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Study on the Characteristics of Unorganized Emission of Volatile Organic Compounds in Chemical Industry--Taking Tianjin Chemical Enterprises as an Example

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Abstract: In order to study on the unorganized emissions characteristics of volatile organic compounds (VOCs) of Tianjin chemical industry, three plants located in a chemical park in Tianjin were chosen. Air samples on the plant boundary and within the enterprise were collected through air bag, and the VOCs emission levels and component characteristics were measured using proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS). The analysis results showed that, (1) the emission level of VOCs of three plants were different. The level of VOCs in tank area was directly related to the tank type, and the level in storage tank area was related to whether it was sealed, (2) the components of VOCs emitted from unorganized sources mainly were saturated alkanes represented by C_2, C_7, C_8, C_9 and C_{11} and oxygenated volatile organic compounds (OVOCs) represented by CH_4O, (3) it was found that alkane substance was a large class of VOCs component in chemical industry plant, so alkanes should be controlled in priority.

Keywords: Volatile Organic Compounds, Chemical Industry, Unorganized Emissions, Emission Levels, Component Characteristics

1. Introduction

Volatile organic compounds (VOCs) were important precursors for troposphere ozone and secondary organic aerosol, which were also main factors driving the increase of atmospheric oxidizing capacity. With the acceleration of industrialization, the emissions of VOCs in China had increased significantly over the past decades, which led to the phenomena that many places in China suffered the pollution dominated by secondary pollutants such as $PM_{2.5}$ and ozone. Monitoring data of year 2016 had showed that rates of change of ozone in the 90th percentile of the 8-hour moving average maximum during year 2013 and 2016 were 139, 145, 150 and 155 μg/m^3 respectively. The concentration of ozone markedly increased, making ozone become the focus of air pollution prevention and control in the future [1]. Besides, previous studies from Ying Chen [2] had predicted the industrial product of VOCs in year 2020 to be 17.51 million tons. Therefore, conducting the study of emission characteristics of VOCs was crucial to air pollution control.

The petrochemical industry, being the primary source of VOCs pollution, took up more than 30% of national VOCs emission amount [3-4]. Additionally, there were larger amount of unorganized VOCs emissions comparing to enterprises' organized emissions of VOCs. In detail, unorganized emitted exhaust gas mainly originated from storage tank area, production plant area, sewage treatment facility area, and loading area [5-6]. According to a survey carried out by EPA of USA in year 2003, volatile storage tank, facility leakage, and sewage treatment in some petrochemical enterprise had the largest VOCs emission amounts, taking up 28%, 27%, 21%, respectively. Peng Wang [7] had applied related calculation through some large petrochemical enterprise's condition, he found out that for the whole

unorganized emitted VOCs, facility leakage took up 49%, sewage treatment took up 16%, tank area took up 11%, and these three unorganized emission took up more than 75% in total.

It was critical for enterprises to realize the significance to strengthen the research of unorganized emission control, not only organized emission. The existing studies of VOCs emission characteristics of petrochemical industries had demonstrated the obvious difference of the characteristics in different countries and ranges [8-11], which made it extremely important to carry out targeted research. This study was aimed at the study on unorganized emission characteristics of volatile organic compounds. It was based on three representative petrochemical enterprises chosen from a chemical park in Tianjin after spot sampling and analytical testing; main sampling points were facility production area, tank area and collecting tank.

2. Materials and Methods

2.1. Sampling Sites

The air samples were collected at three petrochemical enterprises in a chemical park in Tianjin, represented by A, B, C respectively; the selected locations were shown in Figure 1. Unorganized emission sampling points were sited according to HJ/T55-2000 "Technical guidelines for fugitive emission monitoring of air pollutants" [12], all of which were sited on the two sides of the mean wind direction axis. The leeward was sited of sampling spots, and reference sampling spots sited at the windward. During the sampling program, 3 samples were collected at each sampling site on and within plant boundary, sample concentration from each sampling site was the mean value of all three samples collected in equal intervals of time.

Figure 1. *The relative position of each enterprise in the chemical park.*

According to "industry classification standard GB/T 4754-2011" [13], the industry classification of these three enterprises includes basic chemicals manufacturing, resin manufacturing, and plastic manufacturing. Table 1 showed the basic related information about three firms.

Table 1. *Basic information about the firms.*

Enterprise	Principal product	Manufacturing technique	Principal material	Belonged industry
A	Polystyrene	Domestic improved technology	Styrene	Primary form plastics manufacturing
B	2-ethyl hexanol Ethyl alcohol	Low pressure oxo-synthesis process	Propylene	Organic chemical materials manufacturing
C	ABS resin Styrene	Emulsion graft bulk SAN blending method Fina/Badger technique	Benzene, ethylene, butadiene, acrylonitrile	Synthetic resin manufacturing

2.2. Sample Collection Program and Analysis Method

Air samples were collected using air bag sampling method. Firstly, air pump was used to pump the closed negative pressure chamber to create negative pressure inside the camber. Then, the exhaust gas near the unorganized emission point would be collected into good chemical inert air bags due to differential pressure. Sampling bags and connecting

pipes were using Teflon material, bags' volume was 3 L. It was convenient and efficient using air bag sampling method to collect air samples, sealed samples could be delivered directly to labs to make quantitative analysis after sampling [14]. The elevation of the sample inlet was at 1.5 m above ground level.

After sampling, the component and concentration of VOCs in sampling bags were analyzed by proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS). It was noticeable that this method did not contain chromatographic separation process, so it had fast measurement speed and high sensitivity. In addition, all kinds of VOCs were soft- ionized to single ion through proton transfer, producing a few fragment ion, which made it easy to apply mass spectrometry identification [15]. This study used 71 volatile organic compound standard samples, including PAMs testing, as analytical standard substance; each of the standard samples had different relative molecular weight. Five types of VOCs compounds were identified during the process, including alkanes, ene alkynes, halohydrocarbons, benzene series, and oxygenated volatile organic compounds (OVOCs). The TVOCs concentration of each sample was the sum of the concentration of all components in the sample. The average value of all samples' analytical results in the sampling spot represented the actual emission situation of the point.

2.3. Quality Control

New air bags were used for all air sampling. Before sampling, sampling bags were washed two or three times with high pure nitrogen. Samples were delivered to lab right after sampling finishing, and all samples were covered perfectly during the delivery process to avoid direct sunlight. Storing all samples in cool dry room and analyzing them within 24h after sample collection were also important to quality control. Before analysis, calibration was performed using standard mixed gas (containing 56 PAMs gas components of the volume fraction being 10^{-6}) and single standard gas, the correlation coefficients of calibration were all larger than 0.99. All samples would be made zero air blank analysis after standard sample analysis as well as before sample analysis, which was to make sure there was no target left in the analytic system. The analytic results showed that the concentration of all targets was below the method detection limit, quality control index was up to the requirement.

3. Result and Discussion

3.1. Emission Concentration Level Comparison

Table 2 showed total VOCs concentration in measured samples of three enterprises. Overall, a large difference existed in the concentration of sampling points of each enterprise. TVOCs concentration in the tank area of enterprise A had the highest value (5109.3μg/m^3), while TVOCs concentration of upwind in enterprise B was the lowest (1317.1μg/m^3).

A summary of VOCs emission level was presented. The VOCs unorganized emission concentration of tank area in enterprise A was 5109.3μg/m^3, which was three times as much as that of enterprise B. It might be related to the tank type of enterprise A, which was fixed-roof tank; while enterprise B used covered floating roof tank, which helped decrease breathing emission. The emission concentration of production facility area in three enterprises was different from each other. The highest concentration was measured at enterprise A (4840.9μg/m^3); while in enterprise B and C, higher concentration was just 2832.8μg/m^3; it was because most production facilities in enterprise A were old-fashioned and had backward technique, enterprise B and C were just on the contrary. In enterprise B, 2-ethyl hexanol concentration of the primary facility area (2832.8μg/m^3) was higher than that of the secondary facility area (1864.6μg/m^3), which might be related to facilities' condition as well. Besides, storage tank played a role in storing industrial wastewater temporally, and the VOCs concentration of the storage tank in enterprise A and C was 3772.8μg/m^3 and 1493.5μg/m^3 respectively. The reason why VOCs unorganized emission concentration was different between enterprise A and C might be the technique difference in production process, as well as whether there was strict sealing treatment on storage tank.

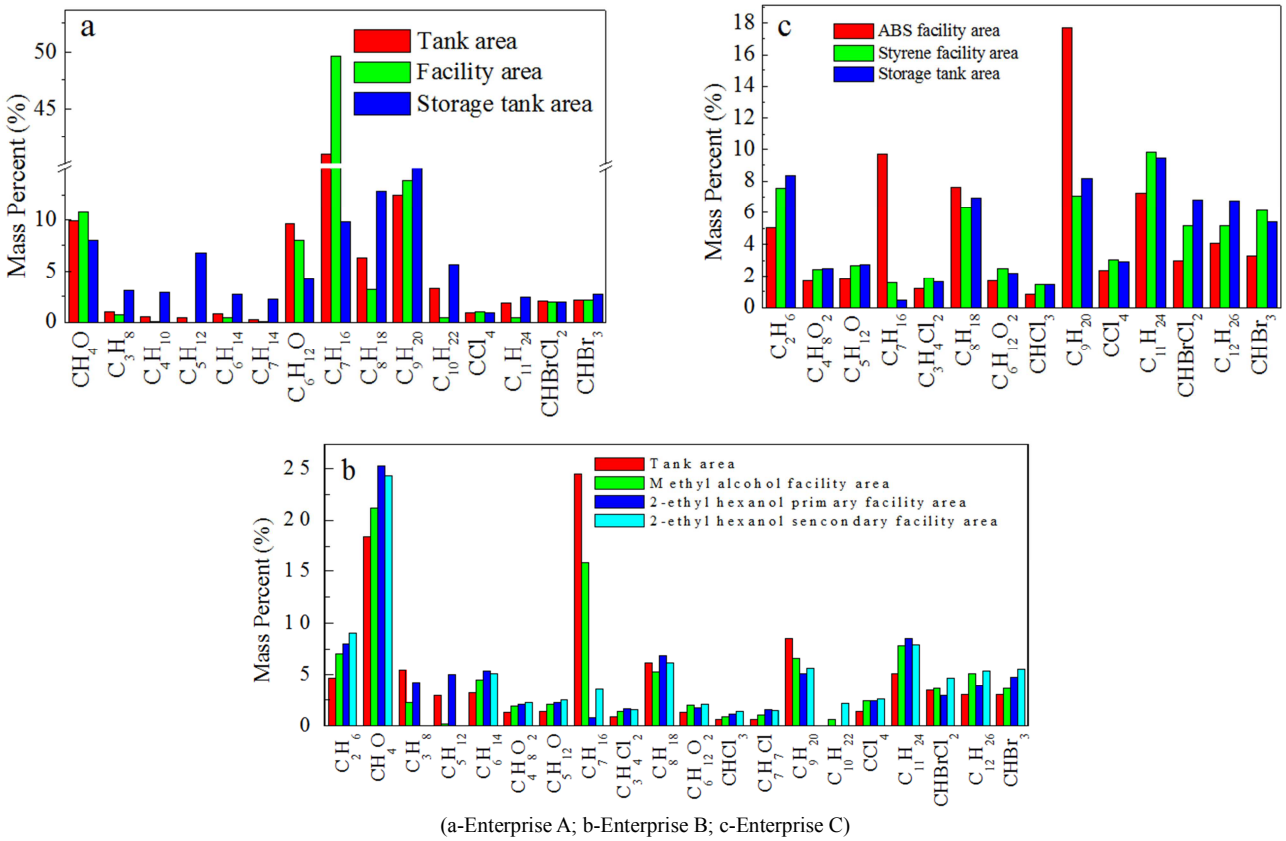
Table 2. *Total VOCs concentrations in the measured samples (μg/m^3).*

Enterprise A		**Enterprise B**		**Enterprise C**	
Sampling point	**TVOCs**	**Sampling point**	**TVOCs**	**Sampling point**	**TVOCs**
Tank area	5109.3	Tank area	1713.2	ABS facility area	2168.3
Production facility area	4840.9	Methyl alcohol facility	1574.8	Styrene facility area	1469.7
Storage tank	3772.8	2-ethyl hexanol primary facility area	2832.8	Storage tank	1493.5
Factory boundary upwind	1611.9	2-ethyl hexanol secondary facility area	1864.6	Factory boundary upwind	1653.8
Factory boundary leeward	1698.7	Factory boundary upwind	1317.1	Factory boundary leeward	3668.9
		Factory boundary leeward	3936.3		

3.2. Component Characteristics and Category

Main VOCs emission components in enterprise A were C_7H_{16}, C_9H_{20}, CH_4O, $C_6H_{12}O$, and C_8H_{18} (Figure 2a). It was noticeable that the proportion of C_7H_{16} in tank area and production facility area was larger than 40%. And emission components in these two sampling points were significantly similar; for example, the proportion of CH_4O was around 10% in both sampling points, while the rest components except the 5 mentioned components were all less than 3%. However, the

emission component characteristics in storage tank area was different from that in tank area and facility area, and emission components detected in the sample from storage tank were similar to the research results of Wei W [16]. The emission components in storage tank were relatively more dispersive. The higher-ranking components were C_9H_{20}, C_8H_{18}, C_7H_{16}, CH_4O, C_5H_{12}, $C_{10}H_{22}$, and $C_6H_{12}O$ respectively. In the production facility area, saturated hydrocarbon C_7H_{15} and C_9H_{20} took up relatively higher proportion, which was directly affected by the polystyrene production technique in enterprise A. Similarly, produced waste water was mainly consist of saturated hydrocarbon, especially the ones whose carbon numbers were 7, 8, and 9.



(a-Enterprise A; b-Enterprise B; c-Enterprise C)

Figure 2. *Characteristics of main compounds of VOCs emitted from each unorganized sampling point.*

Main productions of enterprise B were methyl alcohol and 2-ethyl hexanol. There were 62 components detected at 4 sampling points in enterprise B. Figure 2b showed that CH_4O, C_7H_{16}, C_2H_6, $C_{11}H_{24}$, C_9H_{20}, C_8H_{18}, $C_{12}H_{26}$, $CHBr_3$, and $CHBrCl_2$ were main emission components. The most crucial component was methyl alcohol, whose mass percent in all four sampling points was larger than 15%. Moreover, proportions of methyl alcohol in tank area and methyl alcohol production area were even higher, which was directly related to the storage of raw materials of methyl alcohol in tank area; at the same time, there were unorganized methyl alcohol emission from methyl alcohol facility area. In addition, C_7H_{16} was noticeable in 2-ethyl hexanol facility area, whose mass percent in both primary and secondary area was larger than 15%. Meanwhile, the primary 2-ethyl hexanol facility area had higher unorganized C_7H_{16} emission proportion due to the relatively more old-fashioned equipment. What was different from enterprise A was that emission of halohydrocarbon $CHBr_3$ and $CHCl_2Br$ in enterprise B was relatively more beside saturated hydrocarbon.

Enterprise C mainly produced ABS resin and styrene. The mass percent of CH_4O, C_9H_2O, $C_{11}H_{24}$, C_8H_{18}, C_2H_6, $C_{12}H_{25}$, $CHBrCl_2$, and $CHBr_3$ was relatively high, especially CH_4O, whose proportion was larger than 20% in all three sampling points (Figure 2c). In ABS facility area, proportions of C_9H_2O and C_7H_{16} were obviously larger than that of other components. In styrene facility area and storage tank, $C_{11}H_{24}$, C_9H_{30}, C_8H_{18}, and C_2H_6 had higher mass percent. For enterprise C, main materials used in the production process were ethylene, benzene, butadiene, and acrylonitrile. However, mass percent of these material components was not high in the monitoring results, which was a little different from the result conducted from Mo Zhiwei [17]. The reason might be the difference between production techniques; and that the sampling time was midday, so there was high temperature and low moisture, high radiation intensity made the photochemical activity of olefins and benzene series strong [18]. On the contrary, mass percent of CH_4O was relatively high while there was no CH_4O related materials, intermediate products, or products. It was probably because it was mainly south wind during sampling time, high concentration of CH_4O from enterprise B flowed to enterprise C.

3.3. Precedence-Controlled Pollutants

As shown in Figure 3, unorganized VOCs in all three enterprises were mainly alkanes, OVOCs, and halogenated hydrocarbons, especially alkanes and OVOCs, which had significantly high proportions. Alkanes in both enterprise A and B took up more than 50%; in enterprise C, it was almost 50%. Besides, the percent of halogenated hydrocarbon in both enterprise B and C was more than 10%. Liu Ying [19] had studied the emission recourses of petrochemical industry in Pearl River Delta, he found out that mass percent of alkanes and halogenated hydrocarbons from VOCs emission in some petrochemical industry was larger than 40% and 32% respectively.

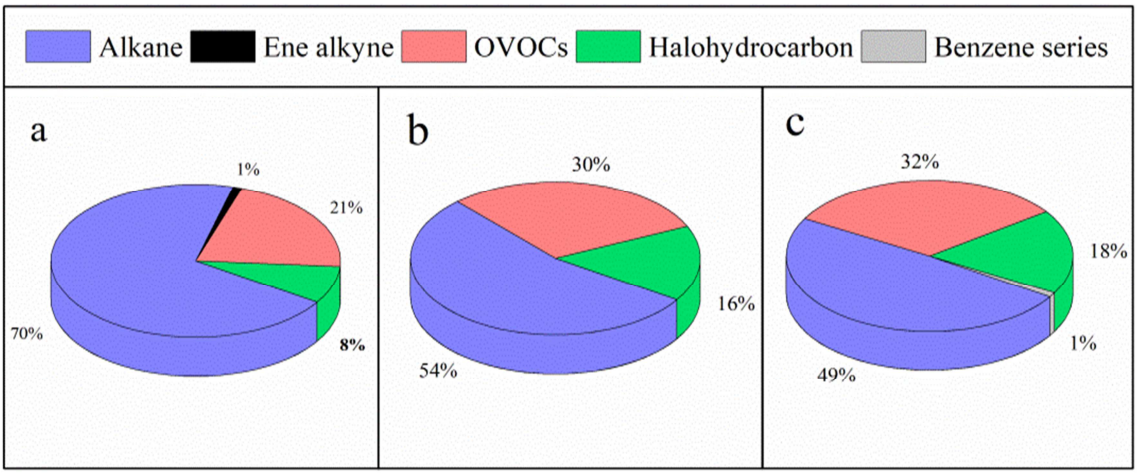


Figure 3. *Species and ratio columns of VOCs emitted from different firms (a-Enterprise A; b-Enterprise B; c-Enterprise C).*

Li Qinqin [20], who researched VOCs unorganized emission in Pearl River Delta, also found that the concentration of alkanes from unorganized emitted VOCs in three facility areas took up more than 50%. They believed that control of alkanes was the priority for petrochemical industry. However, halogenated hydrocarbon was not material or products in production processes of the three enterprises, high proportions might be affected by other petrochemical enterprises in the industrial park.

4. Conclusion

Emission levels of VOCs in three plants were different. The level of VOCs in tank area was directly related to the tank type; the level in storage tank area was related to whether it was well sealed, as well as the difference in production processes.

The components of VOCs emitted from unorganized sources were mainly saturated alkanes represented by C_2, C_7, C_8, C_9 and C_{11} and OVOCs represented by CH_4O.

It was found that alkane substance was a large class of VOCs component in chemical industry plant, so alkanes should be controlled in priority.

At the same time, there was some uncertainty in this study. Firstly, single sample was not representative enough; weather condition (such as sudden change of wind direction) in actual observation could affect sampling results. Secondly, some active VOCs might be lost since the concentration of eneyne hydrocarbon and benzene series was detected to be relatively low, it was a little different from the results of other researches. Thirdly, unorganized emission had many directions, regularity of the emission was not strong, some specific pollutants might not be detected during sampling.

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