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Determination of biogenic amines by 3-(2-furoyl)quinoline-2-carboxaldehyde and capillary electrophoresis with laser-induced fluorescence detection

Xin Liu, Li-Xiang Yang, Ying-Tang Lu*
Key Laboratory of MOE for Plant Developmental Biology, College of Life Sciences, Wuhan University, Wuhan 430072, China

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Abstract

Micellar electrokinetic capillary chromatography with laser-induced fluorescence detection was applied to the determination of biogenic amines including putrescine, histamine, cadaverine, tyramine, tryptamine, 2-phenylethylamine, spermine, and spermidine. A fluorogenic derivatization reagent, 3-(2-furoyl)quinoline-2-carboxaldehyde, was successfully used to fluorescently label these biogenic amines. Different variables that affect derivatization (derivatization reagent concentration, reaction time and temperature) and separation (buffer concentration, addition of organic modifiers and sodium deoxycholate concentration) were studied. The linearities within concentration ranges of up to two orders of magnitudes were achieved for those species with correlation coefficients from 0.9967 to 0.9992. The detection limits (signal to noise=3) of biogenic amines can reach 5×10^{-10} mol l^{-1}, which are equivalent to or better than the detection limits obtained by other analytical methods of biogenic amines. As a preliminary application, this method has been successfully employed to determine biogenic amines in the extract of tobacco leaf.

Keywords: Derivatization, electrophoresis; Biogenic amines; 3-(2-Furoyl)quinoline-2-carboxaldehyde

1. Introduction

Biogenic amines are a group of active organic bases that are usually synthesized by the decarboxylation of amino acids or by the amination and transamintion of aldehydes and ketones. They are widely found in diverse biological systems, and have been associated with many cell processes, including cell proliferation and differentiation, synthesis of nucleic acids and proteins, membrane stability and signal transduction [1,2].

In order to clarify the biological function of biogenic amines in physiological and biochemical processes, it is essential to develop a simpler and more sensitive analytical technique to quantify these compounds in different biological matrixes. There are many analytical techniques developed for the determination of biogenic amines, such as gas chromatography [3], thin-layer chromatography [4,5], high-performance liquid chromatography (HPLC) [6–9] and capillary electrophoresis (CE) [10–13]. Among these protocols, HPLC is the most widely adopted technique for the measurement of biogenic

*Corresponding author. Tel.: +86-27-87682619; fax: +86-27-87666380.
E-mail address: yingtlu@whu.edu.cn (Y.-T. Lu).

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amines in various matrixes. However, HPLC usually requires time-consuming sample treatment and has long analysis time. Complicate operation can limit the application of HPLC in biogenic amines analysis [14]. Recently, CE has been developed as a reliable and efficient separation technique well suited for the determination of biogenic amines, which provides higher sensitivity, lower sample consumption and stronger separation efficiency than HPLC [15].

Due to lack of a strong chromophore or fluorophore, biogenic amines cannot be directly detected at trace level by CE mode. Chemical derivatization in solution has been accepted as an effective modification technique to solve this problem because it can provide highly sensitive detection of these compounds by binding a chromophore or fluorophore that result in products with strong UV absorption and fluorescent emission. It is important to choose an appropriate derivatization reagent for highly sensitive analysis of biogenic amines.

Various derivatization reagents have been applied in the determination of biogenic amines in CE, such as 6-aminoquinoyl-*N*-hydroxysuccinmidyl carbamate (AccQ) [10], *O*-phthalaldehyde (OPA) [11,12,15], fluorescein isothiocyanate isomer I (FITC) [13,16,17], 5-(4,6-dichloro-*s*-triazin-2-ylamino) fluorescein (DTAF) [18], benzoyl chloride [19]. However, the use of these reagents involves a number of drawbacks. Benzoylated amines cannot be detected by fluorescence, and this method used for them is less sensitive than those for other derivatization reagents [19]. AccQ shows a good reactivity toward biogenic amines, but has poor sensitivity as well as benzoyl chloride due to UV detection [10]. OPA can react easily with primary amino compound to form corresponding derivatives, but the OPA derivatives are not very stable. To solve this problem, Oguri et al. separated histamine, tyramine, putescine and cadverine with on-line mode in-capillary derivatization with OPA and *N*-aetylcysteine [11]. Male and Luong described a cyclodextrin-modified CE method coupled with laser-induced fluorescence (LIF) detection for analysis of biogenic amines [12]. The OPA derivatives of biogenic amines can be stabilized in presence of methyl-β-cyclodextrin. Although these methods can effectively overcome the instability of OPA derivatives, they should need complicated on-line derivatization procedure or sample preparation. As a fluorescent derivatization agent in biochemical field, FITC has been also applied in the determination of biogenic amines in soy sauce [13], cheese [16], and wine [17], but those problems associated with kinetics and label chemistry of this reagent can limit the application of these methods. The determination of polyamines was also studied by using DTAF with LIF detection. It reacted with spermidine to form three derivatives. Although all these three derivatives could be used for quantification, multiplex products will interfere the analysis of other amines [18].

The aim of this work is to establish a CE–LIF method for the analysis of biogenic amines that can avoid the drawbacks of above reagents. 3-(2-Furoyl)quinoline-2-carboxaldehyde (FQ) can easily react with primary amino compounds to form highly fluorescent and stable derivatives in presence of KCN [20]. The fluorescent excitation wavelength of their derivatives is close to the wavelength of commercial argon ion laser. Therefore, FQ was widely used in the determination of amino acids [20,21], protein [22,23] and phospholipids [24,25]. However, there are no reports about polyamines analysis using FQ. In this work, FQ was chosen as a derivatization reagent for the determination of biogenic amines including putresine (Put), histamine (Hist), cadaverine (Cad), tyramine (Tyr), tryptamine (Tryp), 2-phenylethylamine (Phe), spermine (Spm) and spermidine (Spd). The derivatization and separation parameters were studied in detail. Under the optimized derivatization and separation conditions, the eight biogenic amines derivatives can be well separated within 30 min by LIF detection. This developed method was also used in the direct determination of biogenic amines in extracts of tobacco leaf.

2. Experimental

2.1. Materials and chemicals

The biogenic amine standards (histamine, tyramine, tryptamine, 2-phenylethylamine, putrescine, cadaverine, spermine, and spermidine) were obtained as the hydrochloride salts from Sigma (St. Louis, MO, USA). Sodium deoxycholate (SDC) and

sodium dodecyl sulfate (SDS) were purchased from Fluka (Buchs, Switzerland). Boric acid, sodium borate, methanol, and acetonitrile were from Shanghai Chemicals (Shanghai, China). Unless otherwise specified, all reagents were of analytical reagent grade. All aqueous solutions were prepared from de-ionized water purified with a Milli-Q system (Millipore, Bedford, MA, USA).

FQ and KCN potassium were from Molecular Probes (Eugene, OR, USA). For storage, FQ was dissolved in methanol, aliquots were dispensed, and solvent was then removed under vacuum. The dried FQ was stored at −20 °C, and was directly used in the derivatization reaction without further treatment.

2.2. Apparatus

CE separations were performed on a G1600A Agilent 3D capillary electrophoresis system (Agilent, CA, USA) equipped with a LIF detection system consisting of a dual laser 488/514 nm Ar-Ion laser (Model: 163D02, Spectra-Physics, CA, USA), a laser-induced fluorescence detector ZETALIF 2000 (Picometrics, Montlaur, France) and Agilent interface 35900E (Agilent, CA, USA). The excitation was performed by a dual laser 488/514 nm Ar-ion laser with 20 mW at a wavelength of 488 nm. The emission intensity was measured at a wavelength of 560 nm filtered by a band pass filter and a notch filter was used to attenuate background radiations. Fluorescence was detected by a photomultiplier tuber. Data collection and process were performed on a G1601A Agilent 3D capillary electrophoresis chemstation (Agilent, CA, USA).

Fused-silica capillaries from Yongnian Optic Fiber Inc. (Hebei, China) with 65 cm (50 cm to detector)× 50 μm I.D×365 μm O.D. were used. A new capillary was pre-treated with 1 mol l^{-1} NaOH and H_2O for 60 min at room temperature prior to use.

2.3. Derivatization procedure

To a 500-μl vial containing 100 nmol dried FQ, 2 μl of aliquots for each amine (1 μmol l^{-1}), and 2 μl 25 mmol l^{-1} KCN were added. The derivatives of FQ with biogenic amines can hardly dissolve in water In order to ensure dissolution of biogenic amines derivatives and homogeneous derivatization reaction process, 6 μl methanol should be added. The vials of mixture were capped, vortexed, and allowed to react at 40 °C for 40 min. Finally; 40 μl of the running buffer were added to stop the derivatization reaction. The derivatives were stored at −20 °C.

2.4. Capillary electrophoresis

The running buffer was consisting of borate buffer (pH 9.35, 25 mmol l^{-1}), SDC aqueous solution (40 mmol l^{-1}) and 10% acetonitrile. Buffer solutions were filtered through a 0.22-μm membrane filter.

Each day before starting analysis, the capillary was rinsed with 0.1 mol l^{-1} NaOH and water for 20 min, then preconditioned with running buffer for 30 min. Between each run the capillary was flushed with 0.1 mol l^{-1} NaOH, water and the running buffer for 5 min. Samples were injected from the anodic end of the capillary hydrodynamically for 5 s at 50 mbar. Separations were carried out at 20 kV constant voltages at 25 °C.

2.5. Plant sample preparation

A sample of 0.5 g of fresh tobacco (*Nicotiana tabacum* cv. SRI) leaf was snipped and grinded to fine powder in the presence of liquid nitrogen. One ml of 5% trichloroacetic acid (TCA) was mixed with this powder in a 1.5-ml microcentrifuge tube. After being vortexed vigorously, the mixture was kept in an ice-bath overnight, then centrifuged at 12 000 *g* for 10 min. The supernatant, containing the free biogenic amines, was stored at −20 °C until derivatization. The extract was diluted 100 times with deionized water, and then derivatized with FQ using the same procedure for the derivatization of standard biogenic amine solutions.

3. Result and discussion

3.1. Separation conditions

The FQ biogenic amine derivatives have poor water solubility and bear no charge. Therefore, micellar electrokinetic capillary (MEKC) chromatography, which has been shown to be useful for the

separation of uncharged analytes, was applied for their separation. A MEKC system is usually obtained by the addition of an anionic surfactant above its critical micelle concentration (CMC) to the running buffer [26,27]. Separation of analyates was resulted from a combination of the electrophoretic mobility of the micelle/analyte and the endoosmotic flow (EOF). Therefore, it is important to choose appropriate surfactants for better separation. The most popular surfactant employed for MEKC is SDS. In preliminary work, when SDS was used as buffer additives, the eight derivatives cannot be separated adequately. In addition, high concentration of SDS cannot improve the resolution of these analytes. Among several ways of manipulating the selectivity in MEKC, the most effective is to change the type of surfactant. SDC, a bile salt surfactant with CMC of 6 m*M* [28], is alternative choice for the separation of hydrophobic analytes, especially for highly hydrophobic analytes, such as polychlorinated biphenyls or polycyclic aromatic hydrocarbons [29]. Furthermore, the cholate system can tolerate high concentration of organic solvents without drastic loss of efficiency and dramatic increase in analysis time [30]. In this paper, the resolution was greatly improved when SDC was used as the additive to borate buffer instead of SDS.

The conditions for the efficient separation of eight biogenic amines derivatives by MEKC were investigated. Several parameters that affect the migration behavior of these derivatives, such as organic modifiers, buffer concentrations, and surfactants concentrations, were studied in detail.

The separation of eight biogenic amines derivatives was incomplete when only SDC and borate were used as running buffer. In MEKC, the addition of organic modifiers to micellar solution has been shown to improve the separation of highly hydrophobic compounds that migrate near or with micelles, because organic modifiers can alter the EOF and extend the migration time windows. Methanol and acetonitrile were tested as organic modifiers in running buffer. The result showed that the addition of acetonitrile could provide better resolution for all eight FQ derivatives than methanol. We compared the effect of acetonitrile concentrations from 0 to 20% in the running buffer on migrate times of FQ-labeled biogenic amines. When acetonitrile concentration was lower than 10%, the peaks for the Put, Cad and Spd derivatives were partially overlapped. However, at higher acetonitrile concentrations (e.g., $>$15%), the resolution of Put, Cad and Spd could be improved but Phe derivative was no longer resolved from the Tryp derivative peak.

In the presence of acetonitrile (10%), the effect of SDC concentration in the running buffer was also investigated. Since the CMC of SDC is 6 m*M*, the tested concentrations of SDC, that means SDC at lower concentration than CMC does not improve resolution. When the concentration of SDC was 30 mmol l^{-1}, the peaks of Tryp and Phe can be overlapped. However, large increases in SDC concentration can produce large electrophoretic currents, thermal gradients within the column, and signification band dispersion. At SDC concentration greater than 50 mmol l^{-1}, all peaks were shifted to longer migration times without an enhancement in resolution due to their peak broadening. Complete resolution of the eight biogenic amine derivatives is almost achieved when SDC concentration is 40 mmol l^{-1}.

The effect of borate concentration on the separation was also examined. The ionic strength of the running buffer is an important factor for the CE separation efficiency. Increasing the borate concentration from 15 to 35 mmol l^{-1} prolonged the migration time of all derivatives analyzed, mainly because of the effect on the EOF. When the borate concentration was lower than 20 mmol l^{-1}, the peaks for Phe and Trp could not be resolved completely. However, the separation time was too long for analysis when the concentration of borate buffer was 35 mmol l^{-1}. Therefore, 25 mmol l^{-1} was chosen as optimum borate concentration used in the running buffer.

Based on these data the optimal condition for the separation of biogenic amines is as follows: 25 mmol l^{-1} borate, 40 mmol l^{-1} SDC and 10% acetonitrile, pH 9.35. Fig. 1 shows the separation of eight biogenic amine standards under optimized conditions.

3.2. Derivatization conditions

Generally, excess derivatization reagents should be applied for the quantitative analysis of biogenic

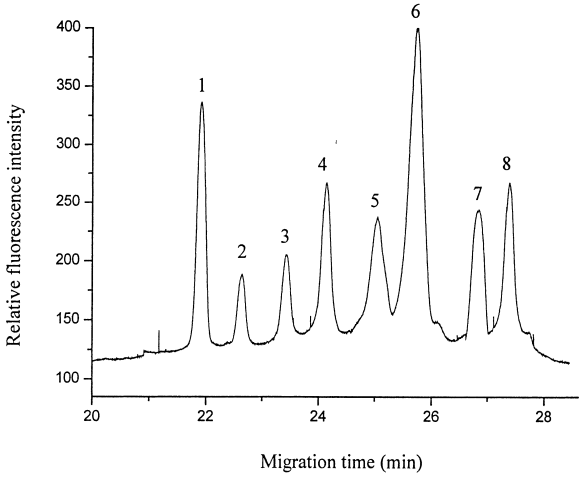

Fig. 1. Electropherogram of eight biogenic amines standards. Peaks: (1) Hist, (2) Put, (3)Cad, (4) Spd, (5) Spm, (6) Tyr, (7) Phe, (8) Tryp. The concentration of each biogenic amine is 1 μmol l^{-1}. Conditions: running buffer, 25 mmol l^{-1} borate buffer (pH 9.35), 40 mmol l^{-1} SDC, and 10% acetonitrile; capillary, 65 cm (50 cm effective length)×50 μm I.D.; injection, 5 s at 50 mbar; separation voltage, 20 kV; temperature, 25 °C.

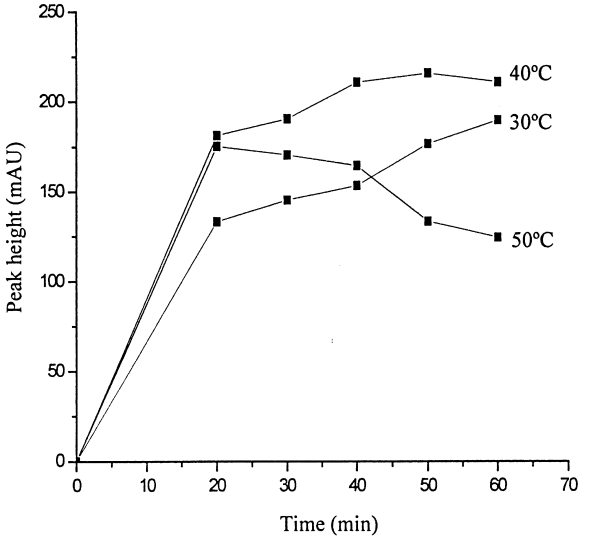

Fig. 2. Effect of reaction temperature and time on the formation of Hist derivatives.

amines, especially polyamines containing two or more amino groups. However, the hydrolysates of excess fluorescent labeling reagents, including DTAF, FITC, and AccQ, etc., may interfere the determination of analytes. As a fluorogenic derivatization reagent, FQ can overcome this shortcoming. Due to weak native fluorescence, excess FQ do not interfere the determination of these analytes.

The influence of FQ/amine ratio on derivatization efficiency was investigated. When the FQ/amine ratio was below 50, many interfering electrophoretic peaks were appeared by the formation of two or more derivatives by polyamines. As the FQ/amine ratio increased, the separation of these derivatives became better. When the amount of FQ exceeded by nearly 100 times that the total concentration of analytes, the derivatization efficiency can reach maximum. Polyamines can also form main derivatives that be used for quantification, respectively.

Reaction temperature is a critical factor for the derivatization reaction. The derivatization reactions of FQ with amino compounds need heating. In this paper, the effect of temperature on derivatization was investigated by using Hist as a representative analyte (Fig. 2). When reaction temperature was 30 °C, the derivatization reaction procedure need more time because low temperature can reduce the reactivity of FQ toward amines. However, when the reaction temperature was 50 °C, the yields of derivatives were also decreased. This is probably due to the unstable characteristics of isoindole ring of FQ-Hist derivative toward high-temperature. Therefore, 40 °C was selected as derivatization reaction temperature.

The effects of the reaction time for the derivatization reaction on the yields of derivatives were also analyzed by changing the reaction time from 0 to 60 min. As can be seen in Fig. 2, the derivatization yield of FQ with Hist reached their maximum plateau in about 40 min and was not increased by prolonging reaction time. The derivatization reaction time was chosen as 40 min. This derivatization procedure using FQ for biogenic amines is faster than using FITC or other derivatization reagents.

3.3. Reproducibility, linear calibration and detection limits

In order to ensure the reproducibility of this method, the capillary should be washed with NaOH, water and then running buffer between runs, which can eliminate the absorption of highly hydrophobic

analyates onto the capillary wall. The reproducibility was evaluated by examining six sequential runs of biogenic amines standard solution (in concentration of 1 μmol l^{-1}) for the migration time and peak area (Table 1). As can be seen, the RSD (relative standard deviate) for the eight FQ-derivatives was from 0.9 to 1.8% for migration time and from 3.4 to 5.8% for peak area. It was shown that the quantification and qualification of biogenic amines could be well done by this CE–LIF method.

A test mixture was diluted to varying concentrations of standard biogenic amines and analyzed using the optimized derivatization reaction procedure and separation conditions for determination of linearity. The lowest detectable amount of biogenic amines was calculated as the amount of biogenic amine that resulted in a peak three times greater than that of the baseline noise. The linear calibration ranges, regression equations, and detection limits of biogenic amines was calculated from peaks and listed in Table 1. The correlation coefficients for these biogenic amines were from 0.9967 to 0.9992, indicating good linearity. The detection limits for the eight labeled amines range from 0.5 nmol l^{-1} for Hist up to 10 nmol l^{-1} for Phe. Increasing the injection time can further lower the detection limits of the developed procedure.

3.4. Analytical application

This developed method has been also applied to the determination of biogenic amines in extracts of tobacco leaf. In order to make the concentration of biogenic amines in linear calibration range and decrease the influence of TCA on derivatization reaction, the real sample should be diluted with water. The sample was derivatized with FQ according to the procedure described in Section 2.3. The peaks were identified by spiking a mixture of standard biogenic amines to the sample solution before injection. The electropherogram of real sample is shown in Fig. 3. As can be seen in Fig. 3, other co-existing amino compounds in tobacco leaf tissue, such as amino acids, ammonia, etc., did not interfere the determination of biogenic amine under the optimized derivatization and separation procedure.

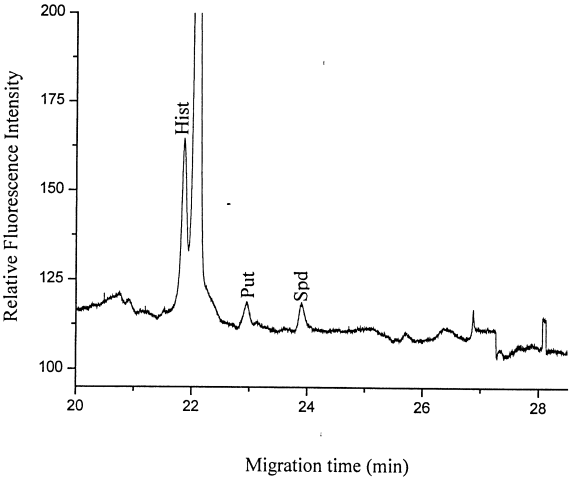

Fig. 3. Electropherogram obtained from extract of tobacco leaf (diluted 100 times). The separation conditions were identical to Fig. 1.

Table 1
Linearity, reproducibility, and calculated detection limits of the proposed method

FQ derivative	Calibration range (μmol l^{-1})	Regression equation	γ	RSD (%)		Detection limit (nmol l^{-1})
				MT	PA	
Histamine	0.01–1	$y = 2.04 \times 10^5 x + 152$	0.9987	0.9	3.4	0.5
Putresine	0.05–1	$y = 9.93 \times 10^4 x + 161$	0.9992	1.2	4.7	5
Cadaverine	0.05–1	$y = 1.40 \times 10^5 x + 328$	0.9990	1.2	4.7	2.5
Spermine	0.05–1	$y = 1.61 \times 10^5 x + 421$	0.9986	1.2	3.8	2.5
Spermidine	0.01–1	$y = 1.39 \times 10^5 x + 305$	0.9989	1.1	4.1	2.5
Tyramine	0.01–1	$y = 2.53 \times 10^5 x + 408$	0.9974	1.3	3.6	1
2-Phenylethylamine	0.05–1	$y = 7.57 \times 10^4 x + 45.6$	0.9996	1.8	4.8	10
Tryptamine	0.01–1	$y = 1.98 \times 10^5 x + 965$	0.9967	1.8	4.4	1

MT, migration time; PA, peak area;
x, concentration of analyte (μmol l^{-1}); y, integrated peak area (mAUs).

Table 2
Analytical results of Hist, Put, and Spd in tobacco with FQ

Amine	Content (nmol g^{-1})[a]	RSD (%, $n=5$)	Recovery (%)
Hist	78	6.7	95
Put	5.4	7.8	94
Spd	8.5	5.4	90

[a] nmol g^{-1} (fresh weight).

This method showed better anti-interference capability compared to other methods used in the determination of biogenic amines. The result indicated that there are small amount of Hist, Put and Spd in tested sample and other biogenic amines were not identified by this method. The contents of Hist, Put, and Spd from tobacco leaf are summarized in Table 2.

4. Conclusion

The proposed method appears to be suitable for the rapid and sensitive determination of biogenic amines. The amines derivatives are stable, highly fluorescent and can be detected in extremely low concentration. The eight amine derivatives were well separated by using optimized running buffer containing borate buffer (pH 9.35, 25 mmol l^{-1}), SDC aqueous solution (40 mmol l^{-1}) and 10% acetonitrile. The detection limits can reach 10^{-10} mol l^{-1} and thus are equivalent to or better than the detection limits obtained by common methods that were used in the determination of biogenic amines. Examples of analysis of biogenic amines from tobacco demonstrate that this proposed CE–LIF method seems to be an attractive choice for the determination of trace biogenic amines in plant tissues and other biological samples.

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