Global NEST Journal, Vol 22, No 4, pp 649-658

Determination and analysis of harmful substances in historical building's fire-retardant coating by gas chromatography

Yang L.[1], Shi D.[2], Liu G.[3], Xiong L.[4] and Luo H.[1]*
[1]College of Civil Engineering and Architecture, Hunan Institute of Science and Technology, Yueyang 414006, China
[2]College of Environment and Resources, Xiangtan University, Xiangtan 411105, China
[3]Staff Development Institute of China National Tobacco Corporation, Zhengzhou 450008, China
[4]CETC Electronics Equipment Group Co., Ltd., China Electronics Technology Group Corporation, Changsha 410205, China
Received: 06/07/2020, Accepted: 04/08/2020, Available online: 22/10/2020
*to whom all correspondence should be addressed: e-mail: gyhvvc@163.com
https://doi.org/10.30955/gnj.003408

Graphical abstract

Abstract

With the emphasis on environment and health, the environmental protection, quality and safety of historical building's fire-retardant coating has gradually become the focus of attention. There are a lot of volatile substances in the fire-retardant coating, which volatilize continuously for a long time after use, directly affect the air quality and seriously harm people's health. Therefore, it is of great practical significance to determine harmful substances in historical building's fire-retardant coating by gas chromatography. The determination is carried out in the way of experiment, including the steps of experimental instrument and reagent, sample formulation, density determination, chromatographic condition, experimental method, gas chromatograph detection, detection method evaluation, and comparative analysis of detection results, etc. The results show that compared with spectrophotometry, electrochemical detection and liquid chromatography, gas chromatography is in content analysis, detection limit, recovery rate of standard addition, relative standard deviation and other aspects should perform better, which proves that gas chromatography has stronger detection performance and is more conducive to the determination of harmful substances in historical building's fire-retardant coating.

Keywords: Historical buildings, fire-retardant coatings, harmful substances, gas chromatography, determination and analysis.

1. Introduction

Coating is a general term for materials that can form a tough protective film when applied to the surface of an object. The paint specially used for decoration of construction engineering is called architectural paint, which is the largest production category in the paint product structure, mainly including interior wall paint, exterior wall paint, roof paint, floor paint, door and window paint, etc. Architectural coatings usually have the function of decoration, protection and special residential improvement. Due to different purposes of use, the proportion of these functions is also different (Kanat and Eren, 2019). Through the way of beautification, it can improve the appearance value of the building and play a decorative role. At the same time, the shape of the building and the size and shape of the base material should match. A layer of coating is applied to form a protective film to isolate the building base material from the atmosphere, prevent or delay the atmospheric erosion, which has a protective effect, so that the building is not affected and damaged by the environment, and the service life is prolonged. The requirements for indoor and outdoor service conditions are quite different, for example, some buildings have special requirements for mildew prevention, fire prevention, heat preservation and insulation, corrosion resistance, etc. For the interior decoration, it is required to have a special residential improvement effect. By applying architectural coating indoors, it can significantly improve the sound insulation, sound absorption, condensation and

Yang L., Shi D., Liu G., Xiong L. and Luo H. (2020), Determination and analysis of harmful substances in historical building's fire-retardant coating by gas chromatography, *Global NEST Journal*, **22**(4), 649-658.

other conditions of the indoor living environment (Masrournia and Vaziry, 2018). However, there are also a lot of volatile substances in the building's fire-retardant coating, which are constantly volatilized in the application process and after a long period of time, directly affect the air quality and seriously harm people's health. Therefore, the qualitative and quantitative analysis of toxic, harmful and volatile substances in fire-retardant coating is very important (Balal *et al.*, 2020; Ogunkunle *et al.*, 2019; Sana *et al.*, 2019; Sarmila *et al.*, 2020).

Because of the toxic, harmful and volatile substances in the coating, it has a great impact on human health. Therefore, it is very urgent to establish accurate, reliable and convenient qualitative and quantitative detection methods for toxic, harmful and volatile substances. At present, the determination methods of toxic, harmful and volatile substances in building's fire-retardant coatings include spectrophotometry, electrochemical detection, gas chromatography, liquid chromatography, kinetic spectrophotometry, fluorescence analysis and titration analysis, among which the first four are most commonly used. The method of distillation is used to process the sample by spectrophotometry. The distilled free formaldehyde acts with the developer, develops the color under appropriate conditions, and measures the absorbance with spectrophotometer under specific wavelength, and quantitatively detects the content of harmful substances in the sample (Hong, Son, and Park, 2018). Electrochemical detection is a kind of instrumental analysis method based on the electrochemical properties of substances in solution. The test substance is regarded as an integral part of the chemical battery, and is measured according to the relationship between a certain electrical parameter (such as resistance, conductivity or current voltage curve) and the concentration of the substance to be measured (Li et al., 2018). The principle of liquid chromatography is to use the similar solubility, that is, the affinity of the tested substance to the two phases is different, so that the mixture is separated in the chromatographic column, and then detected by different detectors, and finally achieve the qualitative and quantitative detection requirements (Zhokhov, Loskutov, and Rybal'chenko, 2018). Gas chromatography is a kind of chromatographic separation and analysis method using gas as mobile phase. The vaporized sample is pushed into the chromatographic column by carrier gas (mobile phase). The molecular force of the stationary phase in the chromatographic column is different from that of the components in the sample. The components flow out of the chromatographic column at different times and are separated from each other (Duan *et al.*, 2019). A chromatogram indicating the time and concentration of each component flowing out of the column is made by using an appropriate identification and recording system. According to the time and order of peak emergence shown in the figure, the compounds can be qualitatively analyzed; according to the height and area of the peak, the compounds can be quantitatively analyzed. It has the characteristics of high efficiency, high sensitivity, strong selectivity, fast analysis speed, wide application and simple operation. It is suitable for qualitative and quantitative analysis of volatile organic compounds. In this paper, gas chromatography is used to determine harmful substances in fire-retardant coatings for historic buildings (Isfarita *et al.*, 2019; Janvier *et al.*, 2020; Muhammad *et al.*, 2020; Nwonumara *et al.*, 2019).

2. Determination of harmful substances in building fire-retardant coating by gas chromatography

Fire-retardant coating refers to the coating on the surface of flammable base materials to reduce the flammability of the material surface and prevent the spread and propagation speed of the fire; or isolate the fire source, prevent the combustion in a short period of time, control the spread of the fire, increase the thermal insulation performance of the base materials, and prevent or weaken the occurrence of the fire, so as to improve the fire resistance of the materials, also known as fire-retardant coating. Building fire-retardant materials are the most important one to apply. Coatings have been developed for many years, with various types and different properties, so they are widely used (Jayanthi *et al.*, 2019). There are many classification methods for coatings, but up to now, there is no one classification method that can include all coatings, so there is no unified classification method. Generally, classification is based on the following methods, as shown in Table 1 below.

Table 1. Classification of Fire-Retardant Coatings for Historical Buildings

Serial number	Classification standard	Type
1	Form of coating	It can be divided into water-based, solvent-based, powder and high solid coatings
2	Method of construction	It can be divided into brush coating, spray coating, dip coating, roller coating and electrophoretic coating, etc.
3	Role in construction	Paint can be divided into putty, primer, varnish, etc.
4	Function of paint	Coatings can be divided into decoration, anticorrosion, heat insulation, fire and high temperature resistant materials
5	Drying method	Coatings can be divided into room temperature drying type, electron beam curing type and wet curing type
6	Status of paint	Paint can be divided into varnish and colored paint
7	Properties of matrix in materials	Coatings can be divided into metal, wood and cement coatings

8	Types of membrane materials	It can be divided into epoxy resin, acrylic resin, unsaturated polyester paint, etc.

In recent years, China began to pay attention to the monitoring and control of indoor air quality problems, and developed a series of corresponding standards to regulate the decoration market behavior. According to the results of medical research, 40% of human diseases are related to indoor pollution. After the coal smoke pollution and photochemical smoke pollution, indoor pollution has become the third generation of urban pollution. Among the many factors that lead to indoor air pollution, there are two main reasons: the toxic substances contained in buildings and decorative materials, among which the main reason is the unqualified environmental quality caused by the harmful substances contained in building materials and decorative materials. It is found that the indoor air contains toxic substances to a certain extent, which will make people have nausea reaction, easy to catch cold, easy to fatigue and lead to the decline of immunity, leading to various diseases (Dar, 2018). Generally, new houses will have unpleasant and irritating smell after decoration, and it can't be dissipated for a long time. Indoor air pollution has become one of the urban environmental problems, which needs to be improved urgently. Therefore, to understand the pollution sources and detect toxic and harmful substances, can take corresponding measures to eliminate or reduce pollution, so that people's health is guaranteed. Paint is composed of pigments, fillers and different auxiliaries, which can release toxic substances, so that residents will be in danger (Zhang *et al.*, 2020). Therefore, countries all over the world have regulated the content of toxic substances in decorative materials. There are many kinds of harmful substances in coatings, such as volatile organic compounds, formaldehyde, benzenes, halogenated compounds, soluble heavy metals, radionuclides and so on. Among them, volatile organic compounds are the most serious. Under standard atmospheric pressure, the organic compounds whose melting point is lower than room temperature and whose initial boiling point or boiling point range is 50 °C-250 °C are called volatile organic compounds (VOC). The main components of VOC are hydrocarbons (halogenated hydrocarbons, oxygen hydrocarbons and nitrogen hydrocarbons, etc.), benzene series, organic halides (chlorides, freon series, etc.), organic ketones, alcohols, unitary compounds, amines, organic acids and petroleum hydrocarbon compounds, etc. Under the action of sunlight, VOC is easy to have photochemical effects with nitrogen oxides and sulfides in the atmosphere, producing secondary pollutants with greater toxicity, forming photochemical smog (Wang *et al.*, 2019). In addition, some halogenated hydrocarbons volatilized to the atmosphere can destroy the ozone layer, which leads to the excessive high-energy ultraviolet rays of the sun reaching the earth's surface, posing a threat to the global environment and human health.

For coatings, VOC refers to the organic compounds whose boiling point (or initial boiling point) is lower than or equal to 250 °C under atmospheric pressure and which participate in the gas-phase photochemical reaction, but do not participate in the gas-phase photochemical reaction, which is called the exempt compound; for indoor air, it is the pollution of any organic compound with boiling point lower than or equal to 250 °C under general pressure conditions, i.e. the amount of TVOC. There are also studies that set the boiling point to a higher temperature, such as 300 °C.

It is estimated that volatile organic compounds (VOCs) released from coatings and rubber are the main source of VOCs, accounting for 5%-10% of air pollutants. The annual output of coatings in the world is about 2.5 × 108 tons, and the growth rate is 3%. Calculated by the average solvent content of 40%, the annual emission of solvents to the atmosphere in the world is about 0.1 × 108 tons. In addition, the release of organic compounds (solvents) also caused a huge waste of resources.

2.1. Experimental instruments and reagents

Volatile organic compounds (VOC) have an impact on the human body, which is easy to cause sensory stimulation, causing visual and auditory impairment and sensory dryness of the human body, neuroticism, stressoriness, depression and apathy and other symptoms in the mental aspect, and stimulation to the mucous membrane. In the aspect of cognitive function, they are disorientation, confusion of long-term and short-term memory, etc. In the exercise body, it will produce weak grip, tremor and incongruity, and volatile organic compounds can easily enter the blood and nervous system through the blood brain barrier, leading to the inhibition of the central nervous system, causing people to have headache, fatigue, drowsiness and uncomfortable feeling. In addition, many volatile organic compounds have genotoxicity and carcinoge-nicity, such as benzene, tetrachloroethylene, trichloroethane, trichloroethylene, etc., which have been proved to be carcinogens or suspicious carcinogens. In this paper, volatile organic compounds (VOCs) are studied, and the harmful substances in fire-retardant coatings for historic buildings are determined by gas chromatography (Xie *et al.*, 2018). The experimental instruments are shown in Table 2. The experimental reagents are shown in Table 3.

2.2. Preparation of samples

First, the coating samples are stirred evenly. About 0.20.5 g (accurate to 0.0001 g) of the above uniformly stirred sample is weighed and put into the beaker, then 5ml of diluent solvent is added (methanol) and stirred with glass rod to make the coating fully disperse. After ultrasonic for 30 min, it is centrifuged with high-speed centrifuge for 5 min, and finally 2 ml of supernatant is taken from syringe and filtered to the sample bottle through a filter membrane with a machine, and it is measured on the gas chromatograph (Lelevic *et al.*, 2020).

2.3. Determination of density

The pycnometer is weighed and its quality is recorded. The fire-retardant coating sample is filled to be tested with pycnometer without bubbles and covered by the pycnometer. the coating outside the pycnometer is wiped off, and the pycnometer filled with the sample to be tested is weighed. The test temperature is 23 °C. The result of density is expressed as mass divided by volume (Lee and Myung, 2019).

2.4. Chromatographic conditions

The injection mode is split flow, split ratio is 10:1, column temperature is 35 °C. After holding for 20 min, the temperature rises to 150 °C at 5 °C/min, and it holds for 10 min; then rises to 230 °C at 20 °C/min, holding for 8 min; the gasification temperature is 250 °C, the detector temperature is 300 °C, N2 is the carrier gas, with the flow rate of 1.5 mL/min (Coimbra, Coelho, and Gamelas, 2019).

2.5. Experimental method

Firstly, 4.0 g of anhydrous magnesium sulfate is measured, 1.0 g of the sample is weighed and put into the sample bottle by electronic balance. After stirring evenly with glass rod, 20 ml of ethyl acetate is added and shook, and finally carried out ultrasonic for 30 minutes. After that, the solution is obtained by filtration, and then determined by gas chromatograph (Talaee *et al.*, 2019).

Table 2. Experimental Instruments

Instrument	Model	Manufacture
Chromatographic column	19091B-115	Agilent, USA
Gas chromatograph	7890A	Agilent, USA
Electronic analytical balance	ESJ60-4	Shenyang Longteng Electronics Co., Ltd
Ultra pure water system	Synergy	Merck millipore, French company
Oven	DZ-30	Shanghai Shenguang Instrument Co., Ltd
Electronic constant temperature water bath	XMTD-6000	Beijing Changfeng Instrument Co., Ltd
Organic filter membrane	13 mm, 0.22 μm	Tianjin Jintang experiment Co., Ltd

Table 3. Experimental Reagents

Experimental reagents	Purity	Company
H3COOC2H5	Analytical purity	Shanghai Ziyi Reagent Factory
C2H3N	Analytical purity	Shanghai Ziyi Reagent Factory
C4H8O	Analytical purity	Shanghai Ziyi Reagent Factory
MgSO4	Analytical purity	Shanghai Ziyi Reagent Factory
CH3OH	Analytical purity	Shanghai Ziyi Reagent Factory
C2H6O	Analytical purity	Shanghai Ziyi Reagent Factory
C3H8O	Analytical purity	Shanghai Ziyi Reagent Factory
CH3(CH2)3OH	Analytical purity	Shanghai Ziyi Reagent Factory
C6H5C2H5	Analytical purity	Shanghai Anpu Instrument Co., Ltd
C6H15N	Analytical purity	Shanghai Anpu Instrument Co., Ltd
C2H6O2	Analytical purity	Shanghai Anpu Instrument Co., Ltd
C4H10O3	Analytical purity	Shanghai Anpu Instrument Co., Ltd
C6H6	Analytical purity	Shanghai Anpu Instrument Co., Ltd
C7H8	Analytical purity	Shanghai Shiyi Chemical Reagent Co., Ltd
C8H10	Analytical purity	Shanghai Shiyi Chemical Reagent Co., Ltd
C4H11NO	Analytical purity	Shanghai Shiyi Chemical Reagent Co., Ltd
C8H16O4	Analytical purity	Shanghai Shiyi Chemical Reagent Co., Ltd
Analysis Sample	Fire-retardant coatings (Medium green matte White alkyd enamel Red matte)	Sample from fire-retardant coating manufacturer

2.6. Detection process of gas chromatograph

Gas chromatograph is the most important scientific instrument in a wide range of applications and a large number of analytical instruments. In the fields of oil, natural gas, fine chemical industry, metallurgy, electric power, medicine, health, grain and oil, food, environmental protection, gas, technical supervision and national defense research, it has almost become one of the necessary analytical instruments in modern analytical chemistry laboratory. With the popularization of gas chromatograph, the customer's requirements for the system have been gradually improved (Liu *et al.*, 2019). It is not only required to have good operation performance, but also to display the working status in real time and intuitively. The operator is required to conveniently adjust the working parameters of the system, data collection, analysis, judgment and parameter display according to the actual situation (Gashimova *et al.*, 2019). For this reason, a visual control system is designed and developed, which can display the status of the system visually, provide a fully graphical operation method, and has low cost. Gas chromatograph refers to the chromatographic analysis instrument using gas as mobile phase (Figure 1).

2.6.1. Principle of gas chromatograph

The basic principle of gas chromatograph technology is (as shown in Figure 2): when the gas sample is sent to the chromatographic system through a certain injection mode, the components of the mixture in the sample are driven by the mobile phase (carrier gas), and the components have different adsorption capacity in the mobile phase through the fixed phase called the chromatographic column (Tienstra and Mol, 2018). When the two phases are in relative motion, each component in the sample will be affected by the above forces repeatedly (103-106) in the two phases, so that each component in the mixture can be separated, and the separated single component will enter the detector system with the carrier gas to obtain non electric conversion, and the chemical component will be converted into an electric signal proportional to its concentration, and then the composition of the sample is analyzed according to the difference of these electrical signals.

Figure 1. Physical picture of gas chromatograph

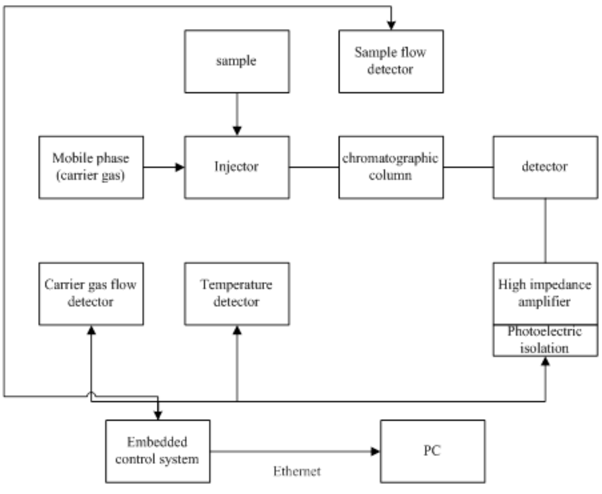

Figure 2. Basic principle block diagram of gas chromatograph technology

2.6.2. Structure of gas chromatograph

The basic structure of gas chromatograph has two parts: analysis unit and display unit. The former mainly includes gas source and control metering device, sample injection device, thermostat and chromatographic column. The latter mainly includes calibrator and automatic recorder. Chromatographic column (including stationary phase) and calibrator are the core components of gas chromatograph (Wu, Li, and Peng, 2018).

(1) The gas circuit of gas chromatograph is a closed pipeline system with continuous operation of carrier gas. The whole gas system requires carrier gas to be pure, airtight, stable and accurate.

(2) Injection system. Injection is to add gas or liquid samples to the top of chromatographic column at a constant speed and quantitatively.

(3) The core of separation system is chromatographic column, which is used to separate multi-component samples into a single component. There are two types of chromatographic columns: packed column and capillary column.

(4) The function of the detector of the detection system is to convert the sample components separated by the chromatographic column into electrical signals according to their characteristics and content, and then record the chromatogram by the recorder after amplification (Dhingra *et al.*, 2018). Common detectors are as follows, see Table 4.

(5) In recent years, the gas chromatograph mainly uses chromatographic data processor. Chromatographic data processor can print and record chromatogram, and print the processed results on the same recording paper, such as retention time, mass fraction of tested components, etc. (Chen *et al.*, 2018; Xiao *et al.*, 2019).

(6) Temperature control system is used to control and measure the temperature of chromatographic column, detector and gasifier, which is an important part of gas chromatograph. Gas chromatographs are divided into two categories: one is gas-solid chromatograph, the other is gas-liquid distribution chromatograph. The two types of chromatographs have different stationary phases, but the structure of the instrument is universal.

2.6.3. Instrument use environment

(1) The room where the gas chromatograph is placed shall have an area of not less than 20 m^2 and be air-conditioned.

(2) The table where the instrument is placed should be strong and stable, preferably cement.

(3) The total power of the power supply used by the instrument shall not be less than 5kW, and it shall be wired separately without interference source.

(4) The power supply must be grounded to prevent interference from other equipment.

2.7. Evaluation of the detection method

2.7.1. *Qualitative analysis*

In the qualitative analysis of the target compound in the sample to be tested, the retention time of the chromatographic peak of the sample is the same as that of the standard substance, and the selected ions in the mass spectrum are all present and the ion abundance ratio is the same as that of the standard substance, then the existence of the target compound can be determined, so as to achieve the qualitative analysis.

2.7.2. *Quantitative analysis*

Firstly, each target compound obtained by qualitative analysis is used to establish the external standard working curve of the target compound standard by using the relationship between different concentration and peak area. Then, when the actual sample is tested by gas chromatograph, the peak area of the sample is brought into the standard curve to achieve quantitative analysis. The specific calculation process is as follows:

Table 4. Detector

Serial number	Detector	Introduction
1	Thermal conductivity detector	The thermal conductivity detector (TCD) belongs to the concentration detector, that is, the response value of the detector is directly proportional to the concentration of the components in the carrier gas. Its basic principle is based on the fact that different substances have different thermal conductivity coefficients and respond to almost all substances. It is the most widely used universal detector at present. Because the sample is not destroyed in the detection process, it can be used for preparation and other joint identification technology.
2	Hydrogen flame ionization detector	Hydrogen flame ionization detector (FID) uses the chemical ionization of organic matter under the action of hydrogen flame to form ion flow, which is detected by measuring the intensity of ion flow. The detector has the advantages of high sensitivity, wide linear range, less harsh operating conditions, low noise and small dead volume. It is commonly used in organic compound detection. However, when the sample is destroyed, it can only detect the organic compounds that produce a large number of carbon positive ions in the hydrogen flame.
3	Electron capture detector	Electron capture detector (ECD) uses the ability of electronegative substance to capture electron and detect it by measuring electron flow. ECD has the characteristics of high sensitivity and good selectivity. It is a kind of exclusive detector, which is the most effective detector for the analysis of trace electronegative organic compounds at present. The stronger the electronegativity of elements is, the higher the sensitivity of the detector is, and it has a very high response to the compounds containing halogen, sulfur, oxygen, carbonyl, amino group, etc. Electron capture detector has been widely used in the determination of organochlorine and organophosphorus pesticide residues, metal complexes, organometal polyhalides or polysulfides. It can use nitrogen or argon as carrier gas, the most commonly used is high-purity nitrogen.
4	Flame photometric detector	Flame photometric detector (FPD) has high sensitivity and selectivity for sulfur and phosphorus compounds. The detection principle is that when the phosphorous and sulfur-containing materials are burned in the hydrogen rich flame, the characteristic spectra are emitted respectively, and the intensity of the characteristic light is measured by the photomultiplier tube through the interference filter.
5	Mass spectro-meter detector	Mass spectrometry detector (MSD) is a kind of mass and universal detector, its principle is the same as mass spectrometry. It can not only give the chromatogram (total ion flow chromatogram or reconstructed ion flow chromatogram) which can be obtained by general GC detector, but also give the mass spectrum corresponding to each peak. The automatic retrieval of the standard library by computer can provide the information of the analytical structure of compounds, so it is an effective tool for GC qualitative analysis. Often called GC-MS analysis, it combines the high separation ability of chromatography with the structure identification ability of MS.

Quantitative calculation of target compounds in samples:

$$Y = \frac{(a-b)c}{2d \cdot e} \tag{1}$$

where, Y is the content of the target compound in the sample; a is the peak area value; b is the intercept of the external standard working curve; c is the amount of diluted solvent methanol; 2 is the injection amount of 2 µL; d is the slope of the external standard working curve; e is the sample mass weighed during the pretreatment.

2.7.3. *The detection limit of the method*

In the process of actual sample detection, the definition of LOD in the established analytical method is generally measured by three times of signal-to-noise ratio. Namely:

$$\mathrm{LOD} = 3 \cdot \frac{g}{h} \tag{2}$$

where, g is the signal strength of the target in the test; h is the noise intensity of the instrument in the test.

2.7.4. *Accuracy and precision of the method*

Whether the analytical method is good or not, or whether the method is satisfactory, is measured by examining the precision and accuracy, while the accuracy and precision are respectively reflected by the recovery rate (R) and the relative standard deviation (RSD). In practice, the standard addition experiment is generally used for the evaluation of analytical methods, that is, by adding three groups of target compounds of different concentrations to the coating samples, the sample pretreatment is processed according to method, to provide to gas chromatograph measurement (Gu *et al.*, 2017). At the same time, four groups are added to each group, and the recovery and relative standard deviation of the final calculation method are calculated. The formula for calculating the recovery of the method is as follows:

$$R = \left[\frac{I-J}{L}\right] \cdot 100\% \tag{3}$$

where, *I* is the concentration of the target compound after adding the standard; *J* is the concentration of the target compound before adding the standard; *L* is the added target compound.

Relative standard deviation of the method is:

$$\mathrm{RSD} = \frac{1}{\bar{x}} \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \cdot 100\% \tag{4}$$

where, x_i is the measured value of the target compound each time; $\bar{x}$ is the average value of the target compound; *n* is the number of experiments.

3. Results and discussion

3.1. Selection of extraction solvent

The extraction solvent of the sample shall be able to completely dissolve the tested substance without affecting the compounds to be analyzed. In order to meet these two requirements, three kinds of organic solvents, acetonitrile, tetrahydrofuran and ethyl acetate, are selected through comparative analysis. Through reading and analyzing a large number of previous work conclusions and experimental studies, it is found that the peaks of acetonitrile and tetrahydrofuran overlap with those of isobutanol. Therefore, ethyl acetate is chosen as the solvent.

3.2. Selection of extraction method

The positive samples containing HBCD are detected by vortex and ultrasonic extraction respectively. The experimental results show that the coating samples can be completely dissolved by ultrasonic extraction for 5 minutes after vortex mixing, and the effect is good, so the samples are extracted by ultrasonic after vortex mixing for 5 minutes.

3.3. Optimization of experimental parameters

In this paper, the column produced by Agilent company in the United States is selected for the detection of VOCs in coatings. The influence of experimental parameters such as different column temperature and different carrier gas velocity on the separation of VOCs in historical building's fire-retardant coating is studied and analyzed, and the column temperature and carrier gas velocity are optimized. The results show that all 23 compounds can be separated effectively when the experimental parameters are suitable. The optimization results of the experimental parameters are as follows: the carrier gas flow rate is 0.5 mL·min^{-1}, the initial temperature is 55 °C and the temperature is controlled for 3 min, then the temperature is increased to 65 °C at the speed of 2 °C·min^{-1}; after 3 min temperature controlling, at the speed of 10 °C·min^{-1}, the temperature is increased to 150 °C; after 2 min tempera-ture controlling, at the speed of 10 °C min^{-1}, the temperature is increased to 200 °C; after 4 min tempera-ture controlling, at the speed of 30 °C min^{-1}, the temperature is increased to 250 °C, then the temperature is controlled for 3 min.

3.4. Analysis of standard components of volatile organic compounds

By means of NIST automatic retrieval and manual spectrum analysis, the chromatographic peaks of volatile organic compounds in three kinds of fire-retardant coatings (medium green matte a, white alkyd enamel b, red matte c) are analyzed and identified, and the types, relative molecular mass and molecular structure of the components are determined. It is concluded that the main volatile organic compounds in the fire-retardant coating are benzene, toluene, ethylbenzene, xylene and C9-C11 hydrocarbon. Figures 3, 4 and 5 are the standard total ion flow chromatograms (TIC diagrams) of samples a, b and c respectively. It can be seen from the figure that the chromatographic peaks of the three samples are not the same, that is to say, the volatile organic compounds contained in the samples are not the same. The three samples come from different manufacturers. Due to the different formulations and raw materials of the fire-retardant coating used by different manufacturers, the volatile organic compounds will be different.

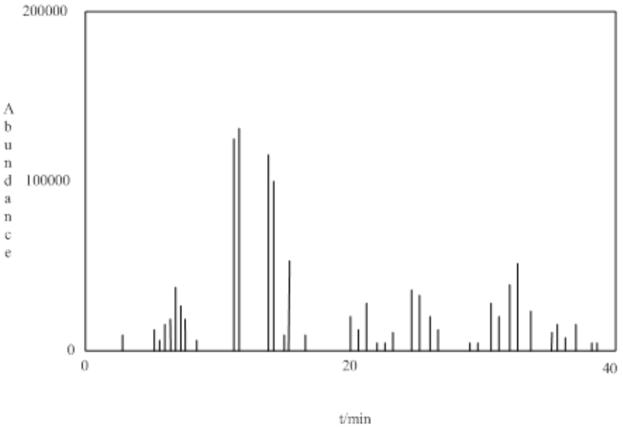

Figure 3. Standard total ion flow chromatogram of sample a

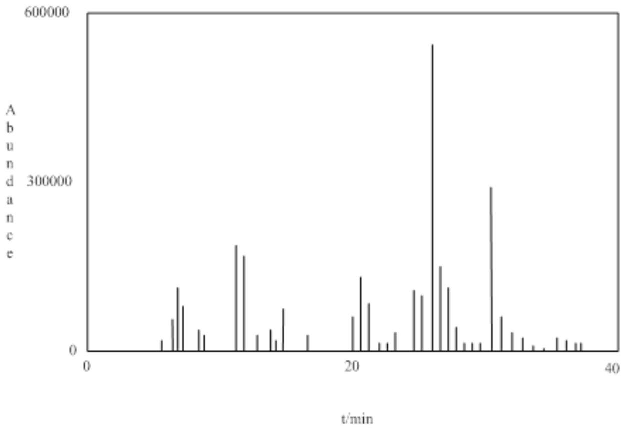

Figure 4. Standard total ion flow chromatogram of sample b

The limit requirements of VOCs in Chinese compulsory national standard coatings are shown in Table 5 below.

3.5. Comparative analysis of test results

In this paper, the green matt paint, white alkyd enamel paint and red matt paint produced by three manufacturers are determined according to the above methods, and the results are compared with those of spectrophotometry, electrochemical detection and liquid chromatography.

(1) Determination results of harmful substances in three samples

It can be seen from Table 6 that the total content of volatile organic compounds in historical building's fire-retardant coating detected by gas chromatography is closer to the true value, indicating that the measurement accuracy of gas chromatography is better than that of spectrophotometry, electrochemical detection and liquid chromatography. In addition, the test results show that the total content of VOCs in the three samples meets the national standards, and they are qualified products.

Table 5. Limit Requirements of VOCs In Chinese Compulsory National Standard Coatings

Project		Limited value	
		Water based wall coating	Water based wall putty
Volatile organic compounds (mg/kg)≤		120 (g/L)	15 (g/kg)
Total of benzene, toluene, ethylbenzene and xylene (mg/kg) ≤		300	
Free formaldehyde (mg/kg) ≤		100	
Soluble heavy metal (mg/kg) ≤	Pb	90	
	Cd	75	
	Cr	60	
	Hg	60	

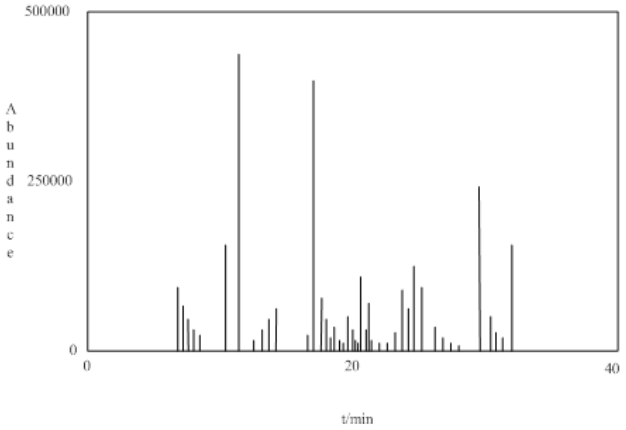

Figure 5. Standard total ion flow chromatogram of sample c

Table 6. Determination Results of Harmful Substances in Three Samples (G/Kg)

Determination method	Sample	Test results (g/kg)
True value	Sample a	52.36
	Sample b	42.33
	Sample c	50.14
Gas chromatography	Sample a	52.30
	Sample b	42.10
	Sample c	52.32
Spectrophotometry	Sample a	55.69
	Sample b	50.14
	Sample c	42.35
Electrochemical detection	Sample a	48.74
	Sample b	38.56
	Sample c	55.88
Liquid chromatography	Sample a	58.39
	Sample b	45.87
	Sample c	45.21

(2) Detection limit of the method

Table 7 shows that the detection limit of gas chromatography is 0.02~0.19 g/kg, and the detection limit of spectrophotometry, electrochemical detection and liquid chromatography is lower, indicating that the detection performance of gas chromatography is better.

Table 7. Detection Limit of The Method

Determination method	Sample	Detection limit
Gas chromatography	Sample a	0.02
	Sample b	0.12
	Sample c	0.19
Spectrophotometry	Sample a	0.25
	Sample b	0.23
	Sample c	0.15
Electrochemical detection	Sample a	0.33
	Sample b	0.30
	Sample c	0.41
Liquid chromatography	Sample a	0.26
	Sample b	0.36
	Sample c	0.32

(3) Accuracy and precision of the method

In order to further study the precision of gas chromatography and the recovery rate of standard addition of the sample, the standard solution of 280 mg·L^{-1} is added to the sample. The accuracy and precision of the measurement results are shown in Table 8.

The results of Table 8 show that the recovery rate of standard addition and relative standard deviation of the three samples with sampling 10 times are 91.7%-111.4% and 1.99%-3.98% respectively. Compared with the results of spectrophotometry, electrochemistry and liquid chromatography, the recovery rate of standard addition is higher and the relative standard deviation is lower, which shows that the performance of gas chromatography is better.

4. Conclusions

Fire-retardant coating is widely used in modern industry and production life. With the attention to environment and health, the environmental protection, quality and safety of fire-retardant coating has gradually become the focus of people's attention. This paper analyzes the toxic and harmful substances in the fire-retardant coating, establishes the detection method of harmful substances, and tests the samples of the fire-retardant coating. The results show that there is no VOC in the coating samples. The volatile organic compounds with high content in the fire-retardant coating samples are analyzed and identified by gas chromatography. The main VOCs are benzene, toluene, ethylbenzene, xylene and C9-C11 hydrocarbon. The total amount of volatile organic compounds in the samples of three fire-retardant coatings is 403-612 g/L, which is in line with the national standards. The accuracy of this method is higher than that of spectrophotometry, electrochemical detection and liquid chromatography to achieve the research goal of this paper.

Table 8. Recovery Rate of Standard Addition and Relative Standard Deviation

Determination method	Sample	Recovery rate of standard addition (%)	Relative standard deviation (%)
Gas chromatography	Sample a	98.6	2.36
	Sample b	91.7	3.98
	Sample c	111.4	1.99
Spectrophotometry	Sample a	85.6	2.68
	Sample b	88.3	3.69
	Sample c	84.2	3.25
Electrochemical detection	Sample a	81.3	3.20
	Sample b	82.7	3.69
	Sample c	83.6	4.02
Liquid chromatography	Sample a	80.2	3.69
	Sample b	85.3	4.03
	Sample c	83.5	3.89

Acknowledgment

Hunan Provincial Department of Education Project in 2018 (Project Number: 18C0129).

References

Balal O., Asghar S. and Eisa S. (2020), Effects of fireworks ancient celebrations on atmospheric concentration of particulate matter in Iran, *Geology, Ecology, and Landscapes*, **4**(2), 104–110.

Chen X.P., Zhang F., Yao H.M.B., et al. (2018), Analyzing multiple pesticides in tobacco leaf using gas chromatography with quadrupole time-of-flight mass spectrometry, *Journal of Separation Science*, **41**(9), 1983–1989.

Coimbra P., Coelho M.S.N. and Gamelas J.A.F. (2019), Surface characterization of polysaccharide scaffolds by inverse gas chromatography regarding application in tissue engineering, *Surface and Interface Analysis*, **51**(11), 1070–1077.

Dar A.A. (2018), Risk assessment, dissipation behavior and persistence of quinalphos in/on green pea by gas chromatography with electron capture detector, *Journal of Separation Science*, **41**(11), 2380–2385.

Dhingra G., Bansal P., Dhingra N., et al. (2018), Development of a microextraction by packed sorbent with gas chromatography -mass spectrometry method for quantification of nitroexplosives in aqueous and fluidic biological samples, *Journal of Separation Science*, **41**(3), 639–647.

Duan H.J., Ji S., Yin T., et al. (2019), Phosphorus–nitrogen-type fire-retardant vinyl ester resin with good comprehensive properties, *Journal of Applied Polymer Science*, **136**(39), 47997.

Gashimova E.M., Temerdashev A.Z., Porkhanov V.A., et al. (2019), Evaluation of the possibility of volatile organic compounds determination in exhaled air by gas chromatography for the noninvasive diagnostics of lung cancer, *Journal of Analytical Chemistry*, **74**(5), 472–479.

Gu F., Guo J., Yao X., Summers P., Widijatmoko S. and Hall P. (2017), An investigation of the current status of recycling spent lithium-ion batteries from consumer electronics in China. *Journal of Cleaner Production*, **161**:765–780.

Hong S.M., Son H. and Park J.S. (2018), Preparation and electrochemical properties of cobalt-phthalocyanine-decorated Fe$_3$O4 nanoparticles, *Journal of Porphyrins and Phthalocyanines*, **22**(7), 1–8.

Isfarita I., Mohd L.H.B.S., Sulong I. and Rozaimi Z. (2019), Root density analysis and wave attenuation ability of Rhizophora Species at Kemaman, Terengganu, *Earth Sciences Malaysia*, **3**(1), 18–24

Janvier H. and Blessing M. (2020), Performance evaluation of irrigation schemes in Rugeramigozi Marshland, Rwanda, *Water Conservation and Management*, **4**(1), 15–19.

Jayanthi D., Victor J.S., Chellan R., et al. (2019), Green processing: minimising harmful substances in leather making, *Environmental Science and Pollution Research*, **26**(198), 6782–6790.

Kanat M. and Eren T. (2019), The synthesis of phosphorus-containing flame retardants and investigation of their flame retardant behavior in textile applications, *Journal of Applied Polymer Science*, **136**(1), 47935.

Lee S.H. and Myung S.W. (2019), An efficient analysis of residual famphur in several species of honey using gas chromatography/mass spectrometry, *Bulletin of the Korean Chemical Society*, **40**(7), 719–723.

Lelevic A., Souchon V., Moreaud M., et al. (2020), Gas chromatography vacuum ultraviolet spectroscopy: A review, *Journal of Separation Science*, **43**(1), 150–173.

Li J.F., Song X.Q., Zhang M.Y., et al. (2018), Simultaneous determination of aminoglycoside residues in food animal muscles by mixed-mode liquid chromatography-tandem mass spectrometry. *Food Analytical Methods*, **11**(6), 1690–1700.

Liu J., Liu Y. and Wang X. (2019), An environmental assessment model of construction and demolition waste based on system dynamics: a case study in Guangzhou, *Environmental Science and Pollution Research International*.

Masrournia M. and Vaziry A. (2018), Preconcentration of Ti(IV) in ore and water by cloud point extraction and determination by UV-Vis Spectrophotometry, *Journal of Analytical Chemistry*, **73**(2), 128–132.

Muhammad F.M.H., Shahbudin S. and Zuhairi A. (2020), Hydrodynamic modelling in inshore reef area within Kuantan Coastal Region, *Journal Clean WAS*, **4**(1), 01–07.

Nwonumara G.N., Mmaduka A.T. and Okechukwu I.O. (2019), Impacts of rock mineralization and poor sanitary system on borehole waters quality and the health implications, *Earth Sciences Pakistan*, 10–13.

Ogunkunle T.J., Adewumi A.A. and Adeyinka O. (2019), Biodiversity: Overexploited but underutilized natural resource for human existence and economic development, *Environment & Ecosystem Science*, **3**(1), 26–34.

Sana B., Haroon R., Abdul N. and Rana A.N. (2019), Spatial and temporal variability analysis of PM2.5 concentration in Lahore city, *Environmental Contaminants Reviews*, **2**(1), 6–10.

Sarmila B., Anisha T., Suraksha B., Sarita B. and Divya P. (2020). Study of improved Mandarin (Citrus Reticulate Blanco) Orchardmanagement practices in mid hills of Gandaki Province, Nepal, *Malaysian Journal of Sustainable Agriculture*, **4**(2), 49–53.

Talaee M., Lorestani B., Ramezani M., et al. (2019), Microfunnel-filter-based emulsification microextraction followed by gas chromatography for simple determination of organophosphorus pesticides in environmental water samples, *Journal of Separation Science*, **42**(14), 2418–2425.

Tienstra M. and Mol H.G.J. (2018), Application of gas chromatography coupled to quadrupole-orbitrap mass spectrometry for pesticide residue analysis in cereals and feed ingredients, *Journal of Aoac International*, **101**(2), 342–351.

Wang M., Zhang D., Cheng Y. and Tan S.K. (2019), Assessing performance of porous pavements and bioretention cells for stormwater management in response to probable climatic changes, *Journal of Environmental Management*, **243**, 157–167.

Wu Y.L., Li Y.Y. and Peng Y.T. (2018), Determination of seven phenolic compounds in mainstream cigarette smoke by gas chromatography-tandem mass spectrometry, *Journal of Chinese Mass Spectrometry Society*, **39**(3), 376–384.

Xiao J., Hu C., Ouyang G., et al. (2019), Impacts of oil implied volatility shocks on stock implied volatility in China: Empirical evidence from a quantile regression approach, *Energy Economics*, **80**, 297–309.

Xie T., Wang D., Ma M.J., et al. (2018), Identification of flavor-active compounds in spiced donkey meat by odor activity value (OAV) calculation and gas chromatography-olfactometry-mass spectrometry, *Food Science*, **39**(8), 123–128.

Zhang T., Wu X., Shaheen S.M., Zhao Q., Liu X., Jörg R. and Ren H. (2020), Ammonium nitrogen recovery from digestate by hydrothermal pretreatment followed by activated hydrochar sorption, *Chemical Engineering Journal*, **379**.

Zhokhov A.K., Loskutov A.Y. and Rybal'chenko I.V. (2018), Methodological approaches to the calculation and prediction of retention indices in capillary gas chromatography, *Journal of Analytical Chemistry*, **73**(3), 207–220.