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Fluorescence determination of acrylamide in heat-processed foods

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ABSTRACT

A simple and rapid fluorescence method has been developed for the determination of acrylamide in heat-processed food samples. In the determination, acrylamide is degraded through Hofmann reaction to generate vinyl amine, and pyrrolinone is produced when the vinyl amine reacts with fluorescamine, resulting in a strong fluorescence emission at 480 nm. Hofmann reaction is a key step for the fluorescence determination of acrylaminde, and the reaction conditions are investigated and optimized. Under the optimal conditions, the fluorescence intensity increases with the increase of acrylamide concentrations. The linear range between the fluorescence intensity and the square-root of acrylamide concentrations is from 0.05 μg mL^{-1} to 20 μg mL^{-1} with the correlation coefficient R^2=0.9935. The detection limit is 0.015 μg mL^{-1} and the recovery for food samples is from 66.0% to 110.6%. In comparison with Specification of Entry&Exit Inspection and Quarantine Bureau of The People's Republic of China (SN/T 2281-2009), the method showed comparable results and demonstrated the accuracy of the method.

1. Introduction

With the development of society and the elevation of living standard, food security is receiving more and more attention. In 1994, acrylamide (AA) was stated with toxicity, probably carcinogenic to humans, by the International Agency for Research on Cancer (IARC) [1]. Since then, its metabolism, dietary exposure, and toxicity have been widely studied [2–5]. Tareke et al. reported that carbohydrate-rich foods exist with relatively high levels of AA as a result of being fried or baked at high temperature [6,7]. It has been demonstrated that AA formation is considered as the product of the Maillard reaction, especially the reaction of an amino acid, asparagines, via water or food matrix model [8,9]. Many heat processed foods contain high levels of AA, such as French fries, fried puffs, fried chicken rolls, bread, biscuits, steamed buns, cakes and coffee [10]. The risk of AA has demonstrated that the exposure of AA to human beings should be controlled to as lower as possible with regard to its inherently toxic properties, such as genetoxicity, neurotoxicity to both somatic and germ cells, carcinogenicity, and reproductive toxicity [11]. Therefore, many analytical chemists have taken high attention to the detection of AA in foods.

Up to now, mass spectrometric (MS) coupled with a chromatographic step either by liquid chromatographic (LC) or gas chromatographic (GC) is the most useful technique for the AA determination [11]. Schieberle et al. [12] developed an HPLC/fluorescence method, and Zhu et al. [13] established a very sensitive GC method combining electron capture detector (GC-ECD) for the AA determination in food samples. Although a derivatization approach in GC–MS would be helpful to increase the determination sensitivity of AA in foodstuffs [7,14,15], the drawbacks such as inconvenience and time-consuming in the derivatization process still limit its applications. Recently, non-derivatization approaches for the AA determination using GC–MS have been reported [16,17], but these methods are still lacking characteristic ion peaks in the mass spectra comparing with non-derivatized AA [18]. LC–MS/MS techniques have been paying more attention to the quantitative analysis [18–21] or exposure survey [22] of AA due to its high sensitivity and without the derivatization steps, but the high cost in instrumentation price and maintenance, and bothersome operations limit their applications. Neither GC nor HPLC approaches are suitable for the rapid and convenient in-site detection of AA [18]. To achieve the target of rapid screening, high-throughput screening and inexpensive cost, some electrochemical techniques are selected for the analysis of large amounts

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of samples [23–30]. Stobiecka et al. introduced a novel electrochemical biosensor for the direct detection of AA in food samples [23]. The easily poisoned electrode caused the unstable signals and resulted in poor reproducibility. More recently, after the derivatization with dansulfinic acid, AA in drinking water could be detected using a thin-layer chromatography (TLC) with fluorescence detection (FLD), and the limit of detection (LOD) was calculated to be 0.025 μg L^{-1} [31]. The AA content in coffee was then successfully determined, and the limit of quantitative at a signal-to-noise ratio of 10 was found to be 48 μg kg^{-1} [32]. Due to its rapid and high sensitivity, FLD has fascinated the attention of many researchers on the rapid detection of trace AA in food samples [31,32].

In this paper, using a novel AA-derivatization approach based on Hofmann reaction, we propose a convenient, sensitive and low-cost FLD method for the AA determination in food samples. This approach shortens the AA-derivatization time using Hofmann reaction. In the process of AA-derivatization, acrylamide is degraded through Hofmann reaction to generate vinyl amine. Pyrrolinone is then produced when the vinyl amine reacts with fluorescamine, resulting in a strong fluorescence emission at 480 nm, which makes it convenient and applicable in the AA determination in complex matrices.

2. Experimental

2.1. Reagents and apparatus

Acrylamide (>99.9%) was provided by Alfa Aesar (Tianjing, China). Fluorescamine (>99.0%) was purchased from Sigma-Aldrich (Shanghai, China). NaClO (active chlorine ≥5.2%), NaOH, H_3BO_3, KCl, NaCl, $CaCl_2$, $FeCl_3$, glucose, acetone, and hexane were all purchased from sinopharm chemical reagent company (Shanghai, China) and used without further purification.

Fluorescamine stock solution (3.5 mmol L^{-1}) was prepared in acetone and stored at 4 °C. 0.05 mol L^{-1} H_3BO_3–NaOH–KCl buffer solutions with different pH values were prepared using 0.2 mol L^{-1} KCl, 0.2 mol L^{-1} H_3BO_3 and proper amount of 0.1 mol L^{-1} NaOH. The pure water for solution preparation in the experiments was from the Millipore Autopure WR600A system (Millipore, Ltd., USA). All food samples used in this study were purchased from local supermarkets in Xiamen and stored at 4 °C if required.

Fluorescence spectra were recorded using an F-4500 (Hitachi, Japan) fluorometer. The pH measurements were operated using a pH-510m (Eutech, Singapore).

The HPLC system consisted of a LC-20AT (Shimadzu, Kyoto, Japan) equipped with DGU-20A degasser and SPD-20A diode array detector. Separation column: Syncronis C18 column (250 × 4.6 mm^2; 5 μm) from Thermofisher USA.

2.2. Sample preparation

Samples were prepared following the method established by Becalski et al. [33]. Briefly, food samples were ground, if necessary, in a blender and then dried at 60 °C. The sample (1.0 g) was homogenized with 10 mL hexane, and centrifuged at 10,000 rpm for 10 min following a 10 min of ultrasonic treatment. The top (hexane) centrifugate layer was promptly discarded, and then another 10 mL hexane was added into the residue to repeat the defatting step. After that, 10 mL water was added into the residue for the extraction of AA. Following with 10 min ultrasonic mixing and 10 min centrifuging at 10,000 rpm, filtrate was collected through 50 μm membranes. Analogously, the extraction procedure was carried out twice. Finally, filtrate was mingled and concentrated to 25 mL, and then stored at 4 °C for usage.

2.3. Derivatization procedure

The improved derivatization procedure was established according to Hofmann degradation built by Hiroo Tanaka and Ryoichi Senju [34]. Reactions were carried out in a thermostated bath at various temperatures for different time (an autoclave was used if the temperature was higher than 90 °C), and then the fluorescence intensity was measured. An aliquot (1.5 mL) of the treated sample was placed in a stoppered borosilicate tube and allowed to reach the temperature equilibrium. NaOH was added before the addition of NaClO. The concentration range of NaOH and NaClO was selected in the range of 0 to 0.1 mol L^{-1} and 0.005 to 0.1 μL mL^{-1} (available $OC1^-$ concentration was kept in the range of 0.0044 to 0.088 mmol L^{-1}), respectively. After the reagents were completely mixed, the derivatization was performed under the controlled bath temperature for a fixed time.

2.4. Detection procedure of fluorescence measurement

In order to keep the solution pH in an appropriate range, 2 mL appropriate borate buffers were initially added into the derivatization product, then, 0.5 mL 3.5 mmol L^{-1} fluorescamine solution was added. After standing for 5 min, the fluorescence intensity of the solution was measured at 480 nm with the excitation wavelength at 385 nm (slit width of 10 nm for excitation and 20 nm for emission). All measurements were carried out in triplicate to insure the stability and reproducibility.

3. Results and discussions

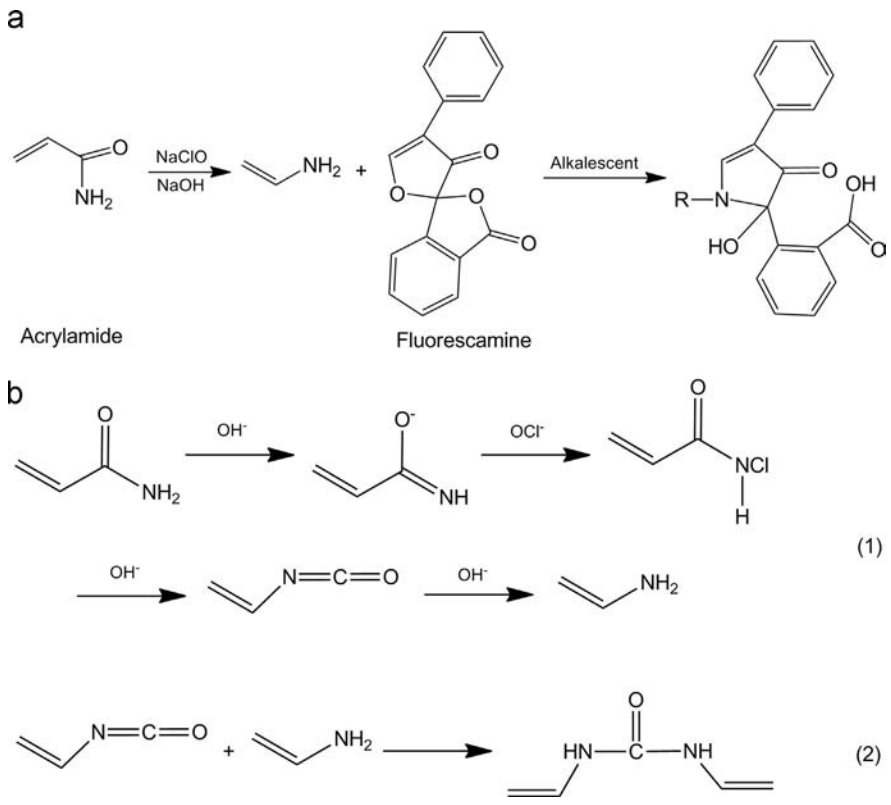
3.1. Fluorescence characteristics and possible reaction mechanism

In the derivatization, the primary amine group in AA reacted with fluorescamine to generate a fluorescent substance (Scheme 1a). In the presence of excess NaOH, AA was chloridized in N atom by NaClO, and then arranged to form an isocyanato group which degraded to a vinyl amine (Scheme 1b) [34]. This primary amine reacted with fluorescamine to form pyrrolinone that emitted strong fluorescence at 480 nm with the excitation wavelength at 385 nm. The fluorescence emission spectra of fluorescamine at different conditions are illustrated in Fig. 1. As shown in Fig. 1, no fluorescence could be found for fluorescamine in water (Line 1 in Fig. 1), while very weak fluorescence in the buffer solution (Line 2 in Fig. 1) indicated its low signal background. The fluorescence intensity of fluorescamine greatly increased when fluorescamine reacted with primary amines even at submicromolar levels [35]. As shown in Line 3 of Fig. 1, in the presence of AA, the increase of the fluorescence intensity at 480 nm indicated that AA could directly react with fluorescamine and result in the increase of its fluorescence intensity. Interestingly, comparing to the intensities of Line 3 and Line 4 in Fig. 1, we can find that AA derivative generated higher fluorescence intensity than that of AA, revealing that primary amine presents higher activity than that of amide. This result indicates that the Hofmann degradation of AA could improve the determination sensitivity of AA.

3.2. Optimization of the experimental conditions

3.2.1. Effect of ClO^- concentration

ClO^- is the essential anion in Hofmann degradation. The effect of its concentration was studied in the range of 0.0044 to 0.088 mmol L^{-1}. As shown in Fig. 2a, the fluorescence intensity increased gradually with the increase of ClO^- concentration until 0.044 mmol L^{-1}, since the halogen for the Hofmann degradation was provided with appropriate concentration of ClO^-. The fluorescence intensity decreased when ClO^- concentration was over



Scheme 1. (a) The generation process of the fluorescent product from AA; (b) The process of Hofmann degradation of AA.

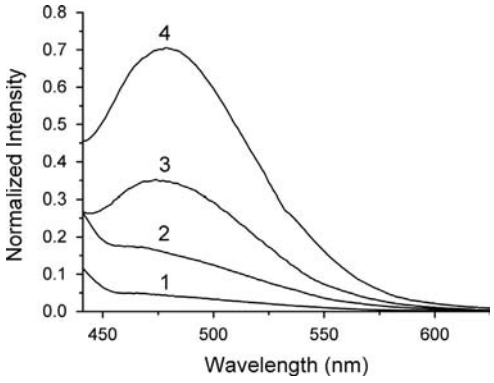


Fig. 1. Fluorescence emission spectra (excitation at 385 nm) of fluorescamine (3.5 mmol L^{-1}) at different conditions: ((1) without AA in water, (2) without AA in buffer, (3) with underivatized AA in buffer, (4) with derivatized AA in buffer). Buffer: H_3BO_3–NaOH–KCl buffer (pH 7.8; 0.05 mol L^{-1}). AA concentration: 10 μg mL^{-1}.

0.044 mmol L^{-1} because the excess strong oxidant, ClO^-, affects the stability of fluorescent product (Scheme 1b). In the experiments, 0.044 mmol L^{-1} ClO^- was selected for Hofmann degradation.

3.2.2. Effect of NaOH concentration

NaOH is another significant factor that influences Hofmann degradation. The fluorescence intensity increased gradually with the increase of NaOH concentration in the range of 0 to 0.025 mol L^{-1}. This result could be revealed by the principle of the Hofmann degradation (Scheme 1b). In general, the rate of N-chlorination is greatly dependent on the NaOH concentration. Therefore, the higher the NaOH concentration, the more abundant the reaction is [36]. Furthermore, as transient intermediates, the isocyanato groups could react with water to yield the objective amine groups in the presence of alkali. Simultaneously, a part of these resulting amine groups gives urea derivatives as a result of the reaction between the amine and isocyanato groups [34]. The excess NaOH is helpful to guarantee the production of amine quickly and cut back the reaction with isocyanato, but much more NaOH (for example, over 0.025 mol L^{-1}) will weaken the activation of fluorescamine, leading to the signal decrease (Fig. 2b). The result coupled with the previous work [37].

3.2.3. Effect of derivatization time and temperature

The reacted temperature and time influence derivatization efficiency immediately [37,38]. Firstly, the effects of temperature between 4 and 150 °C were investigated. As shown in Fig. 2c, the fluorescence intensity was enhanced rapidly as the temperature increased to 90 °C. It could be caused by the high frequency collision between molecules at a higher temperature which accelerates Hofmann degradation. The fluorescence intensity nearly remained constant after 90 °C, revealing that the reaction was nearly to the limit rate. Considering the convenience and cost, 90 °C was selected as the reaction temperature for Hofmann degradation.

The reaction time profile for Hofmann degradation was established by plotting the fluorescence intensity versus the reaction time with a range from 0 to 90 min. As shown in Fig. 2d, the fluorescence intensity rapidly increased from 0 to 15 min and then declined when the time was longer than 15 min. The change indicated that a period time was needed to guarantee the reaction adequately. However, too long reaction time was not beneficial for the formation of vinyl amine because some of the amine groups could be oxidized to nitrogen [37]. Considering these factors, we carried out the experiment for 15 min.

3.2.4. Effect of fluorescamine concentration

Fluorescamine is the luminophore source in the fluorescence determination and its concentration is essential for fluorescence

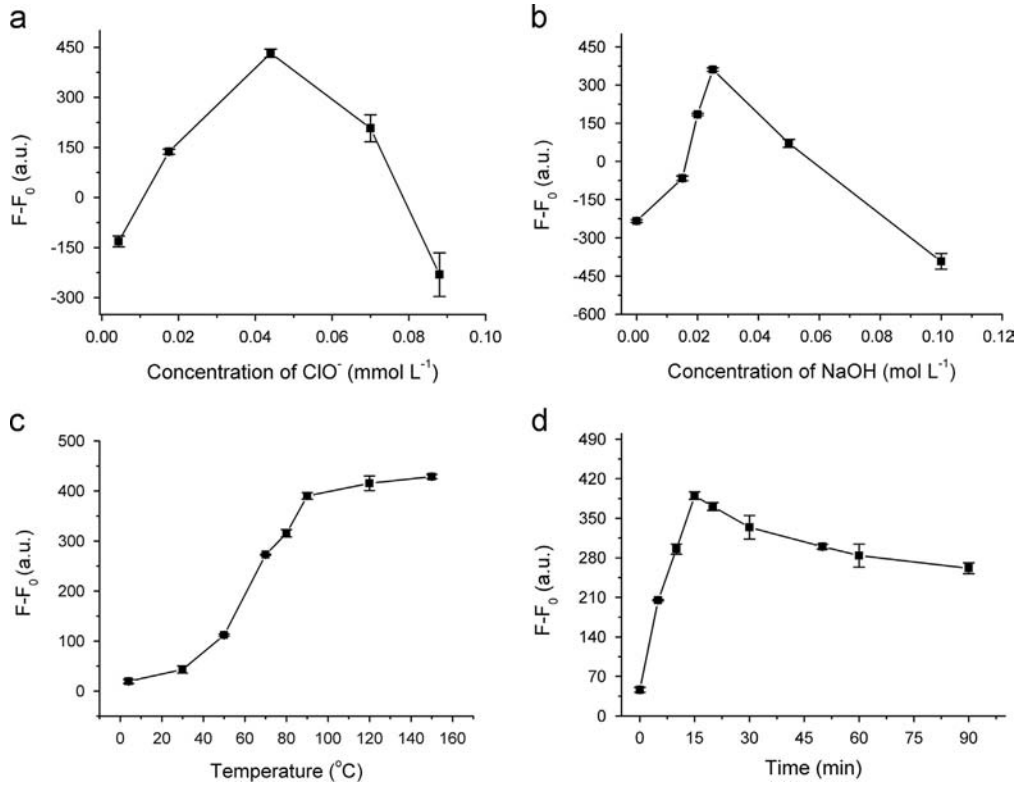


Fig. 2. Optimization of conditions: (a) variation of average fluorescence intensity with concentration of ClO^-; (b) variation of average fluorescence intensity with concentration of NaOH; (c) fluorescence intensity at different temperature; and (d) fluorescence intensity at different time. Excitation wavelength was set at 385 nm. AA concentration: 10 μg mL^{-1}.

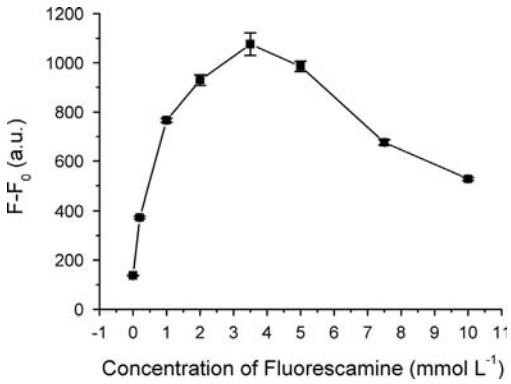


Fig. 3. Variation of average fluorescence intensity with concentration of fluorescamine. Excitation wavelength: 385 nm. AA concentration: 10 μg mL^{-1}.

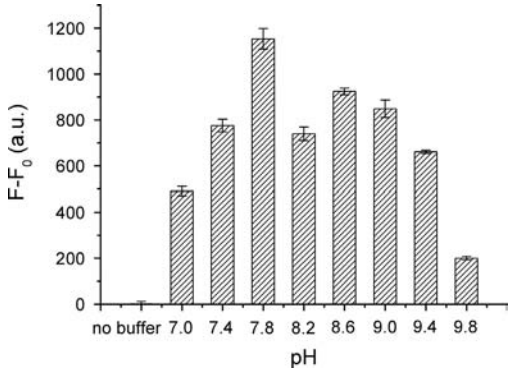


Fig. 4. Fluorescence intensity in 0.05 mol L^{-1} H_3BO_3–NaOH–KCl buffer of different pH (pH from left to right are: 7.0, 7.4, 7.8, 8.2, 8.6, 9.0, 9.4, and 9.8) and no buffer (left). Excitation wavelength: 385 nm. AA concentration: 10 μg mL^{-1}.

intensity. The effect of the fluorescamine concentration from 0 to 10 mmol L^{-1} was investigated. As shown in Fig. 3, the fluorescence intensity obviously increased with the increase of fluorescamine concentration, but decreased when the concentration was higher than 3.5 mmol L^{-1}. Simultaneously, flocculent precipitate with white color was visible when fluorescamine concentration was over 3.5 mmol L^{-1}. Fluorophore–amine interaction appeared to produce the exciplex at high concentration of fluorescamine, while the exciplex emission was often quenched in polar solvents. Meanwhile, high optical densities and turbidity could also result in decreasing fluorescence intensities [39]. Based on this result, a fluorescamine concentration of 3.5 mmol was selected in the subsequent experiments.

3.2.5. *Effect of the buffer pH*

pH value is a crucial parameter to maximize the extent of the fluorogenic reaction. We further investigated the pH effect on the fluorogenic reaction at different buffer solutions. Fluorescence intensities in 0.05 mol L^{-1} H_3BO_3–NaOH–KCl buffer solution with pH 7.0–8.0 were depicted in Fig. 4. The fluorescence intensity of fluorescamine varied greatly at different pH buffer solutions. The maximum intensity could be obtained at pH 7.8, and fluorescence intensity became weaker at either lower or higher pH value. In a lower pH solution, the protonation of amine occurred and made against the reaction. Conversely, hydrolysis of the fluorescamine would predominate over the fluorogenic reaction in a higher pH solution [35]. Therefore, 0.05 mol L^{-1} H_3BO_3–NaOH–KCl buffer solution with pH 7.8 was chosen in the following experiments.

3.3. *Method validation and sample analysis*

Using the optimized conditions, the linearity, limit of detection and repeatability of AA detection were investigated (Fig. 5). The

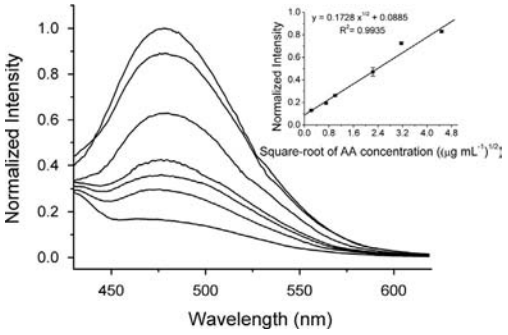


Fig. 5. Fluorescence spectra of fluorescamine in H_3BO_3–NaOH–KCl buffer (pH 7.8, 0.05 mol L^{-1}) in the presence of various concentrations of AA under excitation at 385 nm. The concentrations of AA from bottom to top are: 0 μg mL^{-1}, 0.05 μg mL^{-1}, 0.5 μg mL^{-1}, 1 μg mL^{-1}, 5 μg mL^{-1}, 10 μg mL^{-1}, and 20 μg mL^{-1}. The inset is calibration curve according to the increasing of square-root of AA concentration and maximum emission spectrums.

Table 1
Detection results for acrylamide and recovery of samples ($n=3$).

Food samples	FLD detected (μg kg^{-1} ± SD)	Recovery (%)	HPLC-DAD detected (μg kg^{-1} ± SD)
French fries	940 ± 35	66.0	956 ± 37
Fried puffs	524 ± 23	79.1	529 ± 15
Fried chicken rolls	752 ± 40	78.7	761 ± 30
Bread	103 ± 7	108.8	110 ± 8
Biscuits	232 ± 28	86.2	237 ± 16
Steamed buns	ND	110.6	ND

ND: Not detected.

Table 2
Selectivity of FLD method toward AA over other interferences.

Interferences	ΔF (a.u.)	RSD (%)
Na^+	−65.8	−6.25
Ca^{2+}	−51.1	−4.85
Fe^{3+}	−31.1	−2.95
Glucose	85.9	8.16

$\Delta F = F - F_0$ (F: fluorescence of interference, F_0: fluorescence of AA).
The concentration of both AA and interference were 14 mM.

linearity range was tested by diluting AA standard solution (derivate), and was found to be in the range 0.05 to 20 μg mL^{-1} with a coefficient of determination (R^2) of 0.9935. The limit of determination (LOD), defined as three fold the baseline noise, was 0.015 μg mL^{-1}. The reproducibility was evaluated by detection the fluorescence intensity at 10 μg mL^{-1} of analyte ($n=11$), and the relative standard deviation (RSD) was 4.21%.

The performance of the FLD was studied in the analysis of AA in fried or roasted food samples. As shown in Table 1, the FLD developed could be well applied in the determination of AA in food samples. From the results, we found that fried and deeply roasted foods such as French fries, fried puffs, fried chicken rolls contained a higher content of AA, but there was a lower amount of AA in unroasted or unfried tea sample, indicating that roasting and frying played a key role in increasing the AA content of foods. These results are consistent with other reports [40]. In addition, as shown in Table 1, the recovery of AA spiked at 10 μg mL^{-1} in the samples was found to be in the range of 66.0% to 110.6%. All the results of the food samples illustrate that the developed method is feasible. Then the method was compared with Specification of Entry&Exit Inspection and Quarantine Bureau of The People's Republic of China [41]. The same food samples were detected by both FLD and HPLC-DAD. The results obtained by two different methods showed a good correlation regarding the ultra-trace level (Table 1). This proved the accuracy and efficiency of the newly developed method.

Finally, to test the selectivity of the FLD method in the determination of AA, several interferences common in food were studied as a control: Na^+, Ca^{2+}, Fe^{3+} and Glucose. As shown in Table 2, all the RSD of interferences toward AA in the range of ± 10% proved the good selectivity of the method.

4. Conclusions

Our study provided a simple and rapid FLD method for AA detection based on Hofmann reaction, and followed by fluorescent detection. The inclusion of novel AA-derivatization technique enhanced the detection limit of the technique by forming vinyl amine. The FLD method exhibited their excellent characteristics with convenient operation, short detection time, low cost and good selectivity. The fluorescence intensities were linearly proportional to the square-root of AA concentrations from 0.05 μg mL^{-1} to 20 μg mL^{-1} with the correlation coefficient $R^2=0.9935$. The method also indicated good detection limit with 0.015 μg mL^{-1} and showed a good correlation with Industry Standard in the AA detection in food samples at the ultra-trace level. This sensitive technique provides a more reliable test for AA detection by FLD and encourages the detection of AA by taking more use of fluorescence technique.

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