



Development and validation of ultra-high performance supercritical fluid chromatography method for determination of illegal dyes and comparison to ultra-high performance liquid chromatography method

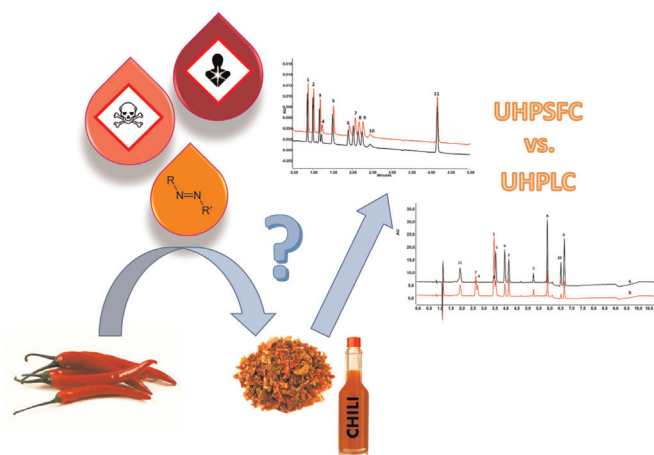
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HIGHLIGHTS

- Efficient and sensitive UHPSFC method was developed and validated.
- Eleven illegal red-orange dyes were separated in less than 5 min.
- The method showed potential for being used to monitor forbidden dyes in food constituents.
- The developed UHPSFC method was compared to the UHPLC-UV.
- UHPSFC method showed better separation and shorter time of analysis while lower consumption of organic solvents.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel simple, fast and efficient ultra-high performance supercritical fluid chromatography (UHPSFC) method was developed and validated for the separation and quantitative determination of eleven illegal dyes in chili-containing spices. The method involved a simple ultrasound-assisted liquid extraction of illegal compounds with tetrahydrofuran. The separation was performed using a supercritical fluid chromatography system and CSH Fluoro-Phenyl stationary phase at 70 °C. The mobile phase was carbon dioxide and the mixture of methanol:acetonitrile (1:1, v/v) with 2.5% formic acid as an additive at the flow rate 2.0 mL min⁻¹. The UV-vis detection was accomplished at 500 nm for seven compounds and at 420 nm for Sudan Orange G, Butter Yellow, Fast Garnet GBC and Methyl Red due to their maximum of absorbance. All eleven compounds were separated in less than 5 min. The method was successfully validated and applied using three commercial samples of chili-containing spices – Chili sauce (Indonesia), Feferony sauce (Slovakia) and Mojo sauce (Spain). The linearity range of proposed method was 0.50–9.09 mg kg⁻¹ ($r \geq 0.995$). The detection limits were determined as signal to noise ratio of 3 and were ranged from 0.15 mg kg⁻¹ to 0.60 mg kg⁻¹ (1.80 mg kg⁻¹ for Fast Garnet) for standard solution and from 0.25 mg kg⁻¹ to 1.00 mg kg⁻¹ (2.50 mg kg⁻¹ for Fast Garnet, 1.50 mg kg⁻¹ for Sudan Red 7B) for chili-containing samples. The recovery values were in the range of 73.5–107.2% and relative standard deviation ranging from 0.1% to 8.2% for within-day precision and from 0.5% to 8.8% for between-day precision. The

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method showed potential for being used to monitor forbidden dyes in food constituents. The developed UHPSFC method was compared to the UHPLC-UV method. The orthogonality of Sudan dyes separation by these two methods was demonstrated. Benefits and drawbacks were discussed showing the reliability of both methods for monitoring of studied illegal dyes in real food constituents.

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1. Introduction

It has been known for a long time that food color is the crucial factor for food perception by a human and a major attractiveness and quality factor. This fact makes producers use the additional dyes in food to improve the intensity of color. Synthetic colorants permitted to be used in foods with a proved safety can be utilized for this purpose. However, due to the wide availability, low cost and chemical stability the banned synthetic dyes are often illegally added to foodstuffs [1,2]. Another reason for the presence of prohibited dyes in food could be the violation of production and/or transportation process, which enables contamination. The red-orange dyes such as Sudan I–IV, Sudan Red 7B, Sudan Red G, Sudan Orange G, Para Red Methyl Red Fast Garnet, and Butter Yellow are fat-soluble dyes usually used in industry for plastic and oils coloring [3]. These dyes have chemical structures that are characterized by the nitrogen-to-nitrogen double azo-bond between aromatic groups as depicted in Fig. 1. Due to the genotoxic and/or carcinogenic activity, the usage of the mentioned dyes and other fat-soluble azo-dyes in food became prohibited in most countries of the world [4]. However, between 2003 and 2005 about 580 food products were withdrawn repeatedly in different countries of the European Union due to Sudan's colorants contamination [5]. The presence of any banned dyes in food was declared to be unacceptable at any level by the European Commission in Decision from May 2005 and thereby the limits of detection were specified as 0.5–1.0 mg kg⁻¹ for the analytical methods used for food control [4]. Nowadays Rapid Alert System for Food and Feed is still reporting the detected contamination of chili products (chili peppers, chili powder, curry powder, sauces, spice mixtures) by Sudan's dyes from India, Ghana, Nigeria etc. [6].

Many analytical methods for the separation and determination of synthetic azo-dyes from Sudan's family in chili-containing foodstuff have been described. Most of them proposed the liquid chromatography (LC) methods with PDA detection [3,7–12] and more sensitive and selective MS detection [13–16]. Not all of the mentioned methods could be characterized as fast because the separation of the four compounds could take up to 71 min [7], 25 min [3] or 20–22 min [8,9].

A faster alternative to LC method for the determination of red-orange illegal dyes, classified as the green separation technique, is supercritical fluid chromatography (SFC). This powerful technique

possesses evident benefits in comparison to other chromatographic techniques [17] due to the low viscosity of the supercritical fluid, resulting in fast diffusion of the compounds in the mobile phase and low pressure drop in the column [18,19]. Moreover, using of sub-2 μm particles column provides further benefits such as enhancing of mass transfer and improved separation [20]. These benefits of UHPSFC compared to LC methods for the separation of closely-related pharmaceuticals and other compounds have been shown previously [18,20–22]. In our work, relatively high molecular weights of studied compounds and low polarity provide hydrophobic properties for studied dyes, which make these compounds suitable also for the separation by SFC. The use of SFC for the analysis of Sudan dyes has been described in very few papers. L. Dolak et al. described the resolution and identification of Sudan I–IV by SFC in 2007 [23]. The separation of the four compounds took about 8 min with the flow rate 4 mL min⁻¹. In 2008 Lefler and Chen briefly described the feasibility study of using SFC for food and beverage analysis, where the improved method for the determination of five azo-dyes using UV detection and the determination of seven dyes using ELSD detection, within 3 min was proposed [24]. No UHPSFC method has been described so far for quantitative determination of studied illegal dyes. In addition, a very limited number of SFC methods have been fully validated up to date due to the well-known complications of earlier SFC systems related to accuracy, repeatability and sensitivity. A comparison of UHPSFC method to UHPLC can provide a better understanding of advantages and disadvantages of both methods.

The aim of the present work was to develop and optimize UHPSFC method for the determination of eleven fat-soluble illegal red-orange dyes, most frequently found in chili-containing spices; to validate UHPSFC method and compare it to UHPLC method.

2. Experimental

2.1. Chemicals and reagents

HPLC gradient grade solvents used were acetonitrile (ACN) and tetrahydrofuran (THF) supplied by Sigma–Aldrich (St. Louis, USA). Methanol (MeOH) was supplied by Lach-Ner (Neratovice, Czech Republic), ethanol absolute (EtOH) was obtained from Fisher Scientific UK, isopropanol (IPA) was from Fluka. Formic acid (Ph. Eur. purity) was obtained from Merck. Ultra-pure water was

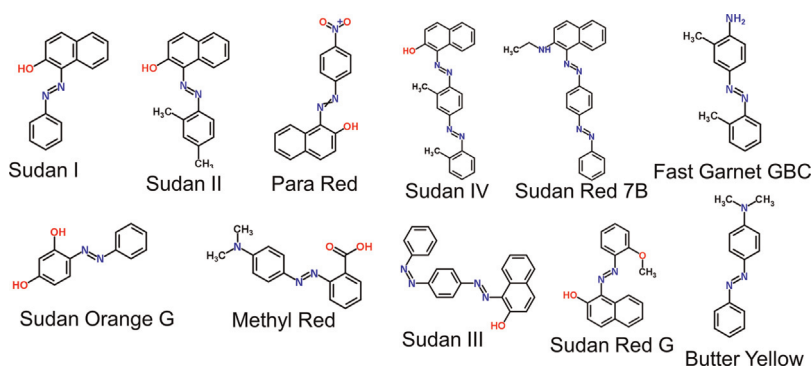


Fig. 1. Chemical structures of studied compounds.

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