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Determination of xanthohumol in beer based on cloud point extraction coupled with high performance liquid chromatography

Ligang Chen, Qi Zhao, Haiyan Jin, Xiaopan Zhang, Yang Xu, Aimin Yu, Hanqi Zhang, Lan Ding*

College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China

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ABSTRACT

A method based on coupling of cloud point extraction (CPE) with high performance liquid chromatography separation and ultraviolet detection was developed for determination of xanthohumol in beer. The nonionic surfactant Triton X-114 was chosen as the extraction medium. The parameters affecting the CPE were evaluated and optimized. The highest extraction yield of xanthohumol was obtained with 2.5% of Triton X-114 (v/v) at pH 5.0, 15% of sodium chloride (w/v), 70 °C of equilibrium temperature and 10 min of equilibrium time. Under these conditions, the limit of detection of xanthohumol is 0.003 mg L^{-1}. The intra- and inter-day precisions expressed as relative standard deviations are 4.6% and 6.3%, respectively. The proposed method was successfully applied for determination of xanthohumol in various beer samples. The contents of xanthohumol in these samples are in the range of 0.052–0.628 mg L^{-1}, and the recoveries ranging from 90.7% to 101.9% were obtained. The developed method was demonstrated to be efficient, green, rapid and inexpensive for extraction and determination of xanthohumol in beer.

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1. Introduction

The hop plant (*Humulus lupulus* L.) is a dioecious plant of the Cannabacea family, and cultivated in most temperate zones of the world [1]. Nowadays, the plant is used in the brewing industry to add bitterness and aroma to beer [2,3]. The hop contains many flavonoid compounds which have positive effect on the human health due to their antioxidant, anticancer, antimicrobial and anti-inflammatory properties [3,4]. Among them, xanthohumol (Fig. 1) shows antiproliferative activity in cancer cell lines derived from human breast cancer, colon cancer and ovarian cancer in vitro [5]. Xanthohumol is characterized as a 'broad spectrum' chemopreventive agent because it is able to inhibit initiation, promotion and progression stages of carcinogenesis by modulating the activity of pro-carcinogen activating enzymes and carcinogen detoxifying enzymes [6]. This compound also exhibits strong antioxidant and free radical scavenging properties [7,8].

The hop is used in the beer production, so one of the main dietary sources of xanthohumol for people is beer [4]. Beer has been attracting interest by consumers over centuries due to its sedative activity, refreshing character, attractive aroma, and typical bitter taste [9]. Thus, the determination of xanthohumol in beer is important.

Xanthohumol has been quantified in beer by high performance liquid chromatography (HPLC) with ultraviolet (UV) detection [10] and mass spectrometry (MS) [4,11], or high performance thin layer chromatography (HPTLC) with UV detection [12]. The MS offered sufficient sensitivity and selectivity for quantitative analysis, but the instrument is expensive. Comparatively speaking, the HPLC–UV apparatus can be easily obtained and used conveniently.

Before HPLC– or HPTLC–UV analysis, the enrichment step is required for determination of trace amount of xanthohumol in beer samples. This was usually performed by liquid–liquid extraction (LLE) [12] or solid phase extraction [10]. Unfortunately, these methods usually are time-consuming or expensive. In particular, the traditional LLE method brings harm to analyst health because large amounts of toxic and volatile organic solvents are required. Therefore, a simple, rapid, less labor-intensive and green extraction method is needed.

Compared with conventional solvent extraction, cloud point extraction (CPE) is an interesting alternative because its high extraction efficiency and enrichment factor, and it requires simple instrument setup and non-toxic organic solvent [13]. Another important merit is that there is no or very little loss of analytes because it is unnecessary to evaporate solvent [14].

CPE is based on the fact that the aqueous solution of nonionic surfactant presents clouding behavior when the experimental temperature is appropriately altered [15]. The critical temperature, called "cloud point" depends on the amphiphile nature and concentration of surfactant [16]. When the temperature rises above the cloud point, the solution is separated into two distinct phases: a surfactant-rich phase and an aqueous phase. The hydrophobic analytes are extracted into the surfactant-rich phase. Compared to

* Corresponding author. Tel.: +86 431 85168399; fax: +86 431 85112355.
E-mail address: dinglan@jlu.edu.cn (L. Ding).

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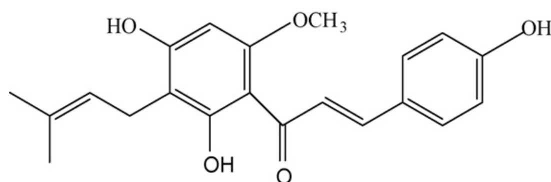

Fig. 1. Chemical structure of xanthohumol.

the initial sample solution volume, the surfactant-rich phase volume is very small, thus a high enrichment factor can be obtained. This leads to an enhanced sensitivity of the analysis without further sample clean-up or evaporation steps [17]. The CPE method has been applied to extract a wide range of analytes from biological, environmental and food samples [18–23].

In this paper, we first report the application of CPE using Triton X-114 as the extraction medium to extract xanthohumol from beer followed by HPLC–UV analysis. All significant variables for CPE were studied including the Triton X-114 concentration, pH, sodium chloride concentration, equilibration temperature and time. The developed method was successfully applied to determine xanthohumol in different beer samples, which demonstrated the feasibility of CPE.

2. Experimental

2.1. Reagents and samples

The standard of xanthohumol was purchased from Sigma–Aldrich (St. Louis, MO, USA). The stock standard solution of xanthohumol (1.0 mg mL^{-1}) was prepared by dissolving an appropriate amount of this compound in methanol. The solution was stored in a refrigerator and found to be stable for 1 month. The working standard solution was prepared daily by diluting the stock standard solution with water.

The nonionic surfactant Triton X-114 was purchased from Sigma–Aldrich. Sodium chloride, sodium hydroxide and hydrochloric acid were of analytical grade and purchased from Beijing Chemical (Beijing, China). Chromatographic grade methanol and acetic acid were obtained from Fisher (Pittsburgh, PA, USA). High purity water with resistivity of 18.2 MΩ cm^{-1} was obtained from a Milli-Q water system (Millipore, Billerica, MA, USA).

Different kinds of beer samples were purchased from the local market. The producing area, original gravity and alcohol degree of these samples are shown in Table 1. Among them, sample 1 was chosen randomly as a representative example in optimization of CPE conditions and validation of the method. In order to demonstrate the applicability of the proposed method, other beer samples were analyzed and used in recovery study.

Table 1
The producing area, original gravity and alcohol degree of beer samples.

Beer sample number	Producing area	Original gravity (°P)	Alcohol degree (%)
Sample 1	Qingdao, China	11	3.7
Sample 2	Qingdao, China	10	3.6
Sample 3	Qingdao, China	10	3.6
Sample 4	Changchun, China	10.5	4.0
Sample 5	Changchun, China	10	4.5
Sample 6	Beijing, China	11	3.7
Sample 7	Beijing, China	10	4.0
Sample 8	Haerbin, China	10.5	4.0
Sample 9	Haerbin, China	10	4.4
Sample 10	Haerbin, China	10	3.6
Sample 11	Siping, China	10	3.6
Sample 12	Tangshan, China	11	4.0

2.2. Apparatus

Chromatographic analysis was performed on an Agilent 1100 liquid chromatograph (Palo Alto, CA, USA) which was equipped with a quaternary pump, a heated column compartment, a UV detector, a LC workstation and a 7725 injection valve. A ZORBAX Bonus-RP C18 column (250 mm × 4.6 mm I.D., 5 μm) was used as an analytical column (Palo Alto, CA, USA).

A KQ3200E ultrasonic apparatus (Kunshan Instrument, Kunshan, China) was used to degas the beer samples. A DK-98-IIA thermostatic bath (Taisite, Tianjin, China) was used to implement the CPE. A SH-36 vortex mixer (Zhenghui, Shanghai, China) was used to mix the CPE solution. A SC-3610 centrifuge (Keda, Beijing, China) was used to accelerate the phase separation process.

2.3. CPE procedure

The beer sample (8.0 mL) was added into a centrifugal tube and degassed by ultrasound for removing the foam, and then the pH was adjusted to 5.0 with 0.1 mol L^{-1} hydrochloric acid. The Triton X-114 (0.2 mL) and sodium chloride (1.2 g) were also added into the centrifugal tube. The mixture was stirred in the vortex for 2 min, and then incubated in the thermostatic bath at 70 °C for 10 min. The phase separation was then accelerated by centrifugation at 4000 rpm for 5 min. The lower aqueous phase was carefully removed by using a syringe with a long needle. The surfactant-rich phase was left in the tube and diluted to 0.5 mL with mobile phase. Then, 20 μL of the diluting surfactant-rich phase was directly injected into the HPLC system for subsequent analysis.

2.4. HPLC–UV analysis

The separation and determination of xanthohumol were carried out by a HPLC–UV system. The mobile phase of methanol–0.5% acetic acid aqueous solution (80:20, v/v) was used. The flow rate was 1.0 mL min^{-1}. The column temperature was 30 °C and the injection volume was 20 μL. The xanthohumol was monitored at the wavelength of 370 nm.

3. Results and discussion

3.1. Optimization of the CPE conditions

The use of CPE for the separation and preconcentration of organic compounds is a useful alternative with the following characteristics: (a) surfactants are less toxic; (b) the experimental operation is simple; (c) no or very little loss of analytes due to no evaporation step; (d) surfactant-rich phase is compatible with the mobile phase used in HPLC and (e) the preconcentration factor can be optimized by modifying the type and concentration of surfactant as well as other experimental conditions [24].

Triton X-114 was chosen as the CPE medium because its low cloud point temperature and high density which facilitate phase separation by centrifugation [24]. Moreover it is easily commercially available and has been successfully applied for the separation and preconcentration of organic compounds before HPLC analysis, such as phthalate esters [25], polycyclicaromatic hydrocarbons [26], estrogens [27], malachite green [28] and crystal violet [28]. Other parameters affecting the performance of the CPE, such as the Triton X-114 concentration, pH, sodium chloride concentration, equilibration temperature and time, were investigated. All experiments were performed using beer sample 1. The extraction yield

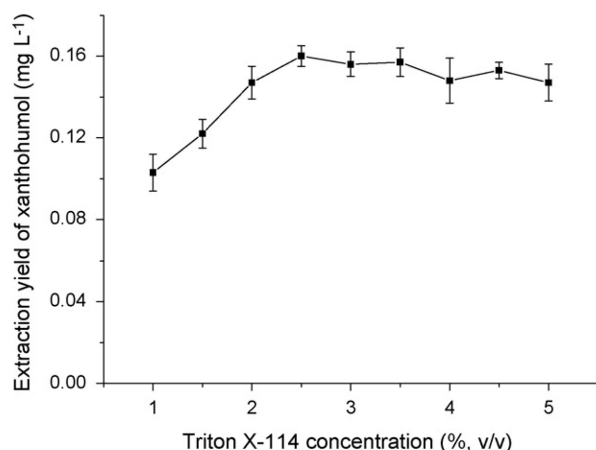

Fig. 2. The effect of Triton X-114 concentration on the extraction yield of xanthohumol ($n = 3$). Other extraction conditions: pH, 5.0; 15% (w/v) of sodium chloride concentration; 70 °C of equilibrium temperature and 10 min of equilibrium time.

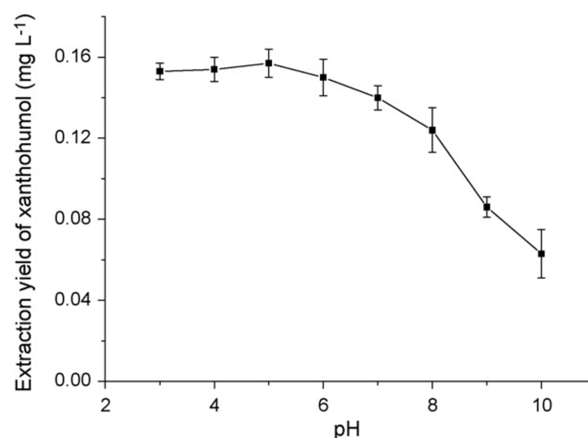

Fig. 3. The effect of pH on the extraction yield of xanthohumol ($n = 3$). Other extraction conditions: 2.5% (v/v) of Triton X-114 concentration; 15% (w/v) of sodium chloride concentration; 70 °C of equilibrium temperature and 10 min of equilibrium time.

of xanthohumol was defined as follows:

$$\text{extraction yield of xanthohumol (mg/L,w/v)} = \frac{\text{mass of xanthohumol extracted from beer}}{\text{volume of beer}}$$

3.1.1. Effect of Triton X-114 concentration

As it is well known, surfactant concentration above the critical micellar concentration is required to achieve the cloud point of the system [22]. The surfactant concentration should be large enough to lead the higher extraction yield. However, the ratio between the volume of aqueous solution to be preconcentrated and the surfactant-rich phase volume increases with the decrease of the surfactant concentration [29]. This shows that the smaller the surfactant concentration, the higher the preconcentration factor [30].

The effect of Triton X-114 concentration from 1.0% to 5.0% on the extraction yield was investigated (v/v, Fig. 2). The extraction yield of xanthohumol increased with the increase of surfactant concentration from 1.0% to 2.5%. The Triton X-114 with small concentration was not enough for the complete extraction. When large concentration of surfactant was used, the surfactant-rich phase obtained after CPE was too sticky and more difficult for subsequent handling. Considering the extraction yield of xanthohumol and maneuverability, 2.5% (v/v) was chosen as the optimum surfactant concentration for further studies.

3.1.2. Effect of pH

The ionic form of analyte does not interact with the micellar aggregate as strongly as its neutral form, and a smaller amount of the analyte is therefore extracted [31]. Thus, pH should be adjusted to ensure that the neutral molecular form of the analyte is present prior to performing the CPE. The effect of pH which was adjusted with 0.1 mol L^{-1} hydrochloric acid or sodium hydroxide on the extraction yield of xanthohumol was studied over the pH range 3.0–10.0 (Fig. 3). The experimental result indicated that the extraction yield of xanthohumol was relative high over the pH range 3.0–6.0. Moreover, the actual pH of beer analyzed in this study is around 5. In the following experiments, the pH was controlled at 5.0 for easy adjustment.

3.1.3. Effect of sodium chloride concentration

The addition of salt can facilitate the phase separation process for some nonionic surfactant systems, since it increases the density of the bulk aqueous phase [32,33]. When the salt concentration is increased, the micelle size and the aggregation number are increased, but the critical micellar concentration remains constant [34]. Available electrolyte also can change the cloud point temperature of nonionic surfactant. The salting-in and salting-out effects can be used to interpret the electrolyte effects on the cloud point of nonionic surfactant [35]. In addition, hydrophobic analyte may become less soluble in the aqueous solution at higher salt concentration and thus contribute to higher extraction yield [22,29].

To study the influence of the electrolyte, different concentrations of sodium chloride ranging from 5% to 25% (m/v) were investigated (Fig. 4). It was observed that the extraction yield of xanthohumol increased with the increase of the sodium chloride concentration from 5% to 15%, and no significant difference was observed above 15%. The sodium chloride concentration of 15% (m/v) was chosen in this study.

3.1.4. Effect of equilibrium temperature

It is known that two phases are formed when aqueous solution of a nonionic surfactant is heated above the cloud point temperature [36]. As the equilibration temperature increases, the volume of the surfactant-rich phase decreases because hydrogen bonds are disrupted and dehydration occurs [22]. The amount of water in a surfactant-rich phase also decreases. The effect of temperature on

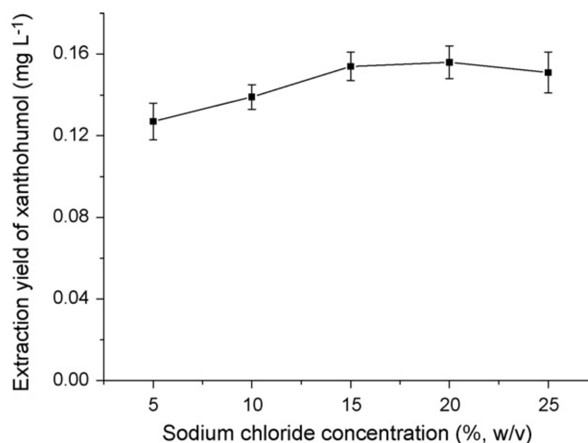

Fig. 4. The effect of sodium chloride concentration on the extraction yield of xanthohumol ($n = 3$). Other extraction conditions: 2.5% (v/v) of Triton X-114 concentration; pH, 5.0; 70 °C of equilibrium temperature and 10 min of equilibrium time.

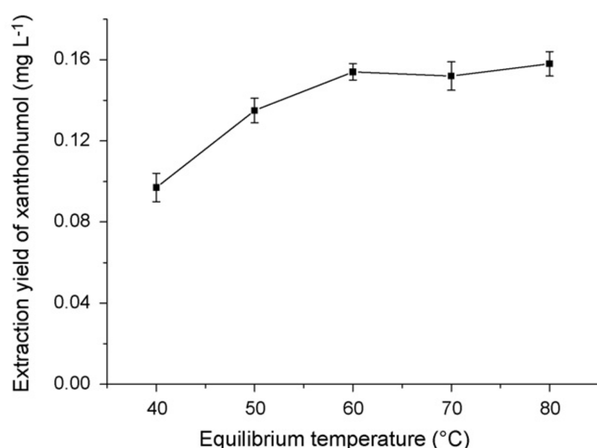

Fig. 5. The effect of equilibrium temperature on the extraction yield of xanthohumol ($n=3$). Other extraction conditions: 2.5% (v/v) of Triton X-114 concentration; pH, 5.0; 15% (w/v) of sodium chloride concentration and 10 min of equilibrium time.

the extraction yield was studied in the range of 40–80 °C (Fig. 5). When the temperature changed from 40 to 60 °C, the extraction yield of xanthohumol increased from 0.097 to 0.154 mg L^{-1}. No significant increment in the extraction yield was observed for higher temperature from 60 to 80 °C. Based on these results, 70 °C was selected as the equilibrium temperature for obtaining the complete extraction.

3.1.5. Effect of equilibrium time

The extraction yield depends on the time that the analyte has to interact with the micelles and get into their core [37]. On the other hand, fast sample preparation procedure is preferred in order to increase the sample throughput of the technique. The effect of the equilibrium time from 5 to 20 min on the extraction yield was investigated (Fig. 6). The extraction yield of xanthohumol increased with the increase of the equilibrium time from 5 to 10 min and did not change from 10 to 20 min. In this work, the equilibrium time of 10 min was chosen. The procedure was then accelerated by centrifugation at 4000 rpm for 5 min, which was enough to get a complete phase separation.

3.2. Preconcentration effect of CPE for xanthohumol

In this study, 2.5% Triton X-114 (pH 5) was chosen for the extraction of xanthohumol from beer samples by CPE technique. The

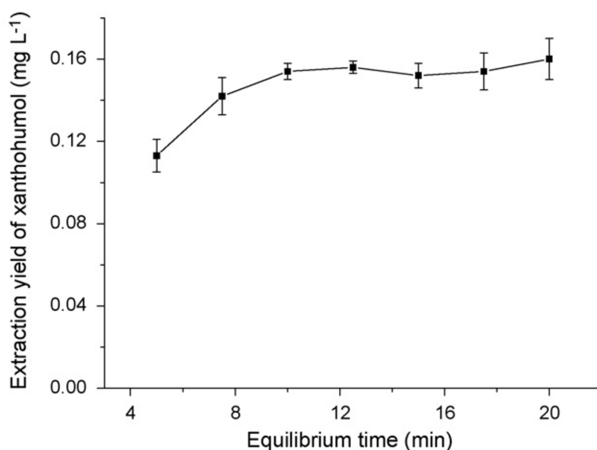

Fig. 6. The effect of equilibrium time on the extraction yield of xanthohumol ($n=3$). Other extraction conditions: 2.5% (v/v) of Triton X-114 concentration; pH, 5.0; 15% (w/v) of sodium chloride concentration and 70 °C of equilibrium temperature.

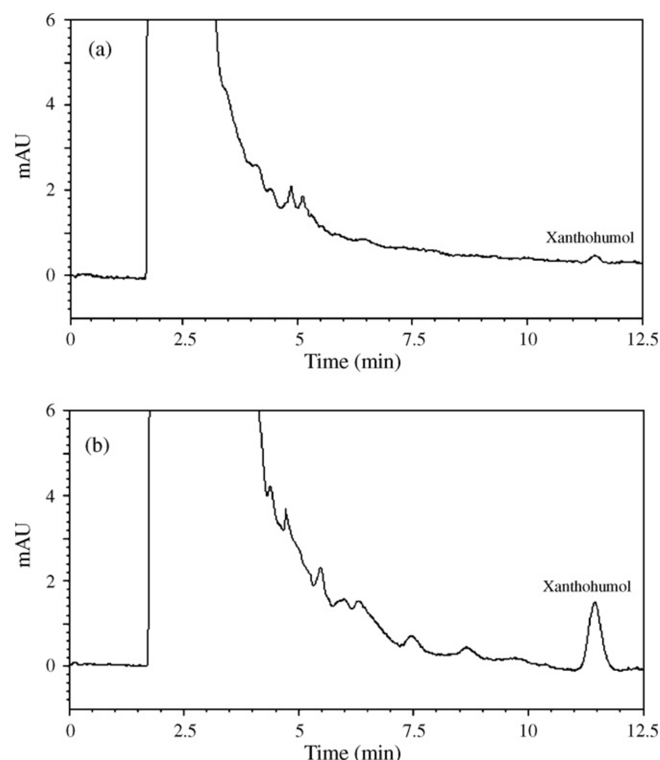

Fig. 7. HPLC chromatograms of the xanthohumol in beer sample 1 prior to CPE (a) and in the surfactant-rich phase after CPE (b). The retention time of xanthohumol was 11.5 min.

separation of the two phases (surfactant-rich phase and aqueous phase) was completed in a few minutes with the help of centrifugation after equilibrium 10 min at 70 °C and adding 15% sodium chloride. The preconcentration effect of the CPE is clearly demonstrated in Fig. 7. Fig. 7a shows a chromatogram of xanthohumol in beer sample 1 prior to CPE. Fig. 7b shows a chromatogram of preconcentrated xanthohumol in the surfactant-rich phase after CPE. The preconcentration factor for this compound is 16.

3.3. Analytical performance

The calibration curve was constructed by analyzing 8.0 mL of xanthohumol standard solution which was prepared in acidified aqueous solution (pH 5) varied in the concentration of 0.01–10 mg L^{-1}. The analytical procedure was the same as the CPE procedure for beer sample mentioned in Section 2.3. The correlation coefficient obtained is 0.999. The limit of detection (LOD)

Table 2
The contents of xanthohumol in different beer samples and the recovery test results.

Beer sample	Original amount (mg L^{-1})	Added amount (mg L^{-1})	Found amount (mg L^{-1})	Recovery (%)
Sample 1	0.153	0.150	0.292	92.8
Sample 2	0.395	0.150	0.538	98.2
Sample 3	0.628	0.150	0.753	96.0
Sample 4	0.325	0.150	0.471	98.8
Sample 5	0.273	0.150	0.414	96.7
Sample 6	0.052	0.150	0.198	92.3
Sample 7	0.214	0.150	0.368	101.9
Sample 8	0.155	0.150	0.299	96.1
Sample 9	0.163	0.150	0.305	95.1
Sample 10	0.054	0.150	0.199	90.7
Sample 11	0.097	0.150	0.243	95.9
Sample 12	0.227	0.150	0.379	100.9

Table 3
Comparison of the proposed method with other methods used in the literatures for analyzing xanthohumol in beer samples.

Sample preparation	Analytical method	LOD ($mg\,L^{-1}$)	LOQ ($mg\,L^{-1}$)	Linear range ($mg\,L^{-1}$)	Recovery (%)	Precision (RSD, %)	Xanthohumol content ($mg\,L^{-1}$)	Simultaneous quantification	Cost	Reference
Direct injection after degassing	HPLC–MS/MS	0.006	0.02	0.01–100	n.r.	n.r.	0.04–0.09 (four samples), not detected (two samples)	Isoxanthohumol, 8-prenylnaringenin, iso-α-bitter acids, α-acids, β-acids	Instrument is expensive	[4]
Direct injection after degassing	HPLC–MS/MS (internal standard was used in calibration)	n.r.	n.r.	0.01–1.0	90–102	3.8	0.002–0.69 (twelve samples), Not detected (one sample)	Isoxanthohumol, 8-Prenylnaringenin, 6-Prenylnaringenin, 6-Geranylnaringenin	Instrument is expensive	[11]
LLE after degassing	HPTLC–UV	0.2	0.5	0.77–7.70	95.7–119.1	1.7–2.3	n.r.	No	Instrument is not expensive	[12]
CPE after degassing	HPLC–UV	0.003	0.01	0.01–10	90.7–101.9	4.6–6.3	0.052–0.628 (twelve samples)	No	Instrument is not expensive	The proposed method

n.r., not reported.

and limit of quantification (LOQ), defined as the concentration corresponding to a signal equal to three and ten times the standard deviation of the blank, are 0.003 and 0.01 $mg\,L^{-1}$.

The intra-day precision was evaluated by assaying beer sample 1 under the optimal conditions six times in 1 day. The extraction yields of xanthohumol obtained were 0.152, 0.159, 0.148, 0.161, 0.142 and 0.155 $mg\,L^{-1}$. The inter-day precision was evaluated by assaying this sample once a day on six consecutive days. The extraction yields of xanthohumol obtained were 0.152, 0.143, 0.161, 0.150, 0.171 and 0.154 $mg\,L^{-1}$. The intra- and inter-day precisions expressed as relative standard deviations (RSDs) are 4.6% and 6.3%, respectively.

3.4. Application of the method

In order to demonstrate the applicability of the proposed method, it was used for determination of xanthohumol in various beer samples (Table 2). The contents of xanthohumol in these beer samples were in the range of 0.052–0.628 $mg\,L^{-1}$. The recovery study was then carried out by spiking beer samples with xanthohumol standard at level of 0.150 $mg\,L^{-1}$. The recoveries of xanthohumol from 90.7% to 101.9% were obtained.

3.5. Comparison of the proposed method with other methods used in the literatures

The analytical results obtained by the proposed method were compared with those obtained by the methods used in the literatures for analyzing xanthohumol in beer samples. The results presented in Table 3 indicated that the proposed method provided similar recovery and precision, and similar or higher sensitivity. The HPLC–MS/MS technique served as an effective analytical tool for analyzing xanthohumol and its related compounds in beer with simple sample preparation [4,11]. But the HPLC–MS/MS instrument is expensive and not can be easily obtained from common analytical laboratory when it was compared with HPLC–UV. Large amount of organic solvent (400 mL of diethyl ether) was required by the LLE–HPTLC–UV method [12].

Xanthohumol contents in beer samples obtained in this study were not in agreement with those obtained in other studies [4,11]. This is because the producing areas of the beer samples analyzed in these studies were different.

4. Conclusions

The proposed analytical method based on CPE proved to be effective for extraction and preconcentration of xanthohumol in beer samples. Under optimized conditions, the enrichment factor of 16 was obtained for the target analyte allowing reaching the low detection limit of 0.003 $mg\,L^{-1}$. An important aspect should be pointed out that is no organic solvent consumption in the CPE process, which turns it into a low cost and environmentally friendly technique.

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