Food Chemistry 192 (2016) 813–824

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Methods for the analysis of azo dyes employed in food industry – A review

Karthik Yamjala [a,*,1], Meyyanathan Subramania Nainar [a,1,*], Nageswara Rao Ramisetti [b]

[a] Department of Pharmaceutical Analysis, JSS College of Pharmacy, Ootacamund, JSS University, Mysore 643001, India
[b] Analytical Chemistry Division, IICT, Tarnaka, Hyderabad, Telangana 500007, India

ARTICLE INFO

Article history:
Received 1 April 2015
Received in revised form 13 July 2015
Accepted 20 July 2015
Available online 22 July 2015

Chemical compounds studied in this article:
Allura Red (PubChem CID: 5360805)
Amaranth (PubChem CID: 5359521)
Brilliant Black BN (PubChem CID: 5359750)
Brown HT (PubChem CID: 9570176)
Carmoisine (PubChem CID: 6321394)
Citrus Red 2 (PubChem CID: 9570225)
LitholRubine BK (PubChem CID: 9571018)
Ponceau 4R (PubChem CID: 54604869)
Sunset Yellow FCF (PubChem CID: 6850717)
Tartrazine (PubChem CID: 164825)

Keywords:
Azo dyes
Extraction
Food matrices
LC–MS/MS

ABSTRACT

A wide variety of azo dyes are generally added for coloring food products not only to make them visually aesthetic but also to reinstate the original appearance lost during the production process. However, many countries in the world have banned the use of most of the azo dyes in food and their usage is highly regulated by domestic and export food supplies. The regulatory authorities and food analysts adopt highly sensitive and selective analytical methods for monitoring as well as assuring the quality and safety of food products. The present manuscript presents a comprehensive review of various analytical techniques used in the analysis of azo dyes employed in food industries of different parts of the world. A brief description on the use of different extraction methods such as liquid–liquid, solid phase and membrane extraction has also been presented.

1. Introduction

Color is one of the important properties by which food is generally evaluated. A wide variety of food colorants of both natural and synthetic origin are added to food products in order to make them more visually aesthetic to consumers and to reinstate their original appearance which was lost during production process. However, most of the dyes obtained from natural sources are unstable and can undergo degradation easily during the processing of food. Therefore, dyes of synthetic origin are widely used, not only because of their stability but also the cost of production is very low when compared to dyes of natural origin (Timberlake, Bridle, & Walford, 1980). Amongst the synthetic dyes employed in the food industry, the azo dyes constitute around 65% of the commercial dye market (Ahlström, Eskilsson, & Björklund, 2005). Azo dyes are synthetic organic colorants, characterized by azo groups (–N=N–) as part of their structure. These dyes offer strong vivid colors and are used for coloring a variety of food products.

Azo dyes are generally resistant to aerobic conditions, but can be readily reduced by intestinal flora to form aromatic amines (Rafii, Hall, & Cerniglia, 1997) which may cause frequent headaches in adults (Hawley & Buckley, 1976), apart from their neurotoxicity (Nagaraja & Desiraju, 1993), genotoxicity (Mpountoukas et al., 2010) and carcinogenicity (Khehra, Saini, Sharma, Chadha, & Chimni, 2006). Because of such problems many countries in the world have banned the usage of most of the azo dyes in food products. Over the last few decades, the use of azo dyes in food has been highly regulated by each country's domestic and export food supplies. Most of the countries generally follow the regulations of those of seven major world markets. The detailed information on

* Corresponding authors.
E-mail addresses: yamjalakarthik@gmail.com (K. Yamjala), meyys@rediffmail.com (M.S. Nainar).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.foodchem.2015.07.085
0308-8146/

approved azo dyes for coloring food (ADF) by different countries are given in Tables 1 and 2.

Few reviews have been published in the literature for the quantification of synthetic food dyes. Ahlström et al. (2005) have reviewed the development of analytical procedures for determination of banned azo dyes in consumer goods. Chung and Cerniglia (1992) have evaluated the mutagenicity effect of azo dyes by structure–activity relationship studies and found that biologically active dyes are mostly limited to those compounds having p-phenylenediamine and benzidine moieties. Kaur and Gupta (2012) have reviewed the determination of water soluble and water insoluble food dyes by spectrophotometry. Kucharska and Grabka (2010) reviewed chromatographic methods for the determination of synthetic dyes. LC-UV–Vis and LC–MS methods for analysis of Sudan I–IV dyes along with their extraction procedure in various food matrices were reviewed by Rebane, Leito, Yurchenko, and Herodes (2010). However, there is not even a single comprehensive review which clearly describes all the analytical methods which are generally used to determine the ADF in food products, which will be quite valuable for not only to the food analysts but also regulatory authorities for monitoring the quality and safety of food products. In order to fill this gap in the literature, the present manuscript describes the various methods used for analysis of ADF and their extraction from complex food matrices.

2. Analytical methods

2.1. Extraction of ADF from food matrices

A wide variety of food products contain azo dyes as colorants. As a consequence, there is no generally accepted/standard method for their extraction in laboratories. Nevertheless, most extraction procedures follow a common path involving the release of desired analytes from their matrices, followed by removal of extraneous matter and a suitable extraction method (solid–liquid or liquid–liquid extraction) (Thompson & Trenerry, 1995; Wu et al., 2013).

2.1.1. Membrane filtration

A membrane is a thin layer of semi-permeable substance that separates substances when an external driving force is applied across the membrane. For ADF in beverages, the most common procedure to collect analytes for further analysis include one-step extraction with membrane filter using water as a diluents (Gosetti et al., 2008; Minioti, Sakellariou, & Thomaidis, 2007).

2.1.2. Solid-phase extraction (SPE)

Solid phase extraction (SPE) is the most commonly used technique in determination of ADF due to its advantages like simplicity and rapidity. It also has the ability of treating large volume of samples free from contaminants with high recoveries. Typical sorbent for SPE include C_{18}, while amino-functionalized low degrees of cross-linking magnetic polymer (NH_2-LDC-MP) (Chen et al., 2014), polyamide, gel permeation chromatography (GPC) (Bonan, Fedrizzi, Menotta, & Elisabetta, 2013; Tang et al., 2014) and styrene–divinylbenzene polymer has good retention towards a few ADF (Soylak, Unsal, & Tuzen, 2011). Different organic solvents have been used in the analysis of ADF and selection of appropriate solvent is not always easy. The structure of analytical matrix and its components play a key role while selecting the solvent for extraction. Solvents such as methanol, acetic acid, ethanol, acetone, ethyl acetate, tetra-n-butyl ammonium phosphate etc., are more appropriate for the extraction of ADF.

A wide variety of SPE methods have been reported for the extraction of ADF from food products Table 3. González, Gallego, and Valcárcel (2003) have determined natural and synthetic colorants in lyophilized foods using an automatic solid-phase extraction system using ammonia, methanol mixture as eluents and RP-C_{18} cotton as stationary phase. Harp, Miranda-Bermudez, Baron, and Richard (2012) have performed the extraction of seventeen food colorants in forty-seven food products employing a simple SPE process. Recently, Tang et al. (2014) have studied the extraction of sixteen synthetic colorants in complex hotpot condiment with high oil content. They have reported that the combination of methanol, acetone (1:1, v/v) and 2 mol/L carbamide solution containing 5% ammonia in methanol had shown excellent extraction efficiency while purification by a GPC column. In recent times, Chen et al. (2014) have investigated the use of NH_2-LDC-MP as a sorbent in SPE under magnetic field to enhance the extraction recoveries of seven synthetic food dyes using pure water (pH 9.0) as an extraction solvent.

2.1.3. Liquid–liquid extraction (LLE)

Liquid–liquid extraction (also known as solvent extraction) involves the separation of compounds based on their relative solubility in two different immiscible liquids, usually organic phase and water. The most common solvents (either alone or in combination) for the extraction of ADF from food products include water, ethanol, methanol, isopropyl alcohol, ammoniacal ethanol, ethyl acetate, ammonia, cyclohexane and tetra-n-butyl ammonium phosphate (Table 3).

In the literature various LLE methods have been reported for the extraction ADF. Yoshioka & Ichihashi, 2008 have used different solvents for the simultaneous extraction of forty food dyes in drinks and candies, and they found that a mixture of ammonia solution and ethanol (1:1, v/v) showed good extraction efficiency after ultra-sonication and evaporation of the sample. Zou, He, Yasen, and Li (2013) observed that the tri-mixture of ethanol, ammonia and water (80:1:19, v/v/v) achieved good extraction recoveries for seven dyes in animal feed and meat samples. Kirschbaum, Krause, and Brückner (2006) analyzed fourteen synthetic food dyes in fish roe using a combination of ammonia solution (25%) and methanol (1:9, v/v). Similarly, Harp, Miranda-Bermudez, and Barrows (2013) determined seven certified food colors in forty-four food products by LC method using ammonium hydroxide and methanol as extraction solvents.

In recent times, the use of eco-friendly extraction solvents has been increased due to their low toxicity profile. Khanavi et al. (2012) developed a green extraction procedure by using non-organic solvents such as ammonia (0.25%, v/v) and water for the extraction of dyes from food products and medicines. Similarly, Vidotti, Costa, and Oliveira (2006) have also developed a simple green method for the extraction of food dyes from artificial juice and gelatin samples using water as a solvent (Table 3).

2.1.4. Other extraction methods

Although solid–liquid and liquid–liquid extraction are the most frequently applied techniques in food samples, other extraction methods for ADF analysis {e.g., microwave-assisted extraction (MAE) and ultrasound-assisted extraction (UAE) have also been used as an eco-friendly extraction alternatives}. These options are beneficial in the laboratory, because conventional extractions with organic solvents are characterized by using high volumes of solvents and time consuming, and they often present low recovery of ADF, low selectivity and precision. Sun, Sun, Li, Zhang, and Yang (2013) have investigated the extraction of twenty-one synthetic colorants in meat by MAE using methanol-acetic acid (95:5, v/v) as a solvent. Similarly, Shen, Zhang, Prinyawiwatkul, and Xu (2014) have developed a method of extraction using two phase solvent (methanol and acetone) and UAE which has resulted in improved extraction recovery of both hydrophilic and hydrophobic pigments. In contrast, there are also a few methods available where