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A single cataluminescence sensor based on spectral array and its use in the identification of vinegars

Jiayi Zeng, Xiaoan Cao *, Yonghui Liu, Jinglin Chen, Keke Ren

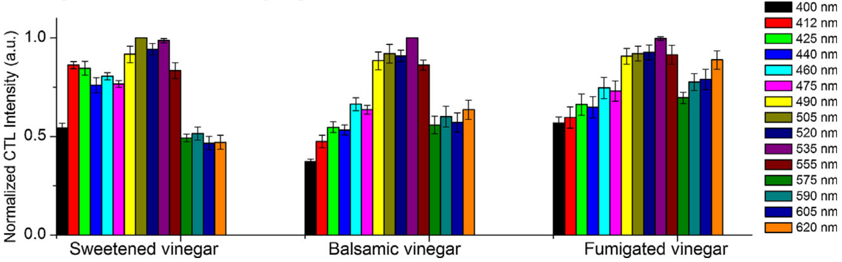
Environmental Science and Engineering Institute, Guangzhou University, 510006 Guangzhou, China

HIGHLIGHTS

- The single CTL sensor for vinegar fast discrimination was simple and stable.
- The spectral arrays of vinegars served as their fingerprints.
- 9 types and 8 brands of vinegar and artificial samples were successfully identified.
- The single sensor was capable of discriminating very similar complex mixtures.

GRAPHICAL ABSTRACT

The spectral arrays of vinegars here served as their fingerprints. Facile discrimination of vinegars was made possible by these unique patterns.



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ABSTRACT

The discrimination of complex mixtures, especially those with very similar compositions, remains a challenging part of chemical analysis. In this paper, a single cataluminescence (CTL) sensor constructed using MgO nanomaterials in a closed reaction cell (CRC) was used to identify vinegars. It may provide an archetype of this type of highly multicomponent system. By scanning the CTL spectra, which were distributed in 15 wavelengths during the reaction period, the spectral array patterns of the vinegars were obtained. These functioned as their fingerprints. The CTL signals of the array were then normalized and identified through linear discrimination analysis (LDA). Nine types and eight brands of vinegars and an additional series of artificial samples were tested; the new technique was found to distinguish between them very well. This single sensor demonstrated excellent promise for analysis of complex mixtures in real-world applications and may provide a novel method for identifying very similar complex analytes.

1. Introduction

Sensor technology provides a versatile approach to chemical analysis. During the past several decades, increasing interest has been drawn to the development of different sensors for specific purposes. The artificial olfactory systems, known as electronic noses and artificial noses, are composed of a group of sensor arrays. They are used for the identification of both simple and complex gas mixtures [1–3]. They have become a common tool for food quality assessment with the advantages of high portability for in situ and on-site testing. They also tend to be low-cost and reliable [4,5]. Studies addressing the evaluation of foodstuffs such as vinegar [6,7], wine [8,9], coffee [10], and tea [11] using electronic noses that have a few to a dozen sensor elements have reported success. However, multiple sensing units are not conducive to instrument stability [12–14]. Alterations of the characteristics of the sensors unit over time affect the final testing results [15]. In order to improve the reproducibility and reduce the need for frequent calibration, a sensor system with as few sensing units as possible is greatly needed.

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* Corresponding author. Tel.: +86 20 39366937; fax: +86 20 39366946.
E-mail address: caoxiaoan2003@aliyun.com (X. Cao).

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In recent years, chemiluminescence (CL)-based detection has become quite a useful detecting tool in the field of food analysis [16,17]. This kind of optical system may facilitate collection abundant information simultaneously, including signal intensity, luminescence lifetime, wavelength, spectral shape, and other factors [18,19]. Nanomaterial-assisted cataluminescence (CTL) sensors can provide stable and reversible responses because their solid sensing nanomaterials are essentially non-expendable during the sensing process [20–23]. Analytes can be wiped out through thermal catalytic degradation after detection. In addition, no light source was needed in CTL sensors so simple instrumentation can be made. These sensors are low-cost and easy to operate, making them attractive for many industrial applications [24–26].

For the discrimination of complex and similar mixtures, one may usually consider a sensor-array approach rather than a single sensor. However, a recent report indicated a novel method for the identification of complex mixtures using a single CTL sensor in a closed reaction cell (CRC). First, 12 medicines were graphically recognized based on their characteristic, multiple-peak CTL response profiles [27]. In order to explore the ability of our single sensor to discriminate other complex mixtures, 72 wine samples were examined as a second trail [28]. By extracting the CTL intensities at different points in time in the response curves as variables and adopting an appropriate algorithm, 72 samples were all assigned to the correct groups.

In order to further improve discrimination among highly similar complex mixtures, a method of CTL spectral array based on the single sensor in CRC was here developed. Commercially available vinegars served as an archetype of such complex analytes.

Vinegar is a popular seasoning worldwide, and its quality directly affects people's health. Many methods of analysis are highly accurate and suitable for assessment of vinegar quality [29–36]. However, most of these methods are costly, require long processing times and focused operators, making them inconvenient for on-site discrimination [37]. A new, fast method of identifying vinegars is necessary.

In the present study, the spectral signals of vinegar on nanosized MgO in CRC were obtained by scanning the CTL spectra repeatedly during the reaction period. These were classified into 15 groups according to the signals' distribution at 15 wavelengths. These were named the spectral array. Then they were normalized and subjected to LDA to classify different vinegars. Vinegars of different types and different brands were discriminated with 100% accuracy. The adulterated samples were distinguished from uncontaminated ones using this method. This simple single sensor demonstrates excellent potential for the analysis of truly complex mixtures in real-life applications and provides a novel approach to identification of complex samples of relatively similar compounds.

2. Experimental

2.1. Materials

Nano-MgO (purity, 99.99%; average particle size, 50 nm) was purchased from Beijing Nacheng Scientific Trading Co., Ltd. (Beijing, China). Nano-ZrO_2 (purity, 99.99%; average particle size, 10 nm) was purchased from Shanghai Zhuerna High-Tech Powder Material Co., Ltd. (Shanghai, China). Nano-Y_2O_3 (purity, 99.99%; average particle size, 30 nm) was purchased from Guangdong Huizhou Ruier Chemical Technology Co., Ltd. (Guangdong, China).

2.2. Vinegars and adulterated samples

Seventeen commercial vinegars (9 types and 8 brands), which could cover an important range of types of vinegar available on the Chinese market, were purchased from a local supermarket. The vinegars were divided into 9 types: baoning vinegar, mature vinegar, red vinegar, sweetened vinegar, balsamic vinegar, fumigated vinegar, white vinegar, apple vinegar, and rice vinegar. The 8 brands of apple vinegar were labeled, “Huashengtang apple vinegar”, “Lecufang apple vinegar”, “Jingcufang apple vinegar”, “Tiandiyihao apple vinegar”, “Youyang apple vinegar”, “Pinger vinegar”, “Maijinli apple vinegar”, and “Hongyuan apple vinegar”. The samples were stored in the laboratory at a constant temperature of $25 \pm 1\,^{\circ}C$ and used directly from their containers without dilution.

Synthesized vinegar consisted of 3.5% acetic acid (analytical-grade), 1.5% lactic acid (analytical-grade), 3% ammonium sulfate (analytical-grade), 1% caramel, 1% maltose, and 90% distilled water according to the work of Qiu [38]. Three different adulterated baoning vinegar samples were obtained by adding 25, 50, and 75 mL/100 mL of the synthesized vinegar. These adulterations were carried out to produce three different adulterated mature vinegar samples. The 4% acetic acid was obtained by diluting the 36% acetic acid (analytical-grade) with distilled water.

2.3. Sensor fabrication

Fig. 1 shows the CTL detection system. The system includes three parts: (1) a CTL chamber (a cylindrical ceramic heater of 5 mm in diameter sintered with 0.5 mm layers of materials was placed in the middle of a quartz tube with an inner diameter of 8 mm. This tube had a sampling port and a gas inlet and outlet with valve switches). (2) A BPCL ultra weak luminescent analyzer (Model BPCL-GP-TGC, Biophysics Institute of Chinese Academy of Science, Beijing, China). There was wheelwork equipped with 15 interference optical filters (1.5 cm in diameter, broadband ±24 nm). These filters showed 15 wavelengths (400, 412, 425, 440, 460, 475, 490, 505, 520, 535, 555, 575, 590, 605, and 620 nm) in the detector (Biophysics Institute of Chinese Academy of Science, Beijing, China). As the wheelwork rotated during the measurement process, the CTL intensities of these 15 wavelengths were measured for each sample. The CTL response profiles of vinegars were determined as the wheelwork was set under each fixed wavelength. The resultant CTL signals were detected and recorded using a photomultiplier tube (Model GDB23, Beijing Nuclear Instrument Factory, Beijing, China). (3) A digital temperature controller (Zhihong Electronic Co., Ltd., Beijing, China). The surface temperature of the nanomaterials was controlled by adjusting the voltage of the heating cylindrical ceramic rod.

2.4. Measurement procedures

Vinegar samples were sprayed on the nano-MgO surface through the sampling port when the two valve switches were closed and then oxidized at a given temperature. The rotation of the wheelwork continued in a loop during the testing process, and CTL signals under the 15 wavelengths were recorded. In this way, the signals' spectral array was obtained for 15 wavelengths per sample. The test lasted 500 s, so the number of rotations was set to 100 cycles and the rotation speed to 5 s per cycle ($s\,c^{-1}$). The samples' CTL response profiles were determined for each given wavelength by setting the wheelwork at a fixed wavelength. In order to remove previous residues on the materials, the sensor was heated at 500 °C for 15 min in air before each measurement (a steady airstream providing by an air pump (Model GA-2600A, Beijing Zhongxing Huili Co., Ltd., Beijing, China) flew through the quartz tube when the two valve switches were unscrewed).

2.5. Data processing and analysis

The signals of spectral array for each sample were determined 5 times and the average was used for analysis. The CTL intensities