Optimization of Coffee Liqueur Manufacturing Process using Caffeine Content

Chang-Hwan Oh

Abstract: ***Coffee liqueur is an alcoholic beverage made by soaking coffee in spirit. Though coffee liqueur is one of the well-known liqueur, few research was made so far. In this research, coffee liqueur was prepared by using different recipes involving liquors with different ethanol concentrations (20, 40, or 80%), and the soaking periods (14, 21, or 30 days) of the coffee liqueur ingredients (roasted coffee beans, coffee bean powder and other ingredients). Volatile and semi-volatile compounds are important for the organoleptic quality of roasted coffee beans. However, the amounts of these compounds in roasted coffee beans are more dependent on roasting conditions than those of non-volatiles. Furthermore, volatiles are more easily lost during storage. On the other hand, caffeine, a well-known compound of coffee is an intrinsic non-volatile chemical, and the caffeine is present in larger than other potential indicator components in coffee beans, ensuring the quantitative consistency of the coffee extracts in the liqueur. Caffeine was quantified from the prepared coffee liqueurs by HPLC after method validation. The average caffeine content of all 54 analyses (6 analyses per sample) was 2081.2 μg/mL. The highest caffeine concentration 2793 μg/mL was acquired in the sample prepared by 80% ethanol liquor. A soaking period of 14 days, was considered inadequate for sufficient caffeine extraction regardless of liquor alcohol content. Caffeine concentration peaked after soaking coffees and other ingredients for 21 days at 80% ethanol concentration. On the other hand, the most consistent caffeine concentrations in liqueurs were obtained by soaking for 21 days in 40% ethanol (RSD 7.8%), thus it could be the optimum coffee liqueur recipe. The consistency of coffee liqueur quality was assured using caffeine content.***

Keywords**:** ***Caffeine, Coffee Liqueur, HPLC, Manufacturing Process, Optimization***

I. INTRODUCTION

Coffee liqueur is a type of alcoholic beverage produced by steeping roasted coffee, sugar and other ingredients in neutral spirit. The most famous coffee liqueur brand is probably Kahlua, which has been made in Mexico since 1936 [1]. However Kahlua has a thick buttery taste, which is not well-like by many alcoholic drink lovers, which is why many people enjoy coffee liqueur made using their own home recipes. Typical ingredients of coffee liqueur include liquor, espresso coffee, roasted coffee bean (and powder), sugar, and vanilla syrup. The discriminative characteristic flavor of coffee is probably a primary reason for choosing coffee liqueur. Over a couple of hundreds compounds contribute to the taste of coffee liqueur. Caffeine is a well-known component of coffee, and also might be a taste factor that influences the complex of coffee liqueur flavors that appeal to coffee liqueur drinkers' palates. Chen reported "two important nitrogenous compounds, caffeine and trigonelline accounted for a maximum 10-30% and 1% respectively, of the total bitter taste intensity of a coffee beverage" [2]. However Voilley et al. suggested that caffeine only accounted for around 10% of the perceived coffee bitterness [3]. The bitterness threshold of caffeine in coffee is 75-155 mg/L. But there are many other coffee chemicals contributing bitterness in terms of the low bitterness threshold (1-90 mg/L), such as pyrazine, quinic acid, caffeic acid, furfuryl alcohol, chlorogenic acid and acetic acid [4]. But the level of caffeine content is high enough imparting co-stimulatory effect on a various coffee flavor. Caffeine levels in homemade coffee liqueurs have been reported by Oh [5], who compared various liquors such as rum, vodka, traditional Korean soju, and fermented ethanol produced liqueurs containing different ratios of coffee ingredients like roasted coffee beans or coffee powder. The composition ratio of coffee powder to coffee bean was observed to have no influence on the extraction efficiency of caffeine during the preparation of coffee liqueur, and the only liqueurs with statistically similar high caffeine extraction efficiencies were those produced using traditional Korean soju or pure fermented ethanol. In the research, all liquors used for coffee liqueur preparation contained around 40% ethanol and the soaking period of roasted coffee beans and powder was fixed at 21 days. Therefore the additional research was required to estimate the caffeine contents by different ethanol ratios of the spirits and the various soaking periods for the preparation of coffee liqueur. This research is the following experiment of Oh's research [5] complementing of the coffee liqueur recipe with consistent quality in terms of the extracted coffee ingredients estimated by the amount of caffeine. In this present research, caffeine contents were measured in coffee liqueurs prepared using liquors with different ethanol concentrations and different soaking periods of coffee liqueur ingredients. High performance liquid chromatography (HPLC) was used for the caffeine quantitative analysis. Quality control of coffee liqueur manufacture was standardized using the caffeine concentrations based on scientific evidence acquired during the present study.

II. MATERIALS AND METHODS

This research is consisted with the preparation of coffee (with roasting), making coffee liqueur by a recipe with two variables (ethanol contents and coffee ingredients soaking time). It is followed that a detail description of the analytical method validation and

Revised Manuscript Received on October 05, 2019
***** Correspondence Author
Chang-Hwan Oh, School of Food and Nutrition, Semyung University, Jecheon, South Korea.

quantitative analysis of caffeine to find the optimum recipe condition for coffee liqueur and to verify the caffeine as a potent quality assurance indicator of coffee liqueur.

A. Coffee and roasting

A single origin high-quality Arabica coffee harvested in the Sidamo province of Ethiopia, "Ethiopia Sidamo G2" coffee bean was used as a major ingredient to make the homemade coffee liqueur. The most distinctive flavor notes found in all Sidamo coffees are “lemon and citrus, with bright crisp acidity” [6]. Raw coffee bean was purchased in Nine Road (Seoul, Korea). Automatic coffee roaster, Gene Café CBR-101 (Genesis, Ansan, Korea) was used for roasting coffee bean. Initial roasting temperature was 180 °C (for 5 min) and ramped to 250 °C (held for 9.3 min) for getting medium brown color. One batch amount of coffee bean for roasting was 180g. The roasted coffee bean was used within 5 hours. Roasted coffee bean (60 g) was ground for 20 seconds for the espresso and 10 seconds for an ingredient of coffee liqueur. Automatic coffee grinder, SP7426 (Wiswell, China) was used. The espresso shot was prepared by an automatic espresso machine (Saeco Royal Type Sup 016, Bologna, Italy). The automatic brewing for one espresso coffee shot (25 mL) took 20 seconds. One shot of espresso equal to 7 g of the roasted coffee bean.

B. Coffee liqueur preparation

The ingredients of coffee liqueur were the roasted coffee bean, roasted coffee bean powder, espresso shot (liquid), brown sugar, vanilla syrup and the fermented rectified ethanol (FRA, diluted to 20, 40, or 80% ethanol). Brown sugar (1 kg, CJ CheilJedang, Seoul, Korea) was obtained from a grocery store in Seoul, Korea. Vanilla syrup (250 mL, Monin, Clearwater, FL, USA) was purchased from Coffee Aroma (Goyang, Geonggi-do, Korea). The FRA (95% v/v) was obtained from “Korea Ethanol Supplies Company” (Seoul, Korea). For the preparation of coffee liqueur, the roasted coffee (43 g), powder (107 g), espresso coffee shot (37.5 mL), brown sugar (150 g) and vanilla syrup (16 mL) were mixed in a 2 L size stainless steel mixing bowl (Kitchen-Art, Incheon, Korea), followed by adding of diluted FRA (20, 40, or 80%) 350 mL. After homogenization by plastic paddle for 5 min, the coffee liqueur ingredients mixture was transferred to a 1 L size glass jar with lid (Ikea, Gwangmyeong, Gyeonggi-do, Korea). Total 9 jars (Each three coffee liqueurs with three different FRA%) were prepared and stored in ambient temperature (17-25°C). Each three jar with FRA 20, 40, or 80% were opened after 14, 21, and 30 days. And each coffee liqueur mixture was filtered by Bűchner funnel with Whatman No. 5 filter paper (110 mm diameter, Cat. No. 1005 110, Little Chalfont, UK) under vacuum. All resulting filtrates were stored in a refrigerator (4°C). They were filtered by 0.45 µm PTFE syringe filter (Advantec, Dublin, CA, USA) just before HPLC analysis was performed.

C. Materials for HPLC analysis

The analytical standards of caffeine (Cat. no. C1778-1VL) and the internal standard (IS) acetaminophen (Cat. no. A3035-1VL) were the product of Sigma-Aldrich (St. Louis, MO, USA). 85% (w/v %) of phosphoric acid in water (Trace metals basis, Cat. No. 345245) was obtained from Sigma-Aldrich Corp. (St. Louis, MO USA). For HPLC grade acetonitrile and water, the product of Burdick & Jackson (Muskegon, MI, USA) were used. The analysis was performed by Prominence HPLC equipped with a photo-diode array (PDA) UV/Vis detector (Shimadzu, Tokyo, Japan). A reversed HPLC column, “Agilent Eclipse plus C_{18} 5 µm (4.6 × 250 mm, Cat. No. 959990-902, Agilent Technologies, Santa Clara, CA, USA)” was used.

D. Quantification of caffeine by HPLC

Caffeine analysis by HPLC was performed by the analysis method of Oh [5]. Gradient mode with two mobile phase (A solution: 0.05N phosphoric acid, B solution: 60% acetonitrile in water) was used. Initial mobile phase condition (75% of A, 25% of B solution) was maintained for 10 min followed by increase of B solution ratio up to 75% within 15 min gradually. HPLC column was kept inside of 35°C column oven during analysis. The filtered sample was injected by Rheodyne injector equipped with 20 µL size loop. Each separated peak was detected by PDA UV/VIS detector at 272 nm. For the quantitative analysis of caffeine, standard curve was prepared with the plotting of the caffeine peak area of the different concentrations (10, 30, 50, 70, and 200 µg/mL) divided by the internal standard peak area (150 µg/mL). All analysis in each concentration point was replicated three times. Method validation for the analysis of caffeine was checked by the method of Oh [5]. The recovery and precision tests were performed by the 6 times replicate quantitative analysis of the 40% ethanol solutions containing 2500 µg/mL of caffeine after 50 times dilution with distilled water. Limit of quantitation (LOQ) was calculated by the equation “ $LOQ = 10 \times \sigma / S$” where S is mean of the slope in the calibration curve derived from the five different concentrations of caffeine (10, 30, 50, 70, and 200 µg/mL) and σ is the standard deviation mean of the intercept. Limit of detection (LOD) was acquired by the equation “ $LOD = 3.3 \times \sigma / S$” .

E. Statistical analysis

Calculation of mean, standard deviation and relative standard deviation (RSD) %, and ANOVA test and regression test were performed by Sigma Plot (*ver.* 13., “Systat Software Inc.”, San Jose, CA, USA).

III. RESULTS AND DISCUSSION

A. Linearity, LOD, LOQ, precision and accuracy of caffeine analysis

The validation result is shown in Table- I. The linearity of

the calibration curve was quite satisfactory for the quantitative analysis. RSD% value obtained by replicate analyses in a day (intra-day) and three days (inter-day), those results were all under 2% which was precise enough.

Table- I. Analytical method validation results for the analysis of caffeine.

Analytical method validation factors	*Results*
Calibration curve formula	y = 5.3624x – 0.1185
Linearity of calibration curve (R^2)	0.999
Limit of Detection (LOD)	1.0 μg/mL
Limit of Quantification (LOQ)	3.0 μg/mL
Precision (intra-day)	1.4%
Precision (inter-day)	1.7%
Recovery	98%

B. Caffeine analysis results of homemade coffee liqueurs

The caffeine contents of coffee liqueurs manufactured using nine different recipes prepared by soaking the ingredients in 20, 40, or 80% ethanol (for 14, 21, or 30 days) are summarized in Fig. 1. The average caffeine content of all 54 analyses (6 analyses per sample) was 2081.2 μg/mL (RSD 24.8%) and the maximum and minimum caffeine concentrations were 3242.7 and 1303.4 μg/mL, respectively. Two-way ANOVA showed mean caffeine contents in 21- or 30-days soaked samples were significantly different, and that the liqueurs produced using 80% ethanol liqueur had the highest mean caffeine content (Table- II). However, mean caffeine concentrations of liqueurs prepared for 14 days using different ethanol concentrations were not significantly different (p<0.05). Thus, a soaking period, of 14 days, was considered inadequate for sufficient caffeine extraction regardless of liquor alcohol content. This was confirmed by the caffeine contents of coffee liqueurs produced by soaking for 14, "21 or 30 days" (for 40 and 80% ethanol but not for 20% ethanol). Furthermore, the average caffeine contents of coffee liqueurs produced by soaking for 14 days in 40 or 80% ethanol were significantly different from those produced by soaking for 21 or 30 days. On the other hand, the caffeine contents of liqueurs produced by soaking for 21 and 30 days were not significantly different. In other words, when coffee liqueurs were manufactured by soaking in a liquor with an alcohol content of 40% or greater than 40%, extracted caffeine contents reach a steady value if the coffee liqueur ingredients are soaked for more than 21 days.

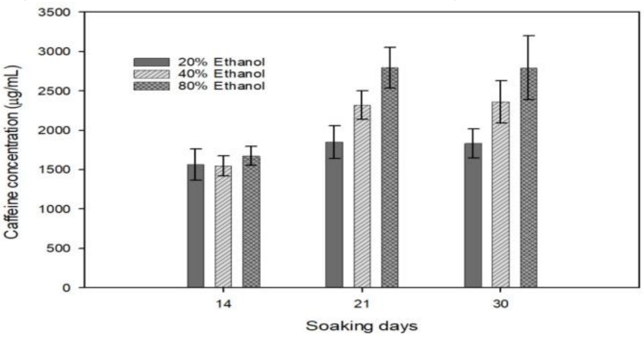

Fig. 1.Caffeine concentration of the coffee liqueur produced by nine different recipes (using 20, 40, or 80% alcohol liquors for 14, 21, or 30 days soaking).

Table- II: Statistical differences between caffeine concentrations (μg/mL) in coffee liqueurs prepared by soaking in 20, 40, or 80% alcohol liquors for 14, 21, or 30 days.

Caffeine / *Ethanol*	14 days		21 days		30days	
	Mean	*RSD %*	*Mean*	*RSD %*	*Mean*	*RSD %*
20%	1563.2[aef]	12.7	1850.5[a]	11.2	1833.0[a]	10.2
40%	1546.1[df]	8.4	2319.1[b]	7.8	2360.2[b]	11.4
80%	1672.7[de]	7.1	2793.8[c]	9.2	2792.5[c]	14.9

[a-f.] Means with same letters are not significantly different (p<0.05).

C. Evaluation of the optimal coffee liqueur manufacturing process

The chemical profile of coffee bean is very complicated, and the roasting of green coffee beans, complicates chemical profiles (consisted with more than 900 volatile and semi-volatiles) due to diverse chemical reactions such as, "Maillard and Strecker reactions, degradation of sugar, trigonelline, chlorogenic acids, proteins etc" [6], [7]. Volatile and semi-volatile compounds are important for the organoleptic quality of roasted coffee beans. However, the amounts of these compounds in roasted coffee beans are more dependent on roasting conditions than those of non-volatiles. Furthermore, volatiles are more easily lost during storage. On the other hand, caffeine is an intrinsic non-volatile chemical, and the caffeine is present in larger amounts than other potential indicator components in coffee beans.

Caffeine concentrations in coffee liqueurs prepared by soaking in 20% ethanol, were not significantly different regardless of soaking time of the coffee liqueur ingredients. Moreover the batch to batch consistencies (precisions) of caffeine concentrations in coffee liqueurs prepared using 20% ethanol liquor were comparatively worse than those of liqueurs prepared using higher ethanol concentrations (RSDs were 10.2-12.7% for 20% alcohol coffee liqueur samples). The relatively high RSD% value for caffeine content, of liqueurs prepared using 20% alcohol indicates inconsistent quality, which indicates 20% alcohol soaking might not be adequate for standardized coffee liqueur manufacture.

Table- III: The optimized coffee liqueur manufacturing process.

Ingredients or process	*Amounts or condition*
Roasted coffee bean	43 g
Roasted coffee bean powder	107 g
Espresso liquid	37.5 mL
Brown sugar	150 g
Vanilla syrup	16 mL
Fermented rectified ethanol (40%)	350 mL
Soaking days	21 days
Temperature for soaking	17 ~ 25°C

Regarding soaking periods, 21 days was considered probably enough to extract caffeine because caffeine contents of 21- and 30-day soaked coffee liqueurs were not significantly different (p<0.05). Most consistent caffeine concentrations in liqueurs were obtained by soaking for 21 days in 40% ethanol (RSD 7.8%). Therefore the optimum coffee liqueur manufacturing process is suggested as Table- III.

IV. CONCLUSION

In the present study, a coffee

liqueur manufacturing process was optimized using liqueur caffeine contents. Soaking of coffee liqueur ingredients in 40% ethanol for 21 days produced the most consistent caffeine concentration in coffee liqueur, and thus, I suggest soaking of coffee liqueur ingredients under these conditions might be satisfactory in terms of consistently extracting caffeine. One of the major non-volatile component, caffeine showed a good precision in the suggested recipe condition, therefore caffeine was proved as a valuable candidate for ensuring the quantitative consistency of the coffee extracts in the liqueur.

ACKNOWLEDGMENT

This research was fully supported by Semyung University Research Grant (March 1st, 2017 – February 28th, 2018). Author thanks "Nine Road" and GM Choi for their advice and support for the sample preparation and analysis.

REFERENCES

1. The Kahlúa Company, *Kahlua the original Coffee Liqueur*. Available from: http://www.kahlua.com/en/products/original/. Accessed Aug. 11, 2019.
2. W. C. Chen. *Studies on the bitter taste of roasted coffee. Relationship between structure and bitter taste of some organic compounds*. PhD thesis, University of Munich, Munich, Germany, 1979.
3. A. Voilley, F. Sauvageot, P. Pierret. "Evaluation des qualités d'une tasse de café: effet de la température de l'eau d'extraction", 9th International Scientific Colloquium on Coffee. June 16-20, 1980, London, UK. Association Scientifique Internationale du Cafe, Paris, France.
4. D. A. McCame. T. M. Thorpe, J. P. McCarthy, "Coffee Bitterness", Vol 25, in *Developments in Food Science*. R. I. Rouseff, Ed. Amsterdam, Elsevier, 1990, pp. 169-182.
5. C. H. Oh, "Investigation of caffeine level in Homemade coffee liqueur", J. Eng. Applied Sci. 12, 2017, pp. 4841-4845.
6. C. A. B. De. Maria, L. C. Trugo, F. R. Aquino Neto, R. F. A. Moreira, C. S. Alviano, "Composition of green coffee water-soluble fractions and identification of volatiles formed during roasting", Food Chem. 55(3), 1996, pp. 203-207.
7. P. Thammarat, C. Kulsing, K. Wongravee, N. Leepipatpiboon, T. Nhujak, "Identification of volatile compounds and selection of discriminant markers for elephant dung coffee using static headspace gas chromatography—mass spectrometry and chemometrics", Molecules, 23, 2018, 1910; doi:10.3390/molecules23081910

AUTHORS PROFILE

Chang-Hwan Oh is a professor in School of Food & Nutrition Science for Bioindustry, Semyung University, Jecheon, South Korea. He studied in Yonsei University from undergraduate to Ph.D. His master and Ph.D thesis were "Flavor Components of *Poncirus trifoliate*" and "Rapid gas chromatographic screening of plant seeds for free non-protein and protein amino acids", respectively. He did his post-doctorate courses in University of Texas at Austin and State University of New York at Stony Brook, U.S.A. He worked as a senior researcher in Korea Food and Drug Administration (Ministry of Food and Drug Safety at present). He also worked as the head of the research institute of Lab Frontier that was a contract laboratory. His research field is the food chemical analysis by instrumental analysis, such as GC, GC-MS, HPLC, etc. He performed more than 50 governmental and private research projects related to the safety evaluation of foods and herbal medicinal materials (for the hazardous compounds like pesticides, heavy metals, organic solvents, PAHs, etc.) by chemical analysis and exposure evaluation. He also published more than 50 research papers about the above research area. He is an editor of SCIE journal "Food Science and Biotechnology". He is the member of many advisory committee of MFDS, such as "Food Hygiene Advisory Committee", "Analytical Examination Development Executive Committee (Chairman)", "New Food Ingredients Advisory Committee", etc.