Colorimetric determination of alcohols in spirit drinks using a reversible solid sensor

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A B S T R A C T

A sensor for the colorimetric estimation of the alcoholic content has been developed based on the entrapment of the reagent (4-N,N-dioctylamino)-4'-trifluoroacetylazobenzene (ETH[T] 4001) into polydimethylsiloxane (PDMS) modified with tretraethylorthosilicate (TEOS). When exposed to an alcoholic media, the sensor delivers ETH[T] 4001 so that it reacts with alcohols, resulting in a change in the solution color. The diffusion of the entrapped ETH[T] 4001 from the polymeric sensor to the working solution depends on the hydrophobicity of both the sensor matrix and the media, while the time of exposure determines whether the reagent reacts with methanol, or with methanol and ethanol. Thus, the sensors are a versatile tool for the estimation of the methanol content in ethanol or in ethanol/water mixtures, and for the measurement of the total alcoholic content (methanol plus ethanol) in an hydroalcoholic media. The proposed sensors are very easy to prepare, and show good precision and long-term stability. Moreover, the reagent delivery is reversible which allows its recovery once the absorbance measurements have been made simply by adding water, so the sensors can be reutilized and the generation of wastes is reduced. The potential utility of the proposed sensors has been demonstrated by measuring the alcoholic strength of commercial spirit drinks, and the methanol content in spiked hydroalcoholic samples.

1. Introduction

The rapid quantification of alcohols in spirit drinks is of great importance because of the high economic significance of this kind of beverages and their negative effect on public health. Ethanol is the predominant alcohol in alcoholic beverages, but methanol can also be found at much lower concentrations. The total content of alcohols in spirit drinks is typically given as alcoholic strength, expressed as the volume of ethanol at 20 °C (% vol). This parameter is used to test the beverage composition during production, and also to assess the quality of the final product. Another important parameter in spirit drinks is the content on methanol because, owing to its intrinsic toxicity, this compound can cause severe diseases such as blindness, coma and death (Paasma, Hovda, & Jacobsen, 2004; Paine & Dayan, 2001; WHO, 2014). The methanol content in spirit drinks produced under standard conditions is limited but relatively high methanol levels can be found in drinks adulterated with industrial products not originally intended for human consumption in order to produce low-cost drinks. For example, methanol contents up to 20–40% have been found in some illegally produced drinks (Lachenmeier, Rehm, & Gmeal, 2007). The

consumption of such products has been identified as the cause of several poisoning and deaths cases all over the world (Paine & Dayan, 2001).

Traditional methods used for the measurement of the alcoholic strength (adopted as official methods in many countries) entail the distillation of ethanol from the sample and subsequent measurement of the density of the collected distillate, generally by pycnometry, electronic densimetry, or densimetry using an hydrostatic balance (Commission Regulation (EU) 2870/2000). For the individual determination of methanol and other alcohols gas chromatography and liquid chromatography are generally used (Chen et al., 1998; E.H.; Soufleros, Mygdalia, & Natskoulis, 2004; Wang, Wang, & Choong, 2004; Stupack, Kocourek, Kolouchova, & Hajslova, 2017). Other alternatives such as those using infrared (Lachenmeier et al., 2010) and Raman spectroscopy (Boyaci, Genis, Guven, Tamer, & Alper, 2012), as well as electric sensors based on the enzymatic reactions (Svensson, Bülow, Kriz, & Krook, 2005) are less common. Distillation-based methods involve long-times of analysis, whereas in chromatographic methods high specialized operators are necessary. Therefore, rapid methods for alcohols are required that can be applied for in-situ quick control of

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alcohols either, during production or in final products (Somboon & Sansuk, 2018).

Colorimetric sensors are ideal for these applications because response can be followed by naked eye or with relatively simple spectrophotometers. However, methanol and ethanol have similar chemical and physical properties thus, the distinction between them is difficult, especially when the amount of methanol is low compared with that of ethanol. For example, Mohr et al. developed different sensors based on the immobilization of azo and stilbene dyes with trifluoroacetyl group into polymeric (PVC, methacrylates) membranes (Mohr et al., 1998, 1999). Under the conditions described by the authors the sensors exhibited comparable responses for ethanol and methanol. More recently, Zhang et al. developed a sensor for the measurement of the alcoholic strength based on the formation of a supramolecular ionic material (SIM) synthetized by ionic self-assembling of an imidazolium-based dication and the dianion 2,2'-azino-bis(3-ethylbenzotiazoline-6-sulfonic acid) with rhodamine 6G (Rh6G) (Zhang et al., 2014). The obtained suspensions are stable in water while in the presence of alcohols (ethanol and methanol) the SIM-Rh6G structure is destructed so that the Rh6G is released, which causes a change in the color of the sample. Deng et al. developed an infinite coordination polymer (ICPs) prepared with 1,4-bis(imidazol-1methyl)benzene and Zn^{2+}, and rhodamine B as sensing probe for alcohols (Deng, Ma, Yu, & Mao, 2015). The same principle was applied with a derivative synthetized with the ligand 2,2'-thiodiacetic acid and Eu^{3+}, and coumarin 343 (Cu343) as fluorimetric tag; this tag is released in the presence of water (Deng, Shi, & Zhou, 2016). So far, only a few sensors have been specifically developed for methanol. A microfluidic chip patterned device was developed by Wang et al. for the colorimetric determination of methanol based on its transformation into formaldehyde and subsequent reaction with fuchsin-sulphurous acid (Wang, Yang, Ju, Wu, & Fu, 2012). A luminescent Zn metal-organic framework (MOF) based on semi-rigid ligand (4-(2-carboxyphenoxy)isophthalic acid was described by Jin et al. for the determination of methanol in ethanol, but the synthetized material was not applied to real samples (Jin et al., 2013). Zhou et al. developed a sensor based on the employment of poly(N-isopropylacrylamide-co-N,N-dimethylacrylamide) copolymers (Zhou et al., 2014). The presence of methanol changed the polymer from a shrinking to a stretched state, causing a change in the transmittance of the solutions which allowed the detection of methanol at a percentage of 2.5% (% vol).

In the past years our research group has developed different colorimetric sensors based on the entrapment of colorimetric reagents into PDMS. The employment of PDMS for the preparation of sensors is a convenient and reliable alternative because it is a low-cost, versatile, non-harmful and optically clear material that can be easily synthetized (Seethapathy & Górecki, 2012). PDMS-based sensors can be used under two main approaches: the sensor acts as a reagent delivery system so that when exposed to the sample the reagent is transferred to the solution and reacts with the analyte, or the analyte diffuses from the sample to the PDMS matrix and then interacts with the reagent. Thus, the presence of the target analyte can be monitored through the color change in the working solution or in the sensor, respectively. Successful examples have been reported with different reagents and a variety of analytes such as aliphatic amines, drugs or biocides (Argente-García et al., 2016a, 2016b, 2017; Campíns-Falcó et al., 2013; Jornet-Martínez et al., 2016; Pla-Tolós, Moliner-Martinez, Molins-Legua, & Campins-Falcó, 2016; Prieto-Blanco et al., 2015).

The aim of the present work was to develop a PDMS-based sensor for the predominant alcohols in spirit samples based on their reaction with the reagent 4-(N,N-dioctylamino)-4'-trifluoroacetylazobenzene (ETH^T 4001). According to the literature, the trifluoroacetil group reacts with alcohols (Fig. 1) producing changes in the absorbances of the reaction media; these changes can be related to the concentration of alcohol (Mohr et al., 1999; Morh et al., 1998). The reagent has been also used for the analysis of aliphatic amines in air (Jornet-Martínez et al., 2016). In the present work, the sensing mechanism for methanol

and ethanol has been studied under different conditions and, on the basis of the results obtained, a method for the rapid determination of alcohols spirit drinks are proposed. The reliability of the proposed approach has been tested by analysis different spirit drinks.

2. Materials and methods

2.1. Reagents

All reagents used throughout the study were of analytical grade. 4-(N,N-dioctylamino)-4'-trifluoroacetylazobenzene (ETH^T 4001) and tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich (St. Louis, MO, USA). HPLC grade ethanol, methanol, 2-propanol and acetone were obtained from Romil (Cambridge, UK). The PDMS Sylgard® 184 Silicone Elastomer Kit (Sylgard® 184 silicone elastomer base and Sylgard® 184 silicone elastomer curing agent) was purchased from Dow Corning (Midland, MI, USA). All aqueous solutions were prepared with Milli-Q water obtained with a Nanopure II system (Sybron, Barnstead, USA).

2.2. Apparatus

Spectrophotometric measurements of solutions were carried out in the 300–660 nm range using a UV-VIS Agilent 8453 diode-array UV spectrophotometer (Agilent Technologies, Waldbronn, Germany). Spectrophotometric measurements of the sensors were carried out using a Cary 60 Fiber Optic UV-VIS spectrophotometer (Agilent Technologies), fitted with a remote fiber optic diffuse reflectance accessory from Harrick Scientific Products (Mulgrave, Victoria, Australia). The absorbance spectra of the sensors were registered in diffuse reflectance mode within the 200–1000 nm range. Data were recorded and processed using a Cary WinUV software (Agilent Technologies).

Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra were recorded with a Cary 630 FTIR-ATR spectrophotometer Agilent Technologies (Böblingen, Germany). Spectra were recorded in the frequency range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1}. For data collection and processing, MicroLab FTIR and ResolutionPro softwares (Agilent Technologies) were used, respectively.

2.3. Preparation of the sensors

Sensors with three different compositions were assayed (Table 1). Pure PDMS sensors were prepared by mixing the appropriate amounts of a solution of ETH^T 4001 in acetone (2.9 mg/mL), the PDMS elastomer base (0.1–0.2 g) and the curing agent; the base elastomer:curing agent ratio was 10:1 [20]. For preparation of the PDMS/TEOS sensors the appropriate amounts of TEOS were mixed with PDMS and curing agent before adding the reagent solution. In all instances the resulting mixtures were stirred for 10 min, and then portions of 200 μL were deposited in well polystyrene plates of 15 mm of diameter, and cured at 40 °C for 6 h.

2.4. Study of the sensor responses

Different mixtures of the ethanol, methanol and water were assayed. Binary methanol/ethanol mixtures were prepared by mixing variable volumes the two alcohols so that the percentages of methanol ranged from 0 to 40% (v/v). Binary ethanol/water mixtures were prepared by mixing variable volumes ethanol and water in order to produce mixtures with percentages of ethanol ranging from 0 to 90% (v/v). Ternary mixtures were prepared by mixing variable volumes of methanol and water with a fixed volume of ethanol; the percentages of ethanol assayed were 50, 60 or 70% (v/v). Aliquots of 1 mL of the mixtures were placed into glass vials, and then exposed to the sensors. Some ethanol/water mixtures were treated with acetone before being exposed to the