Detection and Recognition of Volatile Substances in Mothballs Using Laser-induced Breakdown Spectroscopy and Raman Spectroscopy

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Received: September 14, 2022; Revised: October 28, 2022; Accepted: October 28, 2022; Available online: October 31, 2022.
DOI: 10.46770/AS.2022.231

ABSTRACT: Mothballs are widely used in daily life as an air freshener, but their main components are volatile organic compounds that are harmful to the human body. A system combining laser-induced breakdown spectroscopy (LIBS) with Raman spectroscopy was built for the detection and recognition of volatile substances in mothballs in indoor environments. LIBS is employed for the online in-situ detection of volatile substances in two kinds of mothballs and to find their characteristic spectral lines. A machine learning model is then established to analyze the spectra of air and volatile substance in synthetic mothballs and natural camphor. The model based on principal component analysis and support vector classification achieved a recognition accuracy of 98.33%, indicating that LIBS has significant potential for recognizing volatile substances in mothballs when airborne. By comparing the experimental Raman spectra of mothballs and theoretical Raman spectra of their main components, the spectral fingerprints of mothballs are obtained as a supplement to LIBS detection.

INTRODUCTION

Mothballs, as an air freshener, are one of the most common sources of volatile organic substances (VOCs) in indoor environments. Mothballs are divided into natural camphor and synthetic mothballs. Natural camphor is a substance extracted from the camphor tree.\textsuperscript{1} Its main component is camphor (C\textsubscript{10}H\textsubscript{16}O), which is widely used in medicine and insect control.\textsuperscript{2,3} Because the production of natural camphor is significantly below the market demand, two synthetic products are generally produced as replacements.\textsuperscript{4} Owing to their strong carcinogenicity, synthetic mothballs containing naphthalene have been banned from production in many countries.\textsuperscript{5,6} However, the use of mothballs containing p-dichlorobenzene (C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2}) remains widespread. p-Dichlorobenzene is also toxic and can cause symptoms of poisoning, such as headache, dizziness, and liver damage.\textsuperscript{6,7} The smell of natural camphor and synthetic mothballs is similar, and it is difficult to distinguish them through scent. Therefore, an effective technique for the detection and recognition of these compounds can prevent people from inhaling high concentrations of p-dichlorobenzene from synthetic mothballs.

The detection of volatile substances in mothballs is an urgent requirement. Currently, the most used detection methods are gas chromatography (GC) and mass spectrometry (MS).\textsuperscript{8,9} Gerritsen et al. analyzed VOCs produced by clinical Aspergillus isolates using GC-MS.\textsuperscript{10} Boczkaj et al. studied the characteristics of VOC emission from high-temperature pavement asphalt.\textsuperscript{11} The volatile substances in mothballs have also been detected using GC-MS. Coensel et al. investigated the chemical contamination of clothes...
due to their direct or indirect exposure to moth repellent agents. However, these methods require sample pre-treatment, which is time consuming.

Laser-induced breakdown spectroscopy (LIBS) is an atomic spectroscopy technique with many advantages, including a high detection speed and wide range of detectable elements. It uses a powerful laser to excite material into a plasma. During the plasma transitions from a high energy level to a lower energy level or ground state, information about the elements in the material can be gained from the emission profile. LIBS has also been applied to the analysis of gaseous environments. Dikshit et al. demonstrated the LIBS measurement of atmospheric carbon dioxide. Sturm and Noll also used LIBS for the simultaneous measurement of the elements C, H, N, and O in atmospheric environments. However, these previous studies focused only on the detection of pure VOC samples. Thus far, the online in-situ detection and recognition of VOCs released from daily necessities remains an unaddressed challenge.

Machine learning is a technique for abstracting models from a large amount of data and has been applied to the analysis of spectral data. Michel et al. combined four spectroscopic techniques with machine learning classifiers for the rapid identification of marine plastic debris. Park et al. evaluated the efficacy of several machine learning models for a molecule detection and classification based on the surface-enhanced Raman spectroscopy benchmark dataset of Rhodamine 6G (R6G). The laws governing the training data can be learnt and used to classify or predict the features of new input data. With the assistance of machine learning, differences in the type and content of elements can be traced based on the wavelength or intensity of the characteristic spectral lines, enabling the identification of the category to which a detected substance belongs. Therefore, combining LIBS with machine learning can effectively eliminate interference from impurities and considerably improve the recognition accuracy.

However, because LIBS detects only atoms, this technique does not enable the comprehensive investigation of the sample properties. Raman spectroscopy, as a molecular spectroscopy technique, can provide information about molecular rotation or vibration modes by analyzing the difference in the frequencies of scattered and incident light. For example, Schlüter et al. presented a gas-phase Raman system for measurements in the low-pressure regime. This system overcomes the drawback of the weak Raman effect using a multipass cavity to enhance the Raman signal. Wang et al. introduced a cavity-enhanced Raman spectroscopy gas-sensing method, which can simultaneously detect multi-component gas mixtures, including isotopic gases. The spectral fingerprint determined by this technique can be used as a supplement to LIBS detection.

Herein, an experimental system combining LIBS with Raman spectroscopy is built for the detection and recognition of the volatile substances in mothballs. First, LIBS is employed for the online in-situ detection of the volatile substances from two kinds of mothballs and to find their characteristic spectral lines. Thereafter, spectral data for air and volatile substances from synthetic mothballs and natural camphor are inputted into a self-established model for classification and recognition. By comparing the experimental Raman spectra of mothballs and calculated data for their main components, LIBS detection can be complemented by the molecular spectral fingerprints of mothballs.

**EXPERIMENTAL**

**System.** As shown in Fig. 1, the developed experimental system is composed mainly of LIBS and laser Raman spectroscopy. LIBS was used to determine the elemental composition of the samples. A Q-switched neodymium-doped yttrium aluminium garnet laser was used as the light source, which emits a 260 mJ pulse laser at 1064 nm, with a pulse duration of 10 ns and a repetition rate of 10 Hz. The laser is focused on the sample through a lens and excites it to the plasma at a high energy level. As the plasma returns to the ground state or a lower energy level, the radiated light is collected by the optical fiber coupled to a four-channel spectrometer (AvaSpec-ULS2048–4–USB2, AVANTES), with a detection window ranging from 200 to 900 nm and a detection resolution of 0.08 nm. The spectral data are then inputted into the corresponding software for subsequent analysis. The spectral lines are identified according to the NITS Atomic Spectroscopic database.

The Raman spectroscopy detection of the substances in a mothball sample was performed using a portable laser Raman spectrometer, which consists of a single-mode diode laser with wavelength of 532 nm and a spectrometer (AvaSpec-ULSi2048-USB2-SPC-1, AVANTES). The Raman scattering spectra were collected by the optical fiber coupled to the spectrometer, and

![Fig. 1 Schematic of the experimental system combining LIBS with laser Raman spectroscopy.](image-url)
the light collector was integrated with the laser outlet in a probe. In the experiment, the laser energy was optimized to 100 mW, and the integral time of each measurement was set at 200 ms. To improve the signal-to-noise-ratio of the spectral signal, each Raman spectrum was obtained by averaging twenty measurement results. The mothball samples were stored in a quartz cuvette with an optical path of 10mm and placed 10 cm in front of the probe.

Sample. Because solid mothballs sublime slowly at room temperature, two heating methods were used to extract the volatile substances from the mothballs.

The first method is similar to the water bath heating method. The mothball sample was placed in a beaker which was placed in hot water at ~100 °C. When the laser was focused 2 cm above the mothball sample, both volatile substances and air could be detected. This method can simulate the gradual volatilization of mothballs in the living environment and accelerate the progress of volatilization.

In an alternative method, the mothballs were placed in a 50 mL stainless steel gas sample cell that was then heated to achieve a complete sublimation of the mothball sample. When the valve of the sample cell was opened, the gasified mothballs were emitted as saturated steam. The outlet of the sample cell was placed close to the laser focal point to ensure that the element concentration in the steam was consistent with that in the sample cell. A sufficient number of mothballs was added to simulate a scenario in which a high concentration of gaseous substances is released from mothballs in a confined space.

Two kinds of commercially available mothballs were used: synthetic mothballs and natural camphor. Synthetic mothballs comprise 99% p-dichlorobenzene, and the concentration of Cl in the mothballs is approximately 47.8% based on the mass fraction. Natural camphor is derived from camphor trees and contains more than 94% camphor. Because of the extremely low density of gas, the detection of gas using the Raman spectroscopy system is very difficult. In this experiment, powered mothball samples were analyzed. The mothball samples were ground and passed through a 100-mesh screen before being placed in a beaker, sample cell, or quartz cuvette.

**DESCRIPTION OF THE RECOGNITION MODEL**

Model establishment. An effective machine learning model can distinguish the spectra more rapidly. Because of the high dimension of the selected spectra, principal component analysis (PCA) was applied to reduce the spectra to a lower dimension, and support vector classification (SVC) was adopted as the classification arithmetic to progress the data after dimensionality reduction. The process for establishing the PCA-SVC model is shown in Fig. 2.

The spectral data were divided into a training set and a test set, where the training set accounts for 80%. After standardization, the training data were inputted into PCA for dimensionality reduction. The new principal components with a 99.5% cumulative contribution rate were chosen as classification features and inputted into the SVC model. SVC parameters with the highest classification accuracy were determined via 4-fold cross-validation. Using the same number (N) of principal components and SVC parameters, the PCA-SVC model was re-established for analyzing the test set.

**Model evaluation.** Two performance indexes (accuracy and macro-F1 score) were employed to evaluate the model. The accuracy is the ratio of the correctly predicted samples to the total test data and can be calculated by applying Eq. (1):

\[
\text{Accuracy} = \frac{1}{m} \sum_{i=1}^{m} \mathbb{1}(f(x_i) = y_i)
\]

where, \(y_i\) represents the true value, and \(f(x_i)\) represents the predicted value.

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**Fig. 2** Process for establishing the PCA-SVC model.
Macro-$F_1$ is used to comprehensively investigate the precision and recall in multi-label classification. It can be calculated using Eq. (2).

$$macro - F_1 = \frac{2 \times macro-P \times macro-R}{macro-P + macro-R} \tag{2}$$

Among the parameters, $macro-P$ and $macro-R$ represents the macro precision and macro recall, respectively, as shown in Eq. (3) and (4).

$$macro - P = \frac{1}{n} \sum_{i=1}^{n} P_i \tag{3}$$

$$macro - R = \frac{1}{n} \sum_{i=1}^{n} R_i \tag{4}$$

In the above equations, the parameter $P$ represents the precision, reflecting the percentage of true positive samples among the positive samples predicted by the model. $R$ is the recall, reflecting the percentage of predicted positive samples among the true positive samples.

THEORETICAL CALCULATION METHODS

The molecular structure of $p$-dichlorobenzene and camphor were optimized using density functional theory (DFT)\textsuperscript{28,29} by applying the B3LYP/ 6-311g ++ G (d, p) basis set in the theoretical calculation program Gaussian09\textsuperscript{30}, which has been widely used to study the physical and chemical properties of electrons. The theoretical Raman spectra were also calculated using this basis set.

![Fig. 3 Spectra of volatile substances in synthetic mothballs and natural camphor: 240-260 nm (a); 320-460 nm (b); 460-680 nm (c); and 700-890 nm (d).](image-url)
RESULTS AND DISCUSSION

LIBS identification of volatile substances in synthetic mothballs and natural camphor. In this section, the volatile substances in mothballs after vaporization using the water-bath heating method were qualitatively analyzed. Combining spectroscopic techniques with LIBS to measure the concentration of the substance at the laser focal point allows for the quantitative analysis based on the intensity of the characteristic spectral lines. The volatile substances in synthetic mothballs and natural camphor were respectively tested 1000 times. The spectral lines related to elemental C were used to screen the volatile substances in mothballs. Based on these characteristic lines, 100 sets of spectra were selected for each sample. The spectra after averaging and normalization are shown in Fig. 3.

Overall, the spectrum of the volatile substances in synthetic mothballs is similar to that of natural camphor. C and H are the main elements in camphor balls, with relatively prominent spectral lines. Lines representing Cl and Na are also detected but possess very low intensities so that they are negligible. Although Cl is the main component of synthetic mothballs, the upper energy levels of the two spectral lines of Cl-833.3nm and 837.594 nm are observed at 84,485 cm\(^{-1}\) and 83,894 cm\(^{-1}\), respectively. It is difficult to transform the electrons from the ground state to these excited states. The mean intensity of the spectral line of Na is very low because it is a trace component in the camphor tree and can be found only in a few spectra.

From the analysis of these spectra, the characteristic lines of certain elements or free radicals are chosen as the initial input for the self-established PCA-SVC model, as listed in Table 1. An additional 100 air spectra were collected as the third sample for classification. The characteristic spectrum of air is shown in Fig. S1.

A total of 103 principal components with a 99.5% cumulative contribution rate was extracted. The contribution rate of the first 30 principal components is shown in Fig. 4(a) and the distribution of principal components is shown in Fig. 4(b). In the two-dimensional space composed of PC1 and PC2, the three kinds of spectra are located in different regions. Using the 103 principal components and optimal parameters from the SVC, the PCA-SVC model was re-established for analyzing the test set. According to the results of the algorithm, the accuracy of PCA-SVC can reach 98.33%, and the macro-F1 score can reach 98.37%. These results indicate that the LIBS system can effectively detect and recognize the volatile substances in different kinds of mothballs.

LIBS detection of gaseous components of synthetic mothballs in high concentration. LIBS was employed to detect the gaseous components of synthetic mothballs emitted from the sample cell. A sufficient number of mothballs is employed to simulate a scenario in which a high concentration of the gaseous component of mothballs is released in a confined space. The baseline of the spectrum of gaseous synthetic mothballs measured subsequently was very high. The spectrum after baseline correction is shown in Fig. 5. Elemental Cl from the synthetic mothballs was successfully detected, and a molecular signal of CN free radical was also detected.

Table 1. Spectral lines as original features

<table>
<thead>
<tr>
<th>Element</th>
<th>Spectral lines</th>
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<tbody>
<tr>
<td>C</td>
<td>247.8nm</td>
</tr>
<tr>
<td>CN</td>
<td>357.6-359.0nm; 369.4-388.3nm; 415.2-421.6nm</td>
</tr>
<tr>
<td>H(_\alpha)</td>
<td>656.2nm</td>
</tr>
<tr>
<td>Na</td>
<td>589.0nm; 589.6nm</td>
</tr>
<tr>
<td>Cl</td>
<td>725.6nm; 833.3nm; 837.6nm</td>
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</table>

The spectral lines at 355-360, 380-390, and 410-425 nm in Fig. 5(b) represent \(\Delta\nu=+1\), \(\Delta\nu=0\), and \(\Delta\nu=-1\) modes of the CN band\(^{32}\)

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![Fig. 4 PCA results for the training set: Extracted principal component spectra (a) and principal component distribution diagram (b).](image-url)
When the strong pulse laser ablates the gaseous mothballs and nitrogen and excites them into a plasma, C atoms from the ionization and decomposition of \( p \)-dichlorobenzene may react with N atoms from nitrogen. It can be inferred that the CN free radicals are composed of C atoms from the benzene ring and N atoms from nitrogen.

The spectral lines at 460−480, 500−520, and 540−570 nm represent the \( \Delta \nu=+1 \), \( \Delta \nu=0 \), \( \Delta \nu=-1 \) modes, respectively, of the \( C_2 \) band (Fig. 6). It is also suggested that \( C_2 \) free radicals may be formed by the dissociation of C atoms in the benzene ring under the action of a strong laser. A previous study\(^{33} \) proved that the presence of oxygen can potentially deplete \( C_2 \) emission. Therefore, lines representing the \( C_2 \) radicals were visible when a high concentration of gaseous mothballs was present in the air. Overall, the representative lines of the \( C_2 \) free radical can be used as the characteristic features for detecting a high concentration of synthetic mothballs in the air.
Determination of the Raman spectral fingerprint of mothballs.

Raman spectroscopy is a commonly used molecular spectroscopic technique. Herein, Raman spectroscopy was employed to analyze both synthetic mothballs and natural camphor. The calculated Raman spectrum and the vibration modes of $p$-dichlorobenzene and camphor molecular were obtained based on DFT.

The experimental Raman spectrum of the synthetic mothballs and the calculated Raman spectrum of $p$-dichlorobenzene are shown in Fig. 7(a). Figure 7(b) shows the detected and calculated Raman spectra of natural camphor, and the main characteristic peaks in the experimental and calculated spectra are consistent. Certain molecular vibration modes corresponding to the main peaks are also present in these two figures.

The details of the vibration modes are presented in Table 2. The Raman spectrum of $p$-dichlorobenzene shows characteristic peaks (at 333.18, 1110.18, and 1577.42 cm$^{-1}$) representing the vibrational modes of the C-Cl bonds, and three characteristic peaks of the vibrational modes of C-H bonds (at 637.11, 746.98, and 3080.06 cm$^{-1}$). The Raman spectrum of camphor shows characteristic peaks (at 659.2, 1468.1, 1743.4, and 2956.7 cm$^{-1}$) reflecting different vibration modes of the C-H, C-O, and C-C bonds. The characteristic peaks reflecting the molecular vibration modes can be regarded as the spectral fingerprint of mothballs.

The aforementioned results indicate that the main component of mothballs can be successfully identified using Raman spectroscopy.
CONCLUSION

A system combining LIBS with Raman spectroscopy was developed for the detection and recognition of the volatile components of mothballs in indoor environments. LIBS was employed for the online in-situ detection of the volatile substances from two kinds of mothballs and for identification of their characteristic spectral lines. The spectrum of the volatile substance in synthetic mothballs is similar to that of natural camphor. A PCA-SVC model was established to identify the spectra of air and volatile substances in synthetic mothballs and natural camphor. Based on PCA, the distribution diagram of the first two principal components shows that the three kinds of spectra are located in different areas. The SVC data suggest that the identification accuracy can reach 98.33%, indicating that LIBS has significant potential in recognizing the volatile component of mothballs in air. The characteristic lines representing the C2 free radical can be used as markers in the detection of synthetic mothballs at high concentrations. By comparing the experimental Raman spectra of mothballs with the theoretical Raman spectra of their main components, the characteristic peaks were found to be consistent. These peaks reflecting the molecular vibration modes can be regarded as the spectral fingerprints of mothballs. The aforementioned results show that the system combining LIBS with Raman spectroscopy is effective for the detection and recognition of the volatile substance of mothballs in indoor environments.

AUTHOR INFORMATION

Yuzhu Liu is a full professor and vice director of Jiangsu Key Laboratory for Optoelectronic Detection of Atmosphere and Ocean at Nanjing University of Information Science and Technology (NUIST). He received his PhD in physics from Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences (June 2011). After completing his Ph.D., he came to Paul Scherrer Institute in Switzerland for post-doctoral research. In September 2014, he returned to China and joined NUIST for professorship. His research interests include laser-induced breakdown spectroscopy, Raman spectroscopy, ultrafast molecular dynamics, photoelectron imaging technique, and time-of-flight mass spectrometry. He is currently working on instrumentation developments and investigations for the project of online in situ detection of elements or pollutions in the atmosphere via LIBS. He has published over 100 peer-reviewed scientific papers in ISI-indexed journals.

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Notes
The authors declare no competing financial interest.

ASSOCIATED CONTENT

The supporting information (Fig. S1) is available at www.at-spectrosc.com/as/home

ACKNOWLEDGMENTS

The authors gratefully thank the Natural Science Foundation of China (U1932149) for financial support of this work. The authors are grateful to Dr. Chaochao Qin for the assistance of the theoretical calculation on Gaussian 09 program performed in Henan Normal University.

Table 2. Characteristic peaks and corresponding vibrational modes

<table>
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<th>Experiment/cm⁻¹</th>
<th>Calculation/cm⁻¹</th>
<th>Vibration mode</th>
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<tbody>
<tr>
<td>Synthetic mothballs</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>333.18</td>
<td>315.84</td>
<td>Stretching vibration of C-Cl band; Bending vibration of C-H band</td>
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<tr>
<td></td>
<td>637.11</td>
<td>614.4</td>
<td>Bending vibration of C-H band</td>
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<tr>
<td></td>
<td>746.98</td>
<td>724.84</td>
<td>Stretching vibration of C-Cl band; Bending vibration of C-H band</td>
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<tr>
<td></td>
<td>1110.18</td>
<td>1156.96</td>
<td>Stretching vibration of C-Cl band; Bending vibration of C-H band</td>
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<tr>
<td></td>
<td>1577.42</td>
<td>1550.4</td>
<td>Bending vibration of C-H band</td>
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<td></td>
<td>3080.06</td>
<td>3080.64</td>
<td>Stretching vibration of C-H band</td>
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<td>659.2</td>
<td>619.2</td>
<td>Bending vibration of C-C band</td>
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<td></td>
<td>1468.1</td>
<td>1427.52</td>
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<tr>
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<td>1743.4</td>
<td>1734.72</td>
<td>Stretching vibration of C-O band</td>
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<td></td>
<td>2956.7</td>
<td>2909.76</td>
<td>Stretching vibration of C-H band</td>
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<tr>
<td>Natural camphor</td>
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<td></td>
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<tr>
<td></td>
<td>659.2</td>
<td>619.2</td>
<td>Bending vibration of C-C band</td>
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<td>1468.1</td>
<td>1427.52</td>
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<td></td>
<td>1743.4</td>
<td>1734.72</td>
<td>Stretching vibration of C-O band</td>
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