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Rapid screening of basic colorants in processed vegetables through mass spectrometry using an interchangeable thermal desorption electrospray ionization source

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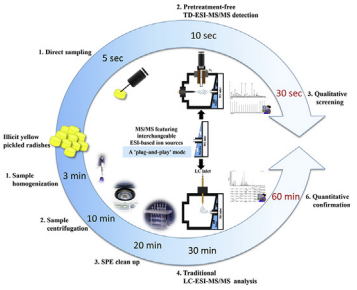
HIGHLIGHTS

- An ambient mass spectrometer featuring an interchangeable TD–ESI and a conventional ESI is reported.
- A dual-working mode—for qualitative screening and quantitative confirmation—is feasible after ion sources switching.
- Qualitative screening analyses and quantitative confirmatory analysis of illegal colorants have been performed.
- Qualitative screening was complete within approximately 30 s for each analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermal desorption electrospray ionization/mass spectrometry (TD–ESI–MS) employing a quickly interchangeable ionization source is a relatively new ambient ionization mass spectrometric technique that has had, to date, only a limited number of applications related to food safety control. With reallocation of resources, this direct-analysis technique has had wider use in food analysis when operated in dual-working mode (pretreatment-free qualitative screening and conventional quantitative confirmation) after switching to an ambient ionization source from a traditional atmospheric pressure ionization source. Herein, we describe the benefits and challenges associated with the use of a TD–ESI source to detect adulterants in processed vegetables (PVs), as a proof-of-concept for the detection of basic colorants. While TD–ESI can offer direct qualitative screening analyses for PVs with detection capabilities lower than those provided with liquid chromatography/UV detection within 30 s, the use of TD–ESI for semi-quantification is applicable only for homogeneous food matrices.

1. Introduction

Food safety is gaining increasing attention because of a sequence of food contamination incidents, including cases

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involving additives (e.g., illegal colorants). Synthetic colorants are considered superior to natural colorants in terms of their color value, uniformity, and applicability in various processed foods. While the use of water-soluble synthetic acid colors (e.g., amaranth, erythrosine, acid red) is generally allowed worldwide, some basic synthetic colorants [e.g., malachite green (MG), auramine O (AO), rhodamine B (RB)] are unauthorized food additives in the United States, the EU, and Taiwan because of their toxicity. Nevertheless, these basic colorants have been detected in various processed foods. The use of MG, AO, and RB has been reported in several developing countries and regions, including Argentina [1], India [2], Vietnam [3], Malaysia [4], the Philippines [5], and Hong Kong [6]. In Taiwan, the use of AO and RB in processed foods has also been reported [7]. In view of the hazardous nature and harmful effects of basic color contaminants, there is a need to develop reliable high-throughput methods for the detection of these compounds in processed foods.

Detecting illegal colorants in food products is a common activity in many of the laboratories conducting regular food safety inspections. One approach to lessen the typical laboratory workload is to increase the throughput of routine inspection analyses. A common sequence in the routine analysis of illegal colorants is a rapid preliminary screening assay followed by confirmatory tests. For example, the Taiwan Food and Drug Administration (TFDA) employs several tests to confirm positive results when screening for illegal colorants, including two preliminary assays [8] (paper chromatography; thin layer chromatography) and six confirmatory tests {two liquid chromatography–UV (LC–UV) [8,9] methods; four liquid chromatography/tandem mass spectrometry (LC–MS/MS) methods [10–13]}. While these conventional screening methods for identifying illegal colorants have broad applicability, throughput is hindered because of the high number of preparative steps and overall duty cycle. Furthermore, the detection limits for the target colorants when using the above-mentioned conventional preliminary assays [8] are high (e.g., 50–100 ng for MG, 500–1000 ng for AO, 50 ng for RB) and can produce a large number of false-negative results. Several new techniques for screening illegal colorants have emerged recently. Of particular interest are those employing ambient ionization mass spectrometry (AMS), which allows samples to be investigated in the open air and without sample pretreatment, including the use of an atmospheric-pressure solids-analysis probe (ASAP) [14], surface desorption atmospheric pressure chemical ionization (DAPCI) [15], paper spray ionization (PS) [16,17], desorption corona beam ionization (DCBI) [18], desorption electrospray ionization (DESI) [19], and direct analysis in real time (DART) [20]. Coupling of these ionization sources to mass spectrometers makes high-throughput screening possible for illegal colorants on and in foods, with little or no prior sample cleanup. Several food matrices (e.g., powdered chili pepper, chili powder, chili oil, tomato sauce, saffron) have been tested during the development of AMS methods for the screening of illegal colorants [14–18]. We are, however, unaware of any previous publications concerning the use of processed foods other than sauces and spices.

AMS is a recently developed technique that requires minimal or no sample pretreatment and dramatically shortens the analytical time from hours to seconds. Based on its high throughput, real-time in situ analyses, and lack of solvent waste, AMS is highly applicable for food safety checks. Nevertheless, because of the source setups, most AMS techniques can analyze only those samples that fit in the confines between the sampling and ionization source and the inlet to the mass spectrometer [21]. Irregularly shaped and large samples must be cut down to an appropriate size and shape prior to analysis, potentially resulting in sample damage. Moreover, while various AMS methods can accommodate requests for higher throughput, techniques are also sought to reallocate resources toward more flexible analytical functions. Thermal desorption/electrospray ionization mass spectrometry (TD–ESI–MS) is a new ESI-based AMS technique that allows the rapid characterization of thermally stable compounds [21–24] in liquids, ointments, and solid samples without the need for extraction or separation. Here, a sampling probe is used to collect analytes directly from a sample in its original physical state; analytes on the probe are then quickly desorbed in a preheated oven prior to ESI and MS detection. With the use of a sampling probe, TD–ESI–MS can conveniently and rapidly analyze samples without the potential damage that arises when cutting them to appropriate shapes and sizes for AMS analysis. On the other hand, by integrating all the temperature, gas, and electrical connections into the source housing, the TD–ESI body becomes interchangeable and can be connected with mass spectrometers in a plug-and-play manner (Fig. 1). Mass spectrometers featuring two readily interchangeable ion sources (e.g., TD–ESI and standard ESI coupled to a chromatographic system) can provide the advantages of dual working modes (pretreatment-free qualitative screening and quantitative confirmation) through simple switching of the ion sources (see the Graphical Abstract). To the best of our knowledge, no previous reports have described the reallocation of ion sources of ESI-based MS systems to provide more flexible analytical functions, particularly both qualitative screening and quantitative confirmatory analysis.

In this study, we conducted a qualitative screening and a quantitative confirmation of basic colorants in processed vegetables (PVs) by using a single mass spectrometer featuring two interchangeable ion sources: a TD–ESI source and a conventional ESI source coupled to liquid chromatography (LC). We explored the quantitative capabilities of the TD–ESI–MS technique for the analysis of colorants in solution. Furthermore, we compared the quantitative data obtained using the TD–ESI–MS method with that from conventional LC/UV detection (LC–UV) and LC/tandem mass spectrometry (LC–MS/MS). We employed three basic colorants and three PVs as model compounds and model matrices.

2. Materials and methods

2.1. Reagents and standards

Solvents for ESI (MeOH, formic acid) were purchased from Merck (Darmstadt, Germany) and Sigma–Aldrich, respectively. Distilled deionized water, purified through a PURELAB Classic UV system (ELGA, Marlow, UK), was used to prepare the electrospray solution and standard sample solutions. Three basic colorants (MG, AO, RB), often used in PVs (green peas, pickled radishes, pickled ginger), were chosen for this study. Illegal basic colorant standards were purchased from Sigma–Aldrich and used without further purification. PVs and fresh radishes were purchased from local stores and markets.

Stock solutions of all standard basic colorants were prepared individually in MeOH at 1 mg mL^{-1} and stored at approximately −20 °C in the dark. Spiking and calibration standard mixtures were prepared at various concentrations by combining aliquots of individual stock solutions, followed by dilution with MeOH.

2.2. Sample preparation

For LC–UV analysis, extraction of basic colorants was performed using the standard method of the TFDA [8]. A sample (1 g) and 6% acetic acid (25 mL) were mixed and then wool threads (0.1 g) were immersed in the sample. The contents were boiled for 30 min until the wool absorbed the color from the solution. The wool threads