



# Direct identification of prohibited substances in cosmetics and foodstuffs using ambient ionization on a miniature mass spectrometry system



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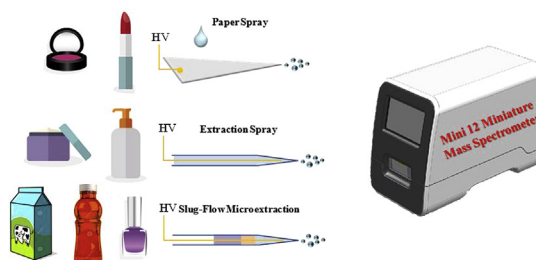
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## HIGHLIGHTS

- Miniature ion trap analytical system with ambient ionization capability for direct chemical analysis.
- Direct analysis of condensed-phase samples in the forms of powder, aqueous mixtures, and cream.
- Optimal conditions identified for real-time sample extraction and analyte ionization.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Significantly simplified work flows were developed for rapid analysis of various types of cosmetic and foodstuff samples by employing a miniature mass spectrometry system and ambient ionization methods. A desktop Mini 12 ion trap mass spectrometer was coupled with paper spray ionization, extraction spray ionization and slug-flow microextraction for direct analysis of Sudan Reds, parabens, antibiotics, steroids, bisphenol and plasticizer from raw samples with complex matrices. Limits of detection as low as 5 µg/kg were obtained for target analytes. On-line derivatization was also implemented for analysis of steroid in cosmetics. The developed methods provide potential analytical possibility for outside-the-lab screening of cosmetics and foodstuff products for the presence of illegal substances.

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## 1. Introduction

In this study, we developed methods using a miniature mass spectrometer and ambient ionization for direct analysis of prohibited substances in food and cosmetic products. Food safety has been drawing public attention due to its relevance to the public health. Although restrictive regulations are enforced worldwide, highly publicized incidents occur from time to time [1,2]. Safety of cosmetic products typically is not getting much public attention, but it is also of a significant concern for public health, simply because of the wide and routine use of these products. Cosmetics cover a wide range of materials that are applied in contact with the human body for cleansing purposes or for altering appearance. Cosmetic products worldwide play an important role in people's daily lives. In addition to the use by adults, cosmetics have also been increasingly used in the care of infants and toddlers. The cosmetic industry represents a tremendous global market, with total sales of about 168 billion Euros in 2014 in the European Union, the United States, China, and Japan [3].

Voluntary addition of illicit substances to lower the costs of production is the most common problem in both the food and cosmetics industry [4–9]. For cosmetic products, illicit substances are also added to enhance short-term cosmetic effectiveness. Common banned additives include antibiotics [10,11], corticosteroids [12–15], sexual hormones (oestrogens [16], progestogens [16], androgen [17]), pharmacologically active substances [16–18], prohibited preservatives (parabens [19–22], methyl-dibromoglutaronitrile [23]), whitening agents [13,24], phthalates [25–28], and nitromusk fragrances [25,28]. Long-term exposure to these substances could cause adverse effects such as skin irritation, allergic reactions, and antibiotic resistance, which represents a severe risk to public health.

The need to enforce product safety and regulatory compliance in both the food and cosmetics industries, calls for the development of effective and convenient methods to identify illicit ingredients with high molecular specificity and sensitivity. The analytical techniques that have been reported for the chemical analysis of food and cosmetic products include thin layer chromatography [29,30], capillary electrophoresis [22,31], gas chromatography (GC) with flame ionization detection [21,32] or coupled with various types of mass spectrometers [19,20,23,25,26,28,33–36], high-performance liquid chromatography (HPLC) using ultraviolet [10,12,16,17,24,37], electrochemical detection [38] or coupled with various types of mass spectrometers [1,11–17,26,35,39]. These methods are typically implemented in analytical laboratories and performed by experienced chemists using bench-top equipment. Sample preparation is usually achieved through multi-step, laborious and time-consuming processes, which also require laboratory procedures such as solvent extraction, dilution, reagent mixing, sonication, heating, centrifugation, and filtration. Although these analytical processes work well for analysis of large numbers of samples at centralized locations, it is also highly desirable to develop fast and easy-to-use methods for on-site screening, especially for situations when rapid decision making is required by inspectors in the field [40,41].

As already demonstrated, mass spectrometry (MS) is a highly sensitive and selective technology which is suitable for both qualitative and quantitative chemical analysis. Conventional laboratory-scale mass spectrometers are bulky and typically used in combination with GC or HPLC, which limits their usage for in-field applications. As opposed to traditional chemical analysis work flow, where samples are brought to the laboratory for analysis, miniaturized mass spectrometers can now be brought to the samples in the field [42,43]. A wide variety of small mass spectrometers have been developed, with a weight as low as 4 kg [44]. However, not all

of them are suitable for analysis of food or cosmetic products, for which a majority of the target analytes are non-volatile. The miniature MS instruments with internal ionization sources, which relies on sample introduction through GC [45], membrane [46], solid-phase microextraction (SPME) [45,47] or sorbents [48], typically can only analyze non- or semi-volatile compounds. To enable the coupling with in-air ionization methods, such as electrospray ionization that is suitable for ionizing non-volatile compounds, atmospheric pressure interface (API) is required for transferring the ions into the mass analyzer under vacuum. Small mass spectrometers with APIs have been developed, among which the Mini 10/11/12 series of instruments [44,49,50] used the discontinuous APIs [51] to achieve the ion transfer without requiring additional pumping capacity. The miniature ion trap instruments also have an advantage of performing MS/MS analysis, which provides additional confirmation of the chemical identity and improved sensitivity for analysis of complex mixtures [42,52].

Sample pretreatment is typically required prior to MS analysis, which would also need to be done quickly in the field to minimize the matrix effects. Ambient ionization has been developed for direct MS analysis of the analytes in untreated samples, and this represents a promising solution for simplification or elimination of sample preparation procedures in on-site analysis [53]. Since desorption electrospray ionization (DESI) [54] and direct analysis in real time (DART) [55] were reported in 2004 and 2005, respectively, more than 40 ambient ionization methods have been developed [53,56]. Sample pretreatment and chromatographic separation, traditionally required for MS-based analysis, can now be bypassed. Notably, a set of ambient ionization methods, e.g., paper spray [57,58], extraction spray [59], or low temperature plasma [60], have been coupled with miniature mass spectrometers, with promising results obtained for on-site applications in food safety [61,62], product authentication [44], environmental monitoring [48,63,64], biomolecule analysis [65,66], homeland security [67] and biomedical diagnosis as well as in forensic investigations [68].

In this study, direct identification of illicit ingredients in food and cosmetic products has been explored by coupling a miniature ion trap mass spectrometry system with ambient ionization methods (Fig. 1). Versatile procedures using paper spray [57,58], extraction spray [59,69], and slug-flow microextraction [70] were developed for direct analysis of a wide variety of food and cosmetic products. In comparison with traditional methods requiring sample pretreatment and separation steps, the methods reported here enable a research to identify illicit ingredients in cosmetics and foodstuffs with significantly improved throughput.

## 2. Experimental

### 2.1. Chemicals and reagents

Sudan Red I (1), Sudan Red II (2), Sudan Red III (3), Sudan Red IV (4), phenylparaben (8), chloramphenicol (10), metronidazole (11), and bis(2-ethylhexyl) phthalate (14) were purchased from Sigma–Aldrich (St. Louis, MO, USA); isopropylparaben (5), isobutylparaben (6), benzylparaben (9), and bisphenol A (13) were purchased from AccuStandard (New Haven, CT, USA); pentylparaben (7) was purchased from Alfa Aesar (Ward Hill, MA, USA); epitestosterone (12) was purchased from Steraloids (Newport, RI, USA). All reference standards had purities greater than 96%, except for Sudan Red II and IV (both 90%). The chemical information for the analytes is listed in Table S1. Ethanol, dichloromethane, methanol, and ethyl acetate of HPLC grade were purchased from Merck (Darmstadt, Germany). Ultrapure water was obtained from a Millipore Milli-Q integral water purification system (Bedford, MA, USA). Other chemicals used in the experiment were purchased

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