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Identification and quality assessment of beverages using a long period grating fibre-optic sensor modified with a mesoporous thin film

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ABSTRACT

In this study, an optical fibre long period grating (LPG) sensor functionalised with a mesoporous thin film was employed for the identification and quality assessment of beverages. The principle of the discrimination of beverages using an LPG sensor is based on the measurement of the change in refractive index of a sensitive film, induced by the binding of the chemical compounds present in the beverage. The sensitive film deposited onto the LPG consisted of poly(allylamine hydrochloride) (PAH) and silica nanospheres (SiO_2 NPs) with diameters ranging from 40 nm to 50 nm. PAH imparts selectivity, while the SiO_2 NPs endow the film with high porosity and enhanced sensitivity. In this study, five different types of beverages, red and white wines, brandy, nihonshyu (sake, a Japanese rice wine), and shochu (a Japanese distilled beverage), prepared via distillation and fermentation, were used to assess the capability of the sensor to identify the origin of the beverages. In addition, a selection of red wines was used to evaluate the use of the sensor in the assessment of the quality of beverages. The results obtained were benchmarked against those obtained using gas chromatography–mass spectrometry for the determination of volatile compounds contributing to the flavours of a set of red wines. Principal component analysis (PCA) was employed for data analysis. This approach enabled both quality assessment of beverages and identification of the methods and materials used for their preparation.

1. Introduction

There is a clear need for simple, rapid, and cost-effective techniques for an objective assessment of the quality of alcoholic beverages, their origin, and the substances used to make them to ensure adequate standards of production, uniformity within a brand, and to avoid falsification [1,2]. The chemical composition of an alcoholic beverage is determined typically by the method of preparation and the chemical composition of the primary products used for its production [3]. While ethanol and water are the main chemicals present in all alcoholic beverages, numerous volatile and non-volatile flavour compounds are also present [4]. Thus, the analysis of the chemical composition of the alcoholic beverages is a challenging task due to the complexity of the media and the presence of hundreds of different chemicals. Among the many factors that contribute to the typicity and quality of a wine, aroma is probably the most important organoleptic characteristic and a key attribute for consumers. Several hundred chemically different flavour compounds, such as higher alcohols, aldehydes, ethyl esters of fatty acids, fatty acids, ketones, monoterpenes, and volatile phenols, have been found in wines [5]. They have slightly different chemical and physical properties, such as polarity and volatility, and their concentrations range from a few ng/L to more than 100 mg/L [6].

Standard methods and procedures for the quality assessment of alcoholic beverages are based on gas and liquid chromatography, often coupled with mass spectrometry for the structural identification of the individual components [7]. For the enrichment of the aroma substances, several methods have been used such as liquid–liquid extraction, column chromatography, solid phase extraction, and solid phase microextraction. The presence of a large variety of compounds that contribute to taste and flavour means that the analysis of the comprehensive spectral data on some wines is not sufficient for assessing their quality. Therefore, pattern recognition approaches have also been applied to the classification of "multi-component" wines and are useful for quality control evaluations [2,8]. In fact, pattern recognition methods for

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classification and identification are used increasingly in fields such as food chemistry, process monitoring, medical sciences, pharmaceutical chemistry, and social and economic sciences. Classification is one of the fundamental methodologies in chemometrics and basically consists of finding a mathematical model capable of recognising the membership of each object to its proper class. Once a classification model has been obtained, the membership of new objects to one of the defined classes can be predicted [8]. Sensory evaluation by trained experts is also employed, but it does not always provide an objective analysis of the consumer products and is an expensive procedure.

Recently, electronic noses and tongues, combined with statistical approaches, and chemometrics have been used intensively for food and beverage identification and ageing and quality assessments [8–12]. Typically, electronic noses and tongues mimic the human olfactory system and are based on an array of nonspecific sensors (or sensors with different selectivities) combined with pattern recognition software. Most electronic nose systems are based on metal oxide sensors or mass sensitive transducers that are inherently highly sensitive to water, making the detection of flavour chemicals present at low concentrations in alcoholic beverages extremely difficult.

In this regard, fibre optic sensors provide an alternative, universally adaptable sensing platform because of the inherent stability of the optical fibres, their high sensitivity, and the ability to multiplex sensors in series [13]. In particular, the combination of optical fibre devices and nanomaterials offers the prospect for the development of measurement techniques using an optical waveguide with a nanostructured coating layer that exhibits changes in its optical properties upon exposure to targeted chemical species. Recently, we have demonstrated a novel chemical sensor based on a layer-by-layer (LbL)-deposited mesoporous film composed of silica nanospheres (SiO_2 NPs) on an optical fibre long period grating (LPG) for the detection of organic compounds [14] and ammonia [15] and for the measurement of the refractive index (RI) of substances [16].

An LPG consists of periodic modulation of the refractive index of the core of an optical fibre with the period lying typically within the range from 100 μm to 1 mm [17]. It couples light from the forward propagating mode of the core of the fibre with a discrete set of co-propagating cladding modes at wavelengths governed by the phase matching condition, as shown in Eq. (1):

$$\lambda_{(x)} = (n_{core} - n_{clad(x)})\Lambda \quad (1)$$

where $\lambda_{(x)}$ represents the wavelength at which the coupling occurs for the linear polarised (LP_{0x}) mode, n_{core} is the effective refractive index of the mode propagating in the core of the fibre, $n_{clad(x)}$ is the effective index of the LP_{0x} cladding mode, and Λ is the period of the grating.

The presence of a coating layer with a sub-μm thicknesses, deposited via LbL film deposition techniques such as Langmuir Blodgett (LB), electrostatic self-assembly (ESA), and dip coating, modulates the transmission spectrum (TS) of the LPG and makes it highly sensitive to the external refractive index. Based on this principle, sensors for pH, humidity, and chemical and biological applications have been demonstrated [17].

Herein, we report the use of an LPG coated with a poly(allylamine hydrochloride)/SiO_2 NPs (PAH/SiO_2) film [14,18] for the identification and quality assessment of beverages. Five different types of beverages, red and white wines, brandy, sake (a Japanese rice wine), and shochu (a Japanese distilled beverage), prepared via distillation and fermentation were used to evaluate the use of the sensor for the determination of the origin of the beverages. In addition, the sensor was used to assess the quality of a selection of red wines. Furthermore, the performance of the sensor for the determination of the volatile compounds contributing to the flavours of a set of red wines was benchmarked against that of gas chromatography–mass spectrometry (GC–MS). Principal component analysis (PCA) was employed for the data analysis, aiding the identification and quality assessment of the beverages. The new sensor enables evaluation of the quality of beverages and the determination of both the methods and materials used for their preparation. In addition, to the best of our knowledge, this method is the first example of the application of an optical fibre LPG chemical sensor that measures refractive index and determines chemical composition of the alcohol for the identification and quality assessment of beverages.

2. Experimental section

2.1. Materials

PAH (M_w: 200,000–350,000, 20% w/w in H_2O) was purchased from Tokyo Kasei, Japan. SiO_2 NPs (SNOWTEX 20L) was purchased from Nissan Chemical. Pure ethanol (EtOH, 99.5%) and acetic acid (99.5%) were purchased from Wako Chemicals, Japan. All of the chemicals were analytical grade reagents and used without further purification. Nihonshyu (sake), shochu, brandy, and a selection of white and red wines were purchased at the local supermarket (Table S1, Supporting information). For the red wine quality assessment, 24 commercially available red wine samples (Table S2) were purchased from a local store. Deionised water (18.3 MΩ cm) was obtained by reverse osmosis followed by ion exchange and filtration (Millipore, Direct-QTM).

2.2. LPG coating

An LPG with a period of 100 μm and a length 35 mm was fabricated in a single mode optical fibre (Fibercore SM750) with a cut-off wavelength of 670 nm using point-by-point exposure to the output from a UV laser source (frequency quadrupled Nd:YAG laser operating at a wavelength of 266 nm) [14–16]. A mesoporous thin film was deposited onto the LPG using an electrostatic self-assembly approach as previously described [14–16]. The LPG was fixed in a Teflon holder constructed with a compartment to accommodate a solution, Fig. 1b [19].

Briefly, the region of the optical fibre containing the LPG was rinsed with deionised water and immersed in a 1 wt% ethanolic KOH (ethanol/water = 3:2, v/v) solution for 20 min, leading to a negatively charged surface. The optical fibre was then immersed sequentially into a solution containing a positively charged polymer, PAH, and a solution containing negatively charged SiO_2 NPs for 20 min each, resulting in the alternate deposition of PAH and SiO_2 NPs layers on the surface of the fibre, Fig. 1a. The fibre was rinsed with distilled water, and dried by flushing with nitrogen gas after each deposition step. A $(PAH/SiO_2)_{10}$ film deposited on the LPG, which was prepared by repeating the two-step sequence for 10 cycles, was previously shown to provide optimal sensor performance in terms of sensitivity and response time [16].

2.3. Beverage identification using the LPG sensor

Prior to analysis of the beverages, the LPG sensor was exposed to known concentrations of ethanol to calibrate its refractive index response, as described previously [16]. Briefly, LPG fibre modified with the PAH/SiO_2 film was immersed into the ethanol solution. Ethanol concentrations ranging from 1% to 40% in increments of 5% were used to simulate the alcohol strengths of the beverages. For comparison, beverages were diluted using water in order to adjust the alcohol strength to the same values as those of the EtOH solutions. The LPG was then immersed in 500 μL of the final