cosmetics

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Review

Analysis of Dyes in Cosmetics: Challenges and Recent Developments

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Abstract: Colour plays a decisive role in the marketing of a cosmetic product. Among thousands of substances used to colour, synthetic dyes are the most widespread in the industry. Their potential secondary effects on human health and different regulatory requirements for their use between the main world markets make analytical control necessary to guarantee the safety of a cosmetic product. However, methodologies for the determination of dyes in cosmetics are scarce with respect to those reported for other cosmetic ingredients such as preservatives or ultraviolet UV filters. In addition, most of the existing methods just consider a part of the total of dyes regulated. On the other hand, many methods have been developed for matrices different than cosmetics such as foodstuff, beverages or wastewater. The current paper reviews the recent developments in analytical methodologies for the control of synthetic dyes in cosmetics proposed in the international scientific literature in the last 10 years (2008–2018). A trend towards the use of miniaturized extraction techniques is evidenced. Due to the hydrophilic nature of dyes, liquid chromatography is the most usual choice in combination with absorbance detectors and, more recently, with mass spectrometry.

Keywords: cosmetics; dyes; cosmetics analysis; sample preparation; matrix solid-phase dispersion; miniaturized extraction techniques; liquid chromatography; mass spectrometry; cosmetics safety

1. Introduction

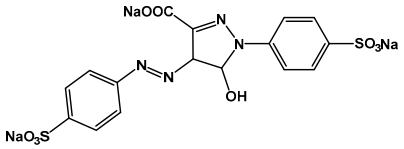
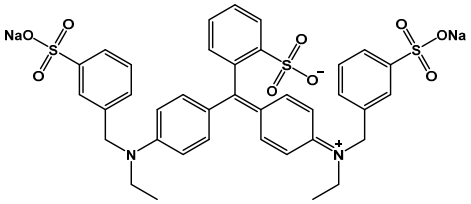
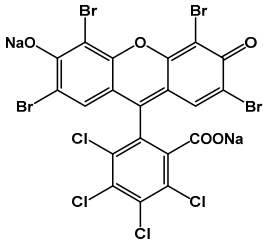
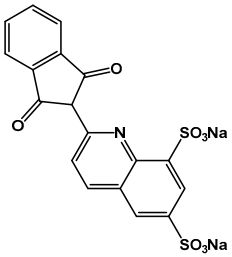
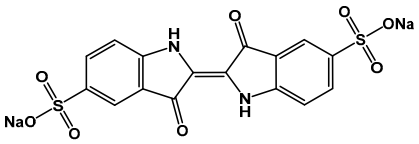
Colour is a key property of a product to determine the attractiveness for consumers and, therefore, its successful marketing. Colouring agents can be added to cosmetics in order to colour the product itself or to colour a part of the body (skin, hair, nails or eyelashes). In this latter case, the so-called colour cosmetic is a sector with a strong growth in the industry of cosmetics, given the increasing concern with body image motivated by the popularity of social media [1]. According to their use, cosmetics can be classified as leave-on, those that are in prolonged contact with the skin such as lipstick, cream or body lotion, and rinse-off, those that are removed after application such as shampoo, gel or soap.

Colorants can be classified according to their structure, source, colour, solubility and application method [2]. Two main categories are established according to solubility: dyes and pigments. Dyes are synthetic organic compounds that are hydro or oil-soluble and they can be found in cosmetics such as skin care products or toiletries whereas pigments are insoluble, they remain in particulate form, and they are mainly employed in toothpastes or decorative make-up [3].

Among the thousands of substances employed as colouring agents, synthetic dyes are preferred over natural (obtained from plants, animals and minerals) given their lower production costs and long-lasting properties such as brightness or greater stability towards light, heat or pH extreme that may occur during the manufacturing process. They can also be classified according to chemical

structure in five main groups: azoic, triarylmethane, xanthenes, indigoid and quinoline. Table 1 shows examples of dyes belonging to each structural family and the corresponding range of Colour Index (CI) number. CI number is a code composed by five numbers used globally to identify these substances. The first two digits indicate the structural category of the dye. Sometimes, they are associated also to an E code, which means that they can be used as food additives.

Table 1. Classification of dyes according to their chemical structure.

Category	CI Range	Example
Azo	11XXX–35XXX	 CI 19140 Tartrazine
Triarylmethane	42XXX–44XXX	 CI 42090 Brilliant Blue
Xanthene	45XXX	 CI 45410 Acid Red 92
Quinoline	47XXX	 CI 47005 Quinoline Yellow
Indigoid	73XXX	 CI 73015 Indigotine

Azo dyes, synthesised from an aromatic amine, are by far the most used in any consumer product due to their lower price. Their characteristic chromophoric azo group, under determined conditions that can take place in intestinal bacteria, liver cells, and skin surface micro flora [4], may be reduced to aromatic amines suspected to cause mutagenic, genotoxic and carcinogenic effects [5]. Although most of epidemiological studies are oriented towards azo dyes, there are also evidences of health risks of other families of colorants. The main route of human exposure to dyes in cosmetics is dermal contact, with special attention to areas close to mucous membranes such as eyes or lips where decorative make-up is daily applied. It has been proven that triarylmethanes are able to enter the blood stream

after systemic absorption [6]. Another study pointed out genotoxic effects caused by the absorption though the skin of Quinoline Yellow [7]. Xanthenes dyes such as Acid Red 92, Erythrosine, or Rose Bengal, which are very popular in cosmetics due to the red shade formed, have been identified as responsible of the formation of rough skin by reacting with proteins on the skin [8]. For other colorants such as Rhodamine B, harmful effects evidenced [9] have led European Union EU authorities to ban the use of these substances in cosmetics.

Among substances intended to colour hair, permanent or oxidative hair dyes are widely used, although they are known as strong allergens [10,11] and thus, the analytical control of these substances is a major concern [12]. However, they have not been considered in this review since they present a chemical nature completely different to synthetic dyes and hence other analytical approaches are needed for their determination in hair dyeing formulations [13]. Only synthetic dyes employed as temporary hair dyes have been included in the methodological review.

On the other hand, it is worth mentioning that the colouring agents employed in tattoos and permanent make-up (PMU), this last consisting on semi (permanent) tattoos used to resemble make-up. The main components are pigments, though dyes are also employed in small amounts, particularly in the form of lake due to their stability. Over 80% of the colorants used are organic and more than 60% of them are azo-pigments, some of which can release aromatic amines as by-products or impurities from synthesis. Raw colour materials employed for tattoos and PMU are not specifically produced for this application, so their purity is generally low. Aromatic amines, polycyclic aromatic hydrocarbons (PAH) or heavy metals can be present and thus a comprehensive analytical control of ingredients as well as unwanted substances is highly needed. However, the lack of a European regulatory framework and harmonized analytical methodologies developed specifically for tattoos and PMU makes the control of these substances difficult and represents a concern that must be dealt with separately [14].

This paper reviews the analytical methodology and developments for the control of synthetic dyes in cosmetics reported in international scientific journals in the last 10 years (2008–2018). Analytical improvements made on both sample preparation and determination are discussed. Recent contributions in this field tended to the development of methods based on micro-extraction techniques and liquid chromatography coupled to mass spectrometry.

2. Regulatory Overview

Dyes are subject to a wide range of regulatory restrictions across countries. These requirements have been exhaustively reviewed by Weisz et al. [15] and Lores et al. [16]. Concerning the use of cosmetics, and consumer products in general, there are three main regulatory authorities: US Food and Drug Administration (FDA) in US, the European Commission (EC) in the European Union (EU), and the Ministry of Health, Labour and Welfare (MHLW) in Japan. They have established positive lists for dyes permitted in cosmetics [15]. Oxidative hair dyes are not considered in this list and the creation of a positive list for this family of ingredients is one of the short- to medium-term objectives of the EU.

The European Regulation of Cosmetic Products (EC 1223/2009) [17], in the Annex IV, lays down the rules for the use of dyes in these products. The cosmetic legislation is frequently being updated, hence analytical methodologies must be constantly improved in order to fulfil the regulatory requirements [16]. In this way, there are no official methods for these compounds. Annex IV lists the 150 colouring agents permitted, sorted in increasing order of CI number. Most of them are not subjected to restrictions of maximum concentrations but some of them are limited to be used in determined types of products. For example, a few can be used only in rinse-off products (36 colorants) and others cannot be applied in mucous membranes (19 colorants) or in eye products (four colorants) [16,17].

Japanese and American regulations are more restrictive with respect to the number of colorants permitted (about 83 [18] and 65 [19] compounds respectively). Moreover, in the case of the US, many colorants, mainly synthetic aromatic organic compounds (also called coal-tar dyes) and their lakes, are subjected to batch certification by the FDA [15]. The different regulatory requirements existing among the main authorities of control hinder the commercialization of cosmetics between

these countries and make the development of analytical methodologies for the control of dyes more necessary. Since some compounds permitted by the European Regulation may be banned by the FDA, the importance of methods available for a broad range of colorants that are both permitted and non-permitted must be highlighted.

3. Analytical Methodology

Traditionally, reported methods for the determination of dyes focused on food matrices [20–23]. The analytical methodology for cosmetics ingredients regulated in the positive lists according to the European Regulation 1223/2009 [17] was reviewed in 2016 [16]. Thus, this paper only considered permitted dyes, and so, methodologies for the analysis of banned compounds were not included. In the current review, the field has been extended to include analytical methods for both permitted and prohibited dyes in cosmetics, which are summarised in Table 2. This table compiles analytical methodologies developed for the determination of synthetic dyes in any kind of cosmetics and reported in international journals between 2008 and 2018. These methodologies are scarce with respect to all those reported for other cosmetic ingredients such as preservatives or UV filters. Moreover, there are no official methods to date in UE, and the existing methods just consider a part of the total regulated dyes. Many methods have also been applied in other matrices such as foodstuff, beverages or wastewater.

Table 2. Analytical methodologies for dyes in cosmetics published in international scientific literature (2008–2018) (underlined compounds are forbidden according to the European Directive on Cosmetics 1223/2009; abbreviations are listed in Appendix A).

Analyte	Sample Matrix	Sample Preparation	Analysis	Year	Ref.
CI 14700, CI 14720, CI 15510, CI 15985, CI 16035, CI 16185, CI 16255, CI 19140, CI 42051, CI 42090, CI 44090, CI 47005, CI 60730, CI 73015	Lip gloss, lip lacquer, lipstick, body lotion, body butter, hand cream, age spot corrector mask, rough skin remover, shampoo, shower gel, products combining both, soap, facial and intimate gels, moisturizing and smoothing masks and toothpaste	Single-step vortex extraction and clean-up 1.5 mL of MeOH and 0.1 g of C18 for clean-up	LC-MS/MS	2018	Guerra et al. [24]
CI 45170	Lipstick	SPE and CPE Using amberlite as adsorbent and surfactant Previous solution in CCl_4	UV-Vis spectroscopy	2018	Bisgin et al. [25]
CI 13065, CI 14700, CI 14720, CI 15510, CI 15985, CI 16035, CI 16185, CI 16255, CI 19140, CI 42051, CI 42090, CI 42640, CI 44090, CI 45170, CI 45410, CI 45430, CI 47005, CI 60730, CI 73015	Children's shampoo, children's toothpaste, face painting, lip balm, coloured hairspray, eye shadow, soap, nail polish	Micro-MSPD Using C18 as sorbent and 2 mL of MeOH for elution	LC-MS/MS	2017	Guerra et al. [26]
CI 45170	Lipstick, rouge and nail polish	DLLME THF and decanoic acid as dispersing solvents	UV-Vis spectroscopy	2017	Ozkantar et al. [27]
CI 45160, CI 45170	Lipstick	MSA-DLLME 1-octanol and acetone as dispersing solvents	HPLC-Vis	2015	Ranjbari et al. [28]
CI 14700, CI 15510, CI 15985, CI 16035, CI 19140, CI 42090, CI 45410, CI 47005, CI 60730	Lip balm, nail polish, eye shadow, toothpaste, shampoo, decorative makeup, perfume and mouthwash	Micro-MSPD Using Florisil as sorbent and 2 mL of MeOH for elution	LC-MS/MS	2015	Guerra et al. [29]
CI 12245, CI 12250, CI 12719, CI 56059, CI 60730	Semi-permanent hair-dyeing formulations	Sample dilution and SPE Strata-X cartridges and ACN/H_2O (1:1) for elution	HPLC-DAD with IL Comparison with LC-MS/MS	2015	Franco et al. [30]
CI 11920, CI 12055, CI 12140, CI 26100, CI 26105	Lipstick	OS-AALLME ILs as extraction solvent	HPLC-UV	2015	Barfi et al. [31]
CI 10316, CI 14700, CI 14720, CI 15510, CI 15850, CI 15850:1, CI 15880:1, CI 15985, CI 16035, CI 16185, CI 16255, CI 17200, CI 19140, CI 42051, CI 42053, CI 42090, CI 45100, CI 45170, CI 45350, CI 45350:1, CI 45370, CI 45380, CI 45380:2, CI 45410, CI 45410:1, CI 45430, CI 47005, CI 59040, CI 60730, CI 61570, CI 73015, CI 75470	Lip product, nail polish, eye product, blush, body glitter, face paint, cream and toothpaste	US and centrifugation Combining DCM, MeOH, HAc and H_2O	LC-PDA	2014	Miranda-Bermudez et al. [32]

Table 2. *Cont.*

Analyte	Sample Matrix	Sample Preparation	Analysis	Year	Ref.
CI 14600, CI 14700, CI 15510, CI 15985, CI 16035, CI 16185, CI 16255, CI 18050, CI 19140, CI 20470, CI 42090	Eye shadow, lipstick and lip gloss	US and centrifugation MeOH-H_2O for eye shadow and $CHCl_3$-H_2O for lip products	UPLC-MS/MS	2013	Xian et al. [33]
CI 14700, CI 15510, CI 15985, CI 26100	Blemish cream and hair dye	Without sample preparation	DESI-MS	2013	Nizzia et al. [34]
CI 40290	Eau de toilette and shampoo	IL-DLLME Adjusted to pH 4	UV-Vis spectroscopy	2013	Guo et al. [35]
CI 45170	Shampoo, pencil and eye shadow	Micro SPE Novel nanocomposite as magnetic sorbent	Fluorescence spectroscopy	2013	Bagheri et al. [36]
CI 45170	Lipstick	SPE Sepabeads SP 70 resin and ACN for elution	UV-Vis spectroscopy	2011	Soylak et al. [9]
CI 15850	Nail preparation, lipstick and rouge	Solvent extraction and centrifugation DMF and MeOH (2:8)	Voltammetry Comparison with LC-UV	2010	Wang et al. [37]
CI 45170	Lipstick	Solvent extraction in hot water (emulsion for micellar determination)	FIA Fluorescence spectroscopy	2008	Wang et al. [38]
CI 45170	Hand washing liquid soap	CPE Aq solution with Triton X-100 in acidic media	UV-Vis spectroscopy	2008	Pourreza et al. [39]
CI 11020, CI 11285, CI 11920, CI 12055, CI 12140, CI 26100, CI 26105, CI 26150, CI 42000:1, CI 61554	Commercial products	Not provided	HPLC-UV and HPLC-MS/MS	2008	Noguerol et al. [40]

Out of 54 dyes considered in the papers reviewed, 16 are banned according to European Regulation (colour index underlined in Table 2) and 38 are permitted, which represents a limited share of the colorants regulated by Annex IV [17]. Figure 1 shows the 10 permitted dyes most determined in cosmetics. They mainly correspond to red shades and seven of them belong to the azoic group. Regarding banned dyes, the majority of studies are focused on the determination of Rhodamine B. Given its genotoxic effects, many methods have been exclusively developed for the analysis of this compound [9,25,27,28,36,38,39], and it will be commented on separately. With the exception of these cases, the current trend is the development of methods for the simultaneous analysis of mixtures of colorants: up to 32 for qualitative analysis [32] or 19 for quantitative analysis [26]. Although out of the period considered in this review, it is worthy to note that in 1997 Rastogi et al. [41] built a useful spectral library consisting of retention times and UV-Vis spectra of 130 organic cosmetic colorants for the purpose of identifying the colouring matter in cosmetic products, and a method based on extraction by SPE and analysis by HPLC-DAD with ion-pair mobile phase was optimized for routine control of colorants in lipsticks and varnishes.

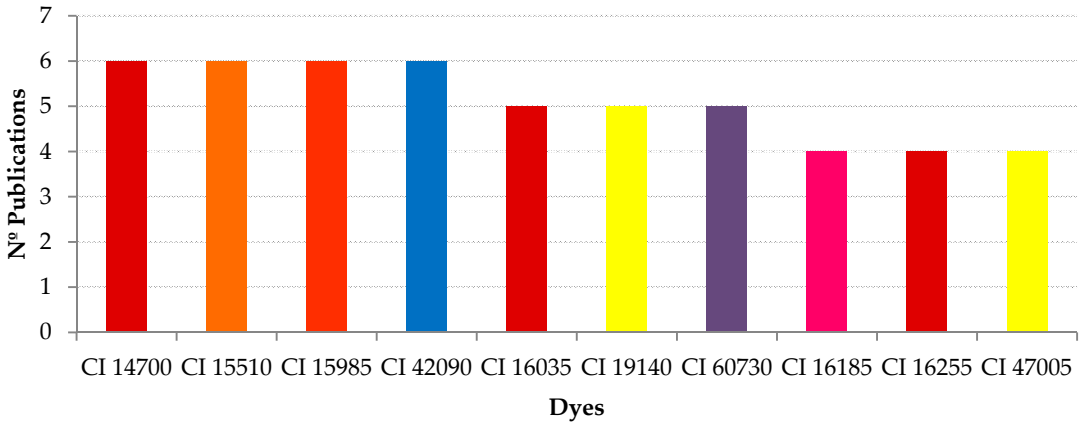


Figure 1. Top 10 permitted dyes analysed in cosmetics in the last 10 years (bar colour corresponds with the shade of each dye).

It should also be mentioned that some methods have been reported for the control of impurities and subsidiary compounds in raw material or other contaminants that can be produced during the manufacturing process [42–45]. Subsidiary colours are a type of impurities which are positional isomers of the dye anion or have higher or lower numbers of substituent groups [43]. The FDA routinely analyses these substances in colorants and their lakes to comply with the regulatory specifications of the batch certification program as was mentioned before. From an analytical point of view, this complex matter requires a different methodological approach which is out of the scope of this revision.

3.1. Sample Preparation

Cosmetics are very different in their form (liquid, semisolid, powder, wax, etc.) and composition. The content of colorants in cosmetics may also vary widely depending on the type of product. Decorative cosmetics such as lipsticks, blushes, face powders, mascaras, eye products or nail polishes, contain the highest percentage of dyes. Therefore, these matrices have been the subject of most of the analytical studies [15].

Sample preparation is a necessary step in the analytical process and it often requires time and energy-consuming operations that imply large amounts of organic solvents, acids or chemicals. Currently, the main priority is the development of sustainable methodologies in accordance with the principles of green chemistry. Simple and rapid methodologies with minimal consumption of reagents and solvents are increasingly demanded by control laboratories. In recent years, there has been a tendency towards the use of microextraction techniques or the miniaturization of conventional procedures of sample preparation. Figure 2 briefs the sample extraction strategies proposed in the methods summarized in Table 2. The amount and type of solvent employed is an important factor to develop more environmental friendly alternatives. In general, methanol or mixtures of methanol and other polar solvents were preferred as eluting or extracting solvent and in particular when the extracts are subsequently analysed by LC, given its compatibility with the mobile phase. However, extraction of dyes from wax-based cosmetics such as lip products often involved the use of toxic organic solvents such as chloroform or dichloromethane.

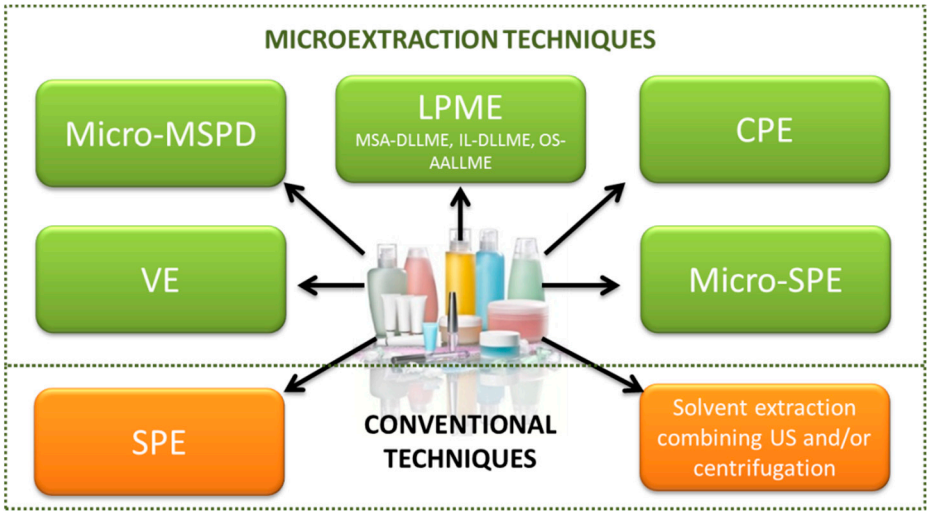


Figure 2. Sample extraction strategies for dyes in cosmetics proposed in the international scientific literature (2008–2018).

Some methodologies focused on the determination of a unique colorant in one or a few cosmetic matrices. In this line, Wang et al. [37] proposed a simple sample treatment for the analysis of Lithol Rubine B (CI 15850) in nail preparation, lipstick and rouge, and Guo et al. [35] developed a method based on ionic liquid dispersive liquid-liquid microextraction (IL-DLLME) for the determination of

Brilliant Blue (CI 42090) in eau de toilette and shampoo. DLLME is a relatively recent micro-extraction technique based on a ternary component solvent system. An adequate extraction solvent and disperser solvent are added to the aqueous sample to form a cloudy solution. To collect the enriched phase with the analytes, a solvent with higher density than water must be used. The conventional solvents for DLLME are chlorobenzene, chloroform, carbon tetrachloride, and carbon disulfide. The use of ionic liquids (IL), considered more environmentally friendly, improve the sensitivity and selectivity, becoming an interesting approach; however, dispersing solvents, heating and cooling down, ultrasonication or additional chemical reagents are frequently required for the dispersion and sedimentation of ILs, resulting in long sampling time. To avoid these additional requirements, Guo et al. [35] employed 1-decyl-3-methylimidazolium tetrafluoroborate ([C10MIM][BF_4]) as the ionic liquid for the sample preconcentration. A full optimization of parameters affecting the micro-extraction such as volume of IL, pH and time of incubation and centrifugation was performed. Since an aqueous media is needed for the dispersion of ILs, this is a selective and sustainable approach only for water soluble samples.

As mentioned before, Rhodamine B is a widely considered dye. In recent years, several methods have been developed for its determination in cosmetics, especially in lipsticks. In 2008, Wang et al. [38] proposed a spectrofluorimetric method with minimal pre-treatment based on dissolution of lipstick in hot water by mechanical stirring. Adding an anionic surfactant during the flow-injection analysis increased the fluorescent sensitivity until 2.5 fold. With this procedure, the authors estimated a sampling rate higher than 100 samples h^{-1}. In the same year, Pourreza et al. [39] developed a method based on cloud point extraction using Triton X-100 as non-ionic surfactant in acidic media. This preconcentration and extraction technique is considered in accordance with the "green chemistry" principles. It is based on the separation, at a certain temperature, of two phases in aqueous solution, one of small volume rich in surfactant and another with low concentration. After separation, the turbid solution is cooled down, so the surfactant rich phase becomes viscous and it is easily separated by decantation. The method was applied to different types of samples including a cosmetic one: hand washing liquid soap.

Solid phase extraction is a well-established preconcentration method generally applied to the analysis of trace amounts of analytes in environmental samples. It has also been proposed as an alternative extraction technique for lipstick [9,25,36]. Soylak et al. [9] developed a method using SPE with Sepabeads SP 70 resin as adsorbent. The purpose was to preconcentrate traces of Rhodamine B in waste water samples and soft drinks but it was also applied to the extraction of the dye in lipstick, previously dissolved in water by heating and stirring. Rhodamine retained in the adsorbent was eluted with 5 mL of acetonitrile and analysed by UV-Vis spectrophotometer. Validation was performed only for the liquid samples so extraction efficiency in lipsticks is not provided. Rhodamine B was identified and quantified in two lipsticks at concentrations of 39 and 127 $\mu g \cdot g^{-1}$. Recently, Bişgin et al. [25] developed two extraction methods based on SPE and CPE (cloud point extraction) for the determination of Rhodamine B in lipstick as well. In both cases, sample was previously dissolved in 25 mL of CCl_4, which is potentially a long-term carcinogenic solvent. For SPE, amberlite XAD-1180 was used as adsorbent and 5 mL of ethanol to elute Rhodamine. For CPE, Tergitol NP-7 was employed as surfactant. In view of the experimental procedure, SPE implies a shorter sampling time, higher preconcentration factor and better repeatability. On the other hand, sensibility is slightly better in the case of CPE. In 2013, Bagheri et al. [36] synthetized a novel magnetic nanocomposite (Fe_3O_4–aniline-naphthylamine) as a high-efficient sorbent for micro-SPE for the determination of Rhodamine in several samples including shampoo, eye pencil and eye shadow. In this case, an amount of 7 mg of sorbent is added to the sample solution and stirred for 10 min. Then, the sorbent is collected with an external magnet and Rhodamine is desorbed with 2 mL of methanol. This alternative sorbent led to higher extraction efficiency due to its increased sorbent surface area and porosity.

Finally, two methods based on DLLME have been developed for the determination of Rhodamine B in decorative make-up (lipstick, rouge and nail polish) [27] and Rhodamine B and 6G (CI 45160)

in lipstick [28]. The first method [27] is based on the combination of two supramolecular solvents, polar and non-polar, such as THF or decanoic acid. Although the experimental procedure is considered fast, prior to micro-extraction a step consisting of solving 0.5 g of sample in 10 mL of ethyl alcohol and shaking for 2 h is needed. In the second case, Ranjbari and Hadjmohammadi [28] optimized a method based on magnetic stirring assisted DLLME (MSA-DLLME), using 1-octanol and acetone as extraction and dispersing solvent, respectively. As mentioned before, DLLME needs extraction solvents with higher density than water, which frequently implies the use of toxic organic solvents. To overcome this limitation, magnetic stirring is introduced in the methodology in order to help to maintain the cloudy solution and to accelerate the mass transfer from aqueous solution to the extraction solvent, without the need for ultrasonication. A home-made glassware extraction cell has been designed to improve the magnet rotation and to simplify the collection of the supernatant organic solvent enriched with the analytes after centrifugation. To apply a technique based on liquid-liquid extraction to a solid sample such as lipstick, a previous treatment is obviously needed. In this case, 0.05 g of lipstick was solved in 50 mL water assisted by ultrasonic waves and mechanical stirring, and then it was filtered and transferred to the extraction cell.

In the context of a growing market of colour cosmetics, multianalyte analytical methodologies are indispensable to satisfy the increased demand of quality control. In the period under consideration, the first extraction method for the determination of a mixture of dyes was proposed by Xian et al. [33] in 2013. Before this work, several multianalyte methods are worthy to consider. Noguerol et al. [40] developed a method based on HPLC-UV and HPLC-ESI-MS/MS for the application to commercial products, but neither the type of sample nor sample preparation method were provided. Nizzia et al. [34] proposed an analytical approach based on desorption electrospray ionization mass spectrometry (DESI-MS), where sample treatment is not required for the analysis. The work published by Xian et al. [33] was focused on the development of a method for the analysis of 11 dyes in cosmetics. In this way, a simple methodology based on vortexing, ultrasounds and centrifugation was successfully applied achieving quantitative recoveries in eye shadow, lipstick and lip gloss. However, for the extraction from waxy matrices, longer sampling time and chlorinated solvents were required though in small volumes (2 mL of chloroform). Similar liquid-liquid extraction using combinations of dichloromethane, methanol, acetic acid and water, was proposed by Miranda-Bermudez et al. [32]. The developed and validated methodology was employed to survey 29 colour additives, including water and methanol-soluble permitted dyes and the most prevalent non-permitted colour additives found by FDA's district laboratories, in 38 samples of lip and eye products, nail polish, blush, body glitter, face paint, cream and toothpaste. Despite the broad range of analytes and samples studied, this methodology was developed only for the qualitative identification of dyes.

Barfi et al. [31] and Franco et al. [30] focused mainly on the determination of illegal dyes in cosmetics. In the first work, a novel, simple and eco-friendly method based on one step air-assisted liquid-liquid micro-extraction (OS-AALLME) was developed to extract Sudan dyes and Orange G in lipstick. In addition, because of the high risk of direct oral ingestion of sample, the validated extraction method was applied to estimate the concentration of a potential biomarker of these dyes, 1-amino-2-naphthol, in human bio-fluids. The advantage of this approach is the application of ILs as extraction solvent, avoiding the use of organic solvent. The immiscibility of ILs in water and their capability to solubilize organic species make them a valuable alternative to conventional solvents. To carry out the dispersion of the IL in aqueous solution, the mixture is repeatedly withdrawn into a glass syringe and pushed out (AALLME), while sonication is performed in order to increase the surface contact between the immiscible liquids and then, to enhance the extraction efficiency. In this way, micro-extraction takes place in one step. On the other hand, Franco et al. [30] developed a method based on sample dilution in water and SPE for the determination of four basic dyes and one acid dye used as semi-permanent hair colorants. Oxidative hair dyes have been the subject of most of the analytical methodologies for the control of hair colorants due to their widespread use and there

are very few methods for semi-permanent dyes. Hair dyeing formulations do not require a complex extraction method. After shampooing, the dyes are retained in the structure of hair through ionic interactions or van der Waal forces.

Recently, Guerra et al. have been working on improving the simultaneous analysis of a great number of chemically different dyes in a broad range of cosmetics, including rinse-off and leave-on products [24,26,29]. In 2015 [29], they introduced the matrix solid-phase dispersion (MSPD) for the first time in the analysis of dyes in cosmetics. MSPD is a valuable approach for solid and semisolid samples for its simplicity and the possibility of performing a clean-up step simultaneously. In this case, miniaturization of the conventional procedure employing a Pasteur pipette as device in order to pack the sample dispersed (see Figure 3), allowed extracting quantitatively nine dyes in many cosmetics including lipstick, nail polish or toothpaste. More recently, they published a new method [26] based on miniaturized MSPD with significant improvements in relation to the previous one. In this work, 19 permitted and banned dyes were analysed, 10 more than in the former, in a broader range of matrices, which involved a re-optimization of the sample preparation procedure using experimental designs. The Pasteur pipette was replaced by a 2 mL syringe to enable an adequate solvent elution employing the dispersant chosen as the optimum, C18. The most recent multi-dye method was also reported by Guerra et al. [24]. Single-step vortex extraction and simultaneous clean-up was applied to the analysis of dyes as well as preservatives in different cosmetics, many of whom have not been analysed yet. In comparison with other approaches based on simple solvent extraction assisted by ultrasounds or centrifugation, this method offers advantages in terms of simplicity, rapidity and minimal consumption of solvents. In addition, it may be considered more environmentally friendly since it avoids the use of solvents such as dichloromethane or chloroform.

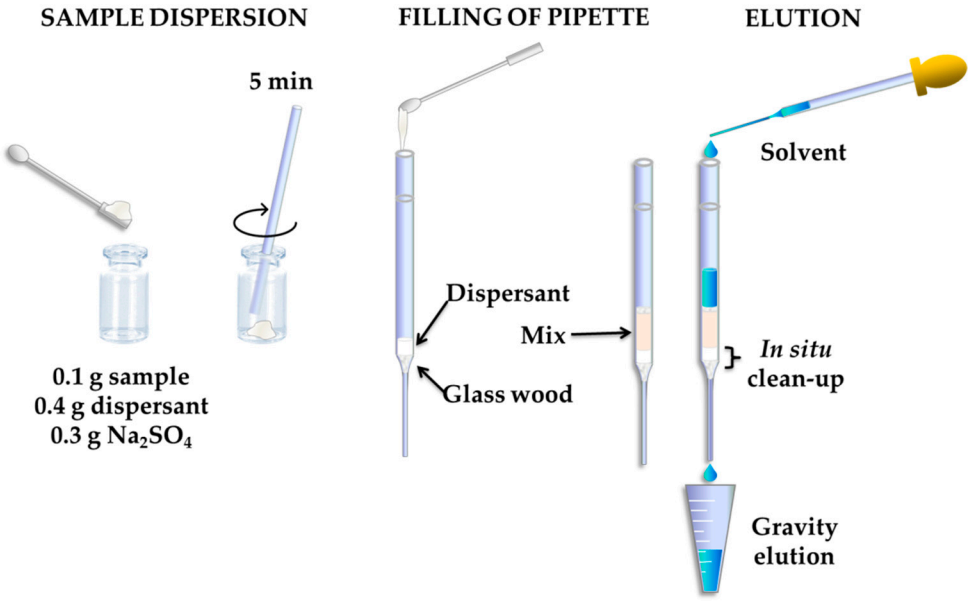


Figure 3. Miniaturized matrix solid-phase dispersion (MSPD) procedure.

3.2. *Analytical Techniques*

In order to identify and quantify properly the dyes in cosmetic samples, a chromatographic separation is frequently required. Liquid chromatography coupled to absorbance or mass spectrometry detectors were proposed in all analytical methodologies for the simultaneous determination of mixtures of dyes (Table 3). Due to the capability of dyes to absorb in the UV-Vis spectrum, DAD or UV-Vis detectors were traditionally the preferred detectors [28,30–32]. In recent years, mass spectrometry has become a valuable choice [24,26,29,33,34], given its enhanced selectivity and sensitivity; it is particularly desired in the analysis of banned compounds. Mass spectrometry overcomes limitations of DAD such

as overlapping of UV-Vis spectra among matrix ingredients. In some studies, a comparison between LC-DAD and LC-MS/MS was established [30,40]. In this way, Noguerol et al. [40] developed two LC methods with UV-Vis detection and with tandem mass spectrometry triple quadrupole in positive ion mode electrospray ionization (ESI) for the routine control of 10 dyes, mainly dyes banned in cosmetics. LC-ESI-MS/MS in full scan mass spectra mode allowed to obtain structural information about multiple peaks observed for some of the studied dyes through HPLC-UV/Vis analysis. The presence of more than one peak for a compound was mainly due to possible isomerization processes, impurities or degradation products. In addition, multiple reaction monitoring (MRM) mode was employed for quantification purposes. In terms of sensitivity, there was a remarkable difference between both methods. Limits of quantification were one or two orders of magnitude lower for the LC-MS/MS analysis, which is particularly valued given the high restriction of those target dyes in the commercial products. This work focused on the development of an analytical method for its implementation in the control of dyes in commercial products, but not specifically for cosmetics.

Table 3. Performance of analytical methodologies for multi-dye determination in cosmetics (2008–2018).

Dye	Recovery (%)	LOD/LOQ	RSD (%)	Ref.
Liquid Chromatography Coupled to Mass Spectrometry				
CI 14700, CI 14720, CI 15510, CI 15985, CI 16035, CI 16185, CI 16255, CI 19140, CI 42051, CI 42090, CI 44090, CI 47005, CI 60730, CI 73015	70.3–117	–/0.070–3.437 μg g^{-1}	<13	Guerra et al. [24]
CI 13065, CI 14700, CI 14720, CI 15510, CI 15985, CI 16035, CI 16185, CI 16255, CI 19140, CI 42051, CI 42090, CI 42640, CI 44090, CI 45170, CI 45410, CI 45430, CI 47005, CI 60730 CI 73015	69.5–121	0.0142–0.476 μg·g^{-1}/–	<15	Guerra et al. [26]
CI 14700, CI 15510, CI 15985, CI 16035, CI 19140, CI 42090, CI 45410, CI 47005, CI 60730	70–120	0.010–0.62/1–5 ng·mL^{-1} (LLOQ)	<15	Guerra et al. [29]
CI 14600, CI 14700, CI 15510, CI 15985, CI 16035, CI 16185, CI 16255, CI 18050, CI 19140, CI 20470, CI 42090	81.6–118.2	1.2–30.3/4.1–100 μg·kg^{-1}	<8	Xian et al. [33]
CI 11020, CI 11285, CI 11920, CI 12055, CI 12140, CI 26100, CI 26105, CI 26150, CI 42000:1, CI 61554	Not provided	4.54–14.3/15.0–47.6 μg·L^{-1}	–	Noguerol et al. [40]
Liquid Chromatography Coupled to Absorbance Detector				
CI 45160, CI 45170	97–100	1.15–1.23/3.82–4.10 ng·mL^{-1}	<2	Ranjbari et al. [28]
CI 12245, CI 12250, CI 12719, CI 56059, CI 60730	Not provided	0.53–2.98 × 10^{-7}/ 1.08–3.66 × 10^{-7} mol·L^{-1}	<5	Franco et al. [30]
CI 11920, CI 12055, CI 12140, CI 26100, CI 26105	86.8–102.3	3.9–84.8 ng·mL^{-1}/–	<6	Barfi et al. [31]
CI 10316, CI 14700, CI 14720, CI 15510, CI 15850, CI 15850:1, CI 15880:1, CI 15985, CI 16035, CI 16185, CI 16255, CI 17200, CI 19140, CI 42051, CI 42053, CI 42090, CI 45100, CI 45170, CI 45350, CI 45350:1, CI 45370, CI 45380, CI 45380:2, CI 45410, CI 45410:1, CI 45430, CI 47005, CI 59040, CI 60730, CI 61570, CI 73015, CI 75470	–	0.1–1.5 mg·L^{-1} (estimated, qualitative method)/–	–	Miranda- Bermudez et al. [32]
CI 11020, CI 11285, CI 11920, CI 12055, CI 12140, CI 26100, CI 26105, CI 26150, CI 42000:1, CI 61554	Not provided	60–890/200–2990 μg·L^{-1}	–	Noguerol et al. [40]
DESI-MS				
CI 14700, CI 15510, CI 15985, CI 26100	–	15–100 ng (<1 ng SRM mode)	9–27	Nizzia et al. [34]

The combination of liquid chromatography and mass spectrometry in the analysis of dyes in cosmetics was reported for the first time by Xian et al. [33] in 2013. Afterwards, Guerra et al. developed several improved methods based on this analytical technique [24,26,29]. Most of the dyes used in cosmetics and so considered in this review are sodium or calcium salts which contain in their structures one or more ionized groups such as sulphonic groups. This fact implies the possible formation of multicharged ions in the ionization source. In addition, the separation of ionic compounds by reverse phase liquid chromatography is a challenging task and more efforts must be done in relation to the separation of neutral compounds. In this respect, the mobile phase (ionic strength, pH, and composition) plays an important role. In some cases, a mobile phase without additives, composed by water and an organic modifier (acetonitrile or methanol), has been employed achieving good sensitivity and a fast analysis [29,33]. The use of UPLC allowed performing the analysis of

11 dyes in 4 min [33]. Similar results were achieved for a mixture of nine dyes with a conventional porous C18 column [29]. Although the use of mass spectrometry allows a selective identification of co-eluted compounds, a chromatographic separation is generally recommended. For this purpose, the addition of volatile neutral salts to mobile phase is necessary in order to avoid interactions between ionized negatively charged compounds and partially ionized residual silanols in the stationary phase [46]. However, the presence of salts in the ion source may cause a suppression of the ionization. Thus, the composition of mobile phase must be investigated to achieve a compromise between good separation and performance. In this way, the use of only 3 mM ammonium acetate in the aqueous mobile phase was proposed [24,26]. This salt concentration was enough to avoid peak tailing while improving the chromatographic separation for quite a number of analytes with satisfactory limits of quantification. In the most recent work [24], other chromatographic parameters were optimized to separate dyes and preservatives.

The matrix effect is the ionization suppression or enhancement of the target compound by others present in the sample and it is very frequent in LC-MS/MS analysis, in particular when electrospray sources are used. In every method for dyes analysis using MS/MS detector, a study of matrix effect was performed. The most comprehensive study was carried out for 19 dyes in seven cosmetic matrices (lip balm, nail polish, hairspray, eye shadow, toothpaste, face painting and gel) [26]. In all cases, the optimized sample extraction procedure allowed obtaining an extract clean enough to perform the analysis with negligible matrix effects, with particular exceptions for some compounds in very few matrices.

In contrast to conventional mass spectrometry techniques, Nizzia et al. [34] investigated the use of DESI-MS for the analysis of common semi-permanent hair colorants in two semisolid cosmetic formulations: a blemish cream and a hair-dye gel. As a novelty, the use of an ambient MS technique allowed a direct analysis without prior sample preparation or chromatographic separation. A thin layer of sample is deposited onto porous Teflon and a pneumatically assisted electrospray is employed to release neutral analytes present on this surface as secondary ions.

On the other hand, UV-Vis and DAD detectors are still often used in the literature for the analysis of dyes in commercial products. Concerning cosmetics, there have been several methods reported in the last 10 years that combine LC and DAD for the quantitative [28,30–32] and qualitative [32] analysis of multiple dyes or that apply direct spectrophotometric measurement when only one dye is considered [9,25,27,35,39] (see Table 4). In these latter methods, good limits of detection were obtained because of the concentration achieved using an extraction technique such as SPE, CPE or DLLME previous to the analysis. Most of these methods were developed to identify and quantify Rhodamine B, so they established a fixed wavelength, 556 nm, which corresponds with the maximum of absorbance of this compound. When a mixture of dyes is analysed, DAD is a useful tool that allows the simultaneous recording of absorbance data from 190 to 800 nm and to match the UV-Vis spectra obtained with spectral libraries.

Table 4. Performance of analytical methodologies for only one dye determination in cosmetics (2008–2018).

Dye	Recovery (%)	LOD/LOQ	RSD (%)	Ref.
		UV-Vis spectroscopy		
CI 45170	85–100	0.7/1.9 $\mu g \cdot L^{-1}$ for CPE, 1.2/3.2 $\mu g \cdot L^{-1}$ for SPE	<7	Bisgin et al. [25]
CI 45170	99–104	0.49/1.47 $\mu g \cdot L^{-1}$/	<6	Ozkantar et al. [27]
CI 42090	99–103	0.34 $\mu g \cdot L^{-1}$	<1	Guo et al. [35]
CI 45170	Not provided	Not provided	<5	Soylak et al. [9]
CI 45170	97–102	1.3 $ng \cdot mL^{-1}$/–	<3	Pourreza et al. [39]
		Fluorescence spectroscopy		
CI 45170	94–99	0.10/0.35 $\mu g \cdot L^{-1}$	<8	Bagheri et al. [36]
CI 45170	98–102.4	5×10^{-10}/1.6×10^{-9} $mol \cdot L^{-1}$	<3	Wang et al. [38]
		Voltammetry		
CI 15850	Not provided	Not provided	<4	Wang et al. [37]

For the determination of basic dyes through LC-DAD, Franco et al. [30] proposed the use of ILs in the mobile phase to enhance peak shapes and to reduce the chromatographic retention times. ILs usually compete with basic groups for the residual silanols on the stationary phase or they can form an ion pair with cationic solutes to improve the shielding efficiency of these silanols. In this way, the analysis was completed in 40 min using an isocratic mode with a mobile phase composed by acetonitrile and water and 2 mL of 0.040 mol·L^{-1} BMIm[NTf_2] solution. The results obtained were compared with those obtained though LC-MS/MS by means of a t-student test. Concentration values obtained in both cases were not significantly different (at 95% confidence level). However, it must be pointed out that the mass spectrum provided chemical structural data that were employed to confirm the presence of the target compounds in the hair-dyeing formulations found by LC-DAD analysis.

Other analytical approaches were reported based on fluorescence measurements [36,38] or voltammetry [37] for the determination of Rhodamine B or Lithol Rubine, respectively. The main advantage of the fluorometric measurement is its high selectivity.

4. Conclusions

Colour increases the marketing success of the consumer products including cosmetics. Synthetic dyes are preferred, particularly azo dyes, even though several studies have evidenced harmful health effects.

There are different regulatory requirements for the use of dyes in cosmetics among the main markets (US, Europe and Japan), which becomes a handicap for the commercialization of a specific product. In the EU, with a powerful cosmetic industry, there are not official methods for the determination of synthetic dyes in cosmetics. The present review of analytical methodologies published in international scientific journals in the last 10 years revealed the lack of methods for the simultaneous analysis of multiple dyes. In addition, the range of coloured compounds analysed is very short in comparison with the total of regulated dyes that can be used in personal care products of daily use. Regarding sample preparation, there is a trend towards the micro-extraction techniques. The low consumption of solvents and reagents make them a valuable choice. For the analysis, liquid chromatography is by far the most preferred separation technique. Since most of synthetic dyes are ionized compounds, special efforts should be made for the optimization of the chromatographic separations. Absorbance detectors are a common approach to be considered, but mass spectrometry brings a significant added value in terms of sensitivity and selectivity, especially for the analysis of banned dyes.

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Appendix A : Abbreviations

ACN	acetonitrile
CI	colour index
CPE	cloud point extraction
DAD	diodo-array detector
DCM	dichloromethane
DESI-MS	desorption electrospray ionization mass spectrometry
DLLME	dispersive liquid-liquid microextraction
DMF	dimethylformamide

ESI	electrospray ionization
FIA	flow injection analysis
HAc	acetic acid
IL	ionic liquid
IL-DLLME	ionic liquid independent disperse liquid-liquid microextraction
LLOQ	lower limit of quantification
LPME	liquid-phase microextraction
MeOH	methanol
MRM	multiple reaction monitoring
MSA-DLLME	magnetic stirring assisted dispersive liquid-liquid microextraction
MSPD	matrix solid-phase dispersion
OS-AALLME	one-step air-assisted liquid-liquid microextraction
RSD	relative standard deviation
SPE	solid phase extraction
SRM	selected reaction monitoring
THF	tetrahydrofuran
UPLC	ultra performance liquid chromatography
US	ultrasounds

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