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Field-amplified sample injection and in-capillary derivatization for sensitivity improvement of the electrophoretic determination of histamine

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Abstract

The feasibility of the combination of field-amplified sample injection (FASI) and in-capillary derivatization was explored for improving sensitivity of histamine in capillary electrophoresis (CE). Naphthalene-2,3-dicarboxaldehyde (NDA) was used as derivatization reagent. The reagent and sample was introduced by tandem mode. The derivatization was accomplished by at-inlet mode with standing time of 1.5 min. The combination of FASI and in-capillary derivatization was successfully achieved with about 400-fold concentration sensitivity enhancement compared to pre-capillary derivatization at the same set-up. The detection limit of concentration for histamine reached 1.25×10^{-11} M by CE and fluorescence detection with S/N = 3. Parameters affecting FASI and in-capillary derivatization process including sample matrix, buffer concentration and reagent injection amount, were investigated.
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Keywords: Capillary electrophoresis; Field-amplified sample injection; In-capillary derivatization; Histamine

1. Introduction

In the past decades, capillary electrophoresis (CE) has been considered a powerful method and applied widely to analyze lots of different substances ranging from small inorganic ion to large bio-macromolecules, due to many advantages, such as the high separation speed and efficiency, very low running costs and low sample volume injected (e.g., 2–10 nl). However, the reduced concentration sensitivity of CE (compared to HPLC), derived from the low injected sample volumes and the short optical path-lengths (e.g., 25–100 μm), is still a big challenge, and makes the detection of trace levels of analytes very difficult [1].

Thanks to the enthusiastic efforts of scientists, several on-line sample pre-concentration methods have been developed to overcome the sensitivity problem, such as isotachophoresis [2,3], dynamic pH junction [4,5], large volume sample stacking [6–10], pH-mediated stacking [11–14], stacking with organic solvent [15–17], high-salt stacking technique [18,19], sweeping [20–23], dynamic pH junction-sweeping [24,25] and field-amplified sample injection (FASI) [26–32]. Among all the above mentioned strategies, FASI, also called head-column field-amplified sample stacking and first used in zone electrophoresis by Haglund and Tiselius [33], has been demonstrated to be the simplest and very effective sample stacking method, especially for cation stacking, up to 10^6-fold enhancement obtained for metal ion analysis [32]. And recently, Quirino and Terabe [34] developed a novel technique (combination of FASI and sweeping) for positively chargeable analytes, rendering about a million-fold sensitivity increase.

On the other hand, derivatization plays an important role in capillary electrophoresis, which increases the detection selectivity and sensitivity by introduction of UV-absorbing or fluorescing groups into the molecules. And without derivatization, some compounds are very difficult to be directly studied by CE. Generally, there are three derivatization modes: pre-column, on-column and post-column, with each of them showing different features. The most favorable features of on-column derivatization compared to pre-column derivatization is the small reaction chamber in the capillary, which means the minimum dilute volume, while compared to post-column mode is the needless of the complex instrument. The main advantage and disadvantage of the above derivatization modes have been described in the literature [35]. Till now, on-column derivatization, also called in-capillary derivatization, has been applied to analyze amino

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acid, biogenic amines and gentamicin by one of the three different strategies [36–43]: zone-passing, at-inlet, and throughout capillary derivatization.

How about introduce the on-line sample pre-concentration method to the on-column derivatization? It is expected that the sensitivity could be sharply increased and this combination strategy would open up a new avenue for the development of CE. Actually, Latorre et al. [44] has successfully increased the sensitivity of amino acid analysis dramatically by using combination of large-volume sample stacking and in-capillary derivatization with 1,2-naphthoquinone-4-sulfonate as the labeling reagent. However, the related study is still very scarce.

In this paper, we first explore the possibility of the combination of FASI and in-capillary derivatization for the determination of histamine with NDA as derivatization reagent. And with this procedure, about 400-fold concentration sensitivity enhancement is achieved compared to pre-capillary derivatization.

2. Experimental

2.1. Apparatus

CE was carried out on a laboratory-built system based on an upright fluorescence microscope (Olympus, Japan), a photomultiplier tube (PMT), a ±30 kV high-voltage dc power supply (Shanghai Institute of Nuclear Research, China) and a uncoated fused-silica capillary of 42–43 cm (32–32.5 cm length to the detector window) × 50 μm I.D. × 365 μm O.D. (Yongnian Optical Conductive Fiber Plant, China). A 100-W high-pressure mercury lamp was used as the excitation radiation. The optical sub-system in the microscope consisted of a 40× objective, a NIB excitation cube including an excitation filter (EX 400–490 nm), a dichroic mirror (DM 510 nm) and a barrier filter (BA 515 nm). The signal from the PMT was monitored using photon-counting device (Beijing Bingsong Photon Technological Corporation, China) and collected by a computer (Inter PIII550) with photon-counting software, and processed with Origin software packages. The conductivity was measured using the DDSJ-308 conductivity apparatus (Shanghai Lei-ci Instrument Plant, China).

2.2. Chemicals

Histamine dihydrochloride purchased from Sigma (St. Louis. MO) were prepared at a concentration of 1.0×10^{-2} M in pure water, and stored in a refrigerator. NDA was obtained from Aldrich. 1.0×10^{-2} M NDA stock solution was prepared in methanol and stored in refrigerator. Two-hundred millimolars NaCN stock solution was prepared with water purified with milli-Q purified system (Millipore, MA, USA). For pre-capillary derivatization: the histamine sample solution was diluted to the desired concentration with water; and 0.5 mM NDA solution was prepared in methanol, 20 mM NaCN solution was prepared in water. For FASI and in-capillary derivatization: the histamine was prepared in 0.15 mM NaCl aqueous solution; NDA solution consists of 0.5 mM NDA, 10 mM borate buffer and 50% methanol (pH 9.1); 15 mM NaCN was prepared in 10 mM borate buffer (pH 9.1). Other chemical reagents were of analytical grade and used without further purification. Carrier electrolyte for capillary electrophoresis was prepared with milli-Q water.

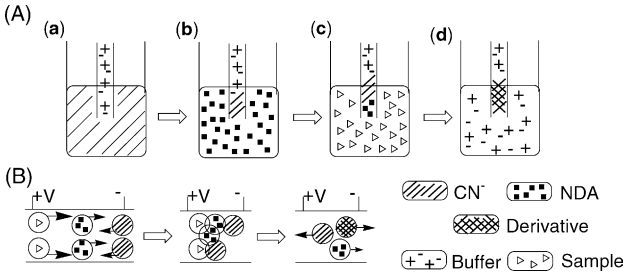

Fig. 1. Scheme of the injection and derivatization process: (A) tandem injection: 38 s at 14 cm height CN^-, 20 s at 14 cm height NDA, 20 kV × 5 s histamine sample; (B) likely mixing mechanism and derivatization process by standing for 1.5 min, and separation at 20 kV.

2.3. Pre-capillary derivatization procedure

Thirty microlitres of histamine solution, 10 μl of 2.0×10^{-2} M borate buffer (pH 9.1), 10 μl of 2.0×10^{-2} M cyanide, and 20 μl of 5.0×10^{-4} M NDA solution was added sequentially and thoroughly mixed. The resultant solution was allowed to stand for 3 min at room temperature prior to injection. The derivatization procedure was the same as previous reported [45]. Sample injection was performed by hydrodynamic mode with sampling height at 9 cm for 30 s.

2.4. In-capillary derivatization and FASI

In-capillary derivatization by the at-inlet technique was performed using tandem mode. Briefly, NaCN solution was first introduced into capillary by hydrodynamic mode with sampling height at 14 cm for 38 s, and NDA solution was injected with sampling height at 14 cm for 20 s, then the sample of histamine was injected with 20 kV for 5 s with cathode at the detector end of the capillary. The derivatization was performed with standing time of 1.5 min in capillary. Fig. 1 shows the injection diagram, and derivatization process.

2.5. Capillary electrophoresis

A new capillary was pre-treated with 1.0 M NaOH, water for 30 min sequentially. Each day before analysis, the capillary was rinsed with 0.1 M NaOH, water for 10 min and preconditioned with running buffer for 10 min at room temperature.

The electrophoresis buffer consisted of 42 mM sodium dihydrogen phosphate (pH 5.15). Separations were carried out at a constant voltage of 20 kV with cathode at the detector end of the capillary.

3. Results and discussion

3.1. In-capillary derivatization reaction process

NDA, a fluorescence derivatization reagent, was developed by de Montigny et al. for derivatization of primary amines in

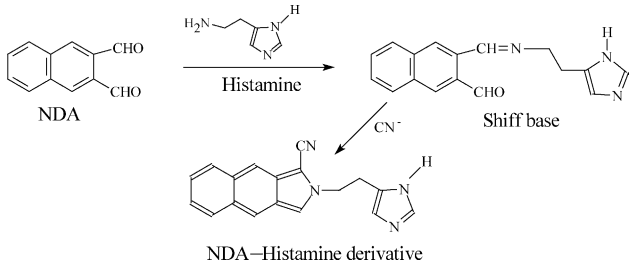

Fig. 2. Derivatization reaction mechanism scheme of NDA with primary amines in the presence of cyanide.

the presence of cyanide to produce high fluorogenic derivatives [46]. The reaction mechanism was showed in Fig. 2. And it has been demonstrated that the addition order of reagents is important in minimizing possible benzoin condensation reactions [47]. Generally, amines were firstly mixed with CN^-, then NDA was added to the mixture solution. This indicated that the mixing of amines, NDA and CN^- is essential for the derivatization reaction in high yield. In our experiment, it was found that NDA can react with CN^- and gradually produce red precipitates with increasing time. And in the previous case, Gilman and Ewing [48] has successfully used the pre-mixed NDA and CN^- solutions to determine the dopamine and five amino acids in single PC12 cell, but the mixed NDA and CN^- solution should be prepared just before each experiment, which increased the reagent costs. The reason might be due to the reaction between NDA and CN^- as we observed. To overcome the above problem, an on-column mixing mode was attempted in this case. It is known in CZE: NDA migrated towards cathode with the electroosmotic flow as other neutral compounds; and histamine (positively chargeable) migrates towards cathode with higher velocity than that of NDA; CN^- would migrate towards the anode, due to its high ion mobility (absolute mobility, also called limiting ionic mobility, μ_{ab} was 8.0×10^{-4} cm^2 s^{-1} V^{-1}, obtained using the formula $\lambda^\infty = \mu_{ab} \times F$, where λ^∞ is the limiting ionic molar conductivity, which can be obtained from Lange's Handbook of Chemistry; F, the Faraday's constant). Therefore, it is possible for them to meet together in the capillary as injected in the order of CN^-, NDA and histamine when high voltage was applied. Fig. 1B shows the likely in-capillary mixing and derivatization process in our case. Thus, in the experiments, the CN^- and NDA were introduced into the capillary sequentially by hydrodynamic mode, and then histamine sample was injected by electrokinetic mode. With this procedure, good experimental results were obtained, meaning that in-capillary derivatization of histamine with NDA/CN^- was successful.

3.2. Effect of sample matrix on stacking in capillary

FASI is one of the most common approaches to improve concentration sensitivity in CE. When the sample matrix has a significantly lower conductivity than that of running buffer, the analytes in the sample zone with high migration speed would decelerate sharply at the boundary of the running buffer, then the stacking was achieved [5]. The higher the conductivity differences between the sample and the running buffer, the larger the stacking effect [34]. Generally, the larger stacking can be obtained when the samples are prepared in pure water instead of diluted buffer. At the very beginning, histamine was prepared in pure water as in general FASI cases, it was found that the combination of FASI and in-capillary derivatization did not occur by multiple repeated experiments, as there was no histamine-NDA derivative peak detected in CE in this case. But when histamine was prepared in 0.4 mM NaCl aqueous solution, the derivatization and stacking in capillary was successful, and good reproducibility was obtained. The examination of the effect of concentration of NaCl in sample solution showed that the relative fluorescence intensity (RFI) gradually decreased when the concentration ranged from 0.16 to 0.56 mM, indicating the decreased stacking effect with increased concentration of sample matrix, similar as in conventional FASI case. But no peak appeared in CE when histamine was dissolved in 0.10 mM or lower than 0.10 mM of NaCl solution, and also, by observing the capillary in detection window with naked eyes by microscope, there is no green fluorescence produced in the capillary in this case. And in the experiments, it was found that the injection current decreased with the increase of the injection time when histamine was prepared in 0.16–0.56 mM NaCl solution, but did not do so with the injection time when histamine was prepared in 0.10 mM NaCl solution or pure water. This phenomenon exactly coincides with whether the peak of NDA-labeled derivative is detected or not, indicating that a little amount of salt is needed for the successful combination of FASI and in-capillary derivatization in this case. Similar phenomena were observed with NaH_2PO_4 as the sample matrix. The relative fluorescence intensity gradually decreased when the concentration of NaH_2PO_4 ranged from 0.24 to 0.56 mM, but no peak was obtained with 0.16 mM or less than 0.16 mM NaH_2PO_4. The different required concentrations of NaH_2PO_4 and NaCl were probably caused by different conductivity of NaH_2PO_4 and NaCl with same concentration. The conductivities of 0.16 mM NaH_2PO_4, 0.24 mM NaH_2PO_4, 0.16 mM NaCl and 0.24 mM NaCl were measured to be 17.04, 23.0, 22.1 and 30.9 μS/cm, respectively. Thus, 0.15 mM NaCl aqueous solution was used as the sample matrix for further study.

3.3. Effect of derivatization pH and the concentration of borate in NaCN and NDA solution

The derivatization pH value would affect the derivatization reaction velocity [46]. The pH value effect was investigated in the range of 7.0–10.8. The optimum pH value was found to be between 9.0 and 9.3, similar to previous results in pre-capillary derivatization [45,46]. To optimize the stacking efficiency, the effect of borate concentration in NaCN and NDA solution were studied in detail, respectively. It was found that the RFI was high with the concentration of borate at 5–15 mM in NaCN solution, but decreased with further increasing the concentration. The peak width at half-height ($W_{1/2}$) increased slowly with the concentration ranging from 5 to 20 mM, but increased rapidly when the concentration is greater than 20 mM. The reproducibility was bad when the concentration was lower than 5 mM. The conductivities of 5, 10, 15, 20, 30 and 40 mM borate in 15 mM NaCN

solution were measured to be 2.17, 2.72, 3.33, 3.85, 5.04 and 6.12 mS/cm, respectively. The conductivity of 42 mM NaH_2PO_4 was measured to be 2.88 mS/cm. Comparing the conductivities of different concentrations of borate in NaCN solutions with that of 42 mM NaH_2PO_4, we considered that the decreased RFI and the increased $W_{1/2}$ with high concentration of borate in NaCN solutions was probably due to the increased conductivity leading to the de-stacking effect of NDA-labeled histamine at the boundary of running buffer. So 10 mM borate was used in NaCN solution. The examination of effect of concentration of borate in NDA solution showed that the RFI increased with the increase of concentration at 0.5–5 mM, and changed slightly within 5–15 mM, then began to decrease with further increasing the concentration. The peak efficiency was also dependent on the concentration of borate. The peak width at half-height decreased slightly with the increase of concentration at 0.5–5 mM, but increased gradually when the concentration ranged from 5 to 40 mM. So 10 mM borate was chosen for further investigation. The conductivities of 0.5, 2.5, 5, 10, 15, 20, 30 and 40 mM borate in 0.5 mM NDA, 50% methanol solution were measured to be 0.05, 0.22, 0.42, 0.81, 1.14, 1.48, 2.20 and 2.80 mS/cm, respectively.

3.4. Effect of concentration of CN^-

The research on pre-capillary derivatization of amino acid [46,47,49] with NDA/CN^- has demonstrated that to ensure the complete reaction, the concentration of NDA and CN^- should be in large excess over that of amino acid, and the optimal ratio between cyanide and NDA was at least 10 [50]. The effect of concentration of CN^- and NDA on derivatization was examined. It was found that 0.5 mM NDA was needed for the rapid derivatization. With NDA at the fixed concentration of 0.5 mM, the effect of concentration of CN^- was examined in the range of 2.5–100 mM. The results showed that at least 5 mM CN^- was needed to obtain the high RFI. Under this conditions, the ratio between [CN^-] and [NDA] was 10, coinciding well with previous reported ratio [50] in the pre-capillary derivatization system. And relatively stable RFI were obtained in the range of 10–30 mM. When the concentration of CN^- was beyond 30 mM, the RFI began to decrease. The peak width at half-height increased slightly when the concentration was between 2.5 and 20 mM, but increased obviously with the concentration at or higher than 30 mM. So 15 mM NaCN was chosen for further studies. The conductivities of 2.5, 5, 10, 20, 30, 50 and 100 mM NaCN in 10 mM borate solution were measured to be 1.58, 1.80, 2.28, 3.12, 4.02, 5.85 and 10.06 mS/cm, respectively. Comparing the conductivities of different concentration of NaCN in 10 mM borate solution with that of 42 mM NaH_2PO_4, it can be considered that the decreased RFI and the increased $W_{1/2}$ under the high concentration of NaCN condition probably was also due to the increased conductivity leading to the de-stacking effect.

3.5. Effect of reagent introduction time

The amount of reagent injected would influence the derivatization reaction and FASI process. With sample height at 14 cm, the optimum injection time of NaCN and NDA solution were investigated, respectively. The results showed that the RFI was high and relatively stable with the injection time of NaCN solution at 30–50 s, and decreased with further increased time. And when the time is less than 30 s, the reproducibility was not very good. The peak width at half-height gradually increased with increasing injection time. To get high RFI and good peak efficiency, 35–40 s was optimum range for the injection time of NaCN solution. Unlike the effect of the injection time of NaCN solution, it was found that the RFI was strongly dependent on the injection time of NDA solution. RFI reached the maximum when the introduction time was 20 s, and then gradually decreased with further increasing time. When the injection time reached 50 s, RFI sharply decreased and the peak width at half-height dramatically increased. The reason was probably that the amount of NDA injected would significantly influence the FASI process and the mixing of sample with labeling reagent in the capillary.

3.6. Effect of reaction time in capillary

In the pre-capillary derivatization study, it has been found that the reaction of NDA with histamine was very quick, and almost completed in about 3 min [45]. The in-capillary derivatization reaction time under the above conditions was optimized. RFI increased with increasing reaction time from 0.5 to 1 min, and was almost unchanged within 4 min. And the peak width at half-height was also almost unchanged within 4 min. But when the time reached 5 min, the RFI decreased dramatically and the peak width at half-height obviously increased. This is reasonable. The pH value of the derivatization buffer in capillary was 9.1, then the ionization of the surface silanol group of capillary increased with the increase of reaction time, then the absorption effect of the capillary wall with NDA-histamine derivative would be stronger, leading to peak tailing. As to the derivatization mechanism, we considered that histamine, NDA and CN^- would mix together during the process of injection of histamine, then the derivatization reaction occur when the voltage is stopped. So, 1.5 min of reaction time was selected.

3.7. Effect of concentration running buffer and the injection time of sample

It was well known that the sample stacking is dependent on the difference of conductivity between the sample and running buffer. The concentrating effect is directly proportional to the enhancement factor or ratio between the conductivity of the background and sample [34]. When the concentration of NaH_2PO_4 buffer increased from 20 to 40 mM, the RFI was proportional to the increase of the concentration, however, further increasing the concentration, the RFI levels off, indicating that at least 40 mM of running buffer concentration was needed for high stacking effect. In this case, 42 mM was used as the buffer concentration for study. Under the above optimum conditions, the sample injection time at 20 kV was also optimized. It was found that the signal increased with increasing the time within 4 s, and almost unchanged from 4 to 5 s, then began to decrease gradually with the increase of the injection

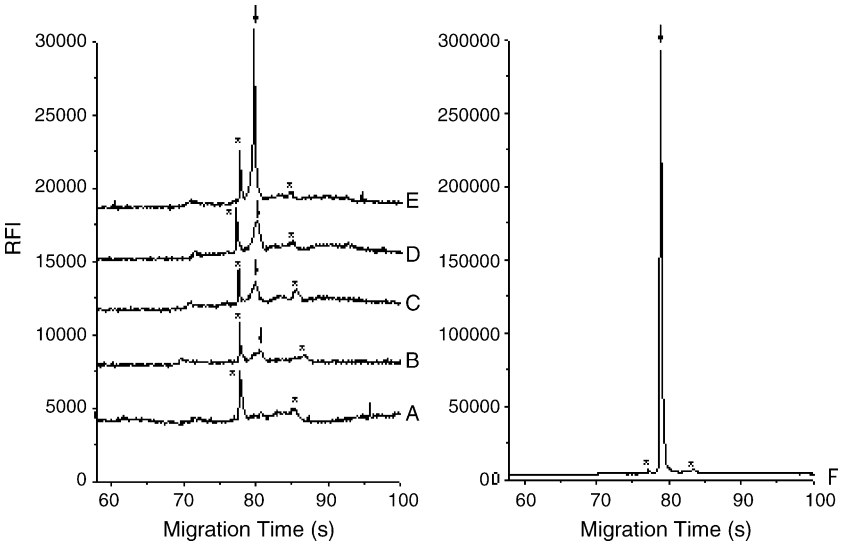

Fig. 3. Electropherograms of histamine with different concentrations with FASI and in-capillary derivatization method under the optimum conditions: (A) 0; (B) 1.25×10^{-11} M; (C) 2.5×10^{-11} M; (D) 5.0×10^{-11} M; (E) 2.5×10^{-10} M; (F) 7.5×10^{-9} M. The peak marked with arrowhead was the peak of NDA-labeled histamine, the other peak marked with (*) were the background.

time, and when the time was 10 s, the RFI and peak efficiency decreased dramatically. So 5 s at 20 kV was used for injection.

3.8. Calibration, reproducibility and detection limit

Fig. 3 shows the electropherograms of a series of histamine sample with different concentration by the combination technique of FASI and in-capillary derivatization under the optimum conditions. Using the fluorescence intensity versus sample concentration, the linear calibration curve was obtained in the range of 1.25×10^{-11} to 7.5×10^{-9} M with regression coefficient of 0.998. The reproducibility was performed by five injection of the standard solution with concentration of 7.5×10^{-9} M. The relative standard deviation (RSD) of the peak height and the migration time were 6.0% and 2.2%, respectively. As shown in Fig. 3B, the detectable concentration limit can be reduced to 1.25×10^{-11} M with S/N = 3.

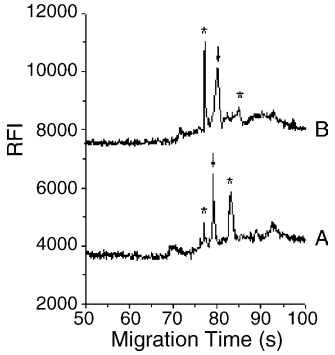

Fig. 4. Comparison of the sensitivity of histamine analysis with pre-capillary derivatization (A) and FASI combined with in-capillary derivatization (B). Histamine concentration: (A) 2.5×10^{-8} M; (B) 5.0×10^{-11} M. The peak marked with arrowhead was the peak of NDA-labeled histamine, the other peak marked with (*) were the background.

3.9. Sensitivity comparison with pre-capillary derivatization

Fig. 4 shows the comparison of the determination of histamine by pre-capillary derivatization and FASI combined with in-capillary derivatization on the same experimental set-up. The peak marked with arrowhead in Fig. 4 was the peak of NDA-labeled histamine. It can be seen in Fig. 4 that the comparative peak height can be obtained with 500-fold diluted sample by the combination of FASI and in-capillary derivatization. By comparing the fluorescence intensity value observed for the 500-fold diluted and undiluted samples, the concentration sensitivity enhancement can be calculated to be about 400-fold.

4. Conclusion

This work illustrated that FASI in combination with in-capillary derivatization was a useful technique for improving the sensitivity of the detection of histamine in CE with NDA as the fluoregenic derivatization reagent. Successful in-capillary mixing of CN^-, NDA and histamine, and derivatization of histamine were obtained with tandem injection order of CN^-, NDA and histamine. Under the optimum conditions, about 400-fold enhancement of concentration sensitivity can be obtained compared to pre-capillary derivatization for analysis of histamine. 1.25×10^{-11} M of detection limit of concentration can be reached. It is expected that the combination of FASI and in-capillary derivatization could be applied to increase the sensitivity of other compounds analysis.

Acknowledgements

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