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An instrument-free method based on visible chemical waves for quantifying the ethanol content in alcoholic beverages

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ABSTRACT

An alternative approach using visible chemical waves for ethanol determination is presented. The method is based on the dynamic change of chemical waves in the Belousov-Zhabotinsky (BZ) reaction by perturbation with ethanol. The observablepropagating waves, generatedina Petri dish, can be recorded by using a smartphone camera. The propagating distances are measured from photographic images and then plotted as a function of time to attain the wave velocity. It is found that wave velocities are inversely proportional to ethanol concentrations. By using this linear relationship, the ethanol content can be efficiently quantified with good intra-day and inter-day precision (< 3% RSD). Validated by the GC technique, the developed method is highly reliable and successfully applied for quantifying the ethanol content in beer, colored whisky, and vodka samples. Hence, this new method provides an alternative practical strategy for simple quantitative detection of ethanol without the need for instruments.

1. Introduction

These days, the consumption of alcoholic beverages has vastly increased worldwide. In terms of quality control and safety to customer health, the alcoholic content must be specified on the products. Thus, the initial assessment of ethanol concentration in alcoholic beverages is an important step in the beverage industry. Many techniques have been developed for the analysis of ethanol in alcoholic samples. For example, the ethanol content in wines can be determined by flow injection spectrophotometry with gas-diffusion and an immobilized enzyme reactor (António, Rangel, & Tóth, 1999), gas chromatography (GC) (Wang, Choong, Su, & Lee, 2003), gas chromatography–mass spectroscopy (GC–MS) (Stupak, Kocourek, Kolouchova, & Hajslova, 2017), full evaporation headspace gas chromatography (Zhan, Lin, Chai, Li, & Barnes, 2015), high performance liquid chromatography–flame ionization detection (HPLC-FID) (Yarita et al., 2002). In beer and whisky samples, the ethanol concentration can be achieved by HPLC-FID (Yarita et al., 2002), sequential injection analysis (SIA) with spectrophotometric detection (Fletcher and Van Staden, 2003), near-infrared spectrophotometry with flow injection (Tipparat, Lapanantnoppakhun, Jakmunee, & Grudpan, 2001), NMR spectrometry (Zuriarrain, Zuriarrain, Villar, & Berregi, 2015), Fourier transform near infrared (FT-IR) and FT-Raman spectrometries (Mendes, Liveira, Suarez, & Rubim, 2003), and amperometric biosensing (Polan et al., 2015). The above-mentioned techniques can provide reliable results with a fast ethanol measurement. However, it is a relatively expensive operation as well as requiring high maintenance of these instruments. For this reason, the development of a simple approach for quantifying the ethanol content is still needed.

The Belousov-Zhabotinsky (BZ) reaction, well-known as the oxidation of an organic compound such as malonic acid (MA) by bromate in an acidic condition with the presence of metal catalyst, has been extensively studied (Epstein and Pojman, 1998; Field and Noyes, 1974; Field, Körös, & Noyes, 1972; Scott, 1994). Depending on the studied conditions, the autocatalytic BZ system can generate two phenomena; temporal oscillations and spatial formations of propagating waves (Epstein and Pojman, 1998). The first can be observed in a stirred system, while the latter occurs in an unstirred one. In general, the temporal oscillations of the BZ system are followed by spectrophotometry and the change of oscillation period is generally employed as an analytical tool to quantify the target analyte based on the analyte pulse perturbation (APP) (Jimenez-Prieto, Manuel, & Perez-Bendito, 1995). This concept has been applied for the analysis of various analytes such as ascorbic acid (Gao et al., 2001), glutamic acid (Goa et al., 2002), hydroquinone (Gao et al., 2002), indium ion (Gao, Wang, Yang, & Yang, 2006), 1-naphthylamine (Gao et al., 2007). However, this

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method is relatively difficult and time-consuming because the BZ reaction is conducted under a stirred condition, thereby requiring time to obtain the stable oscillating patterns. Also, this method still relies on the measurement by an instrument.

To the best of our knowledge, there is no such development for the use of spatial formations of propagating waves as the analytical tool. Herein, we present for the first time an efficient approach for the determination of ethanol by exploiting the propagating waves in the BZ system. The experiments are performed in a simple manner and only a smartphone camera is required to capture the propagating waves. The wave velocity is evaluated and used as a key parameter to assess the ethanol concentration. Moreover, the applicability of the developed method for the quantitative analysis of ethanol in alcoholic beverages is demonstrated and the results are evaluated with those obtained from the GC technique.

2. Materials and methods

2.1. Materials and instruments

Sodium bromate ($NaBrO_3$), sodium bromide (NaBr), and malonic acid (MA) were purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4) was obtained from QRêC. Ferroin ($Fe(o\text{-}phen)_3SO_4$) was purchased from Fluka. Ethanol (EtOH, 99.9%) was obtained from ACI Labscan. Deionized water produced by RiO_s™ Type I Simplicity 185 (Millipore water, USA) was used throughout. The stock solutions of 1 M $NaBrO_3$, 1 M NaBr, 1 M MA, 5 M H_2SO_4, and 2.5 mM ferroin were prepared daily with deionized water. A smartphone (Oppo R7 Lite, 13-megapixel rear camera) was used to record the chemical waves. Gas chromatography (GC-450 series) was also employed to analyze the ethanol content in alcoholic samples.

2.2. Fabrication of catalytic gel dish

The metal catalyst gel was first prepared through the gelation process. The catalyst $Fe(o\text{-}phen)_3SO_4$ was immobilized on a silica-gel matrix to avoid the convection and hydrodynamic perturbations (Yamaguchi, Kuhnert, Nagy-Ungvarai, Müller, & Hess, 1991). The mixture containing 0.4 mL of 2.5 mM $Fe(o\text{-}phen)_3SO_4$, 0.1 mL of 5 M H_2SO_4, and 0.5 mL of deionized water was added drop wise, under continuous stirring, to 2 mL of water glass solution. Then, 3 mL of the solution was poured into a Petri dish (6.99 ± 0.01 cm diameter). After gelation, the gel was washed 3 times with deionized water. To prevent its desiccation, the obtained gel dish was kept by covering with water prior to use. The preparation of catalytic gel usually took roughly 5 min.

2.3. Formation and measurement of visible chemical waves for ethanol analysis

The BZ solution was first prepared by mixing 2 mL of 1 M $NaBrO_3$, 0.4 mL of 1 M MA, 0.3 mL of 1 M NaBr, 0.6 mL of 5 M H_2SO_4, and 1.7 mL of deionized water. Then, the mixture was transferred onto the prepared catalyst gel dish to generate the chemical waves. Eventually, the initial concentration of the BZ solution for chemical waves located in the reaction dish included 0.25 M $NaBrO_3$, 0.075 M MA, 0.25 M H_2SO_4, 0.0375 M NaBr, and 1.25 mM ferroin under atmospheric conditions at a room temperature of 30.5 ± 0.5 °C. For the perturbation of the BZ system with ethanol, appropriate volumes of 99.9% absolute ethanol were first mixed with the BZ solution to obtain the final concentrations of ethanol in the range of 0.2–1.0 %v/v. After that, the mixture was introduced into the catalytic gel dish in order to study its effect on the behavior of waves.

To measure the propagating waves, after a few terraces of propagating waves were generated, the chemical wave dish was carefully set to a position where the wave front was perpendicular to the labeled scale bar (the propagating distance was fixed at 15 mm and the length between the measuring points was 3 mm). Before starting the observation, the circular waves were left to progress until their radii reached approximately 3 mm in order to avoid the curvature effect on the wave velocity. The images of chemical waves at any time were recorded by using a smartphone camera. Finally, the time for the waves to pass through the measuring points, defined as the propagating distance, was obtained. The wave velocity (v), one important dynamic of BZ propagating waves, was derived and utilized to construct a calibration curve for the quantification of ethanol. Usually, it took approximately 5 min for wave formation and measurement.

To validate the proposed method, the intra-day and inter-day experiments were carried out at three ethanol concentration levels (0.4, 0.6 and 0.8 %v/v). The intra-day experiments were performed in triplicate (n = 3) in a day, while the inter-day experiments were conducted over three consecutive days (n = 3 × 3). The average wave velocity (v_{avg}) of each experiment was used for further analysis. It is noted that all the measurements were carried out at the temperature of 30.5 ± 0.5 °C.

2.4. Analysis of ethanol content in alcoholic samples

The content of ethanol in real alcoholic samples was carried out by the proposed method. Nine commercial beverages including four brands of beer, four brands of colored whisky, and one brand of vodka with different labeled contents of ethanol ranging from 5.0 to 40.0 %v/v were purchased from a local market. Prior to ethanol analysis, 0.50 %v/v sample solution of each sample (25 mL) was prepared by a dilution with deionized water using the following sample volumes; 2.5 mL of 5.0 %v/v beer samples (beer 1–3), 2.4 mL of 5.2 %v/v beer 4, 0.36 mL of 35.0 %v/v whisky 1 and 2, 0.33 mL of 38.0 %v/v whisky 3, and 0.31 mL of 40.0 %v/v whisky 4 and vodka. Then, 0.5 mL of the diluted sample solution was used for the determination of ethanol content by the present method, as described in Section 2.3.

To assure the efficacy of the proposed method, the ethanol content in these samples was also determined by GC. The standard ethanol solutions in the range of 1.0–6.0 %v/v were mixed with 1 mL isopropanol used as an internal standard before injecting into GC. The peak area ratio of ethanol to isopropanal at each concentration was plotted to construct a calibration curve. To investigate the ethanol content in the studied samples, colored whisky and vodka samples were diluted to 5.5 %v/v with deionized water, while beer samples were used without dilution. Then, 2 mL of each diluted sample was mixed with 1 mL of isopropanol and injected into GC for analysis. The concentration of ethanol in samples was determined by using the calibration curve. All measurements were carried out at the same temperature (30.5 ± 0.5 °C).

3. Results and discussion

3.1. Chemical waves for ethanol analysis

The chemical waves are based on the ferroin-catalyzed BZ reaction. All BZ reactants were employed and the reaction was conducted on a planar Petri dish which contained the catalyst gel. These chemical waves occur spontaneously after introducing the BZ solution into the dish as a result of autocatalytic reactions coupled with the diffusion of reactants through an excitable medium. The chemical waves can be visible to the naked eye. The dynamics of the waves were recorded by a smartphone camera. The experimental procedure is illustrated in Fig. 1. In this study, as the behavior of the BZ waves is dependent on the recipes of the reactants, a fixed condition consisted of 0.25 M $NaBrO_3$, 0.075 M MA, 0.25 M H_2SO_4, 0.0375 M NaBr, and 1.25 mM ferroin was used throughout to generate the noticeable wave patterns. Fig. 2 illustrates the representative chemical waves at varied times from 0 to 240 s. The wave patterns were generated by adding 0.8 %v/v ethanol into the aforementioned BZ system. As can be seen, the oxidation waves