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Golf ball-assisted electrospray ionization of mass spectrometry for the determination of trace amino acids in complex samples

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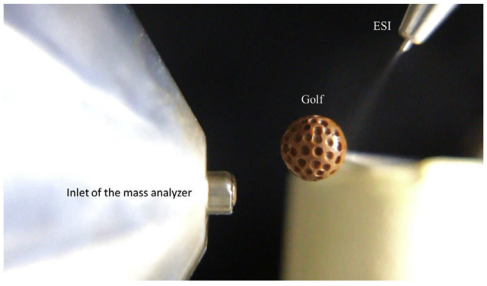
HIGHLIGHTS

- A home-made golf ball was designed and positioned between the ion source and the inlet of the mass analyzer.
- The proposed golf ball device improves the ion focusing and transmission efficiency of LC-MS.
- The golf ball-assisted ESI-MS can be applied to the analysis of trace compounds in complex matrices.

GRAPHICAL ABSTRACT



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ABSTRACT

During the electrospray ionization (ESI) process, ions move through a heated capillary aperture to be detected on arrival at a mass analyzer. However, the ESI process creates an ion plume, which expands into an ion cloud with an area larger than that of the heated capillary aperture, significantly contributing to an ion loss of 50% due to coulombic repulsion. The use of DC and RF fields to focus ions from the ion source into the vacuum chamber has been proposed in the literature, but the improvement of ion transmission efficiency is limited. To improve ion transmission, in this study we propose a novel method using a home-made golf ball positioned between the ion source and the inlet of the mass analyzer to hydrodynamically focus the ions passing through the golf ball. The ion plume produced by the ESI process passes through the golf ball will reduce the size of the ion cloud then be focused and most of them flowed into the mass analyzer. Therefore, the sensitivity will be improved, the aim of this investigation is to study the enhancing of the signal using golf ball-assisted electrospray ionization liquid chromatography tandem mass spectrometry (LC-MS/MS) to determine 20 trace amino acids in complex samples, including tea, urine and serum. The results showed that the analytical performance of the determination of the 20 amino acids in tea, urine and serum samples using the home-made golf ball-assisted ESI source is better than that of a commercial ESI source. The signal intensities of the 20 amino acids were enhanced by factors of 2–2700, 11–2525, and 31–342680 in oolong tea, urine and serum analyses, respectively. The precision of the proposed method ranged from 1–9%, 0.4–9% and 0.4–8% at low, medium and high concentration levels of amino acids, respectively. The home-made golf ball-assisted ESI source effectively increased the signal intensity and enhanced the ion transmission efficiency and is also an easy, convenient and economical device. This technique can be applied to the analysis of trace compounds in complex matrices.

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1. Introduction

Electrospray ionization (ESI) is an excellent ionization technique that is used for analysis of a wide variety of chemical and biological molecules. The ESI process produces ions at atmospheric pressure, and transfer of the ions is necessary for detection in the high vacuum of the mass analyzer. To maintain the high vacuum of the mass analyzer, a differential pumping system composed of separated chambers for pressure reduction is utilized. The ions must transfer through the aperture of a heated capillary that connects to the mass analyzer to arrive at the mass analyzer by the differential pumping system. The ESI process creates an ion plume that expands into an ion cloud with an area larger than that of the aperture of the heated capillary, which significantly contributes to an ion loss of 50% due to coulombic repulsion [1–5].

To overcome ion loss, the use of DC focusing fields at atmospheric pressure and RF fields in specific geometries to focus ions from the ion source into the vacuum chamber has been reported in the literature [6,7]. When using DC focusing fields, the electrical breakdown of the high electric field has resulted in failure of the ions focused towards the aperture to pass through into the vacuum. The ion trajectories that have diverged due to the weaker electric field must be sustained [6]. Conversely, high-field asymmetric waveform ion mobility spectrometry (FAIMS) is a famous technique that uses RF fields in specific geometries. The FAIMS source not only separates ions but also focuses or concentrates ions in front of the aperture. However, the FAIMS cannot focus all ions simultaneously, leading to loss or defocusing of ions [7]. As reviews have shown, much of the literature has reported the use of DC focusing fields at atmospheric pressure or of RF fields in specific geometries to focus ions from the ion source into the vacuum chamber; however, no study has explored the effect of focusing ions from the ion source into the vacuum chamber using physical techniques.

To improve ion transmission efficiency, we propose a novel method in which a home-made golf ball is set between the ion source and the inlet of the mass analyzer to focus ions using the hydrodynamic effects of the golf ball [8–10]. In general, when a jet flows over a smooth ball, the jet fluid would adhere to the ball surface due to the Coanda effect [11], and then the flow formed a boundary layer along the golf ball surface. The fluid in the boundary layer experiences large shear force due to the fluid viscosity and thus a loss of advancing momentum. At certain location downstream of the ball surface, the flow will no longer move farther downstream because the advancing momentum has been dissipated along the flow direction. This will cause the boundary-layer flow to separate from the ball surface, leading to dramatic increase of drag force on the ball and enlargement of the wake width. As the Reynolds number reaches a critical threshold value, the boundary-layer flow becomes turbulent and the delay of boundary-layer separation point is possible. In such case, both the drag and the wake width of the golf ball will be greatly reduced. Based on the hydrodynamics or aerodynamics considerations of the golf ball design, additions of the dimples of proper size (e.g., the diameter and the depth of the dimples) will help delaying the separation point in the boundary-layer along the golf ball surface. As a result of delaying the boundary-layer separation, the width of the wake behind the golf ball will be greatly reduced. In the present study, a home-made golf ball, located in between the ion source and the mass analyzer, employs the combinations of the Coanda effect and the separation delay of boundary-layer to focus the ion flow to the sensing area of the mass analyzer.

Liquid chromatography-tandem mass spectrometry (LC-MS/MS) is an excellent technique with low level detection limits for the analysis of samples with a complex matrix such as tea, urine and serum. However, the LC-MS/MS atmospheric pressure ionization process is accompanied by a matrix effect. Many scientists and researchers have devoted attention to the reduction of this matrix effect by altering the sample preparation [12–14]. As recommended by Stahnke et al. [14], an appropriate dilution can effectively reduce the matrix effects in real samples. Unfortunately, the dilution step cannot enhance the signal.

In the present work, we design a universal signal-enhancing golf ball device-assisted electrospray ionization source combined with a noise-reducing dilution step to determine 20 trace amino acids in complex samples of tea, urine and serum. The results are compared with those of a dilution step on a common ESI source to determine 20 trace amino acids in complex samples, including tea, urine and serum.

2. Materials and methods

2.1. Reagents and materials

Twenty amino acids were determined, including glycine (Gly), alanine (Ala), valine (Val), leucine (Leu), isoleucine (Ile), serine (Ser), threonine (Thr), cysteine (Cys), methionine (Met), proline (Pro), lysine (Lys), arginine (Arg), phenylalanine (Phe), tyrosine (Tyr), tryptophan (Trp), histidine (His), aspartate (Asp), glutamate (Glu), asparagine (Asn) and glutamine (Gln), all of which were purchased from Sigma–Aldrich (Steinheim, Germany). HPLC grade organic solvents, including acetonitrile and formic acid, were purchased from Merck (Darmstadt, Germany). The deionized water (>18 MΩ) used to extract the 20 trace amino acids in tea, urine and serum was purified using a Milli-Q system (Millipore Simplicity, Millipore, France). The ball was made of vespel SP-1 obtained from a local company (Taichung, Taiwan). The vespel SP-1 material was chosen for its good solvent resistance and heat resistance.

2.2. Golf ball device

A home-made golf ball with the diameter 4.7 mm was prepared by drilling dimples into an intact ball. The diameter of the dimples on the golf ball was 0.5 mm. The proposed golf ball was inserted onto a metallic rod to be fixed to the wall of the ESI source housing. To avoid accumulating charge possible on the home-made golf, the metallic rod was chosen as a conductor and a fixture. The golf ball was set between the ion source and the inlet of the mass analyzer. The angle between the ion source and golf ball-MS inlet is approximately 155°. The distance between the golf ball and the ion source is 7 mm. There is 5 mm between the golf ball and MS inlet.

2.3. Oolong tea treatment

The preparation of oolong tea was modified according to Fraser et al.'s method [15]. One milligram of oolong tea leaves was placed in a vial and then extracted with 10 mL of water in a water bath at 90 °C for 5 min with stirring. After cooling to room temperature, the tea solution was centrifuged at 14000 rpm for 5 min at 4 °C. Subsequently, the residual tea leaves were removed, and 5 μL of the solution was injected into the LC-MS/MS.

2.4. Urine and serum treatment

The preparation of urine was modified according to Soga et al.'s method [16]. One microliter of urine was obtained from a volunteer and was diluted with 500 μL of deionized water and then vortexed for 1 min. Because the centrifugal filter device contains trace amounts of glycerin, 10 mL of deionized water was passed through the filter to remove the glycerin. The diluted urine