

In-situ Online Detection of Atmospheric Volatile Organic Compounds Based on Laser Induced Breakdown Spectroscopy: A Review

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ABSTRACT: This review's main purpose is to provide a succinct overview of recent developments in the field of volatile organic compounds (VOCs) detection based on Laser-induced breakdown spectroscopy (LIBS). VOCs are important air pollutants, which have great harm to the environment and human body. It is of great significance to realize the rapid detection of VOCs in the atmospheric environment. LIBS is a novel atomic emission spectroscopy technology, which can achieve the rapid in-situ detection of substances and shows great potential in the online monitoring of atmospheric VOCs. To illustrate the development and difficulties of LIBS technology in atmospheric VOCs detection, some typical cases for various aspects are listed, including the detection of harmful elements in VOCs, source tracing of VOCs, the identification of isomers, and the detection of VOCs in living environment.

INTRODUCTION

In recent years, air pollution has emerged as one of the most pressing environmental challenges for all countries across the world, attracting wide attention of the international community.^{1,2} VOCs are a class of harmful organic pollutants that have high chemical reactivity and volatility in atmospheric environments. The definition of VOCs may vary depending on the country or organization. The World Health Organization (WHO) defines VOCs as a general term for certain VOCs that have a melting point below room temperature and a boiling point between 50 and 260 °C.³ VOCs can typically be categorized into five groups: non-methane hydrocarbons (NMHCs), halogenated hydrocarbons, oxygen-containing organic compounds, nitrogen-containing organic compounds, and sulfur-containing organic compounds. As one of the precursors to the formation of ozone and PM_{2.5}, VOCs could increase tropospheric ozone concentration, urban gray haze, photochemical smog, and other harmful environmental effects,

leading to significant damage to the environment.^{4,6} Additionally, VOCs exhibit physiological toxicity, leading to cancer, deformity, and organ damage in the human body.^{7,8} The sources of VOCs are diverse and can be classified into two categories: natural sources and artificial sources.^{9,10} Natural sources include emissions from wetlands, forests, and oceans, while artificial sources include emissions from industry, agriculture, homes, and transportation vehicles. Among them, industrial and vehicle emissions are the primary causes of VOCs. VOCs emissions have significantly increased due to the rapid industrialization and urbanization, posing a serious threat to the environment.¹¹

To implement effective control measures against these pollutants, a technology that can perform real-time quantitative monitoring of components in the moving air in an open environment is required. Currently, gas chromatography (GC),¹²⁻¹⁴ gas chromatography-mass spectrograph (GC-MS)¹⁵⁻¹⁷ and high-performance liquid chromatography (HPLC)¹⁸⁻²⁰ are commonly used for the detection of VOCs. However, these methods require

plasma is collected by the detector and coupled to the spectrometer, and the spectral information is then displayed on the computer. The laser is the core component of the device, as the plasma excited by it is key to obtaining sample element information, and the laser parameters will affect plasma formation. The spectrometer determines the range and resolution of the spectrum. Different types of lasers and spectrometers need to be selected according to the detection object. The delay trigger device is located between the laser and the spectrometer. By adjusting the delay time, the signal-to-noise ratio of the spectrum can be improved. In addition, when detecting gaseous samples, air pumps are sometimes used to control the gas flow and improve the laser hit rate.

Fig. 1 The schematic diagram of the LIBS experimental setup.

complex sample processing and take a long time to detect, which obviously fails to meet the actual demand.

LIBS is a novel material element analysis technique based on atomic emission spectroscopy.²¹⁻²² It has been widely used in industry,²³⁻²⁵ biomedicine,²⁶⁻²⁸ archaeology,²⁹⁻³¹ environment³²⁻³⁴ and many other fields, showing its outstanding results in element analysis and substance identification. In recent years, LIBS has been developing in the detection of pollutants, and many effective detection methods have been invented.³⁵ Due to its advantages such as fast detection, high sensitivity, multi-component measurement, little damage to the sample and requiring no sample pretreatment, LIBS is expected to emerge as a powerful tool for monitoring ambient air quality. Currently, the LIBS technology has been relatively mature in the detection of metal elements, but there are still few studies on substances that comprise non-metallic elements, such as VOCs. Hence, there is a considerable space for development in this area.

This paper mainly introduces the progress and challenges of LIBS technology in the detection of atmospheric VOCs. From the four levels of the detection of harmful elements in VOCs, source tracing of VOCs, identification of isomers, and VOCs detection in living environment, relevant cases are included to demonstrate the remarkable achievements and great development potential of LIBS in this field.

INSTRUMENTATION

The LIBS experimental system is shown in Fig. 1, which is a typical LIBS system used for the detection of atmospheric VOCs. It consists of a pulsed laser, mirrors, a detector, a spectrometer, a delay trigger device, and a computer. During the experiment, the laser emitted from the laser converges on the sample gas through the mirrors and burns to form a plasma. The light emitted by the

CASE STUDIES

Detection of harmful elements in VOCs. Halogenated hydrocarbons and sulfur compounds are typical classes of VOCs in the atmosphere. Unlike other VOCs composed of carbon, hydrogen, oxygen, and nitrogen, the halogen and sulfur atoms in these compounds can be important features for spectral analysis. However, halogen and sulfur atoms have high ionization energy, and their most intense emission lines lie in the Vacuum UltraViolet (VUV) or Near-Infrared (NIR) region,^{36,37} which makes it difficult for LIBS to detect these elements. In the past few decades, many researchers have modified the experimental environment and samples to improve the detection performance.

For the detection of halogens, it is effective to improve the intensity of halogen lines by conducting experiments in an inert gas environment. Compared with the spectral lines of N, H and O, the intensities of halogen spectral line are relatively weak. But in the environment of inert gas, the spectral line intensity is significantly increased. Usually, helium is used as an ambient gas with better results. Asimellis *et al.* detected F and Cl qualitatively and quantitatively under controlled helium gas ambient atmosphere.³⁸ After optimizing the experimental parameters, the spectral lines of F and Cl could be clearly observed in the upper visible and in the NIR (650–850 nm) region. In the later work, they studied the effect of the ambient atmosphere (pressure and gas species) on Br emission lines.³⁹ The results showed that the signal-to-noise ratio was best in helium under 100 mbar, and the 827.24 nm Br atomic line shifted and expanded asymmetrically when the ambient atmosphere changed. In addition, Barbier *et al.* performed LIBS detection on flame retardants in plastics under different plasma conditions.⁴⁰ It was found that the strength of Br line and Cl line was improved under the helium buffer. However, the enhanced halogen lines in the inert gas atmosphere are mainly located in the NIR region, which requires the spectrometer detection performance to be high. Furthermore, the detection needs to be carried out in the laboratory as it is difficult to create a

controllable inert gas environment in an open environment, limiting the application of LIBS technology in the detection of atmospheric VOCs.

Another common approach is to use molecular emission bands. The intensity of some alkali-halogen molecular bands is stronger than that of halogen emission lines. By replacing the detection of halogen atoms with the detection of molecules formed by alkali metal elements (usually Ca or Ba) and halogens, the sensitivity of detection can be effectively improved, which helps to achieve the quantitative detection of halogens in samples. Fernandez-Mendez *et al.* investigated the spatial and temporal distribution of CaF emission in samples containing Ca and F.⁴¹ Under optimized conditions, the sensitivity of F detection was increased by more than 4 times. Gaft *et al.* obtained and evaluated the spectral signals of halogenated alkali metal compounds such as CaF, CaCl, BaBr, CaI. The results showed that the spectra of halogens combined with alkali-earths elements was easier to be detected than F and Cl atomic lines.^{42,43} Tang *et al.* realized the quantitative detection of F in copper ore based on SrF or CaF molecular emission bands.^{44,45} When there are no alkali metal elements in the sample that can form molecular emission bands with halogens, the sample may require certain manipulation to introduce these elements. The alkali metal elements and halogens combine into molecules in the plasma and can be detected by detectors. Alvarez-Llamas *et al.* developed a novel approach to quantitatively detect F in calcium-free samples based on molecular CaF bands.³⁶ By spraying a calcium solution on the surface of the sample, an intense CaF molecular signal was detected via LIBS system. Mendez-Lopez *et al.* nebulized an aqueous solution of NaF onto the Ca-containing pellets to obtain molecular emission bands of CaF.⁴⁶ This method was used to detect fluorine content in liquids, and the experimental accuracy deviation of the three mouthwashes measured was less than 10%. In addition to solids and liquids, the use of molecular emission bands is also feasible in aerosols. Niu *et al.* detected the spectra of CaCl and CaF radicals in aerosols, which implies the possibility of this method in gas detection.⁴⁷ Besides, since the detection of non-metallic elements may be difficult, combining LIBS technology with other technologies can help improve the detection ability to a certain extent. Nagli *et al.* applied LIBS-MLIF method to detect Cl atoms in concrete samples as a further development of molecular emission applications.⁴⁸ It was found that the detection sensitivity of LIBS-MLIF was better than that of MLIBS. Although molecular emission bands can achieve quantitative and qualitative detection of halogens in samples, it is not a good choice for detecting halogens in atmospheric VOCs. Atmospheric VOCs almost do not contain alkali metal elements. Sample must be processed to obtain the molecular emission bands, which will hinder real-time detection in the actual environment.

Since the LIBS signal intensity of metallic elements is usually much higher than that of halogens, Duerst *et al.* proposed a new

Fig. 2 The characteristic peaks of Cl in the LIBS spectrum and SPAMS spectrum of Freon R11. The figure is taken from REF.⁵⁰

method to confirm the presence of halogens in mineral samples based on the relative intensity ratio of halogens and alkali metals lines.⁴⁹ The LIBS spectra of more than twenty alkali metals and halogens were obtained and the relative intensity ratios of halogen/alkali metal were calculated in the experiment. When testing unknown samples, the peak intensity of alkali metal in the sample can be multiplied by the relative intensity ratio to determine the possible intensity of F, Cl, Br, and I, thus reducing the interference of noise on element identification. Although this method is not yet very mature, it undoubtedly provides a new way of identifying halogen spectral lines in LIBS spectra.

To achieve online direct detection of halogens in atmospheric VOCs, Zhang *et al.* applied LIBS system combined with a self-designed single particle aerosol mass spectrometry (SPAMS) to detect halogen atoms in three typical VOCs (Halon 2402, Freon R11, iodomethane) in the atmospheric environment.⁵⁰ The laser used in the experiment had a wavelength of 1064 nm and an energy of 200 mJ. The time delay was set to 2.5 μ s and the time integration was set to 2 ms. From the obtained LIBS and SPAMS spectra, the characteristic peaks of corresponding halogens in different samples were observed. Fig. 2 shows the LIBS spectrum and SPAMS spectrum of a Freon R11 sample, in which the LIBS characteristic spectral lines and mass spectrum of Cl can be seen. Using mass spectrum as a supplementary analysis, the detection accuracy was improved. Meanwhile, mass spectrum could distinguish halogen isotopes, and the source of pollutants could be traced by calculating the isotope abundance ratio. The Halon 2402 samples were tested by Raman spectroscopy to obtain molecular structure information, as shown Fig. 3. The characteristic peaks corresponding to several vibration modes could be considered as “spectral fingerprints” of the Halon 2402 molecule. Similarly, using the same method, Zhang *et al.* successfully captured the LIBS and SPAMS spectra of halogen atoms in halogenated hydrocarbons.⁵¹ The LIBS spectrum of C₂H₄BrF obtained by the

sulfur concentrations in samples with different concentrations in a helium gas atmosphere under controlled pressure using the NIR spectral lines of sulfur at 869.46 nm.⁵⁷ The optimal ambient pressure measured experimentally was slightly lower than 100 mbar. Weritz *et al.* investigated sulfur in building materials via LIBS in air, argon, and helium atmospheres.⁵⁸ According to the results, the resolution of sulfur spectral lines in the NIR region was best in the helium atmosphere under the same conditions. Jasik *et al.* employed VUV-LIBS to detect trace elements in polyethylene in a 2 mbar Ar atmosphere.⁵⁹ Two atomic lines of sulfur were detected at 180.7 and 182.0 nm and the limit of detection (LOD) in the experiment was 50 µg/g.

Fig. 3 The Raman spectra of Halon 2402. The figure is taken from REF.⁵⁰

Some researchers have also introduced double-pulse technology to improve the sensitivity of LIBS systems. Ma *et al.* quantitatively analyzed sulfur in coal under helium atmosphere using DP-LIBS technique.⁶⁰ Two orthogonally configured nanosecond laser were utilized in the system. The first laser was used to ablate the sample, creating a plasma. The second laser reheated the plasma with a certain time interval. The parameters of the two laser beams were different. Compared with SP-LIBS, the mean strength of the sulfur lines captured by DP-LIBS was 2.3 times higher, and the interference of the oxygen atomic lines was also reduced due to the use of helium gas. The calibration curves were established to quantitatively calculate sulfur concentration. It was found that the best results were obtained when S I 921.3 nm was used. Gaft *et al.* tested and compared the performance of SP-LIBS and DP-LIBS in detecting sulfur concentrations in different minerals.⁶¹ For different kinds of samples and sulfur concentrations, different LIBS devices and detection bands need to be selected. Gondal *et al.* used DP-LIBS system to detect sulfur in the reinforced concrete structures.⁶² The sulfur ionic line was detected at 545.38 nm, which was used as the indicator of sulfur concentration in the sample. The LOD in the experiment was about 38 µg/g. In addition, Ma *et al.* used indirect laser-induced breakdown spectroscopy (ID-LIBS) to improve the detection sensitivity of Cl and S elements.⁶³ Ag and Ba reacted with chloride and sulfate respectively in water to form precipitation. The indirect detection of Cl and S was achieved by measuring the remaining Ag and Ba in water. The results showed that this method could greatly improve the detection sensitivity.

Fig. 4 The LIBS spectrum of C₂H₄BrF. The figure is taken from REF.⁵¹

experiment is shown in Fig. 4. By comparing the theoretical and experimental Raman spectra, two rotational conformations of C₂H₄BrF were identified. It provides reference for rapid identification of halogenated hydrocarbons.

There are similar challenges with halogens when detecting sulfur in samples by LIBS system. Therefore, most researchers select the emission lines of sulfur located in the NIR or VUV region as the research object,⁵²⁻⁵⁴ with only a few studies using spectral lines in the VIS region.^{55,56} In addition, the experiment has certain environmental requirements to enhance the intensity of the characteristic sulfur lines. Asimellis *et al.* efficiently determined

However, most of the current studies using LIBS to detect sulfur are focused on solid samples (coal, steel, ore, *etc.*), because sulfur content is an important standard to measure the quality of industrial production and pollutant emission.^{64,65} There are few studies on the detection of sulfur in gaseous samples. Due to the high mobility of gases in open space, pollutants in the air may be relatively thin. Therefore, the speed and sensitivity of detection are critical, which makes many methods used to detect sulfur in solid samples no longer effective for detecting gases. Researchers are also exploring new ways to achieve accurate measurement of sulfur in atmospheric VOCs.

Fig. 5 Quantitative analysis of sulfur in DMS sample. (a) Sulfur characteristic lines of DMS gas samples at different concentrations, and (b) the calibration curve of sulfur. The figure is taken from REF.⁶⁶

Fig. 6 The characteristic sulfur lines in the LIBS spectra. (a) The CS₂ gaseous sample, and (b) The CS₂ aerosol sample. The figure is taken from REF.⁶⁷

Zhang *et al.* investigated dimethyl sulfide (DMS), a major volatile sulfur-containing organic compound, under normal atmospheric conditions.⁶⁶ The element information of DMS was obtained in this work by using LIBS and Raman techniques, and its molecular configuration. Different volumes of DMS liquid samples were added into the sample cell to fully volatilize to simulate different levels of air pollution. The outlet of the sample cell was placed near the laser focus to ensure that the concentration of the experimentally measured DMS was equal to the concentration of the prepared sample. Under the excitation of laser in 1000 mJ, several ionic lines of sulfur appeared in the 535–570 nm region of the LIBS spectrum. As is shown in Fig. 5, with the increase of DMS concentration, the spectral line intensity of sulfur also increases linearly. The calibration curve of sulfur in air was obtained based on the S II 545.383 nm peak, and the coefficient of determination R^2 was 0.986. In this experiment, the LOD was 46

mg·L⁻¹, which could meet the requirement for sulfur detection in real atmospheric environment. In addition, obvious sulfur ionic lines can be seen in the visible region when detecting gas samples, but often cannot be seen in solid detection. In order to verify whether the sample state influences the intensity of sulfur ionic lines, the LIBS spectra of gas and liquid DMS sample were compared in the experiment. It was found the sulfur ionic lines in gas sample were more easily detected when the experimental conditions were the same except for the sample state.

Chen *et al.* performed LIBS-SPAMS technology on the direct in-situ detection of sulfur in the atmosphere.⁶⁷ Through the detection of CS₂ samples in different states, it was found that the characteristic lines of sulfur ions appeared in the LIBS spectrum of gaseous sample at 540–570 nm, and the signal-to-noise ratio was 28.0±1.2 dB, as shown in Fig. 6. In the aerosol spectrum, the

resolution of the corresponding spectral lines became worse and the signal-to-noise ratio decreased to 17.1 ± 4.2 dB, but the sulfur lines could still be seen faintly. However, in the liquid sample, sulfur lines could not be detected at all in this band. It is also proved that gaseous samples are more easily excited into ionic states under the action of high-energy laser. LIFBASE software⁶⁸ was used to calculate the temperature of CN molecular band. It was found that the vibration temperature and rotation temperature of CN molecular band in gaseous CS₂ experiment were higher than that in aerosol CS₂ experiment, indicating that the increase of plasma temperature was more conducive to the detection of sulfur than the increase of concentration. Besides, the three isotopes of sulfur were well distinguished in the mass spectrum of CS₂. The isotopic abundance ratio of sulfur in the sample was calculated and found to be very close to the natural abundance ratio.

The two examples above confirmed the feasibility of LIBS in detecting harmful elements in atmospheric VOCs. In fact, accurate identification and quantitative detection of these elements is a crucial part in the analysis of VOCs in the atmosphere, which is the basis for the classification of VOCs and the judgment of molecular structure in the follow-up work.

Source tracing of VOCs. Source tracing of VOCs is a crucial step in managing atmospheric VOCs pollution. Only by identifying the sources of atmospheric VOCs can different pollution sources be accurately managed. The types of VOCs produced by different pollution sources are different. If different VOCs in the air can be identified, its possible sources can be determined. Then specific measures are taken to control the emission of pollutants.^{69,70} In previous studies, SPAMS is often used to trace the source of air pollutants. According to the mass spectrum information of particulate matter, the clustering algorithm (ART-2a, K-medians, K-means, Fuzzy clustering, etc.) is used to classify particulate matter into different categories according to the similarity of mass spectrum characteristics, so as to distinguish the source of particulate matter.⁷¹⁻⁷³ In this review, another tracing method based on LIBS combined with machine learning algorithms will be introduced, which can realize the rapid detection and differentiation of atmospheric VOCs.

Machine learning is an important technology in the field of artificial intelligence, which can automatically improve the prediction and decision-making abilities of computers through data or experience. Since the 1950s, machine learning has gone through multiple stages of development and has gradually matured. Many classical algorithms, such as Logistic Regression (LR), K-Nearest Neighbor (KNN), Classification and Regression Tree (CART), Error Back Propagation (BP), Artificial Neural Network (ANN), Convolutional Neural Network (CNN), Support Vector Machine (SVM), Adaptive Boosting (AdaBoost), Random Forest (RF), have been produced successively, promoting machine learning to penetrate into more different fields.^{74,75} At present,

machine algorithms can be roughly divided into three categories: supervised learning, unsupervised learning, and reinforcement learning. They play a crucial role in many application scenarios such as image recognition,⁷⁶⁻⁷⁸ natural language processing,⁷⁹⁻⁸¹ traffic prediction,⁸²⁻⁸⁴ medical diagnosis⁸⁵⁻⁸⁷ and so on. In recent years, LIBS combined with machine learning algorithms has become a hot topic.⁸⁸ Chen *et al.* proposed a new method to identify inferior charcoal based on LIBS technology.⁸⁹ Principle Component Analysis (PCA) was used to reduce the dimension of spectral data. On this basis, combined with the optimized KNN and SVM methods, the classification accuracy of fruit charcoal, mechanism charcoal and bamboo charcoal reached 96.0% and 97.3%, respectively. Liu *et al.* used the LIBS-HIS technology combined with machine learning algorithms to build recognition models of rice geographical origin.⁹⁰ In the experiment, the recognition accuracy of the Partial Least Squares Discriminant Analysis (PLS-DA), the SVM, and the Extreme Learning Machine (ELM) algorithms reached 99.08%, 99.85% and 99.47%, respectively. Rzecki *et al.* tested the classification effect of seven machine learning algorithms (DT, KNN, RF, SVM, PNN, MLP, GRNN) on LIBS spectra of paper-ink samples, and the results showed that the RF algorithm had the best classification effect, with an accuracy of 99.08%.⁹¹

Lu *et al.* proposed a method of atmospheric VOCs source tracing based on LIBS combined with machine learning algorithms.⁹² The source tracing model of VOCs is shown in Fig. 7. The five haloalkanes used in the experiment were C₂H₄BrCl, C₂H₄Cl₂, C₂H₃Cl₃, C₂H₂Cl₄ and CH₃I. To simulate environmental pollution, liquid reagents were added to a closed box filled with air at atmospheric pressure and heated to accelerate the evaporation of the reagent until the gas in the box became stable. Firstly, LIBS were used to detect the polluted air. Atomic lines of Cl, Br and I, ionic lines of Br and I, CN molecular emission bands and some common elements in the air were respectively observed in different samples. For different VOCs samples, 300 spectra were selected and the data was standardized to carry out PCA. When the entire spectral region was selected for PCA, the data sets corresponding to different VOCs overlapped significantly on the two-dimensional plane composed of PC1 and PC2. When the bands of C, H, Cl, Br, I and CN were selected for PCA, different VOCs could be well separated on the two-dimensional plane

Fig. 7 The source tracing model of VOCs based on LIBS and BP-ANN. The figure is taken from REF.⁹²

Fig. 8 The PCA results based on LIBS spectra. (a) Principal component contribution rate and cumulative contribution rate, and (b) result of differentiation. The figure is taken from REF.⁹²

composed of PC1 and PC2. The analysis results are shown in Fig. 8. On this basis, BP-ANN was used to establish the classification model of VOCs. 1500 pieces of spectral data were divided into training set and test set, with the training set accounting for 80% and the test set accounting for 20%. There were 5 neurons in the output layer of the model by using one-hot encoding. A hidden layer was established. After model training, the recognition accuracy could be calculated by comparing the label predicted and the actual ones. It was found that the recognition accuracy was highest when the number of neurons in the hidden layer was 4. In order to better evaluate the performance of the model, ten times ten-fold cross-validation was adopted, and the average value was taken as the final recognition accuracy. When the number of hidden layer neurons was 4, the recognition accuracy reached 99.77%.

Identification of isomers. Cis-trans isomers, also known as geometric isomers or E and Z isomers, are a type of stereoisomers that have the same molecular formula and bond connectivity but differ in the spatial arrangement of substituents around a double bond.⁹³ There are also many isomers in VOCs. The structures of VOC isomers are different, and their degree of atmospheric pollution may vary. The study of isomers is important in many fields, including chemistry,^{94,95} biochemistry,^{96,97} and pharmacology,^{98,99} as they can have different physical, chemical, and biological properties.

Recent research on cis-trans isomers has focused on developing new methods for their synthesis, separation, and characterization. For example, advances in spectroscopic techniques, such as NMR and IR spectroscopy, have enabled researchers to distinguish

between cis and trans isomers more accurately. Saman *et al.* characterized a highly-thermoreistant POSS, the octa(aminophenyl)silsesquioxane (OAPS) by using IR and NMR spectra.¹⁰⁰ Abikhodr *et al.* demonstrated a method in which ion fragments produced by collision-induced dissociation (CID) are separated using IMS and identified using the vibrational fingerprints of only a few standards.¹⁰¹ In addition to infrared spectroscopy, there are some other spectral determination methods. Buhrow *et al.* measured the concentrations of endoxifen and its metabolites Z- and E-isomers in the plasma of estrogen receptor-positive breast cancer patients by liquid chromatography-mass spectrometry.¹⁰² Additionally, computational methods, such as molecular modeling and quantum chemistry calculations, have been used to predict the stability and properties of cis and trans isomers. Zhang *et al.* studied the effect of molecular structure on oxidation properties of propanol isomers at elevated pressure.¹⁰³ Anthony *et al.* studied the internal rotation splitting in the spectra of three NT isomers to analyze the influence of isomers on the internal rotation barrier.¹⁰⁴

In recent years, a new method has been proposed to determine and classify the isomers of VOCs in the atmosphere by LIBS technology. Zhang *et al.* studied rapid identification of VOCs and their isomers in the atmosphere.¹⁰⁵ LIBS technology was developed to online distinguish VOCs and their isomers in the air. In this work, dibromoethane and fluorobromobenzene were used as experimental subjects. Dibromoethane and fluorobromobenzene are important commodity chemicals and indispensable synthetic intermediates in modern chemistry. There are two isomers of dibromoethane, 1,1-dibromoethane and 1,2-dibromoethane. Fluorobromobenzene has three isomers, such as,

2-fluorobromobenzene, 4-fluorobromobenzene, and 3-fluorobromobenzene. Their structure diagram is shown in Fig. 9. LIBS technology combined with machine learning was used to classify and identify isomers in the work. Firstly, the LIBS spectra of dibromoethane and fluorobromobenzene were quickly identified by machine learning. The recognition results are shown in Fig. 10. The point cluster distribution of fluorobromobenzene samples is relatively concentrated, and the scores of both principal components in the distribution area are negative. The distribution of data points for dibromoethane is relatively scattered, and the principal component score of the distribution area is positive.

Fig. 9 The optimized molecular configuration diagram of the four VOCs. The figure is taken from REF.¹⁰⁵

Secondly, the LIBS spectra of the isomers of dibromoethane and fluorobromobenzene are classified by machine learning, and the results are shown in Fig. 11. Based on PCA algorithm, BP-ANN is used for accurate identification and classification. The following data come from BP-ANN algorithm. The optimal recognition accuracy of dibromoethane is 98.25%, and the precision and recall rate are 96.08% and 97.5%, respectively. The optimal recognition accuracy of fluorobromobenzene is 81.25%. The PCA distribution maps of the two isomers of p-fluorobromobenzene in Fig. 11 are highly overlapped, but the best recognition rate after combining BP-ANN is still higher than 80%. The precision and recall are 74.63% and 71.25%, respectively.

From the results, the classification of VOCs isomers by LIBS technology combined with machine learning is successful.

Fig. 10 Distribution of the scores of the first two principal components of dibromoethane and fluorobromobenzene samples. The figure is taken from REF.¹⁰⁵

VOCs detection in living environment. On a global scale, the contribution of natural sources to the atmospheric VOCs is relatively large, but the natural sources are beyond the scope of human control. Thus, it is difficult to alter their emissions in the atmosphere, and artificial sources should be given special attention. VOCs emission objects in artificial sources are complex. In addition to transportation and industrial production, which are two of the most familiar sources of emissions, many common household items also emit VOCs, causing local air pollution and damaging human health. Therefore, it is significant to apply LIBS detection technology to the monitoring of VOC sources in daily life. In this review, two common types of VOCs in living environments are presented as examples, as shown in Fig. 12.

Fig. 11 Scatter point distribution diagram of the first two main components of the two isomers. (a) Dibromoethane, and (b) fluorobromobenzene. The figure is taken from REF.¹⁰⁵

Fig. 12 VOCs in the living environment.

Fig. 13 PCA results of air, synthetic mothball, and natural camphor spectra. (a) Principal component contribution rate and cumulative contribution rate, and (b) result of differentiation. The figure is taken from REF.¹⁰⁹

of the two samples were similar, but the intensity of C and CN lines in the synthetic mothballs spectra were significantly higher. C, CN, H α , Na and Cl spectra lines were used as the original features of PCA to reduce their dimensions. The principal component contribution rate and cumulative contribution rate is shown Fig. 13(a). On the two-dimensional plane formed by PC1 and PC2, the samples of air, natural camphor and synthetic mothballs could be distinguished, as shown in Fig. 13(b). The SVC data showed that the recognition accuracy could reach 98.33%. C₂ free radicals were also detected in high concentrations of synthetic mothballs volatile gases. In addition, Raman spectra of natural camphor and synthetic mothballs indicated that the characteristic peaks of the molecular vibration modes could be used as spectral fingerprints to distinguish mothballs.

Fig. 14 LIBS spectrum of pesticides and deltamethrin in the 350 nm–430 nm band. The figure is taken from REF.¹¹⁴

Mothballs are one of the important sources of indoor VOCs. Mothballs can be divided into natural camphor (the main component is C₁₀H₁₆O) and synthetic mothballs (the main component is C₆H₄Cl₂ or naphthalene, which is harmful to human health).¹⁰⁶⁻¹⁰⁸ Since the production of natural camphor is relatively low, synthetic mothballs is commonly used as a substitute in the market. However, the smell of the two species is so similar that it's difficult to distinguish them directly via sensory means. Therefore, a technique for identifying mothball species is needed.

Sun *et al.* successfully realized the distinction between two kinds of mothballs (camphor and p-dichlorobenzene) via LIBS combined with machine learning algorithm (PCA-SVC).¹⁰⁹ It could be seen from the experimental results that the LIBS spectra

Pesticide is an important means to control pests and diseases and maintain food production, which is widely used in modern agricultural production.^{110,111} Because many pesticides need to be applied in the form of spraying, the VOCs in them can easily enter the atmosphere, contaminating the ambient air and harming human health.^{112,113} Therefore, it is necessary to monitor the air near farmland.

Zhang *et al.* detected and analyzed the LIBS spectra of clean air, pesticide Decis and its active ingredient deltamethrin (C₂₂H₁₉Br₂NO₃, CAS:52918-63-5).¹¹⁴ CN molecular band, C₂ molecular band and Ca atomic line (422.672 nm) were detected in both pesticides and deltamethrin, as shown in Fig. 14 and Fig. 15. Two Br atomic lines (827.294 nm and 833.470 nm) were also seen in the spectrum of deltamethrin. In the above two spectra, it is found that some characteristic lines cannot be caught in the air, which indicates that it is feasible to use LIBS technology to monitor pesticide aerosols or VOCs emitted by pesticides.

Fig. 15 LIBS spectrum of pesticides and deltamethrin in the 460–680 nm band. The figure is taken from REF.¹¹⁴

CONCLUSION

Air pollution is a significant environmental challenge that affects human health and well-being. As nations worldwide become more aware of the impact of air pollution, there is an urgent need for advanced methods to prevent and control it. VOCs are one of the main air pollutants. The detection and source tracing of VOCs is essential to implementing control measures effectively. In this review, a method for detecting atmospheric VOCs based on LIBS is introduced. LIBS is a new method for material element analysis. Although it has been used more frequently to detect solid and liquid samples, its advantages of high sensitivity, high efficiency and requiring no sample pretreatment also make it ideal for the online detection of gas samples.

In this review, applications of VOCs in online detection based on LIBS technique are briefly introduced, and accurate qualitative analysis of halogenated hydrocarbons and sulfur-containing compounds was achieved by the spectra of halogen and sulfur elements, respectively. Then, according to the spectral characteristics of different VOCs, LIBS is combined with machine learning algorithm to successfully realize the source tracing of VOCs. In addition, in the listed cases, it is proposed that there are also differences in the spectra between isomers, and good classification results are obtained by LIBS combined with machine learning. Finally, the application of this technology to life scenes (detection of mothballs and pesticides) is briefly described.

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Notes

The authors declare no competing financial interest.

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