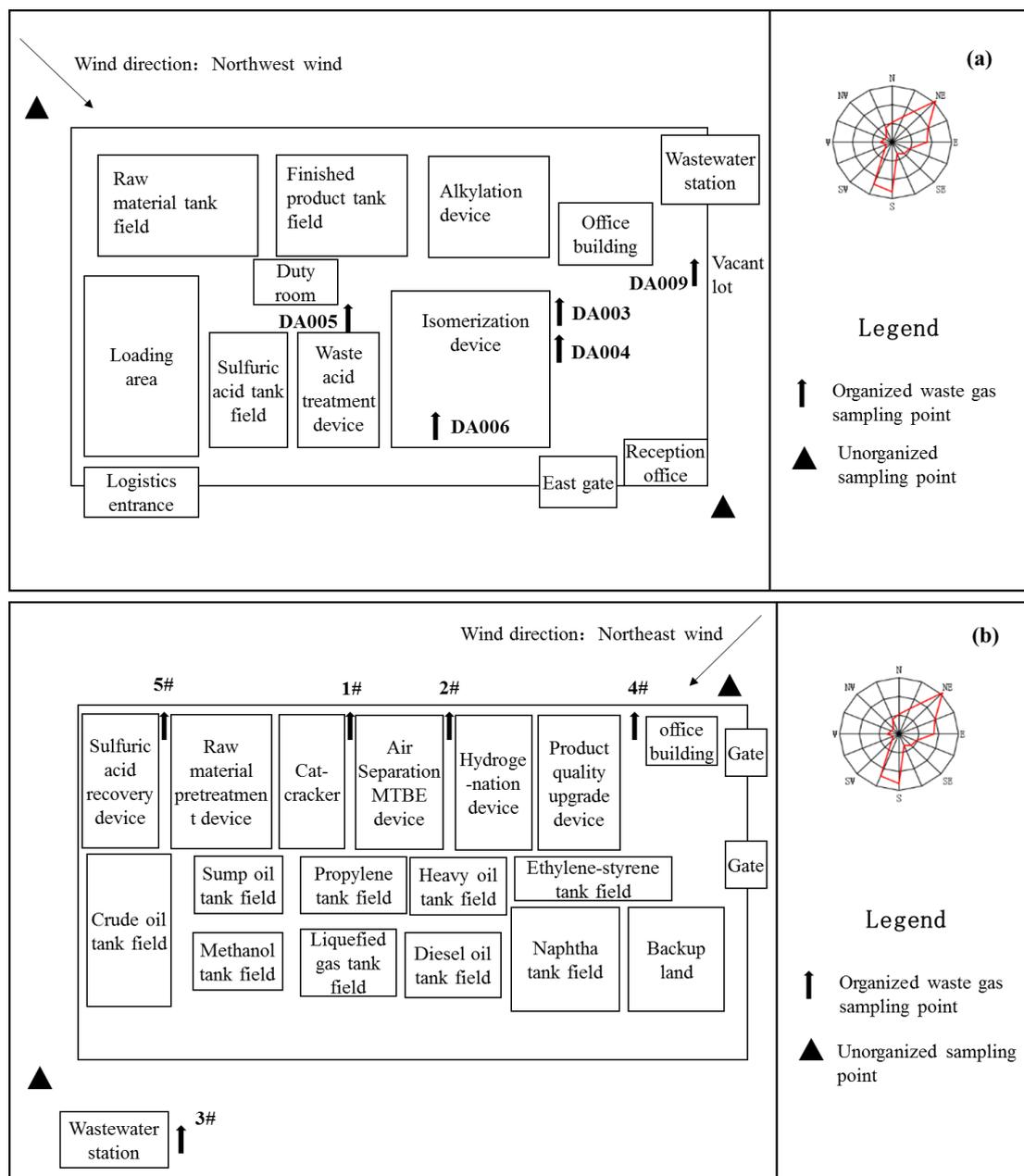


Figure. 1 (a) Sampling layout Enterprise A; (b) Sampling layout in Enterprise B

The enterprise process furnace mainly collected and analyzed the particulate matter, SO<sub>2</sub> and NO<sub>x</sub>, and the acidic gas recovery device mainly analyzed and collected sulfur dioxide and sulfuric acid mist; but other devices related to organic processing, such as wastewater treatment and organic waste gas collection device, product refining deodorization device and enterprise factory bound analysis device, mainly collected and analyzed SO<sub>2</sub>, NO<sub>x</sub> and particulate matter, as well as NMVOCs and its main components. During sampling, due to the small sampling port diameter of the isomerization regeneration device of Enterprise A, the probe of the smoke detector could not enter. Therefore, the particulate matter, SO<sub>2</sub> and NO<sub>x</sub> of the device were not tested. The oil and gas recovery device of Enterprise A malfunctioned during sampling, at the same time, the torch assembly which was running intermittently had no sampling port, so the two devices were not sampled.

### 2.2 Test instruments and devices

In order to ensure the authenticity and representativeness of samples taken, in this study, according to the stationary source collection standard of Ministry of Ecological Environment, the gas sampling location was in the vertical sections, avoiding the flue elbow and the jumpy cross sections. The sampling location was set at the place of no less than 6 times the diameter in the downstream direction of elbow, valve, reducer and distance, and the place of no less than 3 times the diameter in the upstream direction of the above parts. For gaseous pollutants, the sampling location was not subject to the above restrictions due to relatively uniform mixing, but the eddy zone should be avoided to ensure that the sampler can operate safely and take the central point of the discharge pipe as the sampling point<sup>[11]</sup>.

Unorganized gas was sampled in the process device where the ambient gas was scattered around, and the sampling points should be located in the respiratory zone at the height of 1.5 m. When surrounded by tall buildings, the sampling point should be moved to a position which had an angle of less than 30 ° with the obstacles. The sampling point should be not affected by surrounding plants or buildings; generally, there are 270 ° free space, and free of the influence of other pollutants<sup>[12]</sup>.

The samples were collected using activated carbon tube and air bag to synchronously collect the gas containing NMVOCs. For these two sampling methods, the gas was processed respectively by thermal desorption device and three-stage cold trap gas precooling and concentration device, and then the gas chromatograph was used for quantitative determination. For other pollutants, such as SO<sub>2</sub>, NO<sub>x</sub>, and particulate matter, brown-acid titrator was used respectively. Visible spectrophotometer and flue gas tester were used for determination. Sulfate, nitrate and ammonium were measured by ion chromatograph.

### 2.3 Quality control and quality assurance

In order to ensure the representativeness and authenticity of samples collected, the sampling points, sampling methods and monitoring frequencies of fixed pollution sources are determined mainly according to the sampling standards issued by the country or industry for fixed pollution sources monitoring<sup>[12-14]</sup>. Before sampling, the pitot tube and sampling tip were checked intact; the sampling bag was checked whether there was leakage phenomenon such as rupture and damage; the filter tube was observed to check if there was any damage; the air tightness of the sampling system was checked. New sampling air bag, new activated carbon tube and new filter tube were used for sample collection. Before the analysis of samples in the laboratory, the quality control of 19 test studies was carried out in various ways, including personnel, environment, methods, reagent materials and equipment. At the same time, measures such as blank sample, parallel sample, quality control sample and standard recovery were taken in the monitoring process to ensure the accuracy and reliability of the monitoring results. Standard curve should be drawn for each batch of samples, and the correlation coefficient should be no less than 0.999. The laboratory blank level should not be greater than 10 ng. The relative deviation of duplicate samples should not be greater than 25% and that of standard recovery should not be greater than 20%. For the sample's standard recovery, two sets of parallel sampling device should be set at the same sampling point. One of them contained all the standard mixtures of target compounds, and the standard labeled concentration was controlled at 40~60% of the sample concentration based on the pre-sampling results.

### 2.4 Estimation of NMVOCs emission inventory at sampling points

Through literature review<sup>[15]</sup>, the estimation formula of organized pollution sources in this study is as follows:

$$E_i = \sum_{n=1}^N \left\{ Q_n \times \left[ 1 - (f_{H_2O})_n \right] \times \frac{T_o}{T_n} \times \frac{P_n}{P_o} \times (C_i)_n \times H \times 10^{-9} \right\} \quad (1)$$

Where,  $E_i$  is the emissions of pollutant  $i$ , t/a.  $N$  is the annual number of measurements;  $n$  is the

measurement number, for the  $n$ th measurement;  $Q_n$  refers to the flow rate (wet basis) of the process waste gas during the  $n$ th measurement,  $\text{m}^3/\text{h}$ ;  $(f_{H_2O})_n$  refers to the water content of the process waste gas during the  $n$ th measurement, in volume fraction;  $T_o$  is the temperature in the standard state, 273.15K;  $T_n$  is the temperature at the  $n$ th measurement of flow, K;  $P_n$  is the average pressure when measuring flow in the  $n$ th measurement, kPa;  $P_o$  is the average pressure in the standard state, 101.325 kPa;  $(C_i)_n$  is the concentration (dry basis and standard state) of pollutant  $i$  in the process waste gas during the  $n$ th measurement,  $\text{mg}/\text{m}^3$ ;  $H$  is the time interval between the two measurements,  $h$ .

### 2.5 Analysis of photochemical activity characteristics of NMVOCs at sampling points

The danger of volatile organics lies not only in its own toxicity, but also in its close correlation with photochemical ozone formation [16-17], which can be evaluated by using ozone formation potential (OFP). Currently, OFP research methods mainly include: equivalent propylene concentration method, photochemical ozone creation potential method (POCP), OH radical reaction rate method (LOH) and maximum incremental reaction method (MIR) [18-21]. MIR represents the maximum ozone concentration that components can generate. Its calculation takes into account both the kinetic activity of VOCs and the reaction mechanism activity of VOCs, which can reflect the ozone formation contribution capacity of VOCs as a whole. Therefore, this study adopted the MIR method to study the characteristics of VOCs photochemical pollution in petrochemical enterprises. The calculation formula is as follows:

$$\begin{aligned} \xi_{MIR,i} &= \max[\partial p(O_3) / \partial p(VOCs)_i] \\ \varphi_{OFP,i} &= \xi_{MIR,i} \times p(VOCs)_i \end{aligned} \quad (2)$$

Where,  $\rho(O_3)$  refers to ozone mass concentration ( $\text{mg}/\text{m}^3$ ).  $\rho(VOCs)_i$  refers to the mass concentration ( $\text{mg}/\text{m}^3$ )/ emissions (t) of VOCs component  $i$ ;  $\varphi_{OFP,i}$  is the maximum OFP in the component  $i$ ;  $\xi_{MIR,i}$  is the maximum incremental reactivity of component  $i$ . In this study, the MIR coefficient values are mainly from the research results of literatures.

## 3. Results and discussions

### 3.1 Laboratory analysis results

#### 3.1.1 Total concentration analysis of pollutants at each sampling points

(1) Analysis results of Enterprise A's emission sources

The total concentration of particulate matter,  $\text{SO}_2$ ,  $\text{NO}_x$ , and tested NMVOCs from organized process devices and unorganized (ambient) air in Enterprise A is shown in Table 1. It is shown from Table 1 that the concentrations of particulate matter,  $\text{SO}_2$  and  $\text{NO}_x$  from process heating furnace were  $190.4 \text{ mg}/\text{m}^3$ ,  $869 \text{ mg}/\text{m}^3$  and  $877.3 \text{ mg}/\text{m}^3$ , which seriously exceeded the emissions standard of particulate matter ( $20 \text{ mg}/\text{m}^3$ ),  $\text{SO}_2$  ( $50 \text{ mg}/\text{m}^3$ ) and  $\text{NO}_x$  ( $100 \text{ mg}/\text{m}^3$ ) in the process heating furnace in petroleum chemical industry enterprises by the Ministry of Ecological Environment [22], so the enterprise should install higher-efficient flue gas based nitrogen, phosphorus, dust removal device. The concentration of  $\text{SO}_2$  in the acidic gas recovery device was up to  $436 \text{ mg}/\text{m}^3$ , which was 3.3 times higher than the  $\text{SO}_2$  emission limit ( $100 \text{ mg}/\text{m}^3$ ) set by the Ministry of Ecological Environment, and the concentration of various pollutants in the unorganized ambient air around the factory also seriously exceeds the emission limit set by the Ministry of Ecological Environment. The concentrations of NMVOCs detected by wastewater treatment and organic waste gas collection device and isomerization device in Enterprise A were relatively close. In general, the tested concentrations at the sampling points in the enterprise seriously exceeded the national emission standards, and the enterprise should add equipment and facilities with higher efficiency of pollutant removal in each process.

Table 1 Summary of total concentration ( $\text{mg}/\text{m}^3$ ) of pollutants detected in Enterprise A

Detecting process	Particulate matter	SO <sub>2</sub>	NO <sub>x</sub>	Total tested NMVOCs
Process heating furnace	190.4	869	877.3	-----
Acidic gas recovery device	-----	436	-----	-----
Wastewater treatment and organic waste gas collection device	99.7	438.7	439.3	598.3
Isomerization device	-----	-----	-----	541.3
Unorganized (ambient) air around the factory	77.2	371.3	384	218.7

## (2) Analysis results of Enterprise B's emission sources

Table 2 shows the total concentration of particulate matter, SO<sub>2</sub>, NO<sub>x</sub>, and tested NMVOCs from the organized process devices and unorganized (ambient) air in Enterprise B; similar to Enterprise A, the detected pollutant concentration in the enterprise also seriously exceeded the emissions limits released by our country. Among them, the NMVOCs emissions from product refining deodorization facilities accounted for the most, compared with those from other sampling points, which is mainly because there were more organic compounds containing sulfur and ammonia in the product refining deodorization facilities. Desulfurization and denitrification device contained a relatively small amount of NMVOCs, which is mainly because Enterprise B enterprise integrated the catalytic cracking catalyst regeneration flue gas device and sulfur recovery device, and the tail gas of two processes was discharged to the desulfurization and denitrification device, then was discharged together after treatment, so the tail gas in the later device was the total tail gas from three devices, which led to the complex composition of pollutants in the device, at the same time, when the flow was measured, the hourly flow in the device was found more than those in other devices. The measured emission rates in three times were 8.13 kg/h, 12.84 kg/h and 17.18 kg/h, respectively.

Table 2 Summary of total concentration ( $\text{mg}/\text{m}^3$ ) of pollutants detected in Enterprise B

Detecting process	Particulate matter	SO <sub>2</sub>	NO <sub>x</sub>	Total tested NMVOCs
Process heating furnace	176.3	861	862.7	-----
Wastewater treatment and organic waste gas collection device	93.7	434.7	435	591
Desulfurization and denitration device	93.3	414	415	33.4
Product refining deodorization facilities	-----	-----	-----	627.9
Unorganized (ambient) air around the factory	84.2	414	443.7	320.5

By comparing the test results of Enterprise A and Enterprise B in Table 1 and Table 2, it is found that the pollutant concentrations in the two petrochemical enterprises in Hainan Province were seriously over the standard. Relevant departments of Hainan Province should strictly supervise and control the pollutants in these petrochemical enterprises. First of all, Hainan petrochemical enterprises should step up the installation of waste gas treatment device with higher recycling and treatment efficiency enterprises so as to effectively reduce the emission of NMVOCs. The operation of the installed tail gas treatment device should be monitored in real time, and the monitoring and statistics system of NMVOCs in petrochemical enterprises should be improved; besides, intelligent monitoring equipment that can be remotely controlled should be installed in the plant area of petrochemical enterprises, so as to supervise and urge the enterprises to meet the emission standards. On the other hand, clean production should be vigorously promoted to reduce NMVOCs emissions from the source.

The components tested for particulate matter in process organized emission (fixed emission source) were organic carbon, black carbon, sulfate, nitrate and ammonium salt. The contribution characteristics of each component are shown in Fig.2. Black carbon is the largest in particulate matter components in 2 enterprises, accounting for 57.7% and 31.8%, respectively. Black carbon is the main

absorbent of atmospheric aerosol [23-24], which will reduce atmospheric visibility [25], lead to health damage and erosion of buildings, and impact on regional and global climate change. Therefore, it is necessary to control black carbon pollution in Hainan petrochemical enterprises. The organic carbon in the fixed source emissions of the 2 enterprises has a high proportion, which is 25.1% and 29.5%, respectively. The high proportion of organic carbon is relatively predictable, and volatile organic compounds are highly reactive. The secondary organic aerosols are generated in a relatively short time. The ammonium salt, accounts for 3.6% and 10.2% in Enterprise A and B respectively, which is the least.

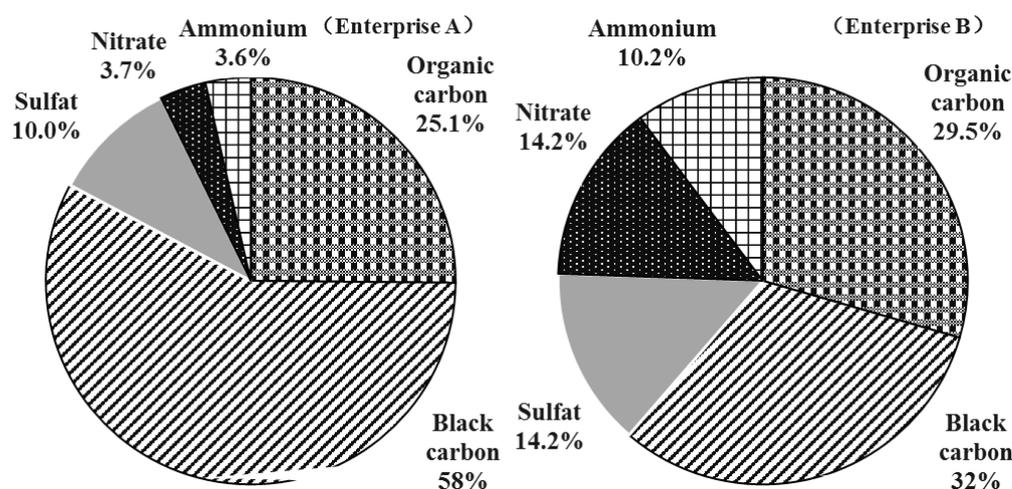


Figure. 2 The characteristics of particulate matter composition of organized emission sources in Enterprises A and B

### 3.1.2 Component analysis of NMVOCs at different sampling points

Field sample test results show that there were 22 kinds of substances that could be detected by the components of NMVOCs in the seven sampling sites of the two enterprises, of which the substances that could be detected by 100% included benzene, toluene, o-xylene, m-xylene, p-xylene, ethylbenzene, styrene, ethylene, chloroethylene, propane, n-hexane and ethane.

Fig.3 shows the NMVOCs composition concentration of the two enterprises at different sampling points. The three maximum components in the wastewater treatment and organic waste gas collection device of Enterprise A are acetaldehyde, methanol and butane, the combined concentration of which accounts for 34.7% of the total concentration. The wastewater of wastewater treatment and organic waste gas collection device mainly comes from cooling water, washing water and caustic washing water in the production process, which contained dissolved NMVOCs substance. The treating process included acidification, aeration and anaerobic wastewater treatment operation, and the waste gas was collected into the waste gas treatment device through the induced draught system, and treated with the biological deodorant system. Finally, the waste gas was discharged into the atmosphere through the exhaust funnel. But it cannot be treated 100% in the process, so there was still a lot of organics in the final exhaust. The three maximum components in the isomerization device were acetaldehyde, methanol and o-xylene. The sum of the three substances takes up 35.2% of the total concentration, and the sum of the three substances takes up 69.0% and 69.3% of the total concentration of the two sampling points respectively, among which isopropanol accounts for 57.7% and 58.0% of the total concentration respectively. The waste gas of the isomerization regeneration device mainly came from the gas produced in the process of isomerization. As the isomerization reaction takes place over a period of time, polymer olefin product cracking the made hydrocarbon deposited on the surface of the catalyst in the form of coke, resulting in a decline in the activity of the catalyst. Therefore, the catalyst must be regenerated after being used for a period of time to improve its activity. Under the high temperature environment, the coke on the catalyst surface was converted into CO<sub>2</sub> and discharged into

the atmosphere through the exhaust funnel. Due to insufficient combustion, the tail gas of the isomerization regeneration device comprised substances including acetaldehyde, methanol and some benzene series, which contained NMVOCs. The three maximum substances detected at unorganized emissions (ambient air around the factory) were xylene, ethyl benzene and p-xylene, which were aromatic hydrocarbon compounds, accounting for 42.7% of the total concentration in the ambient air around the factory detection. The components with high content detected in the ambient air around the factory were significantly different from the first three components in the two organized discharge process, such as dispersion in production, leakage and volatilization of storage in tank field, which indicated that the benzene series in the organized discharges device of the process is highly active and more prone to volatilization and leakage.

The first three maximum substances of Enterprise B's wastewater treatment and organic waste gas collection device is acetaldehyde, methanol and butene, the concentration of which accounted for 34.9% of the total concentration of the process. It is the same as the components of the process in Enterprise A. It suggests that the types of contaminants in the same process are very similar, even though in different enterprises. The first three maximum substances in the desulfurization and denitrification device of Enterprise B are acetaldehyde, methanol and o-xylene, accounting for 35.3% of the total concentration of the process. The desulfurization and denitrification device of B Enterprise B is used to treat the SO<sub>2</sub> and NO<sub>x</sub> containing in the tail gas. Desulfurization adopted limestone - paste wet desulphurization process, and main process technology were as follows: the limestone was mixed with water and stir into absorption slurry in the absorption tower; absorption slurry was mixed in contact with the flue gas; the SO<sub>2</sub> in the flue gas and the CaCO<sub>3</sub> in the slurry and the air-oxidized air in the air were absorbed by chemical reaction to remove SO<sub>2</sub>; the end product was gypsum; the flue gas after desulphurization removed fogdrop through the mist eliminator and was discharged into the atmosphere from the exhaust funnel. Denitration adopted selective catalytic reduction (SCR), and the main technological process was: flue gas was led into the SCR reactor in 310-410°C position of the boiler; under the action of catalyst, NO<sub>x</sub> in flue gas reacted with reducing agent NH<sub>3</sub> to form N<sub>2</sub>, thus reducing the emission concentration of NO<sub>x</sub>; after denitration, the flue gas was drawn into the boiler for combustion and finally discharged into the atmosphere through the exhaust funnel. Due to the combustion efficiency of the device itself, the waste gas comprised substances containing NMVOCs such as isopropyl alcohol, non-methane total hydrocarbon and some benzene series. Products refined deodorization devices were most abundant in acetaldehyde, ethylene, and methanol, accounting for 31.2% of the total process concentration. Products refined deodorization device was used to treat gas, dry gas, liquefied petroleum gas from catalytic cracking device and gas holder gas from the oil and gas recycling facilities. The waste gas of the device was discharged into the atmosphere through the exhaust funnel after being treated by the deodorization device. The deodorization device mainly deals with odorous gases such as H<sub>2</sub>S and NH<sub>3</sub>, but organics can still be detected in the final flue gas due to the high volatility of NMVOCs. The three most abundant substances detected in ambient air around the factory were meta-xylene, o-xylene and p-xylene, which all belonged to aromatic hydrocarbons. These three substances accounted for 41.5% of the total NMVOCs concentration of the test, similar to species categories of much content detected in Enterprise A. It indicates that aromatic hydrocarbons should be the focus of attention and governance for petrochemical enterprises.

According to the emission limit of organic pollutants in the exhaust under the Release of Pollutant Discharge Standard in Petrochemical Industry<sup>[22]</sup> issued by the Ministry of Ecological Environment, the 14 pollutants with emission limit and its emission limit in this study are as follows: benzene (4 mg/m<sup>3</sup>), methylbenzene (15 mg/m<sup>3</sup>), xylene (20 mg/m<sup>3</sup>), ethylbenzene (100 mg/m<sup>3</sup>), styrene (50 mg/m<sup>3</sup>), chloroethylene (1 mg/m<sup>3</sup>), formaldehyde (5 mg/m<sup>3</sup>), acetaldehyde (50 mg/m<sup>3</sup>), acrolein (3 mg/m<sup>3</sup>), normal hexane (100 mg/m<sup>3</sup>), methyl alcohol (50 mg/m<sup>3</sup>) and acetone (100 mg/m<sup>3</sup>). It can be found through comparison between the detection value of each pollutant and emission standard that only five components meet the standard, including methylbenzene, ethylbenzene, styrene, normal hexane and acetone, and other components severely exceed the limit, especially the xylene, of which the detection concentration doubles the emission limit. Xylene organics have a relatively high

atmospheric reactivity<sup>[26]</sup> and deemed as vital precursor to ozone formation. It is a matter of great urgency to effectively control these components out of limits.

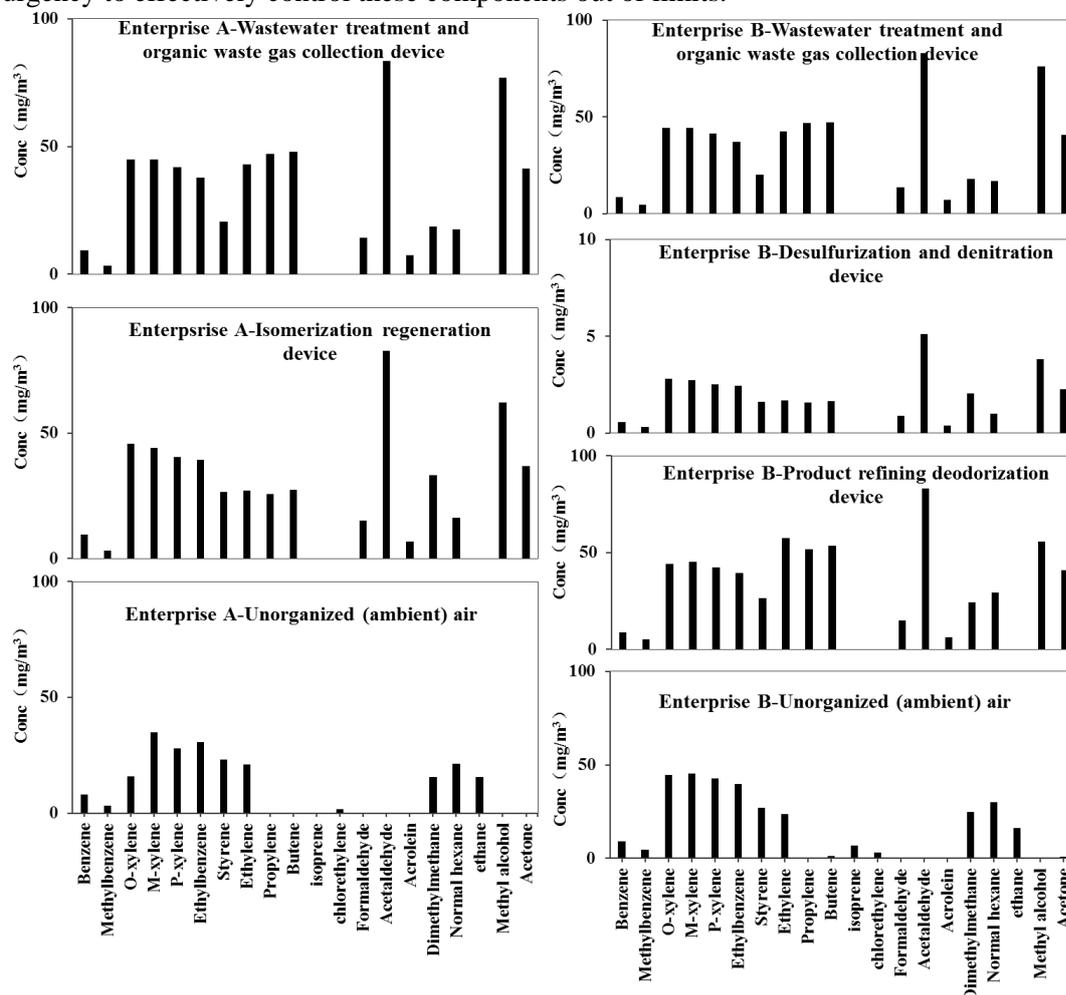


Figure. 3 Characteristic Spectra of NMVOCs components at different sampling points in Enterprises A and B

### 3.2 Analysis on emission characteristics of NMVOCs in emission inventory of petrochemical industry

#### 3.2.1 Emission characteristics of NMVOCs components at different sampling points

Through investigation on flow of different sampling apparatus and annual operation time in Enterprises A and B and in combination of emission concentration of NMVOCs detected, the emission inventory of NMVOCs at different sampling points can be obtained based on Formula 1. Table 3 shows wastewater treatment and organic waste gas collection device in Enterprises A and B and key component emissions of NMVOCs in desulfurization and denitration device in Enterprise B in 2017. Component emissions of NMVOCs in wastewater treatment and organic waste gas collection device in Enterprise B is almost twice as much as Enterprise A, because the former's scale is larger than the latter's. Benzene series and aldoketones are considered the much pollutants emitted from Enterprises A and B.

Table 3 Emission characteristics of NMVOCs components of fixed sources in Enterprises A and B

Wastewater treatment and organic waste gas collected device in	Wastewater treatment and organic waste gas collection device in	Desulfurization and denitration device in Enterprise B
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	<b>Enterprise A</b>	<b>Enterprise B</b>	
Benzene	0.39	0.60	0.87
Methylbenzene	0.13	0.33	0.49
O-xylene	1.91	3.14	4.44
M-xylene	1.91	3.15	4.31
P-xylene	1.77	2.92	3.95
Ethylbenzene	1.60	2.63	3.86
Styrene	0.87	1.42	2.55
Ethylene	1.83	3.00	2.63
Propylene	2.00	3.31	2.47
Butene	2.03	3.34	2.59
Formaldehyde	0.60	0.97	1.42
Acetaldehyde	3.55	5.89	8.09
Acrolein	0.31	0.50	0.62
Dimethylmethane	0.79	1.27	3.24
Normal hexane	0.74	1.20	1.54
Methyl alcohol	3.26	5.39	6.05
Acetone	1.76	2.87	3.58

### 3.2.2 OFP in each detection process

According to the component emissions of NMVOCs in each process and in combination of MIR coefficient, the OFP of different organized emissions during process can be obtained. Table 3 shows the OFP of different VOCs components at three sampling points in Enterprises A and B. The top three materials in contributions of OFP for the wastewater treatment and organic waste gas collection device point location are the same, which are propylene, acetaldehyde and butane, accounting for 45.6% and 45.7% in total contributions respectively in two enterprises. Two of the three substances are olefins, so olefins are the principal photochemistry pollutants in wastewater treatment and organic waste gas collection device. Furthermore, the contribution of OFP from arene substances cannot be neglected, and merely three types of xylene substances account for 30% of total amount. The top three substances in contributions of OFP for the desulfurization and denitration device point location are acetaldehyde, m-xylene and o-xylene, which account for 47% of total amount. Two of these top three materials are arene substances. Therefore, the olefin substances are the principal photochemistry pollutants in the process. To sum up, key harnessing on arene substances in petrochemical industry is very important.

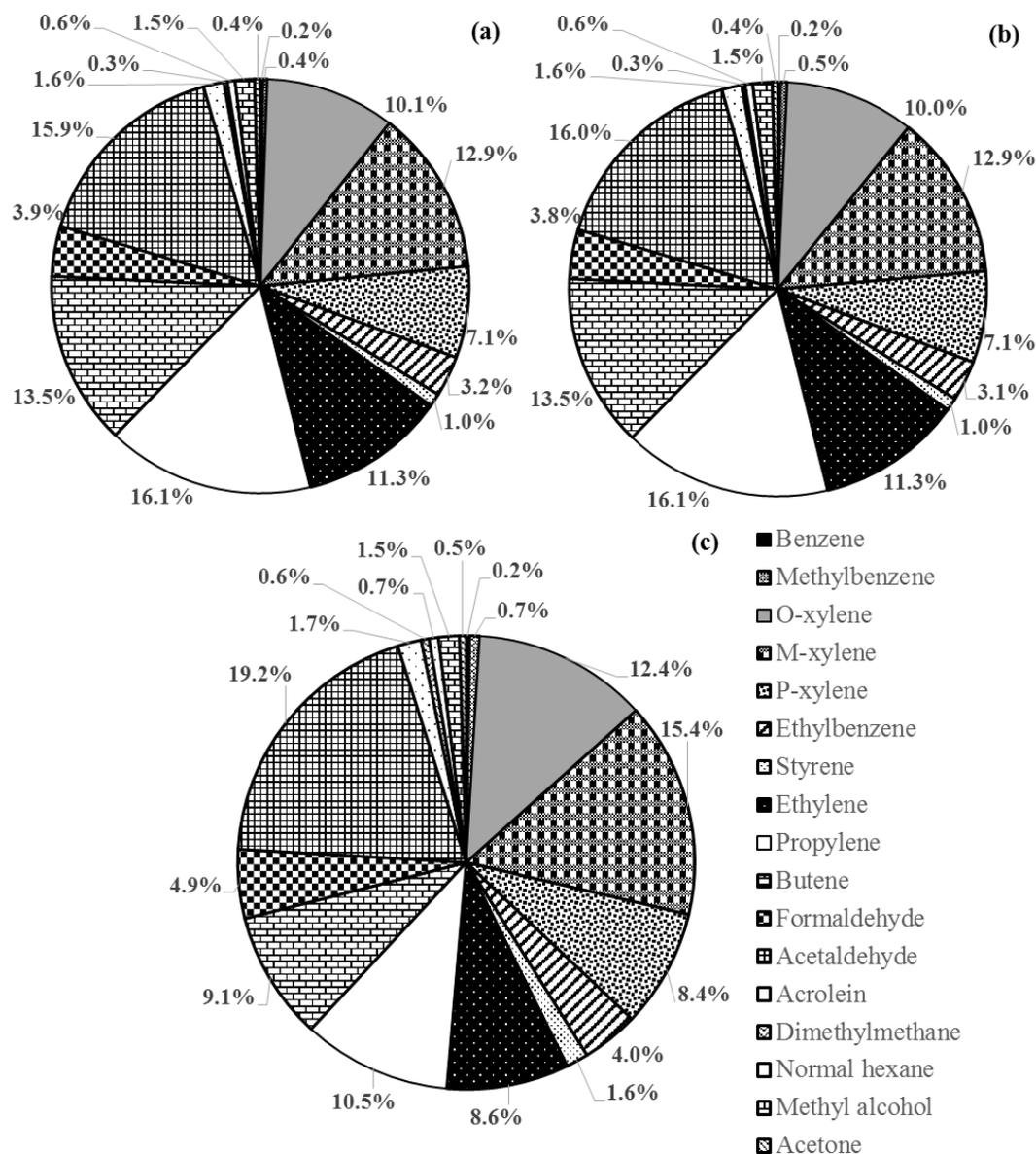


Figure. 4 (a) The wastewater treatment and organic waste gas collection device in Enterprise A, (b) The wastewater treatment and organic waste gas collection device in Enterprise B, (c) OFP of NMVOCs in the desulfurization and denitrification device of Enterprise B .

#### 4. Conclusions

(1) The mass concentrations of particulate matter,  $\text{SO}_2$ ,  $\text{NO}_x$  and NMVOCs in the process in petrochemical industries in Hainan Province, are 77.2-190.4, 371.3-869, 384-877.3 and 33 -627.9  $\text{mg}/\text{m}^3$ , respectively. The data are far above the emission standards of process devices in petrochemical industry released by the Ministry of Environmental Protection, and enhancement in the treatment of pollutions is further needed for the petrochemical industry in Hainan Province.

(2) All of polluting emission links, 21 components of NMVOCs have been detected. Among these components, acetaldehyde, methyl alcohol and acetone are at a high concentration and aromatic hydrocarbons and olefin compounds are classified into vital photochemical pollutants, which mainly include xylene, propylene and butane.

(3) Key components in process emission sources in the petrochemical industry in Hainan Province

include organic carbon, black carbon, sulfate, nitrate and ammonium salt, among which black carbon and organic carbon have a high proportion, accounting for 57.7%-32% and 25.1%-29.5% respectively.

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