CHEMICAL ENGINEERING TRANSACTIONS
VOL. 68, 2018

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Selena Sironi, Laura Capelli

ISBN 978-88-95608-65-5; **ISSN** 2283-9216
DOI: 10.3303/CET1868011

Test on Noxious Gases in Urban Sewage Pipe Based on Odor Classification

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Urban sewage pipes are filled with flammable, explosive, toxic and other noxious gases, which have brought hidden troubles during system maintenance and operation. To ease these threats to the urban sewage pipeline network, we should perform spot inspection and take some measures against safety risks that may occur on them. But of those, the test of noxious gases is the most challenging. Based on the odor classification method, we take an urban sewage pipe network in Chongqing as a study case for sample collection and spot inspection. The purpose of this paper is to classify and test the methane CH4 and hydrogen sulfide H2S by different methods. Data available from individual supervision spots are compared and analyzed in parallel, in order to explore how to measure these noxious gases and what's the distribution and concentration change laws of them in urban sewage pipes, hoping to provide the clues to the early warning and safety operation of urban sewage pipeline network.

1. Introduction

Urban sewage pipeline network as the infrastructure used to collect, transport and treat residents' domestic water and industrial sewage in urban areas serves as a significant part that can guarantee normal operation of city life and production (Yu et al., 2013). Urban sewage pipelines will retain the spate of contaminants in a humid, non-ventilated environment all year round, which will produce huge mass of toxic and harmful gases after oxidation or microbial decomposition (Li et al., 2013). Toxic and explosive gases in the urban pipe network will possibly triggered the safety risk for the urban sewage treatment system. In this regard, many accidents such as gas poisoning caused by harmful gas leakage from urban sewage pipes have occurred at home and abroad, causing great personal injuries and property losses. In this context, it is of great significance to study the test and measurement methods for harmful gases in urban sewage pipelines (Emmanuel et al., 2005).

There are main components of harmful gases such as CH_4, H_2S, CO_2, CO, SO_2, etc., in urban sewage pipelines, all of which will pose threat to the lives and property of urban residents when they reach a certain concentration in the local area of underground pipelines (Thoman, 2008). For example, in 2015, several workers were poisoned by hydrogen sulfide when they perform maintenance and cleaning jobs for underground pipelines in Germany, resulting in one death and 8 injuries. In China, the similar poisoning accidents also happened occasionally since people always cling to low awareness of pipeline safety and the maintenance job of urban pipelines is also not performed frequently. According to available figures, since 2000, there have been 1000 cases of casualties caused by the explosions due to the accumulation of explosive gases in underground pipelines in domestic cities (Roehrdanz et al., 2017). To ensure the safety warning and operation of urban sewage pipe network, the key is how to test the harmful gases by effective methods and master the distribution law of harmful gases in it.

Take the underground sewage pipeline network in Chongqing city as an example, and methane and hydrogen sulfide as the sampling objects. As methane belongs to a colorless and odorless gas and hydrogen sulfide has a foul smell, the sampling gases should be first classified based on the odor classification model, and then the gas chromatography is used to test the methane, the methylene blue for hydrogen sulfide. In the test, it is found that the odor features and test concentration of gases in urban sewage pipe network are different since they may be subjected to change with different environment, temperature and depth of sewage test. Generally, the higher the temperature, the greater the gas concentration, so that the odder the odor gets. Methane in the urban pipe network of wells and septic tanks is the highest, while the hydrogen sulfide in the sewage pipeline is higher (Langård et al., 2015). The study provides the clues to the operation safety of urban sewage pipe network, and has multiple effects in the economy, society and environmental protection.

2. Formation and field collection of Harmful gases in urban sewage pipe network

2.1 Formation of harmful gases

There are various types of sewage such as domestic sewage, medical sewage, chemical sewage, etc., deposited in the urban sewage pipe network. As a result, not only does urban sewage contain complicated chemical components, but its odor is also ever-changing. The urban sewer network is a pipeline for urban sewage collection and transmission. Additionally, it also acts as a biochemical reactor for wastewater (Leckner et al., 2004). Specific substances that have a conversion reaction mainly includes four components: carbon, nitrogenous and sulfur-containing substances, as well as oxygen supply. See Figure 1 for the characteristics of material sublimation reaction and the generation process of gases in the sewage pipe network. The full line in the figure is the aerobic process of biochemical reaction, and the dotted line is the anaerobic reaction process:

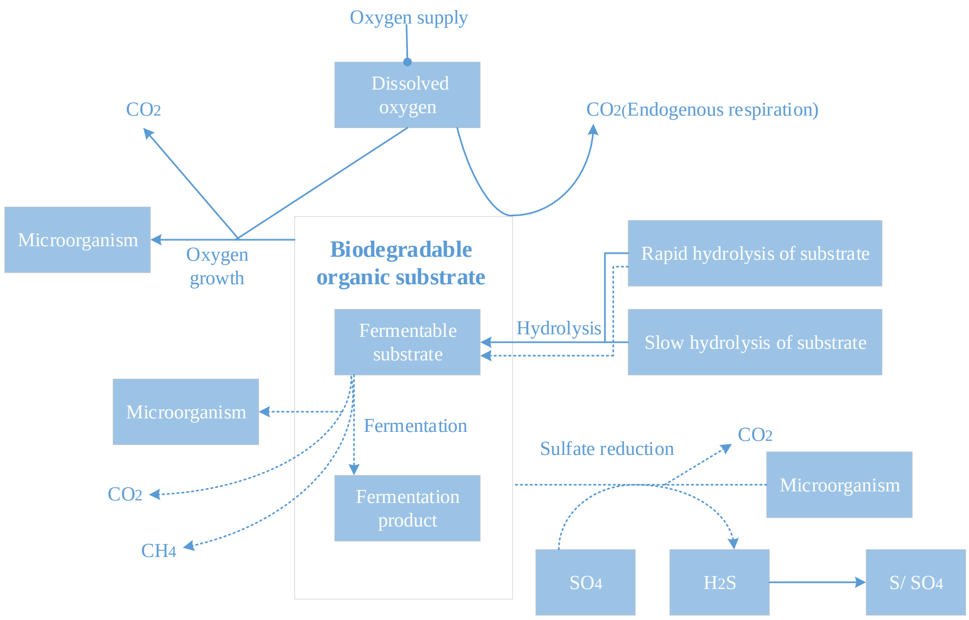

Figure 1: The progress of gas from sewerage system

The anaerobic process of biochemical sewage reaction is the main process of methane formation: in the phase 1, hydrolytic fermentation reaction occurs; in the phase 2, biochemical reaction produces hydrogen and acetic acid, and in phase 3, methane generates based on the biochemical reactions in the previous two phases (Mun et al., 2009). The factors affecting the formation of methane in the sewage system include the composition and fluidity of the sewage, the properties of the solid pollutants, the ratio of organic carbon to nitrogen in the sewage (Wang and Zhang, 2018), trace metals, toxic and inhibitory substrates, temperature, and pH value (Formisano et al., 2004).

Oxidation of inorganic sulfides under acidic conditions or reduction of organic sulfides under anaerobic conditions are the mechanisms for the formation of hydrogen sulfides (Lu et al., 2004). Equations 1 and 2 can generate the hydrogen sulfide from iron sulfide and lead sulfide in the case of non-soluble metal sulfides under acidic conditions:

$$FeS + 2H^{+} \leftrightharpoons H_2S \uparrow + Fe^{2+} \tag{1}$$

$$PbS + 2H^{+} \leftrightharpoons H_2S \uparrow + Pe^{2+} \tag{2}$$

As shown in Equation 3, the decomposition and reduction of sulfur-containing organic matter under anaerobic conditions:

$$SO_4^{2-} + 2C + 2H_2O \rightarrow 2HCO_3^- + H_2S \quad (3)$$

The main factors that affect the formation of hydrogen sulfide include the properties of the sewage phase, fluidity, sulfide concentration, wastewater retention time, redox point location, sewage temperature, pH value, drainage facilities, etc.

2.2 Determination of test areas of harmful gases in urban sewage pipe network

This paper takes the underground pipe network in Chongqing as a study case to carry out the test. By 2017, the sewage pipe network of Chongqing has reached 6,500 kilometers, passing through 21 natural river basins for water repellence, including the Yangtze River and the Jialing River, eventually forming the underground sewage pipeline network of the levels 1, 2 and 3. The sampling and testing areas are mainly divided into three categories: residential area, commercial areas, and public toilets.
(1) For the residential area, it instantiates the Meteor Garden Community in Jiangbei District;
(2) For the commercial area, it instantiates the Huayu Pizza in Jiangbei District;
(3) For the public toilets, the public toilet in Jialing Park in Jiangbei District is representative.
The urban sewage pipe network is mainly composed of sewage pipelines and septic tanks. Test areas as determined for harmful gases basically covers the typical areas of urban sewage pipe networks.

3. Test on harmful gases in urban sewage pipelines

3.1 Introduction of odor classification method

First, an electronic nose fingerprint is used to measure the concentration of the sample gas with foul smell. When the measured concentration is greater than 100, the sample is first used for hydrogen sulfide test, otherwise for methane test.

3.1.1 Gas Chromatography - Methane test

Gas chromatography uses an inert gas as the mobile phase to carry the test sample gas into the column and exit it after the adsorption-desorption-release process. Due to the separation behavior of the components of the gas to be tested, after a certain column length, they are separated from each other, and sequentially leave the column and access to the tester. Then they convert into an electrical signal to form a chromatographic elution profile. Gas chromatograph includes carrier, sampling, separation, measurement and recording systems (Bull et al., 2000).

3.1.2 Methylene blue-hydrogen sulfide test

In general, the test methods for hydrogen sulfide include iodometry, methylene blue, oxidized micro coulometric method, hydrogenolysis-rate meter colorimetric method, lead acetate reaction rate single-path detection method, etc. (Yongsiri et al., 2004). Since the above methods all refer to the methods used in natural gas examination, the advantages and disadvantages, test range and precision are different from each other. Based on the characteristics of the integrated urban sewage pipe network and the concentration change of hydrogen sulfide, the methylene blue is chosen to test the gases with the classification identification.

3.1.3 Test instrument

1. Methane test
Electronic nose fingerprint, gas chromatograph, 2ml, 8ml, 10ml, 32ml, 100ml syringe, column, sample injector, methane standard gas, carrier gas (hydrogen).
2. Hydrogen sulfide test
Electronic nose fingerprint, spectrophotometer, colorimetric tube, thermostatic water bath, N-dimethyl-p-phenylenediamine hydrochloride, ferric chloride, zinc acetate, potassium dichromate (reference reagent), sodium thiosulfate, iodine, potassium iodide, anhydrous sodium carbonate, soluble starch, hydrochloric acid, glacial acetic acid, sodium sulfide, colorimetric tube holder (Hvitvedjacobsen et al., 2005).

3.2 Test procedure and results of odor classification

3.2.1 Methane test

The test is conducted on the methane, provided that air tightness must be ensured. Oven is set to 120 °C and the carrier gas to the flow rate of 40 mL/min. the standard gas methane in the column and the gas components in the sewage pipe sample under test are compared for retention time under above chromatographic column and operating conditions. If the retention times t_R are consistent, the gas to be measured is methane, provided that it is ensured that there is no interference. Measure the peak area of methane in the sample gas (Valencia et al., 2018), and calculate the volume fraction of methane according to Equation 4:

$$\varphi_{CH_4} = \varphi_s \times \frac{A_{CH_4}\ or\ h_{CH_4}}{A_s\ or\ h_s} \tag{4}$$

φ_{CH_4} is the content of methane in the sample gas; φ_s is the content of standard gas methane, 10^{-6}; A_{CH_4} and A_s are the peak areas of methane in the sample gas and in standard gas, respectively.

3.2.2 Test results of Methane

The methane concentration of underground sewage pipeline wells 1# ~ 7# of the popular garden community and the curve of the methane concentration of the 1# and 2# wells as the depth are shown in Figure 2.

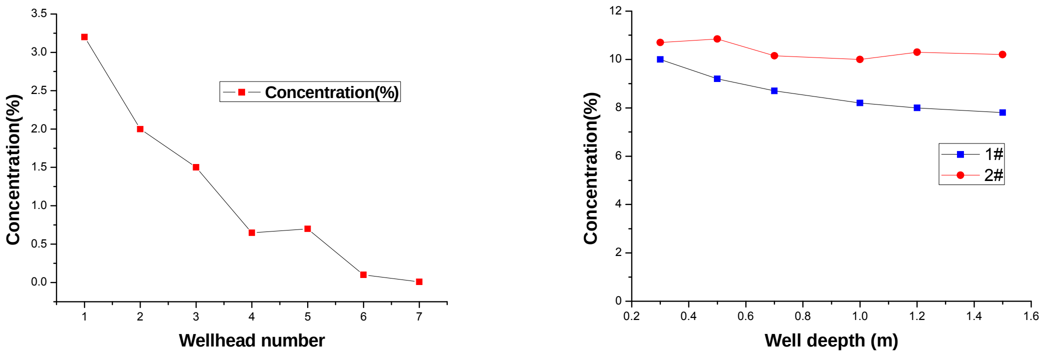

Figure 2: The concentration curve of CH_4 in residential area

The average values in the figure are available by two parallel measurements, and the absolute deviation between the two measurements fall within the range of the basic tolerance of methane. The error of gas chromatography method is less than 5% in accordance with the monitoring standards for methane concentration in urban sewage pipeline.

3.2.3 Hydrogen sulfide test

In the hydrogen sulfide test, first a solution of hydrochloric acid, zinc acetate, N-dimethyl-p-phenylenediamine hydrochloride, iodine, sodium thiosulfate and other solutions should be prepared, and then add a color developer to plot a standard curve (Zhang et al., 2008). In the end, the results calculated are analyzed by the color development process and the absorbance measurement, as shown in Equations 5 and 6.

$$V_n = V \times \frac{p-p_v}{101.3} \times \frac{293.2}{273.2+t} \tag{5}$$

$$\rho = \frac{m}{V_n} \tag{6}$$

Where ρ represents the mass concentration of hydrogen sulfide; V_n is the gas sample correction volume; *V* is the sample volume; *P* is the atmospheric pressure of sample; *Pv* is saturated vapor pressure of water at the temperature *t*, and *t* represents the average temperature of the gas sample.

3.2.4 Test results of hydrogen sulfide

As shown in Figure 3, it is a comparison of hydrogen sulfide concentrations in residential areas measured by a five-in-one gas tester and methylene blue.
As shown above, the five-in-one gas tester and the methane blue determine the hydrogen sulfide concentration with a basically coincided curve, which means that the methylene blue has a good test precision, and the error falls within less than 5%, in accordance with sewage pipeline specification.

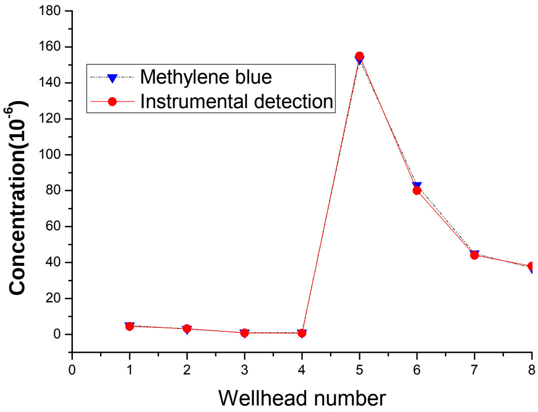

Figure 3: The concentration curve of H_2S in residential area by methylene blue and instrumental detection

3.3 Distribution law of main regional components of urban sewage pipelines

The gas chromatography and the methylene blue are used to randomly and regularly sample the residential area, commercial area and public toilet for the urban sewage pipe network. The average odor concentrations measured with electronic nose in the residential area, commercial area and public toilet are 67, 135, 344, respectively, based on which, the methane and hydrogen sulfide in the sample gas are classified and identified for the test. In the end, the test results are counted up and the average value is solved. The methane distribution is shown in Table 1, and the hydrogen sulfide distribution is shown in Table 2:

Table 1: The distribution of the CH_4 in three regions

Regions/Concentration	mean concentration	Max concentration	Min concentration	Odor intensity
Residential area	3.415	11.542	0	67
Commercial district	0.527	2.982	0	135
Public lavatory	8.213	44.603	0	344

Table 2: The distribution of the H_2S in three regions

Regions/Concentration	mean concentration	Max concentration	Min concentration	Odor intensity
Residential area	33	236	0	67
Commercial district	58.8	520	0	135
Public lavatory	20.6	298	0	344

As shown in Table 1, the methane concentrations in residential areas and public toilets have reached the lower limit of explosion, so that there is a risk of methane leakage and explosion; from Table 2, we can learn that the average concentration of hydrogen sulfide climbs the top level in the commercial area as a highly dangerous area where the hydrogen sulfide poisoning accident will be prone to occur. In addition, a comprehensive study is also made on the temperature, sewage well depth and other factors in the test. It is found that the temperature is proportional to the concentration of harmful gas in the urban sewage pipeline. Methane appears at the places of shallow well or closer to the ground.

4. Conclusion

Urban sewage pipes are filled with a variety of hazardous gases produced by complex biochemical reactions, which poses a threat to artificial maintenance and rebuilding works for them. And worse, massive accumulation and leakage of hazardous gases may cause dangers such as poisoning and explosion. In this paper, the odor classification recognition method is introduced to test the hazardous gases, i.e. methane and hydrogen sulfide, in urban sewage pipeline network, for example, in Chongqing city. Through experiment analysis, the main conclusions are drawn as follows:

4.1 Based on the principle of odor classification, it is possible to initially classify hazardous gases in urban pipes so as to facilitate the subsequent detection on the concentrations of noxious gases.

4.2 Gas chromatography has a better test precision for methane while the methylene blue does better for the hydrogen sulfide in accordance with the standard specifications, so that both apply to the detection of hazardous gases in urban sewage pipelines.
4.3 As the concentrations of noxious gases in urban sewage pipes are subjected to various factors such as environment, temperature and well depth, we should increase the frequency of sampling and supervision to avoid massive accumulation of them in urban pipeline network.

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