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Analytical Methods

Tuneable surface enhanced Raman spectroscopy hyphenated to chemically derivatized thin-layer chromatography plates for screening histamine in fish

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ABSTRACT

Reliable screening of histamine in fish was of urgent importance for food safety. This work presented a highly selective surface enhanced Raman spectroscopy (SERS) method mediated by thin-layer chromatography (TLC), which was tailored for identification and quantitation of histamine. Following separation and derivatization with fluram, plates were assayed with SERS, jointly using silver nanoparticle and NaCl. The latter dramatically suppressed the masking effect caused by excessive fluram throughout the plate, thus offering clear baseline and intensive Raman fingerprints specific to the analyte. Under optimized conditions, the usability of this method was validated by identifying the structural fingerprints of both targeted and unknown compounds in fish samples. Meanwhile, the quantitative results of this method agreed with those by an HPLC method officially suggested by EU for histamine determination. Showing remarkable cost-efficiency and user-friendliness, this facile TLC-SERS method was indeed screening-oriented and may be more attractive to controlling laboratories of limited resource.

1. Introduction

Histamine (His), the enzymatic decarboxylation product of histidine, was commonly recognized as a critical marker for food decomposition. However, the last decade witnessed increasing awareness of its impacts on food safety. It had been well documented that food containing high levels of His seriously endangered consumers that are allergic to its potential toxicity (Linares et al., 2016; Mohammed, Bashammakh, Alsibaai, Alwael, & El-Shahawi, 2016). Despite stringent regulations, His was still ranked among the most problematic bio-contaminants, especially in fish products. According to the 2014 annual report of the rapid alert system for food and feed, the number of food safety incidences exclusively due to His grossly account for 7.4% of total notifications on food poising cases around European Union.

Among the large varieties of methods available, HPLC linked with different detectors, especially mass spectrometry, was regarded as the "gold-standard" for assaying His in bio-tissues (Daniel, dos Santos, Vidal, & do Lago, 2015; Evangelista et al., 2016; Mohammed et al., 2016; Yesudhason et al., 2013). Though achieving remarkable specificity and sensitivity, these methods shared common drawbacks intrinsic to column separation like poor throughput and laborious sample preparation. Against this background, increasing attention was paid to thin-layer chromatography (TLC) as a powerful and facile platform for screening tasks (Agatonovic-Kustrin, Morton, & Yusof, 2016; Bernard-Savary & Poole, 2015; Cretu & Morlock, 2014; Jyotshna, Srivastava, Killadi, & Shanker, 2015; Lebot, Do, & Legendre, 2014). While enabling simultaneous separation of many samples, TLC hyphenated with state-of-the-art detections, like mass spectrometry (Chen & Schwack, 2013; Cheng, Huang, & Shiea, 2009; Morlock & Schwack, 2010), atomic fluorescence spectrometry (Liu, Zhu, Zheng, & Hu, 2012), biosensor (Chen & Morlock, 2015; Chen & Schwack, 2014; Choma & Grzelak, 2011; Klingelhöfer & Morlock, 2015; Teh & Morlock, 2015) and Raman spectroscopy (Li et al.,

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2011; Lucotti et al., 2012; Zhang, Liu, Liu, Sun, & Wei, 2014) was a new interdisciplinary frontier in analytical chemistry. Because of much superior specificity and simplicity, the combination of TLC with surface enhanced Raman spectroscopy (SERS) was particularly attractive. Apart from the high sensitivity (even to single molecules), SERS essentially mirrored the advantages of normal Raman spectroscopy, offering characteristic fingerprints unique to analyte structures. Therefore, SERS can even replace the roles of analyte standards in routing screening. These advantages ultimately endued outstanding usability of TLC-SERS, therefore extremely suitable for straightforwardly identifying targeted spots based on unambiguous molecular information.

In previous researches, SERS measurements were exclusively performed with intact TLC layers. But, this did work with UV/vis-invisible compounds like His, because the aiming of the incident laser must be precisely adjusted. Facing this problem, an alternative using programmable scanning on large area of plate layers deposited with SERS substrate was proposed by Sepaniak and Zhang (Freye, Crane, Kirchner, & Sepaniak, 2013; Zhang et al., 2014). But this strategy was obviously not a smart choice for rapid screening tasks, concerning the expensive instrumentation and time-consuming procedures. For this reason, direct SERS measurements on derivatized TLC plates was especially more attractive for on-site screening.

To keep up with the concept of simple and reliable principles, the objective of this work was to establish a TLC-SERS method for direct identification and quantitation of His visualized by fluram. Facing the masking effect caused by derivatization, the joint use of classic silver nanoparticles (AgNPs) colloid in combination with NaCl aqueous solution was optimized to achieve intensive and specific fingerprint spectra of the analyte. Furthermore, the performances of the proposed method was validated with fish samples.

2. Experimental

2.1. Reagents and devices

Histamine dihydrochloride (>99% purity), fluram (>99% purity) and other chemical reagents of analytical purity were purchased from Sigma Aldrich (Shanghai, China). Water was bi-distilled. Silica gel 60 glass plates from Merck (10 × 20 cm, SN. 1.05626.0001) were washed by pre-developing with methanol, dried at 120 °C by TLC heater III (CAMAG, Muttenz, Switzerland) for 20 min and stored in a ziplock. Fresh and stored Ribbonfish and Tuna samples were purchased from local supermarket.

2.2. AgNPs preparation and characterization

Sodium citrate reduced AgNPs colloid was synthesized according to the classic method of Meisel (Lee & Meisel, 1982) and characterized by UV–vis spectrometer and Scanning Electronic Microscopy (Fig. 1S). Then, following the method of Chen (Shi, Liu, & Chen, 2016), 5 mL raw AgNPs colloid was concentrated by centrifuging (4000 r/min, 10 min) and carefully discarding upper 4.5 mL supernatant, respectively. The final 0.5 mL residue was re-suspended by vigorously shaking with a vertex for 1 min, resulting in 10-fold concentrated AgNPs colloid.

2.3. Sample preparation

Standard solution of His was freshly prepared in methanol at concentrations of 0.05 mg/mL. The extraction and cleanup of fish samples were principality based on the method of Yesudhason et al. (2013) and Gloria (Evangelista et al., 2016) but simplified. Briefly, 10 g fish muscle was sufficiently minced with 10 mL of 10% trichloroacetic acid in water using a homogenizer. If necessary, the homogenate was spiked with His standard, resulting in artificial contamination at 5, 10, 15 mg/kg. The homogenate neutralized by 0.1 mL 0.25 g/mL NaOH solution was centrifuged at 3000 r/min for 5 min and 2 mL of the supernatant was then filtered through a 0.45 μm membrane filter.

2.4. TLC procedure

Using 0.5 MPa nitrogen gas as carrier, 2–4 μL His standard and fish samples were precisely sprayed onto TLC plates (10 × 10 cm) as 6 mm bands using by Linomat 5 with a 100 μL syringe (CAMAG), with 8 mm distance from the button, 12 mm from the left side, and 1.7 mm distance between the tracks. The development was performed by ADC-2 (CAMAG) with 10 mL methanol/acetone/ammonia (25%), 3/7/0.5 (v/v/v) to 50 mm from the lower edge. Before development, the chamber saturation was achieved by placing another 10 mL mobile phase together with a piece of filter paper into the second trough. The developed plate was sufficiently dried (80 °C 3 min) and dipped into 0.1 mg/mL fluram in acetone, using a TLC Immersion Device III (CAMAG) with a vertical speed of 2 cm/s and 2 s immersion time. After heating at 80 °C for 3 min, the images (0.10 mm/Pixel resolution) of plates was carried out with Visualizer 4 (CAMAG) under 366 nm lighting.

2.5. TLC-SERS procedure

After instrumental TLC procedures, plates were visualized under 366 nm irradiation. Bands of visible fluorescence were slightly marked with a soft pencil. To the marked area, 3 μL AgNPs colloid and 3 μL NaCl aqueous solution at various concentrations were sequentially deposited by capillary pipettes. SERS measurement was performed by LabRAMAM HR Evolution (Horiba Jobin Yvon S.A.S, France) equipped with a CCD camera and a helium-neon laser (633 nm). Guided by a red bean and the microscopic image, the marked area was carefully aimed. Every Raman scattering signal was averaged of three accumulations and the acquisition time of each run was 10 s. The obtained data were processed and interpreted by LabSpec5 software.

2.6. HPLC determination of fish samples

A HPLC method officially recommended by EU was used for monitoring His contents of investigated fish samples in parallel. Sample extraction, derivatization and analytical conditions were same to that proposed by Altieri, Semeraro, Scalise, Calderari, and Stacchini (2016). The separation and determination of samples were carried out by a Waters HPLC system equipped with autosampler, ZORBAX SB-C18 column (4.6 × 150 mm, 5 μm) and Diode Array Detector (DAD).

3. Results and discussion

3.1. TLC-SERS method development

As mentioned before, the perquisite of successfully applying SRES on TLC plate relied on precisely knowing where the target was. Practically, location by visual guidance was the most facile method, because it enabled the most straightforward impression. Moreover, eye-inspection allowed semi-quantitative estimation of the separation results. Therefore, huge time and energy with many negative samples can be saved in this way, while SERS confirmation and quantitation was only focused on violently non-compliant samples.