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Determination of five alcohol compounds in fermented Korean foods via simple liquid extraction with dimethyl-sulfoxide followed by gas chromatography-mass spectrometry for Halal food certification

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ABSTRACT

An analytical method for the determination of five alcohols (methanol, ethanol, n-propanol, n-butanol and n-pentanol) in fermented Korean foods using gas chromatography-mass spectrometry (GC/MS) was validated in terms of precision, accuracy, sensitivity and linearity. GC/MS separation was performed on a silica-based INNOWAX column (film thickness 0.25 μm, i.d. 250 μm, length 30 m) coated with polyethylene glycol and a mass selective detector set to determine specific selected ions for each alcohol. The limits of detection and quantification of the GC/MS analyses ranged from 0.25 to 1.16 mg/kg. Intra-day and inter-day RSDs for individual alcohol compounds were below 7%, and calibration curves exhibited good linearity ($r = 0.999$) within the tested ranges. Recovery values ranged from 90.79 to 101.50%. These results suggest that the analytical method described in this study could be used to determine the concentrations of five alcohols in a variety of fermented Korean foods such as *Gochujang*, *Kimchi* and soybean sauce (paste, solid and liquid sample) for Halal food certification.

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1. Introduction

Alcoholic drinks or beverages are totally prohibited in Islam, and even a small amount of alcohol in foods or drinks will render the products *haram* and thus forbidden (Najiha, Tajul, Norziah, & Nadiah, 2010), as alcohol leads to *Sukr* (intoxication). For Muslims, any agent or process that disconnects a person from a state of awareness or consciousness (a state in which the person may forget the creator) is called *Sukr* and is *haram* (Ahmed, Memish, Allegranzi, & Pittet, 2006). Currently, it is well-known that alcohol is a significant disease burden and is associated with premature death and disability (Rhem, 2009). In a classification of harmful substances, a recent paper claimed that alcohol is more dangerous than heroin (Lee & Forsythe, 2011).

In chemistry, an organic compound in which a hydroxyl functional group is bound to a saturated carbon atom, such as methanol, ethanol, propanol, butanol and pentanol, is an alcohol compound. However, only one type of alcohol (ethanol) is considered *haram* for Muslims (Jahangir et al., 2016). Trace amounts of ethanol that are naturally present or are used during food processing could be *halal* if the amount is insufficient to cause intoxication (Najiha et al.,2010). The LPPOM MUI (Lembaga Pengkajian Pangan Obat-Obatan Dan Kosmetika Majelis Ulama Indonesia) has defined the following regulations regarding acceptable trace alcohol levels: the alcohol must not be a byproduct of the *khamr* (alcoholic beverage) industry, the use of alcohol in the production of food and beverage products is allowed as long as the alcohol levels in the final product are not detectable, and alcohol levels in intermediate products (products that are not consumed directly) must not be higher than 1% (LPPOM MUI, 2012). Because of these regulations, we considered five alcohols (methanol, ethanol, n-propanol, n-butanol and n-pentanol) as target compounds that could occur naturally in

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fermented foods and potentially lead to *Sukr*.

Numerous studies have reported naturally occurring ethanol in traditional fermented Korean foods such as red pepper paste (*Gochujang*) (Choi, Lee, Park, Sun, & Noh, 1997; Kim & Yang, 2004), soybean sauce (Choi, Kwon, Nam, Shin, & Yang, 1992; Kwon et al., 2003), and *Kimchi* (Cho & Rhee, 1991). Because an official method for analyzing solid or paste-type food samples does not exist, the analytical methods used in all of the above studies were modified distillation methods (the most common method) derived from AOAC Official Method 984.14 (AOAC, 1988) for liquid beer samples. There has been an attempt to determine ethanol concentrations in solid matrices (cooked meals) using Solid Phase Micro Extraction (SPME) – GC/MS (Mateus, Ferreira, & Pinho, 2011). However, this method was not used to detect several alcohol compounds simultaneously, and full validation parameters for the precision and accuracy of the method were not determined. Moreover, quantification methods for alcohols are almost completely restricted to alcoholic beverages or liquid sample matrices (Shishov et al., 2016; Wang, Wang, & Choong, 2004; Zhang, Lin, Chai, Li, & Barnes, 2015).

Many other analytical methods for measuring alcohols as volatile compounds have been reported. Recently, GC/MS coupled with distillation (Dragone, Mussatto, Oliveira, & Teixeira, 2009), GC/MS coupled with Head Space (HS) – SPME (Ding, Wu, Huang, & Zhou, 2016; Xiao et al., 2014; Yang et al., 2016), GC/MS coupled with Stir Bar Sorptive Extraction (SBSE) – Dynamic Head space (DHS) detection (Ha, Wang, Jang, Seog, & Chen, 2014) and Nuclear Magnetic resonance (NMR) detection (Baiano et al., 2015) have been used to profile (but not quantitatively analyze) alcoholic compounds in various food samples.

Therefore, our study focused on evaluating a quantitative analysis method for the determination of five alcohols in solid (*Kimchi*), paste (*Gochujang*) and liquid (Soybean sauce) fermented Korean food matrices. This analysis method employs GC/MS following a simple liquid extraction with dimethyl sulfoxide to determine alcohol levels for Halal food certification.

2. Materials and methods

2.1. Samples and reagents

All reference materials, including methanol (99.9%), pure ethanol (100%), n-propanol (99.9%), n-butanol (99.7%) and n-pentanol (99.0%) were obtained from Sigma (St. Louis, MO, USA). The internal standard (IS, n-hexanol, 99.0%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Standard stock solutions of each reference alcohol were dissolved in dimethyl sulfoxide (DMSO) at concentrations ranging from 2.54% to 2.65%. IS was prepared at a concentration of 2.51%. All external and internal standard stock solutions were transferred to glass vials whose interiors were treated with trimethyl silane. Stock solutions were stored at 4 °C. Because the freezing point of DMSO is 18 °C, stock solutions were frozen at 4 °C. To prepare working standard solutions, each external stock solution was diluted with DMSO to concentrations of 0.31, 1.22, 4.88, 19.53, 78.13, 312.50 and 1250.00 mg/kg. IS was added to all working standard solutions to a final IS concentration of 250.00 mg/kg. The test samples used in the method validation process (*Gochujang, Kimchi* and soybean sauce) were produced in large mass production factories and artificially contained ethanol as a food additive. These test samples were purchased from local retail stores in Seoul, Korea. The test samples used in the application test (*Gochujang* and soybean sauce) were produced using traditional Korean manufacturing processes and were purchased at local markets in Sunchang-gun, Jeollabuk-do, the most famous region for traditional fermented Korean food. Each sample was minced using a BÜCHI mixer B-400 (BÜCHI, Flawil, Switzerland) for complete homogenization and stored at 4 °C prior to analysis. DMSO was purchased from Sigma (St. Louis, MO, USA). Ultra-pure water was obtained from a Milli Q system (Millipore, Bedford, MA, USA).

2.2. Sample preparation

Approximately 0.5 g of sample (1.0 g of *Kimchi*) was added to a 22 mL gas-tight vial (Supelco, Bellefonte, PA, USA) containing a magnetic stir bar (10-mm length, 6 mm i.d.) (Bel-Art products, Wayne, NJ, USA) and 1.0 mL of IS (n-hexanol, 2500.00 mg/kg). DMSO (8.5 mL but 8.0 mL for *Kimchi*) was gradually added to each vial, and the vials were tightly capped. Vials were placed on a Twister (GERSTEL, Gerstel em Blaarthe, Netherlands) and extracted at 25 °C for 60 min with agitation at 1300 rpm, until the upper lipid layers were completely separated from the DMSO and crushed samples. After extraction, vials were stored in the dark for 5 min at room temperature. The upper lipid layer was then removed and discarded using a Pasteur pipet. Supernatants were filtered through a 0.45 μm syringe filter (Whatman, Maidstone, UK) and transferred to small glass vials for GC/MS analysis.

To allow the analytical results for methanol and ethanol to be compared with results obtained using the official method, a distillation method modified from AOAC Official Method 984.14 (AOAC, 1988) was performed in parallel. Approximately 5 g of sample was weighed in a 300 mL Kjeldahl flask, and 50 mL of water was added. The flask was connected to a distillation apparatus maintained at 120 °C and distilled for 30 min. After distillation, distillates were poured into 25-mL volumetric flasks and diluted to 25 mL with water. The aforementioned solutions were diluted with additional water to bring their methanol and ethanol concentrations within calibrated concentration ranges. After filtering through 0.45 μm syringe filters, solutions were transferred to small glass vials for GC-FID analysis. To avoid errors resulting from analyst bias, all of the analyses using the AOAC method, including instrument analyses, were carried out at the Japan Food Research Institute (JFRL).

2.3. GC/MSD analysis conditions for five alcohols

The GC/MSD system was an Agilent 6890 GC system (Agilent, Santa Clara, CA, USA) coupled to an Agilent Mass selective detector 5973 quadruple mass spectrometer (Agilent, Santa Clara, CA, USA). Target compounds were separated using a DB-INNOWAX silica base polyethylene glycol column (30-m length, 250 μm i.d., 0.25 μm film thickness, J & W Scientific Inc., Folsom, CA, USA). The carrier gas was helium, with a flow rate of 1.0 mL/min. Split mode (split ratio 40:1) was used. The column oven temperature program was as follows: initial temperature of 40 °C (hold 5 min), increase to 240 °C with a ramp rate of 10 °C per min, hold at 240 °C for 9 min. The quadruple temperature, transfer line temperature and MS source temperature were 150, 280 and 230 °C, respectively. The inlet temperature was fixed at 160 °C, and the injection volume was 1.0 μL. The mass spectrometer was operated in electron impact ionization mode (70 eV), and Selected Ion Monitoring mode (SIM mode) was used. The SIM conditions were as follows: the initial selected ions were 29, 31, 32, 45 and 46 *m/z* (hold 4 min for methanol and ethanol), then changed to 31, 59 and 60 *m/z* (hold 2 min for n-propanol), changed to 31, 41 and 56 *m/z* (hold 2 min for

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