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Simultaneous determination of biogenic amines and estrogens in foodstuff by an improved HPLC method combining with fluorescence labeling

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ABSTRACT

Biogenic amines (BA) and estrogens (ES) have attracted increasing attentions due to their significance on food safety and food quality. In this study, a novel HPLC-FLD method using ethyl-acridine-sulfonyl chloride (EAC) as fluorescence labeling reagent has been developed for simultaneous determination of BA and ES in food samples. The labeling conditions including labeling time, pH of borate buffers and amount of EAC were optimized. The simultaneous labeling of BA and ES can be finished in as little as 6 min. This method without complex pre-treatment offered the low LOD of 0.27–0.69 ng/mL. It was applied to analyze several food samples (beer, cheese, fish, sausage and shrimp), and showed excellent applicability.

1. Introduction

Biogenic amines (BA) and estrogens (ES) have attracted increasing attentions due to their significance on food safety and food quality (Qin, Wang, Kaneko, Hoshi & Sato, 2004; Shalaby, 1996). BA are low molecular-weight organic bases with aromatic, aliphatic or heterocyclic structure. They occur naturally in a wide variety of protein-rich and fermented foodstuffs. The presence of BA may induce headache, heart palpitation, hypotension, hypertension, nausea, emesis and even intracerebral hemorrhage, anaphylactic shock syndrome and death in very severe cases (Özdestan & üren, 2009). The estimation of BA is also an important indicator for degree of freshness or spoilage of food, the extent of ripening and the quality of storage.

Estrogens are often illegally used to improve feed conversion efficiency and promote growth rates in livestock production. After they are used, a portion is discharged into the water environment by excretion and the rest remain in the animal's body. These compounds may be transferred into water, foods and food webs if not well controlled (Shao et al., 2005; Yager & Davidson, 2006). Estrogens exposure has been recognized as a risk factor for the dramatic increase of estrogen dependent diseases (Härkönen & Mäkelä, 2004; Qin et al., 2004). Many countries such as European Union Countries have banned the use of estrogens as growth promoters, whereas some other countries allow their restricted use (Impens, De Wasch, Cornelis & De Brabander, 2002). Simultaneous analysis of BA and ES can provide important information for food safety and food quality because BA and ES may coexist in many foodstuffs (especially the unqualified foods) such as fermented foodstuffs (e.g. beer, cheese), meat and meat products (e.g. fish, prawn) (Malik, Blasco & Picó, 2010; Núñez, Gallart-Ayala, Martins & Lucci,2012). However, the HPLC method for simultaneous determination of BA and ES remains poorly investigated. Thus, development of a sensitive and selective method for simultaneous determination of BA and ES is not only of general interest, but also of great importance.

Most BA occurring in foodstuff show low UV absorption, and are often present at low concentration. Their determination by spectrophotometry is difficult. The fluorescence labeling is often

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employed to increase sensitivity and selectivity. Although many different types of labeling reagents have been developed such as o-phthaldialdehyde (OPA), 9-fluorenyl methyl chloroformate (FMOC), 5-furoylquinoline-3-carboxaldehyde (FQ) 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC), phenyl isothiocyanate ester (PITC), dansyl chloride (Dns-Cl) and so on, a variety of shortcomings in their applications have also been reported such as poor stability of the derivatives, short detection wavelengths, bad reproducibility, low detection sensitivity, long labeling time, tediously analytical procedure, limiting to primary amino and serious interferences in chromatogram (McKenzie et al., 2002; Özdestan & üren, 2009; Zhao & Suo, 2008). Recently, a novel fluorescent labeling reagent named ethylacridine-sulfonyl chloride (EAC, purity by HPLC: 98%) has been reported in our recent study and this reagent showed excellent photoluminescence property (You et al., 2009). In the present study, EAC was developed for simultaneous determination of BA (putrescine, histamine, cadaverine, 2-phenylethylamine, 1,6-hexamethy lenediamine, tyramine, spermidine and spermine) and ES (estrone, estradiol and estriol) in food samples by HPLC-FLD. To the best of our knowledge, this is the first attempt of using fluorescence labeling for simultaneous determination of trace BA and ES in food samples by HPLC-FLD. The herein reported method is capable of offering higher detection selectivity and sensitivity than the previous reported methods for BA or ES determination (Gosetti, Mazzucco, Gianotti, Polati & Gennaro, 2007; Huang et al., 2009; Kim et al.,2011; Kovacs, Simon-Sarkadi & Ganzler,1999; Li, Wang, & Yuan, 2009; Lu et al.,2007; Mao, Sun, Zhang, Li & Wu, 2004; Proestos, Loukatos & Komaitis, 2008). Obtaining the optimum conditions for simultaneous labeling of BA and ES was an important step in the method development. In this study, response surface methodology (RSM) was employed as an efficient tool to optimize the labeling reaction, ensuring the sufficient and rapid labeling of BA and ES. This developed method was also validated to assure high accuracy and precision, and the reliability of its results. When applied to the food sample analysis (beer, cheese, fish, sausage and shrimp), it showed excellent applicability.

2. Materials and methods

2.1. Instrumentation

Experiments were performed using an Agilent 1100 Series high-performance liquid chromatography (Agilent Technologies, Palo Alto, CA, USA). The HPLC system consisted of an online vacuum degasser (model G1322A), a quaternary pump (model G1311A), an autosampler (model G1329A), a thermostated column compartment (model G1316A) and a fluorescence detector (FLD). The mass spectrometer (MSD Trap SL, model G2445D) from Bruker Daltonik (Bremen, Germany) was equipped with an atmospheric pressure chemical ionization (APCI) source (model G1947A). Ion source conditions: APCI in positive ion detection mode; nebulizer pressure 60 psi; dry gas temperature, 350 °C; dry gas flow, 5.0 L/min. APCI Vap temperature 350 °C; corona current 4000 nA; capillary voltage 3500 V.

2.2. Chemicals

All standards (purity $\geq$ 98%), including estrone (E_1), estradiol (E_2), estriol (E_3), putrescine (PUT), histamine (HIS), cadaverine (CAD), 2-phenylethylamine (2-PHE), 1,6-hexamethylenediamine (HEX), tyramine (TYR), spermidine (SPD) and spermine (SPM), were at the highest purity commercially available and purchased from Sigma (St. Louis, MO, USA). HPLC grade acetonitrile (CH_3CN, ACN) was purchased from Yucheng Chemical Reagent Co. (Yucheng, Shandong Province, China). EAC was synthesized in our laboratory (You et al., 2009; purity by HPLC: 98%). Other chemicals were analytical grade from Jining Chemical Reagent (Jining, Shandong Province, China).

2.3. Preparation of standard solutions

The mixed standards for HPLC analysis were prepared by diluting the corresponding stock solution (1.0×10^{-2} mol/L) with 0.1 mol/L HCl solution. EAC solution (5.0×10^{-2} mol/L) was prepared by dissolving 32 mg EAC in 20 mL ACN. The corresponding low concentration of labeling reagent solution (5.0×10^{-3} mol/L) was obtained by diluting the stock solution with ACN.

2.4. Sample preparation

All food samples (beer, cheese, fish, sausages and shrimp) were purchased from a marketplace (Jining, Shandong province, China). The extractions of BA and ES were carried out according to several reported studies with minor revision (Saaid, Saad, Hashim, Mohamed Ali & Saleh, 2009; Ternes, Andersen, Gilberg & Bonerz, 2002). All solid samples were treated as following: 5 g of sample was extracted twice with 15 mL 5ml/100ml trifluoroacetic acid (TCA) in an ultrasonic cleaner (25 min each extraction) and then centrifuged for 5 min at 3000 rpm; the residue was ultrasonicated twice for 25 min with 15 mL methanol. The mixture was then centrifuged at 3000 rpm for 10 min. All supernatants were combined, and 4 mL of the mixture were evaporated to dryness by a gentle nitrogen stream, and then the residue was re-dissolved by 2 mL 5ml/100ml TCA. Liquid samples were diluted five times with the 0.1 mol/L HCl.

2.5. Derivatization procedure

10 μL mixed standard solution (or 100 μL prepared sample solution), 150 μL derivatization reagent, 100 μL of sodium borate buffer (pH = 9.7) were successively added to a 2 mL vial. The vial was sealed and then shaken for 6 min at 55 °C. After the reaction was completed, the mixture was cooled to room temperature in a water-bath, and then 50 μL of 50ml/100ml acetic acid and 200 μL ACN were added. The diluted solution (10 μL) was injected into the LC system.

2.6. HPLC separation

HPLC separation of the labeled analytes was carried out on a reversed-phase Hypersil BDS C_{18} column (200 mm × 4.6 mm, 5 μm) with a gradient elution. The mobile phase A was 25ml/100ml ACN containing 0.1ml/100ml ammonium formate and B was 100% ACN. The mobile phase solutions were degassed and filtered through a 0.45-μm filter and pumped at a flow rate of 1 mL/min. The column temperature was set at 36 °C. The injection volume was 10 μL. The fluorescence excitation and emission wavelengths were set at λ_{ex} 270 nm and λ_{em} 430 nm, respectively. The gradient elution program was as follows: 0 min = 15% B, 10 min = 17% B, 25 min = 24% B, 40 min = 65% B, and 50 min = 100% B. Before injecting the next sample, the column was equilibrated with the initial mobile phase for 10 min.

2.7. Method validation

The linearity, repeatability, accuracy, precision, sensitivity, recovery, and limits of detection (LOD) were validated according to United States Food and Drug Administration (FDA) guidelines and several reported studies (Li, You, Suo, et al., 2011; Li, You, et al., 2011). For linearity evaluation, standard solutions at a series of concentrations (0.005 μmol/L–2.5 μmol/L) were prepared and injected into the HPLC system. Calibration curves were constructed

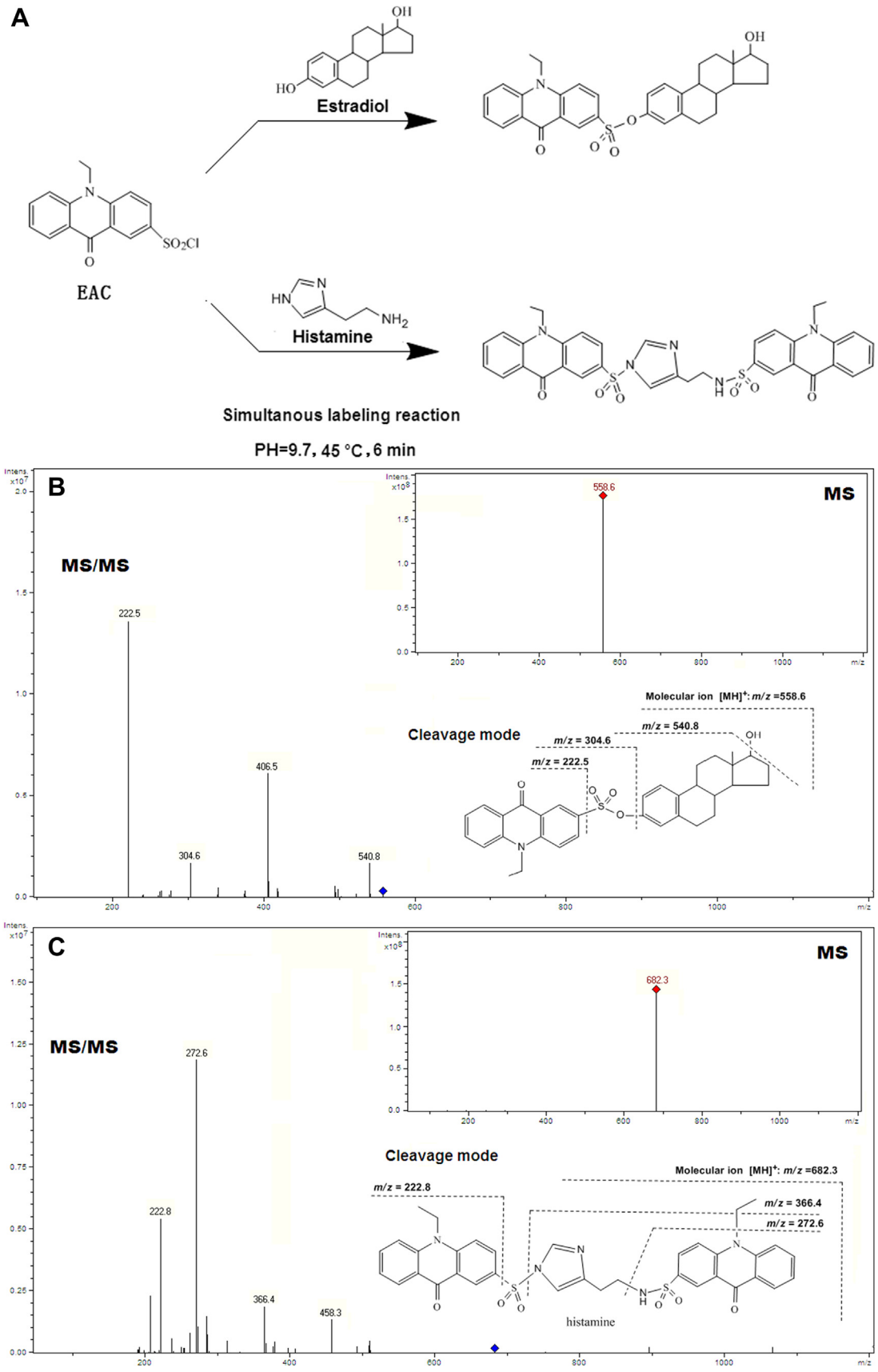

Fig. 1. The representative labeling schemes for estradiol and histamine under the optimum conditions (A) and their MS data (MS and MS/MS) and cleavage mode for estradiol (B) and histamine (C) derivative.

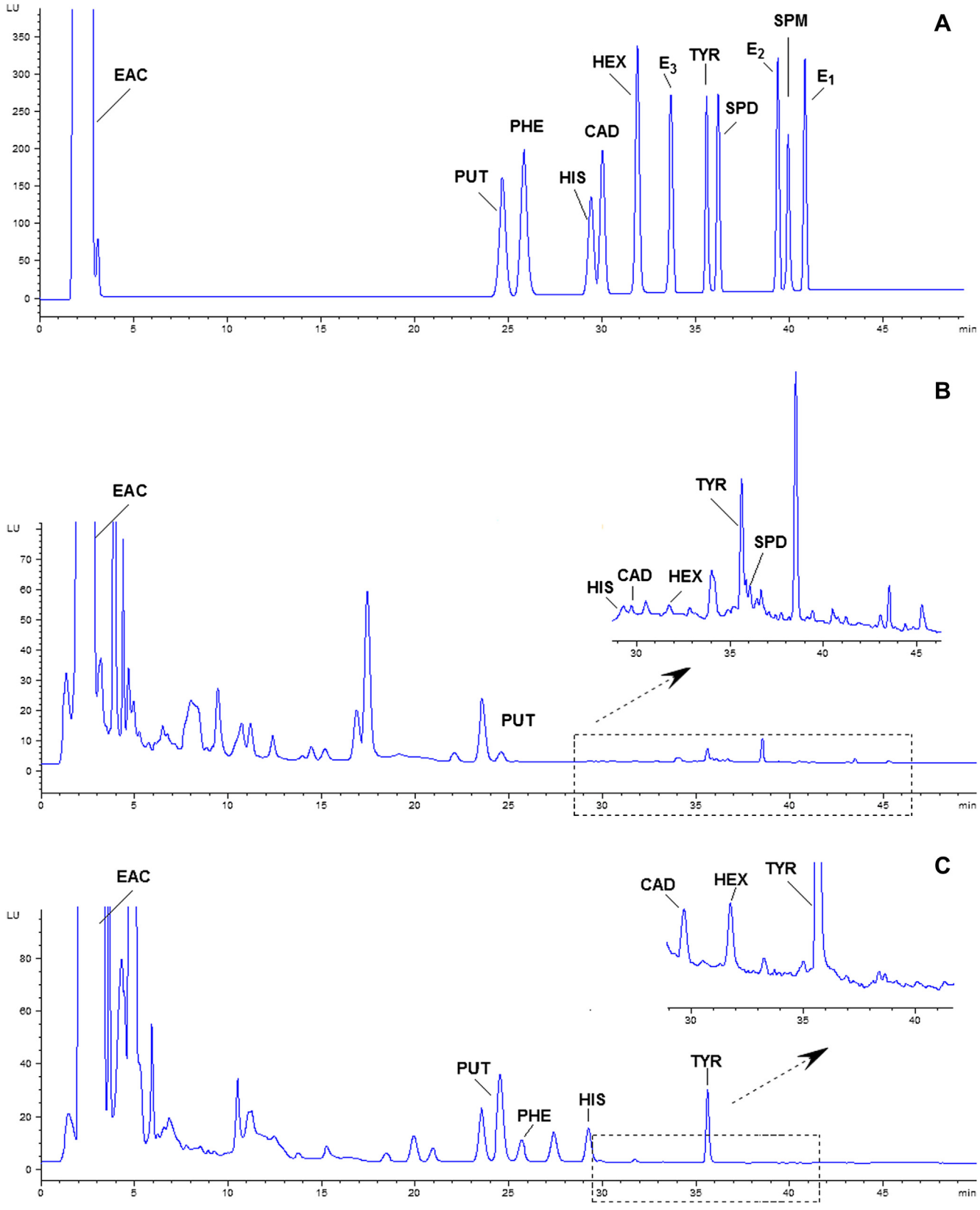

Fig. 2. The representative chromatograms for 11 standards (A), beer sample (B) and shrimp sample (C). HPLC conditions: analyte separation was carried out on a reversed-phase Hypersil BDS C_{18} column (200 mm × 4.6 mm, 5 μm i.d.); the mobile phase A: 25ml/100ml ACN containing 0.1ml/100ml ammonium formate and B: 100% ACN; flow rate: 1 mL/min; the column temperature: 36 °C; the fluorescence excitation and emission wavelengths: λ_{ex} 270 nm and λ_{em} 430 nm.

by linear regression of the peak area (Y) versus the concentration (x). The LOD were calculated at the signal-to-noise (S/N) ratio of 3. A 10-μL standard sample was injected into the chromatograph by an automatic sampler ($n = 6$), and the method repeatability was investigated by measuring the relative standard deviations (RSD) for peak area and retention time. The accuracy of the analytical method was determined by spiking a known amount of standards into food samples and analyzing the percentage recovery. The precision was expressed as the percentage relative standard deviation (R.S.D. %).

3. Results and discussion

3.1. Optimization of fluorescence labeling

The main parameters for the simultaneous labeling of BA and ES were optimized by response surface methodology (RSM). The optimization process was carried out according to our previous methods (Li, Cui, et al., 2011; Li, You, Suo, et al., 2011). Firstly, the labeling temperature was evaluated in the range of 20–60 °C, and results indicated the full labeling reaction can be achieved at 45 °C. In these pre-tests, borate buffers performed best and were therefore selected for further method development. The parameters including labeling time, pH of borate buffers and amount of EAC (mole ratio of EAC to BA and ES) were chosen for optimization by RSM. Estradiol and histamine were used as the tested compounds, and the labeling schemes are showed in Fig. 1. Results indicated that by increasing labeling time (2–10 min), the labeling yield increased as well, reached a maximum value and the further increase of the labeling time had slightly effect on the labeling yield. With a given labeling time, the labeling yield increased with the increasing pH of borate buffers and reached a maximum value, followed by a decline with its further increase. The optimal conditions given by RSM were as follows: labeling time = 6 min, pH of borate buffers = 9.7 and molar ratio of EAC to the analytes = 7.5. The fluorescence labeling experiments were carried out to test the validity of the optimum conditions given by the response surface analysis. Results indicated the BA and ES can be sufficiently labeled under the proposed conditions. The experimental peak area was 4030 ($n = 3$), which was close to the theoretical predicted value of 3994, indicating that the experimental design model may better reflect the labeling parameters.

3.2. Stability of EAC and the labeled analytes

EAC was dissolved in pure acetonitrile and stored at 4 °C in darkness for two weeks, and the labeling yields were found with the little change of <2.0%. The labeled BA and ES were stored at 4 °C in darkness for a period of 7 days, and they were analyzed six times during these days. Results indicated these labeled analytes were stable enough to be analyzed at least 48 h later, with the peak areas varies of <2.70%.

3.3. HPLC separation and MS identification

The development of the HPLC method started with selection of various analytical columns, mobile phase composition and flow rate to obtain satisfactory separation. Methanol and acetonitrile were used as the basis for different mobile phases. A series of analytical columns including Hypersil BDS C_8 (200 mm × 4.6 mm, 5 μm), Hypersil C_{18} (200 mm × 4.6 mm, 5 μm), Hypersil BDS C_{18} (200 mm × 4.6 mm, 5 μm) and Spherisorb C_{18} (200 mm × 4.6 mm, 5 μm) were investigated, and results showed that Hypersil BDS C_{18} (200 mm × 4.6 mm, 5 μm) could result in good resolution. The best mobile phases were found to be Eluent A acetonitrile/H_2O (25:75; v/v) and Eluent B pure acetonitrile. The optimum flow rate and column temperature were 1 mL/min and 36 °C, respectively. The typical chromatogram for 11 standards is presented in Fig. 2A.

Chromatographic peaks were simultaneously identified by the retention time and online post-column APCI/MS in positive mode. The MS data indicate that both EAC-BA and EAC-ES derivatives exhibited intense quasi-molecular ion peak of $[M+H]^+$, and produced the abundant product ion at m/z 222, which corresponded to the molecular core structure. Fig. 1B and C present the cleavage mode and MS data (MS and MS/MS) for the representative estradiol (E_2) and histamine (His) derivative. E_2 derivative produced an intense molecular ion peak at m/z 558.6 and the specific fragment ions at m/z 540.8, m/z 304.6, and m/z 222.5 (Fig. 1B). Histamine derivative gave an intense molecular ion peak at m/z 682.3 and the specific fragment ions at m/z 366.4, m/z 272.6, and m/z 222.8 (Fig. 1C).

3.4. Method validation

The results of method validation including linearity, detection limits (LOD), precision, and reproducibility of retention time and peak are shown in Table 1. The correlation coefficients were of >0.9994, indicating excellent linearity (Table 1). The proposed method with fluorescence detection offered the low detection limits of 0.27–0.69 μg/L. With fluorescent detection, RSD for retention time and peak area are in the range of 0.01–0.05% and 1.26–1.85%, respectively (Table 1). The inter- and intra-day variability were investigated to evaluate the precision of the proposed method and expressed as relative standard deviation (R.S.D. %). The intra-day assay variability ranged from 1.98 to 3.80% for the target analytes (Table 1), while inter-day assay variability was from 3.24 to 5.63% (Table 1). The results for method accuracy are shown in Table 2. The method accuracy were in the range of 93.74–104.02%.

Table 1
Linear regression equation, correlation coefficients (R), LOD, reproducibility of retention time and peak area, intra- and inter- day precision.

Analytes	Linearity		LOD (nmol/L)	LOD (ng/mL)	Repeatability R.S.D (%) ($n = 6$)		Precision R.S.D (%) ($n = 6$)	
	$Y = AX + B$[a]	R			Retention time	Peak area	Intra-day	Inter-day
Putrescine	$Y = 42.94X + 0.91$	0.9995	3.1	0.27	0.03	1.85	2.57	4.90
Phenylethylamine	$Y = 52.6X + 8.90$	0.9998	2.4	0.29	0.05	1.31	2.26	5.42
Histamine	$Y = 40.46X + 3.25$	0.9997	3.2	0.36	0.02	1.58	3.04	5.11
Cadaverine	$Y = 46.04X + 5.0$	0.9998	2.7	0.27	0.03	1.34	3.50	4.80
Hexamethylenediamine	$Y = 45.83X + 7.64$	0.9999	2.9	0.34	0.01	1.44	2.61	5.63
Estriol	$Y = 53.35X + 6.04$	0.9999	2.2	0.69	0.02	1.30	2.52	3.72
Tyramine	$Y = 49.62X + 7.64$	0.9996	2.8	0.38	0.03	1.83	3.30	5.01
Spermidine	$Y = 43.84X + 4.62$	0.9997	2.6	0.37	0.03	1.26	3.00	4.76
Estradiol	$Y = 59.87X + 4.06$	0.9999	2.3	0.63	0.05	1.60	1.98	3.24
Spermine	$Y = 36.15X + 2.53$	0.9994	3.3	0.67	0.04	1.55	2.53	4.37
Estrone	$Y = 52.03X + 2.60$	0.9998	2.5	0.68	0.02	1.72	3.80	5.52

[a] X: the injected amounts (pmol); Y: the peak area detected with fluorescence detector.

Table 2
Analytical results for biogenic amine and estrogen in selected food samples ($n = 6$).

Samples	Analytes	Original (μg/g or μg/mL)[a]	Added (μg/g or μg/mL)	Found (μg/g or μg/mL)	Recovery (%)	RSD (%) $n = 6$
Beer	Putrescine	244.22	250	516.45	101.50	2.61
	Phenylethylamine	4.56	5	9.56	100.02	2.44
	Histamine	7.34	10	16.58	95.61	1.83
	Cadaverine	6.70	10	15.70	94.10	2.61
	Hexamethylenediamine	5.52	10	15.07	97.08	2.59
	Tyramine	123.15	130	251.96	99.53	3.20
	Spermidine	17.41	20	38.91	104.02	2.51
	Spermine	10.43	10	19.44	95.17	2.74
Cheese	Putrescine	306.66	310	596.66	96.76	3.13
	Cadaverine	53.25	60	112.30	99.17	2.24
	Hexamethylenediamine	12.74	20	33.19	101.38	2.98
	Tyramine	14.60	20	32.86	94.98	2.26
	Spermidine	31.61	40	66.22	96.48	2.51
	Estradiol	0.13	2	2.08	97.65	2.69
	Spermine	18.94	20	39.14	100.52	1.76
Fish	Putrescine	428.62	500	960.84	103.47	2.09
	Phenylethylamine	19.21	20	38.85	99.07	1.80
	Histamine	526.35	500	983.35	95.81	3.00
	Hexamethylenediamine	146.76	150	298.27	100.51	2.43
	Tyramine	847.08	900	1753.72	100.38	1.85
	Spermidine	1.42	5	6.17	96.12	3.10
	Spermine	0.85	5	5.76	98.54	2.00
Sausage	Putrescine	81.65	90	165.43	96.37	2.89
	Histamine	2.32	5	7.42	101.39	3.31
	Cadaverine	9.03	10	18.80	98.81	3.52
	Hexamethylenediamine	6.85	7	13.79	99.54	1.62
	Tyramine	33.44	40	71.99	98.02	2.79
	Spermidine	77.37	80	158.14	100.48	1.40
	Spermine	46.36	50	93.02	96.53	3.04
Shrimp	Putrescine	927.34	1000	1992.90	103.40	2.42
	Phenylethylamine	389.71	400	740.27	93.74	2.18
	Histamine	808.69	800	1484.35	97.26	2.41
	Cadaverine	13.82	20	34.27	101.36	2.95
	Hexamethylenediamine	14.57	20	35.42	102.45	3.02
	Tyramine	520.91	520	990.74	95.18	2.80

[a] the unit for solid sample is "μg/g"; for liquid samples, the unit is "μg/mL".

These results demonstrated the suitability of the proposed method for determination of trace BA and ES from food samples.

3.5. Sample analysis

Food samples including beer, cheese, fish, sausage and shrimp were collected and analyzed by the proposed HPLC-FLD method. The chromatographic peaks were doubly identified by retention time and online MS. The representative chromatograms for beer and shrimp are shown in Fig. 2B and C. The analytical results are presented in Table 2. Estradiol was only detected in cheese sample. In other samples, only BA was detected (Table 2). Eight biogenic amines were detected in beer sample, and the contents were in the range of 4.56–244.22 μg/mL.

3.6. Comparison with the reported methods

The overall comparison of the new method and reported methods is presented in Table 3. The proposed method without complex pre-treatment offered the LOD of 0.27–0.67 μg/L for BA,

Table 3
The overall comparison of the new methods and reported methods.

Methods	Reagents	Labeling conditions	LOD	Reference
The reported methods for biogenic amine determination				
CE-LIF	AccQ	Borate buffer, 55 °C, 10 min	1000–40,000 nmol/L	Kovacs et al., 1999
CE-FL	OPA	20 mM phosphate-borate buffer, pH = 10.0	1000–5000 nmol/L	Oguri, Watanabe, & Abe, 1997
HPLC-DAD	DnsCl	NaOH saturated $NaHCO_3$,40 °C, 30 min	50–250 μg/L	Lu et al.,2007
HPLC-UV	CNBF	$Na_2B_4O_7$ buffer, pH = 9.5, 60 °C, 30 min	100–2000 nmol/L	Kim et al.,2011
HPLC-MS	DnsCl	$NaHCO_3$ 0.25 M, 40 °C, 20 min	1.7–22.5 μg/L	Gosetti et al., 2007
SPE-HPLC-FLD	AQC	$Na_2B_4O_7$ buffer, pH 8.8, 40 min.	5–50 μg/L	Huang et al., 2009
HPLC-FLD	DnsCl	Na_2CO_3 solution, pH 7.8, 40 °C,	20–180 μg/L	Proestos, Loukatos, & Komaitis, 2008
HPLC-FLD	EAC	$Na_2B_4O_7$ buffer, pH 9.7, 45 °C, 6 min	2.4–3.3 nmol/L or 0.27–0.67 μg/L	This work
The reported methods for estrogen determination				
SPE-HPLC-FLD	PNC	Buffer: no mention,25 °C, 30 min	2.7–8.3 μg/L	Mao et al., 2004
SPE-HPLC-MS	NO	No labeling	4–300 μg/L	Volmer & Hui, 1997
SBSE-HPLC-DAD	NO	No labeling	25–100 μg/L	Masunaga et al., 2000
CPE-HPLC-UV	NO	No labeling	1.0–3.8 μg/L	Wang et al., 2007
SPE-HPLC-DAD	NO	No labeling	2.4 μg/L	Li, Wang, & Yuan, 2009
HPLC-FLD	EAC	$Na_2B_4O_7$ buffer, pH 9.7, 45 °C, 6 min	0.63–0.69 μg/L	This work

SPE = solid-phase microextraction; SBSE = stir bar sorptive extraction; AccQ = 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate; OPA = o-phthaldialdehyde; CNBF = 4-chloro-3,5-dinitrobenzotrifluoride; DnsCl = dansyl chloride; AQC = 6-aminoquinolyl-N-hydrosysuccinimidyl carbamate; PNC = *p*-Nitrobenzoyl chloride.

which were significantly lower than the reported methods in Table 3. EAC can perform the sufficient labeling of the analytes in as little as 6 min, which is more rapid than CNBF (30 min), PNC (30 min) and AQC (40 min). Furthermore, OPA and AQC were incapable of secondary amines, and the quantification is difficult as a result of the instability of OPA (Zhao & Suo, 2008). The developed method here provided the low LOD of 0.63–0.69 μg/L for ES that were lower than the reported methods in Table 3. Furthermore, to the best of our knowledge, it is the first trial of using fluorescence labeling for simultaneous monitoring of BA and ES by HPLC-FLD in food samples, which is another added benefit of this developed method.

4. Conclusion

In the presented study, a novel fluorescence labeling method using EAC as labeling reagent was developed for simultaneous determination of BA and ES in food samples by HPLC-FLD. The proposed method showed many advantages than the reported methods. Meanwhile, the developed method here also exhibited powerful potential for accurate determination of BA and ES from other food samples.

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