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Short communication

Determination of soluble sugar profile in rice

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ABSTRACT

Soluble sugars in rice are the main components affecting sweetness taste of rice. In this paper, an accurate, precise and rapid method for simultaneous determination of multi soluble sugars in rice by using ion chromatography equipped with pulsed amperometric detector was presented. Pretreatment and parameters of ion chromatography and pulsed amperometric detector were optimized. Regression coefficients (R) of 0.9998, 1.0000, 0.9979, 0.9998 and 0.9998 were obtained for glucose, fructose, sucrose, raffinose and maltose, respectively. The recovery ranges of five sugars were 92.9–112.0% for milled rice matrix. Repeatability and reproducibility of the method were 0.8–9.7% and 1.9–7.6%, respectively. Method LODs of 3.1–34.6 μg g^{-1} were obtained for soluble sugars in milled rice matrix.

1. Introduction

Rice is one of the most important staple foods for world population [1]. The taste of rice is primarily associated with soluble components such as soluble sugars and amino acids. It was reported that soluble sugars in rice such as glucose and sucrose are the main components affecting sweetness taste of rice [2,3]. Hence, soluble sugar content and profile is an important index to rice quality especially taste quality. Sucrose, glucose, fructose, maltose and raffinose are the major soluble sugars in rice [4–6]. It's necessary to assess the soluble sugar profile of rice kernels for rice quality assessment.

There are many methods reported to determine sugar content in food [7,8]. Hydrometer [9], refractometer [10] were used to measure the total sugar content. Electronic tongue[2,11] and near infrared spectroscopy (NIR) [12] were also applied for assessing the sweetness of samples. However, the results were strongly influenced by the prediction training. High pressure liquid chromatography(HPLC) [9,13], gas chromatography (GC) [14] and capillary electrophoresis were also used to determine sugar content in samples. As sugars do not absorb ultraviolet or visible wavelengths, it is not possible to determine sugars using HPLC with ultraviolet-visible detector unless proper derivatization was implemented. Evaporative light-scattering detector (ELSD) and differential refractive index detector (RID) are universal detectors, hence they were widely used for sugar analysis, needing no derivatization [9–12]. ELSD is based on the ability of particles to cause photon scattering, and hence, it can detect most compounds less volatile than mobile phase [9]. However, high purity quality of mobile solution was required for stable baseline. ELSD calibration response curve is non-linear which might cause errors in quantification [7]. Furthermore, it possesses relatively low sensitivity, and consequently is not suitable for trace analysis. RID works as a differential refractometer that measures the difference in refraction index of eluent induced by solute [15]. The signal is highly dependent on wavelength, temperature and density of solute, hence gradient elution is not applicable to RID. Pulsed amperometric detector (PAD) is also used for detecting sugars and fructan in fruit and vegetable extracts. Compared to ELSD and RID, PAD is seen to more sensitive and reliable as a detector for carbohydrates. Besides, PAD is not sensitive to the changes of mobile solution. Hence, PAD is a more suitable detector for sugar analysis. As aqueous solution is much more appropriate for electron conductivity during redox at the electrodes than organic solution, PAD is usually coupled with ion chromatography (IC) [16–18]. IC-PAD method has been applied for sugar analysis in inulin [17,18], olive plant [19], rice wine [20], raw sugar [21]. However, it has not been applied for sugar analysis in rice. Soluble sugars in rice were extracted and concentrated before introduced into HPLC with RID [2,6], making the determination tedious.

This work reported a sensitive and reliable method for determining multi soluble sugars in rice by using IC-PAD. The pretreatment for rice sample and the condition for separation and detection were optimized. The performance of the IC-PAD method was investigated.

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2. Material and methods

2.1. Chemicals and materials

High-purity (≥99%) glucose, fructose and sucrose were obtained from National Institute of metrology, China. High-purity (≥99%) maltose and raffinose were purchased from Dr. Ehrenstorfer GmbH, Germany. 30% sodium hydroxide aqueous (NaOH) were purchased from Merck KGaA, Germany. All solutions were prepared with deionized water using a Millipore advantage 10 system (Millipore Co. USA).

2.2. Rice samples and pretreatment

Five rice samples were provided by Rice Product Quality Supervision and Inspection Center, Ministry of Agriculture. Before testing, rice samples were husked. Then half of husked rice sample were milled until most of bran and part of embryo had been removed. After that, both husked rice samples and milled rice samples were ground into flour by using a Cyclotec 1093 sample mill(Foss Tecator, Sweden). The rice flour samples were stored in −20 °C before use.

During extraction, an aliquot of flour sample (0.25 g for husked rice flour while 0.5 g for milled rice flour) was weighed and extracted with 10 mL of 50% ethanol aqueous solution. The mixture was kept on a mechanical shaker for 30 min at the room temperature. After centrifuged at 3000 rpm for 10 min, the supernatant was collected. The process was repeated twice and supernatants collected were evenly mixed. Finally, the mixed supernatant was filtered through a 0.45 μm filter and ready for the following measurement.

2.3. Determination of soluble sugars

Soluble sugars were determined by 850 Professional IC equipped with 871 Advanced Bioscan (Metrohm, Shanghai, China). IC separation was performed on a Metrosep Carb 1 column (5.0 μm, 150 mm × 4.0 mm) with a Metrosep guard column. The isocratic mobile phase was consisted of solvent A (250 mmol L^{-1} NaOH) and solvent B (H_2O) at a ratio of 40:60. The flow rate for mobile phase solution was 1 mL min^{-1}. The eluted analytes were detected and quantified by an 871 Advanced Bioscan with PAD mode (Metrohm, Shanghai, China). Gold electrode and Ag/AgCl electrode were used as working electrode and reference electrode, respectively. The detail parameters for PAD was as following: E_1 = 0.1 V, t_1 = 0.4 s, E_2 = 0.7 V, t_2 = 0.2 s, E_3 = −0.1 V, t_3 = 0.4 s, t_{sample} = 40 ms. Here, E_1, E_2, and E_3 were defined as the detection potential, oxidation cleaning potential and reduction cleaning potential, respectively, and t_1, t_2 and t_3 represented time duration to apply E_1, E_2 and E_3, respectively. T_{sample} was defined as detection time at the end of E_1.

3. Results and discussion

3.1. Sample pretreatment

Three extraction methods were compared by repeating extraction for twice. With shake treatment method, the mixture was kept on a mechanical shaker for 30 min. The mixture was treated with ultrasonic for 30 min in ultrasonic treatment method. However, it was found that sample flour was deposited at the bottom of centrifuge tube due to gravity during ultrasonic treatment. Hence, in ultrasonic and shake treatment method, the mixture was kept in an ultrasonic instrument for 30 min during which the mixture was shook with a vortex shaker for 5 times to avoid sample flour being deposited at the bottom. The results were showed in Fig. 1a. It was found that ultrasonic treatment method resulted in the lowest sugar content. It was mainly because of incomplete extraction caused by the deposition of sample flour at the bottom. Shake treatment method resulted in highest contents of all sugars except sucrose content. The highest sucrose content was

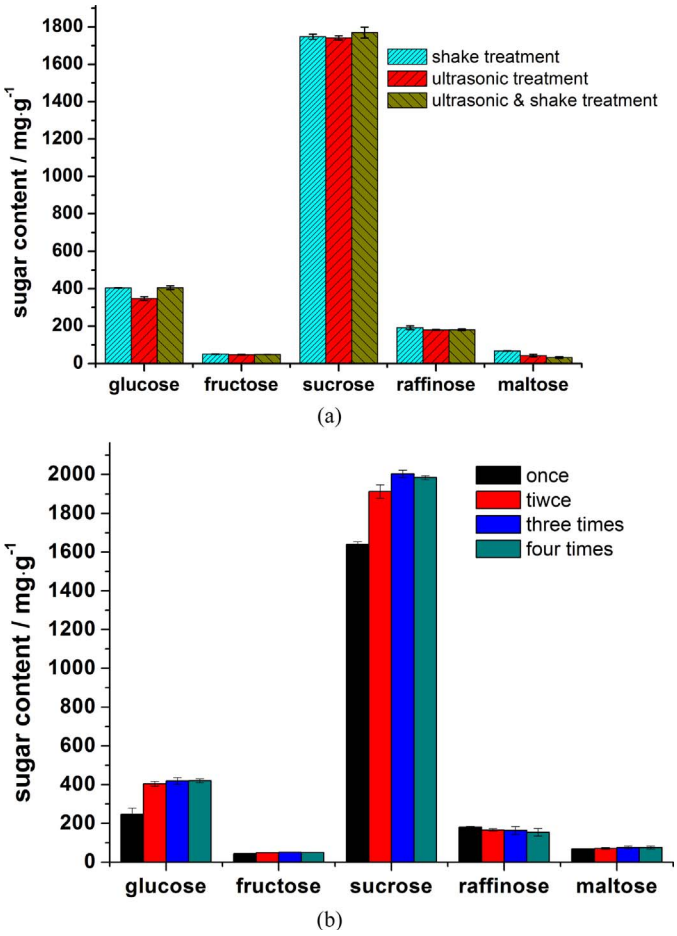

Fig. 1. Influence of pretreatment on the final result. (a) Sugar contents obtained with three sample extraction methods; (b) sugar contents obtained with different times.

obtained by using ultrasonic and shake treatment method. However, the operation of ultrasonic and shake treatment method is quite cumbersome. Hence, shake treatment method was chosen taking account of extraction efficiency and ease of operation.

The number of extraction times was also investigated. With extraction times increased from 1 to 2, glucose, fructose, sucrose and maltose content increased while raffinose content decreased (Fig. 1b). However, the increase flatted when extraction times increased from 2 to 4. Hence, the extraction was repeated twice in the following work.

3.2. Detection potential

Detection potential had great effect on the signals of object sugars (Fig. 2a). The peak areas of glucose and fructose increased rapidly with the detection potential increased from −0.05 V to 0.1 V, and then leveled off. Similar trends were observed for other three sugars, except for the turning points of 0.2 V for sucrose and raffinose, and 0.05 V for maltose. Meanwhile, detection potential affect the baseline and baseline noise as well. As seen from Fig. 2b, sharp decline of baseline drift in 30 min was observed with detection potential increased from −0.05 to 0.05 V, and then it leveled off at the detection potential of 0.05–0.20 V, and finally the baseline drift increased with the increase of detection potential up to test voltage. A lowest baseline drift was obtained at the detection potential of 0.1 V. The baseline noise sharply decreased with the increase of detection potential up to 0.1 V, and then sharply increased again with the increased of detection potential up to test voltage. A lowest of baseline noise was obtained at detection potential of 0.1 V. Hence, a detection potential of 0.1 V was employed to balance signal sensitivities of all sugars and baseline condition.