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Simple and sensitive method for determination of glycoalkaloids in potato tubers by high-performance liquid chromatography with chemiluminescence detection

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Abstract

A novel, simple and sensitive high-performance liquid chromatographic method for the determination of the potato glycoalkaloids, α-solanine and α-chaconine, based on the chemiluminescent reaction of tris(2,2′-bipyridine)ruthenium(III) has been developed. The calibration graph was linear in the range of 5 ng/ml–10 μg/ml for both α-solanine and α-chaconine. The detection limits of α-solanine and α-chaconine were 1.2 and 1.3 ng/ml, respectively. This method was successfully applied to a potato tuber sample without cleanup, pre-concentration, and derivatization steps. The recoveries (mean ± standard deviation, %) of α-solanine and α-chaconine spiked in tuber pith at 10 μg/g ($n = 6$) were 101.0 ± 4.4% and 103.6 ± 7.1%, respectively.

Keywords: Potato glycoalkaloids; α-Solanine; α-Chaconine; Chemiluminescence; $Ru(bpy)_3^{3+}$; HPLC

1. Introduction

Glycoalkaloids (GAs) are naturally occurring compounds in all parts of the potato plant. Major GAs in tubers of commercial potato varieties representing 95% or more of total GAs are α-solanine and α-chaconine (Fig. 1) [1]. The generally accepted safe upper limit for GAs in potato tubers in the USA is 20 mg of total GAs per 100 g of tuber. Consumption of potato containing higher than normal levels of GAs is associated with human deaths and poisonings and a lot of livestock deaths [2]. In the potato plant high concentrations of GAs occur in the peel of the tuber, in the sprouts, and in the flowers [1]. The concentration of GAs in tubers also increases in response to a number of factors, including physical injury, poor growing conditions, climate, and storage conditions [1,3]. It has long been known that exposure of tubers to light can rapidly cause a large increase in GAs concentrations [4]. This can occur during growth, transport, and storage. Therefore, there is a strong need for a method to monitor the GAs in potato.

A number of methods, such as gas chromatography [5], high-performance liquid chromatography (HPLC) [4,6–8] enzyme immunoassay [9], high-performance thin-layer chromatography [10], capillary isotachophoresis [11], and enzyme biosensor [12], have been used for the determination of GAs in potato. HPLC separation and UV detection method is now becoming the most widely used method, because it is rapid, accurate, and reproducible. However, GAs do not have a suitable UV chromophore, and therefore absorbance is measured at around 200 nm, where many compounds absorb light. This drawback dictates the need for relatively large sample sizes and a sample cleanup to overcome background noise.

In recent years, the chemiluminescent reaction of tris (2,2′-bipyridine)ruthenium(III), $Ru(bpy)_3^{3+}$, has received considerable attention in chemical analysis. This chemiluminescent reaction is useful for the determination of oxalate [13], aliphatic alkylamines [14], amino acids [15–17], and active methylene

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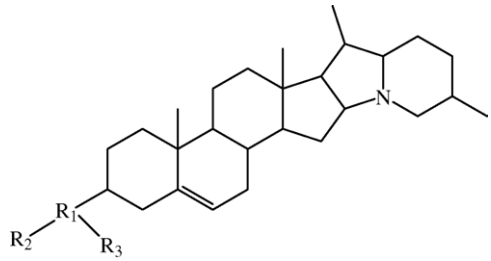

Fig. 1. The structure of α-solanine and α-chaconine present in potato. The suger group for α-solanine consists of R_1 = β-D-galactose, R_2 = β-D-glucose and R_3 = α-L-rhamnose, and R_1 = β-D-glucose, and $R_2 = R_3$ = α-L-rhamnose for α-chaconine.

compounds [18]. Many analytical applications of $Ru(bpy)_3^{3+}$ as a chemiluminescent reagent for flow injection analysis (FIA) [19], HPLC [20], capillary electrohoresis, and micro total analytical system (μ-TAS) [21] have been reported. Its analytical importance is shown in a certain number of recent reviews [22–25].

Since Noffsinger and Danielson first investigated the chemiluminescent reaction of $Ru(bpy)_3^{3+}$ with amine compounds, a large variety of compounds having an aliphatic tertiary amine moiety that is the most suitable reducing agents for the $Ru(bpy)_3^{3+}$ chemiluminescent reaction were detected by this chemiluminescent reaction [19–21]. α-Solanine and α-chaconine are trisaccharide glycosides with a common tertiary amine aglycone solanidine. Therefore, HPLC with chemiluminescence (CL) detection using $Ru(bpy)_3^{3+}$ can be expected to be applicable for determining α-solanine and α-chaconine.

In this study, we attempted to establish a simple and sensitive HPLC determination method of α-solanine and α-chaconine in potato based on the post-column $Ru(bpy)_3^{3+}$ CL detection system.

2. Experimental

2.1. Chemicals

α-Solanine and α-chaconine were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Stock standard solutions of α-solanine and α-chaconine were prepared in methanol at 0.2 mg/ml and kept in the dark and cool. The stock solutions were diluted with the mobile phase before use. Tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate ($Ru(bpy)_3Cl_2{\cdot}6H_2O$) was prepared according to a published procedure [26] in our laboratory. A 0.5 mM $Ru(bpy)_3^{2+}$ solution was prepared by dissolving a weighed quantity of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ in a 10 mM sulfuric acid or a 100 mM sodium sulfate containing 1 mM sulfuric acid. Water for all solutions was purified using a GS-200 automatic water distillation apparatus (Advantec, Tokyo, Japan) and then a Mill-QII water purification system (Millipore, Bedford, MA, USA). Acetonitrile was of HPLC grade (Wako Pure Chemical, Osaka, Japan). All other chemicals were of analytical reagent grade and used without further purification.

2.2. Apparatus

HPLC experiments were done with the CL detection system shown in Fig. 2. A HPLC assembly consisted of a GL Science PU611 pump (GL Science, Tokyo, Japan) equipped with a Ryeodyne 7125 sample injector (20 μl, Cototi, CA, USA) and Chromolith Performance RP-18e column (100 mm × 4.6 mm I.D., Merck, Darmstadt, Garmany). The $Ru(bpy)_3^{2+}$ solution was delivered with a CL Science PU 611 pump at a flow rate of 0.3 ml/min and oxidized to $Ru(bpy)_3^{3+}$ by the controlled-current electrolysis method (Galvanostat Comet 3000, Comet, Kawasaki, Japan). Because $Ru(bpy)_3^{3+}$ in an aqueous solution is unstable, the $Ru(bpy)_3^{3+}$ solution has to be prepared freshly from the $Ru(bpy)_3^{2+}$ solution before use. The eluent and $Ru(bpy)_3^{3+}$ solution were mixed and pumped continuously through the spiral flow cell in a comet 3000 chemiluminescence detector. Chromatograms were recorded with a Hitachi D-2500 Chromato-Integrator (Hitachi, Tokyo, Japan). The eluent and the $Ru(bpy)_3^{2+}$ solution were purged with a Shodex degass KT-355 of membrane type degasser (Showa Denko, Tokyo, Japan). All connecting PTFE tube was 0.5 mm I.D. UV detection was performed on a Hitachi L-4200 UV–VIS detector (Hitachi, Tokyo, Japan).

For FIA experiments, the column was removed from the system represented in Fig. 2. In the pH study, a 100 mM phosphate buffer was pumped with a GL Science PU611 pump at a flow rate of 0.1 ml/min in order to control the pH of the CL reaction and mixed with the carrier solution after the injector.

2.3. Sample preparation

Potato tubers were bought from a local supermarket. The tubers were rinsed in tap water and wiped with a clean cloth. One tuber (tuber A) was stored in the dark and the other tuber

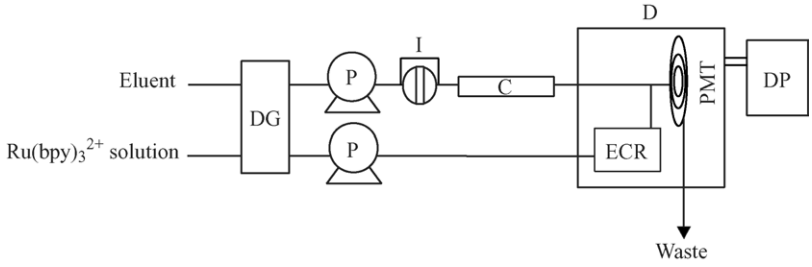

Fig. 2. Schematic diagram of the HPLC-CL system. P, pump; I, injector (20 μl); C, column; D, chemiluminescence detector; ECR, electrochemical reactor; PMT, photomultiplier tube (biased at 450 V); DP, data processor.

(tuber B) was exposed to the sunlight (tuber B) for 3 weeks. After 3 weeks, tuber B was greening. These tubers were divided into skin (about 1 mm thick) and pith (heart of tuber). Recovery experiments were made only with homogenized tuber pith with addition of 10 μg/g of α-solanine and α-chaconine (six replicates).

2.4. Extraction procedure

GAs were extracted in the same way from all kinds of sample. Extraction solution was 5% acetic acid in water. 0.1 g of sample and 10 ml of extraction solution were blended for 4 min. The resulting slurry was poured into a centrifuge tube, and then centrifuged at 3500 rpm for 10 min. The supernatant was filtered through a 0.45 μm filter. Prior to injection, skin sample extracts were diluted 1:20 and pith sample extracts were diluted 1:2 with the eluent and at that time the pH values of all solutions were adjusted to 7–8 with a 5 M sodium hydroxide. For UV detection, all extracts were diluted 1:2. A 20 μl aliquot was used for HPLC analysis.

3. Results and discussion

3.1. Chemiluminescence conditions

To develop the suitable CL conditions, some preliminary experiments were performed by FIA system.

The CL intensity for amine compounds is greatly affected by the pH of reaction condition [14]. The effects of pH on the CL intensity are shown in Fig. 3. As the pH of the effluent increased, the signal-to-noise (S/N) ratio increased significantly up to pH 6.4, and then decreased. In general, the CL intensity of the amines and amino acids increased as the pH became higher, showing that enhanced CL occurs when the pH is greater than the pK_a of the amine moiety [17]. However, hydroxide ion reacts with $Ru(bpy)_3^{3+}$ [28] and cause a high back ground as shown in Fig. 3. As a result, the best S/N ratio was obtained at pH 6.4. Hence, this effluent pH value was selected in further experiments.

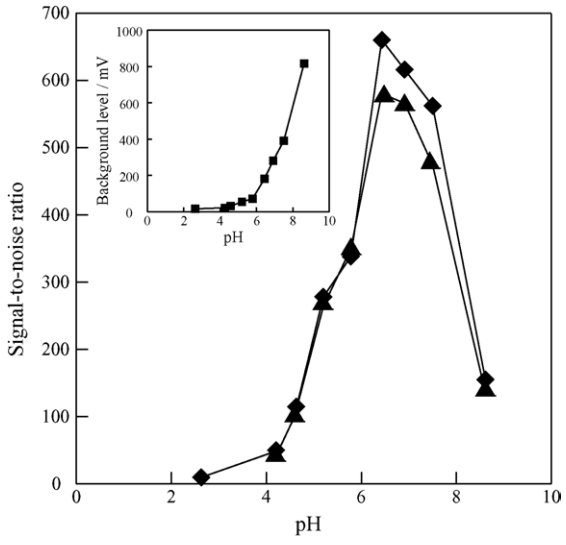

Fig. 3. Effect of the pH on the CL intensity for α-solanine and α-chaconine obtained by FIA. Sample: 100 ng/ml α-solanine (■), 100 ng/ml α-chaconine (▲). *Conditions*: carrier, water–acetonitrile (6:4, v/v); $Ru(bpy)_3^{2+}$ solution, 0.5 mM $Ru(bpy)_3^{2+}$ in a 100 mM sodium sulfate containing 1 mM sulfuric acid; buffer solution, 100 mM phosphate buffer, flow rate of carrier, 0.5 ml/min; flow rate of $Ru(bpy)_3^{2+}$ solution, 0.3 ml/min; flow rate of buffer solution, 0.1ml/min. Inset: Background level as a function of pH.

The $Ru(bpy)_3^{3+}$ solution has to be prepared from the $Ru(bpy)_3^{2+}$ solution before use. Three main methods were reported to obtain $Ru(bpy)_3^{3+}$ from $Ru(bpy)_3^{2+}$: chemical [14,21], photochemical [29], and electrochemical [13,15,16] oxidation. The electrochemical oxidation method has three modes, external, in situ solution, and in situ immobilized mode. W.-Y. Lee and T.M. Nieman have reported comparison of these three modes [30]. In this report, we have employed the external electrochemical oxidation method. The electrolytic current of a electrochemical reactor is one of important parameters for the oxidation of $Ru(bpy)_3^{2+}$. The effect of the electrolytic current of a electrochemical reactor on the CL intensity was characterized. In this experiment, the carrier was a 20 mM phosphate buffer (pH 6)–acetonitrile (65:35, v/v) and the 0.5 mM $Ru(bpy)_3^{2+}$ solution was prepared by a 100 mM sodium sulfate containing 1 mM sulfuric acid. The carrier and the $Ru(bpy)_3^{2+}$ solution were delivered at flow rates of 0.6 and 0.3 ml/min, respectively. With increasing the electrolytic current, both the CL intensity and noise-level increased. The CL intensity increased with increasing current up to at least 110 μA, while high S/N ratio was indicated at 50 μA. Hence, the electrolytic current was set at 50 μA in further experiments.

A maximum in CL intensity should be located at the point where the solution delivery rate matches the reaction rate. The effect of the flow rate on the CL intensity was characterized. In order to hold conversion efficiency from $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$, the flow rate of the $Ru(bpy)_3^{2+}$ solution was maintained at 0.3 ml/min. The flow rate of the carrier was varied. An increased CL intensity was observed up to 0.5 ml/min. Increasing the flow rate from 0.5 to 1.0 ml/min led to an almost constant CL intensity.

3.2. HPLC conditions

The HPLC separation conditions were examined using a mixture of α-solanine and α-chaconine based upon the results of the FIA studies (pH, electrolytic current, and flow rate). The retention mechanism of the GAs on reversed phase columns involves both hydrophobic interaction with alkyl chain and ion-exchange interaction with residual silanol groups on the silica packing. An ion-exchange process can result in peak tailing and excessive retention times. One approach to prevent or reduce the ion-exchange interaction is to use a low pH buffer, which inhibits the ionization of the silanol groups. Another approach is to use a high pH buffer, which depresses the protonation of the GA. As the optimal pH value of the CL reaction is about 6.5, the eluent was a 20 mM phosphate buffer (pH 7.8)–acetonitrile (65:35, v/v) and delivered at a flow rate of 0.6 ml/min. Because hydroxide ion reacts with $Ru(bpy)_3^{3+}$ to yield CL [28], it is unfit that

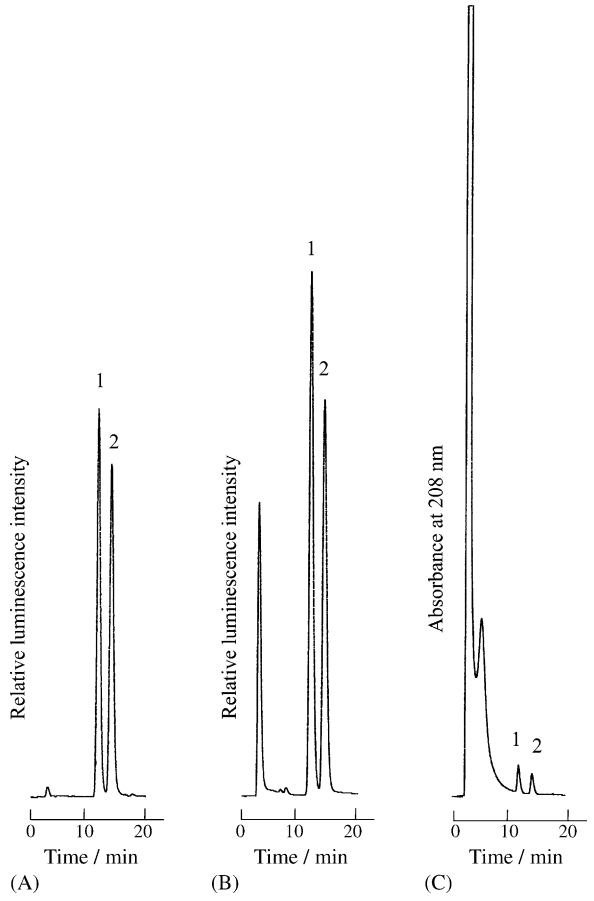

Fig. 4. Chromatograms obtained with CL detection for (A) a standard α-solanine and α-chaconine solution and (B) a 20 times diluted tuber B skin sample extract, and with UV detection for (C) a two times diluted tuber B skin sample extract. Peak identification: 1, α-solanine; 2, α-chaconine. Analyte concentration: (A) 1.00 μg/ml α-solanine and α-chaconine; (B) 1.27 μg/ml α-solanine and 1.09 μg/ml α-chaconine; (C) 11.9 μg/ml α-solanine and 10.7 μg/ml α-chaconine. *Conditions*: eluent, a 20 mM phosphate buffer (pH 7.8)–acetonitrile (65:35, v/v); $Ru(bpy)_3^{2+}$ solution, 0.5 mM $Ru(bpy)_3^{2+}$ in a 10 mM sulfuric acid; flow rate of eluent, 0.6 ml/min; flow rate of $Ru(bpy)_3^{2+}$ solution, 0.3 ml/min.

a $Ru(bpy)_3^{2+}$ solution is prepared in a high pH value solution. The $Ru(bpy)_3^{2+}$ solution was prepared in a 10 mM sulfuric acid and delivered at a flow rate of 0.3 ml/min. When the eluent and the $Ru(bpy)_3^{2+}$ solution were used, the pH of the effluent was near 6.5 and the separation of α-solanine and α-chaconine was achieved within 20 min. Fig. 4A shows a typical chromatogram of α-solanine and α-chaconine.

3.3. Calibration graphs, detection limits, and comparison with other methods

The calibration graphs for α-solanine and α-chaconine with HPLC-CL, using the peak area, were linear from 5 ng/ml to at least 10 μg/ml (coefficient of determination, $r^2 = 0.9999$). The relative standard deviations within a day tested with a concentration of 10 ng/ml α-solanine and α-chaconine were of 2.6 and 2.4% ($n = 6$), respectively. The detection limits of α-solanine and α-chaconine were of 1.2 ng/ml (1.4 nM, 28 fmol) and 1.3 ng/ml (1.5 nM, 30 fmol), respectively. The detection limits were calculated as three times the signal from the base line noise (S/N = 3). As can be seen from Table 1, the present method is more sensitive than previously reported methods.

Table 1
Comparison of the detection limit and the linear range for α-solanine using the present methodology with those of some previously reported techniques

Method	Detection limit	Linear range	Reference
GC-FID[a]	3 ng	–	[5]
HPLC-UV (208 nm)	–	1.0–50.0 μg/ml	[6]
HPTLC-FL[b]	10 ng	0.2–2 μg	[10]
Capillary ITP[c]	–	5–25 μg/ml	[11]
Enzyme biosensor	0.5 μM	0.5–100 μM	[12]
Present method	1.2 ng/ml (1.4 nM, 24 pg)	0.005–10 μg/ml	

[a] Flame ionization detector.
[b] Fluorescence detection.
[c] Isotachophoresis.

The drawback of the present method is the need continuously to deliver the expensive $Ru(bpy)_3^{3+}$ solution. Since $Ru(bpy)_3^{3+}$ can be electrochemically recycled, this problem has been solved by immobilizing $Ru(bpy)_3^{3+}$ on an electrode surface which cannot only minimizes the consumption of $Ru(bpy)_3^{3+}$, but also allow simple instrumentation [30].

3.4. Determination of GAs in potato

To test the applicability of the proposed HPLC method to real samples, α-solanine and α-chaconine in potato were determined. The most commonly used cleanup method for GAs determination by HPLC is solid-phase extraction (SPE). SPE is a powerful method to concentrate and purify the analytes of the complicated matrixes. However, it has been reported that main losses of GAs occurred during the SPE procedure inclusive of selected SPE sorbents and sorbent volume [6,7,31]. As the $Ru(bpy)_3^{3+}$ CL detection method was sensitive and selective, we applied this method to the determination of α-solanine and α-chaconine in potato without SPE procedure. Fig. 4B shows a chromatogram with CL detection obtained for a tuber B skin sample. The chromatogram indicates that well-defined peak would be obtained without SPE procedure.

There is a variety of extraction solutions employed in published methods. Most are based on a weak solution of acetic acid with the addition of other solvents or salts. In most cases, silica based octadecyl (C_{18}) sorbents have been used for SPE. Therefore, organic solvent requires removal before any SPE step as many organic solvents prevent adsorption of GAs onto C_{18} SPE sorbents. Heptanesulfonic acid as an ion-pair reagent was also used to enhance complete adsorption of GAs onto C_{18} SPE sorbents. However, SPE procedure is not necessary in the present method. Hence, several extraction solutions were examined in order to find suitable extraction for the present method. Fig. 5 shows the extraction profile of α-solanine and α-chaconine with different extraction solutions. As a result, the 5% acetic acid solution was employed as an extraction solution.

Fresh potato was assumed to have water content of 80% [27]. When a sample size is large, a volume change of an extraction

Table 2
Contents of α-solanine and α-chaconine in potato tubers[a]

Sample	Content (mg/100 g)					
	α-Solanine		α-Chaconine		Total GAs[b]	
	CL	UV	CL	UV	CL	UV
Tuber A						
Skin	21.8 ± 0.1	nd	48.4 ± 0.5	nd	70.1 ± 0.6	–
Pith	0.30 ± 0.01	nd	0.45 ± 0.01	nd	0.75 ± 0.01	–
Tuber B						
Skin	254 ± 1	233 ± 6	220 ± 2	213 ± 4	473 ± 3	447 ± 10
Pith	3.21 ± 0.08	nd	4.97 ± 0.15	nd	8.19 ± 0.20	–

CL, CL detection; UV, UV detection at 208 nm; nd, not detected.
[a] Values are means for four determination ± standard deviation.
[b] Total GAs = α-solanine + α-chaconine.

solution cannot be ignored. In the present procedure, the sample size (0.1 g) was small as against the extraction solution (10 ml). Therefore, the volume change of the extraction solution can be ignored. The volume change is less than or equal to 1%. The recoveries (mean ± standard deviation, %) of α-solanine and α-chaconine spiked in tuber pith at 10 μg/g ($n = 6$) were 101.0 ± 4.4% and 103.6 ± 7.1%, respectively.

In order to evaluate the sensitivity and selectivity of the proposed method, the same samples were analyzed using UV detection. The calibration graphs for α-solanine and α-chaconine with HPLC-UV detection at 208 nm were linear from 5 μg/ml to at least 100 μg/ml (coefficient of determination, $r^2 = 1$). α-Solanine and α-chaconine could be determined with UV detection for only tuber B skin sample. Fig. 4C shows a chromatogram with UV detection obtained for a tuber B skin sample.

Total GAs (α-solanine and α-chaconine) content of potato tubers are given in Table 2. Data of Table 2 shows that the content of the α-solanine and α-chaconine, as measured by the proposed method, was in agreement with that obtained by UV detection. There were significant differences between tuber A and tuber B. The skin and pith of green potato exposed to the sunlight contained more GAs in those of potato stored in the dark. It is clear that the concentration of GAs is affected by sunlight.

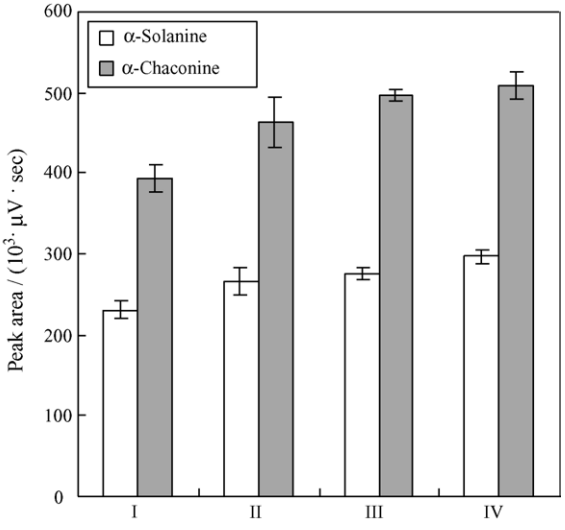

Fig. 5. Extraction profile of α-solanine and α-chaconine from potato tuber with different extraction solutions. (I) Water; (II) 0.1% acetic acid; (III) 1% acetic acid and (IV) 5% acetic acid. Values are means for four determination ± standard deviation.

4. Conclusions

This highly sensitive and selective detection method permits the HPLC determination of GAs in potato at a small sample size without any cleanup or concentration steps. Since the present method does not require a time-consuming sample preparation procedure prior to analysis, it is suitable for rapidly screening a large number of samples. As this CL detection method can be applied to other analytical instrument, such as capillary electrophoresis and μ-TAS, more rapid determination method should be developed. Other GAs, such as β-solanine, β-chaconine, γ-solanine, and γ-chaconine, will also be determined by this CL method, because they contain solanidine structure. In addition, when the $Ru(bpy)_3^{3+}$ solution was sprinkled on the cut surface of potato tubers, the emission of light was observed by visual observation in a darkroom. This result may be applicable for imaging of GAs distribution.

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