J. Electrochem. Sci. Eng. **00(0)** (2022) 000-000; http://dx.doi.org/10.5599/jese.1507

Open Access : : ISSN 1847-9286
www.jESE-online.org

Review paper

Electrochemical sensors for the safety and quality control of cosmetics: An overview of achievements and challenges

Totka Dodevska✉, Dobrin Hadzhiev and Ivan Shterev

Department of Organic Chemistry and Inorganic Chemistry, University of Food Technologies, Plovdiv, Bulgaria

Corresponding author: ✉dodevska@mail.bg; *Tel.: +359-32-603-679; Fax: +359-32-644-102*

Received: September 5, 2022; Accepted: November 19, 2022; Published: November 22, 2022

Abstract

Due to the rapid growth of the cosmetic industry in recent years, the development of new, reliable, cost-effective, ease of use and rapid methods to assay cosmetics' quality is of particular importance. Modern electrochemistry provides powerful analytical techniques with excellent sensitivity, instrumental simplicity and portability, providing reliable alternatives to conventional analytical methods. This review aims to give readers a clear view of advances in areas of electrode modification, successful strategies for signal amplification, and miniaturization techniques used in electroanalytical devices for cosmetics control and safety. We have summarized recent trends in the nonenzymatic electrochemical sensor systems applied in the analysis of cosmetic products revealing that there are a variety of efficient sensors for whitening agents, preservatives, UV filters, heavy metals, etc. In conclusion, current challenges related to the sensors design and future perspectives are outlined.

Keywords

Personal care products; ingredients; analytical methods; electroanalysis

Abbreviations

AdsASV	adsorptive anodic stripping voltammetry
AR	arbutin (4-hydroxyphenyl-β-D-glucopyranoside)
BP	butylparaben
BZ3	benzophenone-3
CC	catechol (1,2-dihydroxybenzene)
CPE	carbon paste electrode
DPAdSV	differential pulse adsorptive stripping voltammetry
DPV	differential pulse voltammetry
EP	ethylparaben
ErGO	electrochemically reduced graphene oxide
Fc	ferrocene
FIA	flow injection analysis
GCE	glassy carbon electrode
HQ	hydroquinone (1,4-dihydroxybenzene)

8-HQ	8-hydroxyquinoline
IL-GO	ionic liquid functionalized graphene oxide
LOD	limit of detection
LOQ	limit of quantification
LSV	linear sweep voltammetry
MB	methylene blue
4-MBC	4-methylbenzylidene camphor
MIPs	molecularly imprinted polymers
MP	methylparaben
MWCNTs	multi-wall carbon nanotubes
NPs	nanoparticles
OCR	octocrylene
OMC	octyl-methoxycinammate
PHBA	*p*-hydroxybenzoic acid
PP	propylparaben
PPD	*p*-phenylenediamine
RS	resorcinol (1,3-dihydroxybenzene)
SPE	screen-printed electrode
SWAdSV	square wave adsorptive stripping voltammetry
SWV	square wave voltammetry
TCS	triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol
TGA	thioglycolic acid
ZPT	zinc pyrithione (bis[(2-pyridyl-1-oxo)-thio]zinc)

Introduction

In general, cosmetics (body and personal care products) are mixtures of substances intended to be applied to the external parts of the human body for the purposes of cleaning, moisturizing, beautifying, keeping them in good condition or correcting body odors. As cosmetic preparations are repeatedly applied directly to the human body (epidermis, hair, nails, lips, external genital organs, teeth), they should be efficient and safe for health. To ensure the safety and quality of cosmetics, all the ingredients used in cosmetic products meet certain regulatory requirements.

Variety substances are allowed within certain limits as they may produce pharmacological or toxic effects at higher concentrations. In terms of safety, some other important aspects should be considered, which include the possibility of long-term effects. Recently, it was recognized that some topically applied substances penetrate through the skin and produce human systemic exposure. Unfortunately, using cosmetic products in some cases is related to the occurrence of unfavorable effects resulting from the intentional or accidental presence of toxic chemical ingredients [1]. Such substances may be a major component of the raw materials used in cosmetic manufacture or are deliberately added in cosmetics. It is considered that a small part of substandard cosmetics is falsified. The rest result from poor manufacturing practices, incorrect storage or inappropriate packaging.

Comprehensive coverage of the specific analytical procedure for various analytes and cosmetics samples, as well as the most recent developments in global legalization governing the cosmetics industry, were provided by Salvador and Chisvert [2]. A wide range of analytical techniques is used to accurately characterize and quantify ingredients in cosmetics. Conventional methods such as high-performance liquid chromatography (HPLC), gas chromatography, spectrophotometry, chemiluminescence, and fluorescence have been established for the analysis of cosmetic products. However, most of these methods have some disadvantages, such as specific expensive equipment, the need for complex pretreatment resulting in large time consumption and use of organic solvents in excess volumes, complicated operation, or a narrow linear range. Therefore, the development of a precise and easy-to-handle alternative for quick and efficient quantitative detection of various ingredients in cosmetic products is necessary for consumer safety [3]. New analytical methodologies are expected to use modern and efficient techniques with highly selective detectors, as well as rapid and simple sample preparation procedures with a high level of automation [4].

Electrochemical techniques have attracted significant interest due to their high sensitivity, low detection limit, simple operation, extremely low sample consumption, and rapid analysis. Electrochemical detection is also advantageous in terms of sensor fabrication cost, power consumption and miniaturization capability [5]. The following part will provide an overview of how advances in electroanalytical technology have contributed to developing sensor devices to screen for safety and quality markers associated with cosmetics and personal care products.

Current stage of electrochemical sensors for the analysis of cosmetics ingredients

Whitening agents

Hydroquinone, catechol, and resorcinol

The popularity of skin-lightening (whitening/bleaching) products has grown markedly in recent years. The motivation for skin whitening may be to treat a pigmentary disorder, but it is often simply for cosmetic enhancement, as skin complexion is considered one of the most important beauty features. Nowadays, skin lightening is a global phenomenon, with the highest rates in Africa, Asia, and the Middle East.

One of the most frequent targets for the development of hypopigmenting agents is tyrosinase - a copper-containing enzyme that catalyzes the rate-limiting step of melanin biosynthesis. The skin-lightening agents act by inhibiting of tyrosinase activity, thereby reducing the conversion of dihydroxybenzoic acid to melanin. The isomers of dihydroxybenzene hydroquinone (1,4-dihydroxybenzene, HQ), catechol (1,2-dihydroxybenzene, CC), and resorcinol (1,3-dihydroxybenzene, RS) specifically inhibit the melanogenesis in cells and are used in hair dyes and medical whitening creams [6]. The most commonly used treatment of hyperpigmentation for over 50 years is topical HQ. Although very effective, its long-term application causes a number of adverse reactions, including skin irritation, burning sensations, leukoderma, ochronosis, and degenerative changes followed by the skin's loss of elasticity and may have a cytotoxic effect on melanocytes. RS is an endocrine disruptor that can affect thyroid function by inhibiting thyroxin peroxidase. After prolonged exposure to RS, suppression of thyroid hormone synthesis in humans, hematological abnormalities, carcinogenesis, and fatal cases of human fetus poisoning have been observed [7]. HQ, CC, and RS are included among the substances prohibited for use as skin whitening agents in cosmetic products (Annex II and Annex III) to Regulation (EC) No 1223/2009 [8]. In the USA, the Food and Drug Administration has proposed concentrations of HQ between 1.5 and 2 % in skin lighteners [9]. According to China's hygienic standard for cosmetics, HQ is limited to oxidation colorants for hair dyeing, with a maximum allowable concentration of 2 wt.% [6]. However, in developing countries, whitening cosmetics containing HQ are circulating illegally, not to mention that the concentration level is relatively high [10].

HQ, CC and RS are electroactive substances that can be detected using various electrochemical methods. Conventional working electrodes, such as glassy carbon, graphite, carbon paste electrodes, and boron-doped diamond electrodes, have low reproducibility and stability for phenolic compounds detection because the redox reaction that occurs usually produces a polymer layer that adsorbs on the surface of the electrode, resulting in a fouling effect. This phenomenon severely affects the analytical performance in terms of sensitivity and linearity of the electrode signal. In order to reduce this effect and improve the electrode efficiency, modification of the working electrodes with nanomaterials (metal/metal oxide nanoparticles, CNTs), graphene or polymers has been extensively investigated.

Cotchim *et al.* reported a simple electrochemical sensor for the determination of HQ at trace levels using a carboxylic acid-functionalized graphene-modified glassy carbon electrode (Gr-COOH/GCE) for adsorptive anodic stripping voltammetry (AdsASV) [9]. The electroanalytical procedure involves two steps: i) accumulation or preconcentration of the analyte at the electrode surface, and ii) stripping of the accumulated analyte from the electrode surface by using a potential sweep. Gr-COOH acts as an adsorbent, resulting in HQ being closely adsorbed on the electrode surface. As a result, the detection efficiency increases, leading to high sensitivity and a low limit of detection (LOD). The Gr-COOH/GCE exhibited good electrochemical oxidation behavior of HQ with sensitivity ten times higher than the bare GCE. The authors point out that after each experiment, the modified electrode was cleaned in the supporting electrolyte at a potential of +1.0 V (*vs.* Ag/AgCl) for 60 s to minimize electrode fouling and improve the electrochemical response. Under the optimized conditions, the analytical performance of the proposed method was validated and exhibited a wide linear range (0.1 to 40.0 µM), high sensitivity (19.86 µA μM^{-1} cm^{-2}), LOD of 0.04 µM, good selectivity, high accuracy and precision. The modified electrode provides rapid response and good repeatability, and it successfully detects trace HQ in cosmetic and skin-lightening products. Concentrations of HQ determined by the proposed sensor and by UV-derivative spectrophotometry showed no significant differences, indicating that the developed method can be successfully applied for the determination of HQ in various cosmetic products.

A simple electrochemical sensor based on nano-sepiolite clay-modified carbon paste electrode was developed for the analysis of HQ in cosmetic samples by using differential pulse adsorptive stripping voltammetry (DPAdSV) and square wave adsorptive stripping voltammetry (SWAdSV) [11]. The electrode has the advantages of high sensitivity, large linear range, low limit of detection, ease of preparation, practical surface renewal, and low cost. The authors reported that in order to prevent electrode fouling before all assays, surface cleaning of carbon paste sensors was carried out by washing with a water-ethanol mixture (1:1). The proposed sensor was applied to the analysis of HQ in the cosmetic sample (Expigment cream) with satisfying results. According to the presented results, the proposed methods have definite precision and accuracy.

Electrochemical techniques in combination with screen-printed electrodes (SPEs) have been proven as capable sensors to accelerate the change from conventional benchtop techniques/equipment to low-cost, robust and quick sensing devices [12]. With respect to the most used glassy carbon electrodes, SPEs show numerous advantages such as easy customization, cost-effectiveness, miniaturization, measurements that consume only a few microliters of sample, suitability for in-field analysis, and the absence of surface pre-treatment or polishing. It is therefore considered a potential tool for on-site applications [13]. A small and portable graphene-modified carbon paste sensor for HQ was developed using the screen-printing technique [14]. The electrochemical detection is based on a one-drop analysis (60 µL of the sample). A linear calibration was achieved in the range of 10^{-4} to 5×10^{-3} M HQ (LOD = 7×10^{-5} M). The authors stated that the sensor provided good precision and accuracy with an analysis time of less than a minute. This device was applied to determine the presence of HQ in whitening cosmetic products. The results obtained from the developed sensor satisfactorily agreed with HPLC, indicating the reliability of the electrochemical method.

An anodically pretreated screen-printed ring disk carbon electrode (SPRDCE*) coupling with a flow injection analysis (FIA) system was developed as a simple, rapid, sensitive, and self-validated HQ sensor [15]. Using carbon-based electrode preanodized in phosphate buffer (a nontoxic solution), the sensitivity of electrochemical detection of HQ was significantly improved owing to the increase of the polar oxygen-containing functional group during the anodization. The developed anodized SPRDCE* presented high ability and feasibility for HQ detection. Under the optimized conditions, a linear range of 0.25 to 160 ppm and LOD = 0.024 ppm for HQ were defined. Using this method, HQ in cosmetic products was successfully quantified without any pre-treatment. SPRDCE* combined with the FIA system offers important practical features for routine analysis of HQ in cosmetic products (Figure 1).

A carbon paste electrode spiked with ferrocene (Fc/CPE) was constructed by incorporation of ferrocene in a graphite powder–paraffin matrix [16]. Ferrocene (Fc) is a stable organometallic complex of iron. Fast and reversible redox reactions involving the Fc/Fc$^+$ couple make it a suitable mediator that accelerates electron transfer in the electrochemical systems. Linear sweep voltammetry (LSV) data confirm that Fc/CPE possesses good analytical performance - working range of 0.20 to 10 µM, a sensitivity of 10.436 µA µM^{-1}, and a detection limit of 0.06 µM HQ.

An efficient and economically viable electrochemical sensor for the quantitative determination of RS based on 77Maghemite/multi-wall carbon nanotubes (M/MWCNTs) modified carbon paste electrode was developed by Manasa *et al.* [17]. Quantitative analysis of RS was performed in PBS (pH 7.0) using differential pulse voltammetry (DPV) and two linear ranges (0.5 to 10 and 10 to 100 µM) were obtained as a result of the kinetic limitation at the electrode/solution interface; LOD was found to be 0.02 µM. Furthermore, to demonstrate the feasibility of the M/MWCNTs/MCPE, the amounts of RS in hair dye samples were tested by DPV, which showed good recovery and practical applicability.

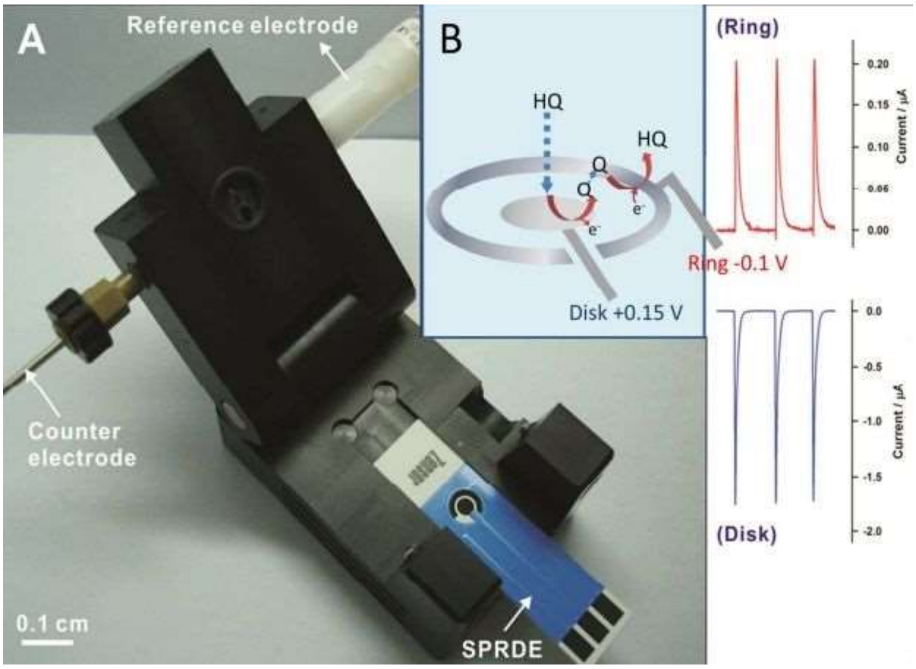

Figure 1. *Schematic representation for monitoring of HQ at the SPRDCE* using FIA.*
Reproduced from Ref. [15] with permission from the Royal Society of Chemistry

Nowadays, the effective simultaneous detection of phenolic compounds that have analogous chemical features is a subject of major study interest in the field of analytical chemistry [18]. Because of the similar electrochemical behaviour of HQ, RS, and CC, their redox peaks tend to overlap and cannot be effectively distinguished using conventional glassy carbon electrodes [19]. Therefore, to improve the detection sensitivity and selectivity of electrochemical sensors, it is necessary to search for new nanomaterials that are eco-friendly, economical, and show good catalytic performance. Electrodes modified with magnetic nanomaterials present stable conductivity and accelerate the redox process. Feng *et al.* studied the electrochemical behavior of dihydroxybenzene isomers on N-doped nickel carbide spheres (N-NiCSs/GCE) in 0.1 M PBS (pH 7.0) using cyclic voltammetry (CV) and

DPV. N-NiCSs/GCE has been applied to the simultaneous determination of HQ, CC and RS with a wide linear range, good stability, reproducibility and high sensitivity, which fully meet the requirements of cosmetics testing [6]. Under the experimental conditions, the three analytes are distinguishable by their peak potentials. The detection limits of HQ, CC, and RS were 0.00152, 0.015 and 0.24 mM, respectively. The N-NiCSs/GCE sensor has been successfully used to detect simultaneously HQ, CC, and RS in local tap water, hair dye, and whitening cream samples with satisfactory recoveries demonstrating its practicability and reliability. The authors have concluded that their future research will focus on appropriate reverse electrode passivation materials to reduce the effect of fouling.

Ascorbic acid (AA), known as vitamin C, is a naturally occurring water-soluble organic compound with antioxidant properties. Ascorbic acid plays a key role in maintaining skin health. It provides protection against UV-induced photodamage and participates in the formation of skin barrier lipids and collagen in the dermis. Although the antipigmentary and skin-protective mechanisms of AA still need to be clarified, AA has been used widely as a skin-lightening, anti-aging, anti-oxidant and anti-inflammatory agent in commercially available cosmetics such as creams and lotions, designed to protect and rejuvenate photoaged skin [20].

A new sensor based on copper oxide (CuO) nanostructures modified glassy carbon electrode (CuONPs/GCE) was designed for the simultaneous electrochemical determination of AA and HQ [21]. CuONPs with nanoflakes morphology were synthesized through an aqueous chemical growth method using copper acetate as precursor salt and sodium hydroxide as a reducing agent. CuONPs were deposited on the GCE surface by drop casting method. Under the optimal conditions, the prepared electrode CuONPs/GCE reveals excellent sensitivity, selectivity and stability with a wide linear dynamic range (0.0001 to 0.30 mM for AA, and 0.0003 to 0.355 mM for HQ) and limit of detection (0.01 µM for AA, and 0.009 µM for HQ). The proposed sensor has shown a potential for the simultaneous determination of AA and HQ and can be effectively used in real samples of skin-lightening creams.

Here it should be pointed out that the drop-casting approach could be characterized by some drawbacks, such as low homogeneity and stability of the resulting modified surface. A phenomenon known as the "coffee ring" effect was observed due to capillary forces present as a result of solvent evaporation which can push the modifier to the edges of the underlying electrode [13]. Agglomeration of particles upon electrode surface modification during the drop-casting process affects many physical and chemical properties, thus affecting sensing performance by decreasing the fraction of electroactive nanoparticles. Due to NPs agglomeration, these modified electrodes may lack reproducibility. Additionally, the modifier that has been physically adsorbed onto the electrode surface may be gradually stripped off in long-term operations.

A sensor based on electrochemically reduced graphene oxide (ErGO), carboxylated multi-wall carbon nanotubes (cMWCNT), and gold nanoparticles (AuNPs) was developed by Domínguez-Aragón *et al.* for the simultaneous detection of dihydroxybenzene isomers [22]. The authors emphasize that carbon-based nanocomposites of ErGO and MWCNT can be prepared within a single step, avoiding common drawbacks such as agglomeration and restacking of layers. Carboxylated MWCNT shows good mechanical properties, porous structure, high surface area, enhanced hydrophilicity, excellent chemical stability, ability to promote electron transfer reactions and higher attachment properties due to the functional groups on their surface. Therefore, cMWCNT can help to generate a more homogeneous surface with the better electrochemical activity of the material compared with MWCNT. The ErGO-cMWCNT nanocomposite can be used as an excellent scaffold for catalytic nanomaterials deposition. On the other hand, AuNPs are of great significance for electrode modification because they provide additional features such as excellent conductivity, high surface area and catalytic properties that make them excellent materials for the electrochemical detection of a wide range of analytes [23]. Under optimized conditions, using differential pulse voltammetry, the GCE/ErGO-cMWCNT/AuNPs sensor exhibited a linear concentration range of 1.2 to 170 µM for HQ and CC, and 2.4 to 400 µM for RS with detection limits of 0.39, 0.54 and 0.61 µM, respectively. The proposed sensor showed a great potential for the simultaneous, highly sensitive, precise, and easy-to-handle detection of HQ, CC and RS in complex samples such as tap water and commercial skin-lightening cream (Figure 2).

Edris and Sulaiman presented a novel highly sensitive composite of electrochemically reduced graphene oxide-poly(Procion Red MX-5B)/gold nanoparticles modified glassy carbon electrode (GCE/ErGO-poly(PR)/AuNPs) for voltammetric detection of HQ, CC, and RS [18]. The involvement of azo dye (PR) with multi-functional groups as a mediator makes the ErGO more soluble as well as stabilizes the AuNPs in the composite. The synergistic effect makes the composite have better electrochemical catalytic activity for dihydroxybenzene isomers. The composite material showed the feature of high specific surface area and high conductivity that enhanced the electrocatalysis of HQ, CC, and RC. The proposed sensor displays a linear range of 0.1 to 90 µM for HQ, 0.4 to 90 µM for CC, and 4 to 350 µM for RS. The limits of detection are extremely low: 53, 53, and 79 nM for HQ, CC, and RC, respectively. The GCE/ErGOpoly(PR)/AuNPs was used for simultaneous voltammetric detection of HQ, CC, and RS in the cosmetic sample (Melashine cream 4 %) with satisfactory recoveries. The nanocomposite possesses adequate reproducibility, good stability and acceptable recoveries for wastewater and cosmetic samples analyses.

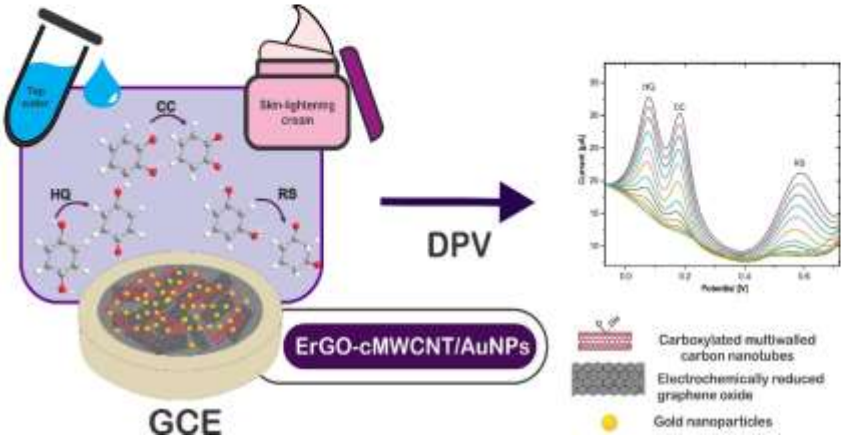

Figure 2. *Schematic representation for the simultaneous detection of HQ, CC, and RS at the GCE/ErGO-cMWCNT/AuNPs sensor. Reproduced from Ref. [22]. Licensee MDPI, Basel, Switzerland (2021)*

Butwong *et al.* [19] described a simple strategy for the fabrication of a new modified electrode exploiting the synergetic effect of CNTs and AgNPs capped by cysteamine (Cst) for simultaneous detection of HQ and CC [19]. Cysteamine stabilized AgNPs and binds strongly to CNTs to form a stable and sensing layer on a GCE surface. The resulting AgCst-CNTs/GCE possesses a large active surface area, high conductivity and excellent catalysis, with a detection limit of 10 and 40 nM for HQ and CC, respectively. The sensor was demonstrated for the analysis of river water and a topical cream, as manifested by high accuracy and reproducibility.

Arbutin

Arbutin (4-hydroxyphenyl-β-D-glucopyranoside, AR), is a naturally occurring skin-lightening agent and has been found in the species of various plant families such as marjoram, cranberry, blueberry, and several pear species. AR is often used in skin care products as it is an efficient agent for the treatment of hyperpigmentation disorders and shows less melanocyte cytotoxicity than HQ.

The practical applicability of hydroxyapatite-ZnO-PdNPs modified carbon paste electrode (HAP-ZnO-PdNPs/CPE) [24], and a sepiolite clay-modified carbon paste electrode (Clay/CPE) [25] to detect AR electively in cosmetics was tested and satisfactory results were obtained. HAP-ZnO-PdNPs/CPE for simultaneous quantitative detection of AR and AA (vitamin C) was developed by Shahamirifard *et al.* [24] DPV data reveal that the modified electrode has exhibited excellent electrocatalytic activity towards the oxidations of AR and AA in buffer solution (pH 7.0). The corresponding electrochemical signals have appeared as two well-resolved oxidation peaks with a potential difference of 0.23 V (*vs.* Ag/AgCl, 3.0 M KCl) which is high enough for the simultaneous determination of the concentration of AR and AA. The linear response ranges were 0.12 to 56 µM for AR and 0.12 to 55.36 µM for vitamin C, with detection limits of 85.7 and 19.4 nM, respectively. The practical applicability of the fabricated sensor was confirmed in commercial lightening Seagull cream.

Online derivatization followed by a disposable electrochemical sensor was also used to determine AR in cosmetic products [26]. The AR was chemically oxidized by MnO_2 and subsequently reduced at a screen-printed carbon electrode using a low detection potential which improved the selectivity of the method.

The so-called "green synthesis", using mild reaction conditions and natural resources such as plant extracts, has received more attention as a cost-effective and valuable alternative for environmentally safe and energy-efficient production of metal nanoparticles (MNPs) [20]. Unlike chemical and physical processes, bio-inspired synthetic methods restrict the use of toxic chemicals, energy and sophisticated instruments. Nowadays, there is convincing evidence that green synthesis of MNPs has the potential to provide a new direction in the fabrication of cheap and effective electrocatalysts applicable in pharmaceutical, environmental, and food analysis. Khatoon *et al.* [27] reported for the first time utilization of bell pepper (BP) extract as a capping, stabilizing, and reducing agent for the cost-effective and environmentally safe synthesis of AgNPs and applicability of the nanoparticles for the development of an electrochemical sensor for AR detection [27]. The fabricated electrochemical platform based on BP-AgNPs-GCE exhibits a linear current response in the concentration range from 10 to 350 µM, LOD of 0.03 µM, and LOQ of 0.09 µM, respectively. The applicability of this sensor for sensitive detection of AR in real samples was confirmed in commercially available skin whitening creams.

Here we must note that the experimental data published so far show that the surfaces modified with biosynthesized MNPs remain challenging as they are often not as stable and reproducible as one would hope. It is important to ensure that metal nanoparticles produced by the plants or plant extracts remain stable during their storage without changes in their morphology and size before using them in practical applications. Further research needs to be done to address these issues and improve the electrode performance in terms of higher operational and storage stability of the electrocatalysts modified with nanoparticles synthesized in a green way.

Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is classified as an antimicrobial agent, cosmetic biocide, oral health care agent, and oxidizing agent. Hydrogen peroxide can often be found in many day-to-day life cosmetic products such as hair dyes, hair bleaches (diluted H_2O_2 mixed with ammonium hydroxide solution is used as a constituent), tooth whitening products and sold as an antiseptic. The EC restricts the amount of H_2O_2 that may be present in cosmetic products. These restrictions included a maximum concentration of 4 % in products applied to the skin and 12 % in products applied to the hair; dyes intended to be used on eyelashes (professional use only) are safe when they contain up to 2 % H_2O_2 [28]. Since H_2O_2 is an aggressive oxidizer that damages human skin, a higher concentration of H_2O_2 (> 20 %) is considered to be highly hazardous.

The determination of H_2O_2 plays an important role in clinical research, medical diagnostics as well as in many industrial applications (food processing, paper, textile, pharmaceuticals, cosmetics, cleaning and disinfection products) [29]. The electrochemical nonenzymatic detection of H_2O_2 can provide many attractive characteristics, such as simple fabrication, ultrahigh sensitivity, and excellent stability. Considering the rapid expansion of nonenzymatic H_2O_2 detection using advanced nanomaterials, several review papers were devoted to the design strategies for electrocatalysts used in H_2O_2 sensors by focusing on the sensing performance, electrocatalytic mechanism, and morphology of electrode materials [30-33]. Here we refine the search and present exclusively the electrochemical sensors applicable in the H_2O_2 analysis of cosmetics, medical and cleaning products. Copper oxide/graphitic carbon nitride composite (CuO/g-C_3N_4) dropped onto GCE [34], nanosized bismuth particles modified electrode (SPAgE-Bi^{nano}) [35], carbon paste electrode modified with nano-composite of reduced graphene oxide and $CuFe_2O_4$ nanoparticles (RGO/$CuFe_2O_4$/CPE) [36], CuO/Cu wire [37], 3D printed graphene electrode with Prussian blue (3DGrE/PB) (Figure 3) [38], as well as carbon electrodes modified with perovskites-type oxides [39-42] were developed, characterized and successfully used as working electrodes for the electrochemical detection of H_2O_2 in a wide range of cosmetics and antiseptic products (Table 1).

Table 1. *Comparison of the analytical parameters of electrochemical nonenzymetic sensors for the determination of H_2O_2 in cosmetics, medical and cleaning products*

Electrode material	Method	Linear range	LOD	Real sample	Ref.
CuO/g-C_3N_4/GCE[1]	DPV[4]	0.5 – 50 µM	0.31 µM	makeup remover	[34]
SPAgE-Bi^{nano} [2]	CV[5]	100 µM – 5 mM	56.59 µM	hair dyes	[35]
RGO/$CuFe_2O_4$/CPE	Amp.[6]	2 – 200 µM	0.52 µM	hair dye, mouthwash solution	[36]
	DPV[4]	2 – 1000 µM	0.064 µM		
CuO/Cu wire	Amp.[6]	10 – 1800 µM	1.34 µM	Listerine mouthwash	[37]
3DGrE/PB[3]	Amp.[6]	1 – 700 µM	0.11 µM	mouthwash	[38]
$LaNi_{0.5}Ti_{0.5}O_3/CoFe_2O_4$/GCE	Amp.[6]	0.1 µM – 8.2 mM	23 nM	toothpaste	[39]
$La_{0.66}Sr_{0.33}MnO_3$/CPE	Amp.[6]	–	–	cleaning product	[40]
$LaNi_{0.6}Co_{0.4}O_3$/CPE	Amp.[6]	10 nM – 100 µM	1 nM	toothpaste	[41]
$La_{0.7}Sr_{0.3}Mn_{0.75}Co_{0.25}O_3$/CPE	Amp.[6]	0.5 – 1000 µM	0.17 µM	toothpaste, medical solution	[42]

[1] CuO/g-C_3N_4/GCE: copper oxide/graphitic carbon nitride composite/glassy carbon electrode; [2] SPAgE-Bi^{nano}: three-in-one screen-printed electrode assembly containing nano bismuth species deposited silver as working, pre-oxidized silver as a reference and unmodified silver as counter electrodes; [3] 3DGrE/PB: 3D printed graphene electrode with Prussian blue; [4] DPV: differential pulse voltammetry; [5] CV: cyclic voltammetry; [6] Amp.: amperometry.

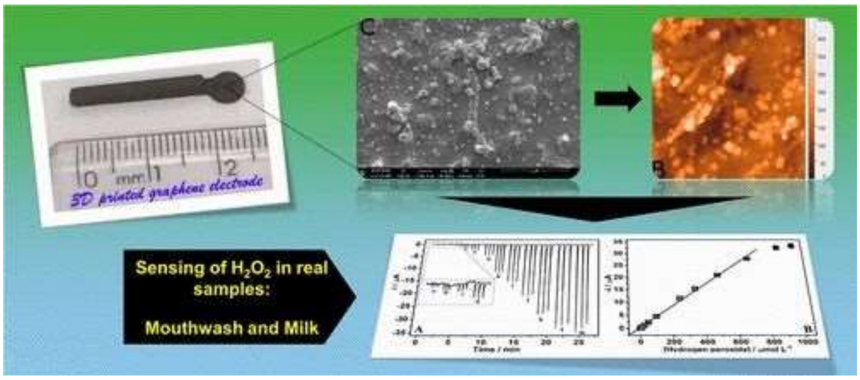

Figure 3. *Schematic representation for the detection of H_2O_2 using 3D printed graphene electrode with Prussian blue (3DGrE/PB). Reprinted with permission from Ref. [38]. Copyright (2019) American Chemical Society*

Preservatives

Preservatives are added to cosmetics in order to prevent microbial spoilage, and therefore prolonging products' shelflife. Parabens, aldehydes, phenoxyethanol, glycol ether, isothiazolinones, quarternary ammonium compounds and organic acids (benzoic acid, hydroxybenzoic acid, dehydroacetic acid, sorbic acid, *etc*.) are commonly added as preservatives to a wide range of cosmetics. Michalkiewicz *et al*. [43] reviewed the research achievements on modified carbon materials in the electroanalysis of preservatives most frequently used in food, cosmetic, and pharmaceutical preparations [43].

p-hydroxybenzoic acid

p-hydroxybenzoic acid (4-hydroxybenzoic acid, PHBA) is a frequently used preservative substance in cosmetics. Moreover, PHBA is the hydrolysis product of parabens, a popular preservative in cosmetics and foodstuffs. A few published works have reported the detection of PHBA using an electrochemical technique.

Electrochemical determination of PHBA is required for efficient surface modification. Nickel titanate ($NiTiO_3$) nanoceramics, synthesized by the sol-gel method, were used to fabricate a modified carbon paste electrode ($NiTiO_3$/CPE) for quantitative detection of PHBA [44]. DPV results suggest that the modified electrode exhibits an electrocatalytic effect on the oxidation of PHBA, resulting in a marked enhancement of the peak current response at 1.0 V (*vs.* Ag/AgCl, 3 M KCl). Under the optimized conditions in Britton-Robinson buffer solution (pH 2.0), the oxidation peak current was linearly dependent on the concentration of PHBA in the ranges of 0.7 – 80 μM and 80 – 1000 μM. The detection limit was estimated to be 62 nM. Common interfering ions, such as Na^+, K^+, NH_4^+, Cl^-, CO_3^{2-}, NO_3^- and I^-, do not influence the DPV response of PHBA with deviations below 5 %. However, the authors reported that methylparaben and propylparaben have the same oxidation potential and show interference effects. The ability of the nanostructured modified electrode was examined in the detection of PHBA in an oil-free liquid cream foundation. The satisfactory results from the analysis proved the practical applicability of $NiTiO_3$/CPE towards the determination of PHBA in real samples.

The same electrode was tested for the simultaneous voltammetric determination of *o*-hydroxybenzoic acid (OHBA) and *p*-hydroxybenzoic acid (PHBA) [45]. Peak overlap in voltammetry is a challenge for the quantitative analysis of electroactive isomers. The experimental results show that the optimum pH 2.0 can be used for the determination of OHBA and PHBA individually. But, when OHBA and PHBA determine simultaneously at pH 2.0, only one peak in DPV was registered at about 1.05 V. In order to obtain improved voltammetric peak separation, the authors used a higher pH value. In electrolyte Britton-Robinson buffer solution (pH 5.0), DPV shows an oxidation peak of PHBA at about 0.8 V, whereas an oxidation peak of OHBA was observed at about 0.9 V. However, from the presented voltammogram, it is clear that the signals are not completely resolved. Therefore, it is doubtful that the peak current can be measured accurately. The results would be more convincing if the authors presented the DPV records for various concentrations of PHBA and OHBA, respectively, in the presence of a constant concentration of the counterpart.

Recently, Charoenkitamorn *et al.* proposed the anodized SPGE (SPGE*) for PHBA detection [46]. The facile electrode preparation for PHBA detection and the utilization of phosphate buffer solution is environmentally friendly that could be counted as a green chemistry process. Under optimal conditions, the detection limit for PHBA was achieved at 0.073 μM. The results from the interference tests revealed that the ionic substances have no effects on PHBA detection, whereas uric and ascorbic acid can interfere after adding a concentration 50 times higher than PHBA. The oxidation potentials of both species were found to be 0.30 and 0.40 V (*vs.* Ag/AgCl), respectively, which is closed to the oxidation potential of PHBA and caused a lower tolerance limit than those obtained from other studied species. The established feature would limit the use of this sensor for PHBA analysis in cosmetics with high vitamin C content. Here it should also be noted that the interference of parabens has not been investigated. Five samples of skin lotions were determined to verify the practical performance of the proposed SPGE*. The HPLC, a standard method for PHBA analysis, was performed in parallel with the same samples. The obtained results reveal that the proposed SPGE* has a highly effective feasibility for the determination of PHBA in cosmetics. Not least, the SPGE* can be applied using a portable potentiostat, which is accessible and eligible for the end-users to operate onsite.

Parabens

Parabens (alkyl esters of *p*-hydroxybenzoic acid) have been used for over 70 years in cosmetics, foods, and pharmaceuticals as preservatives due to their broad antimicrobial spectrum, effectiveness and low price. Methylparaben (MP), ethylparaben (EP), propylparaben (PP) and butylparaben (BP) are most frequently used in commercial applications. The antimicrobial activity of parabens increases with the increasing length of the ester group, but water solubility decreases. In practice, shorter esters (MP and EP) are commonly used because of their high solubility in water. Product ingredient labels typically list more than one paraben in a cosmetic product. Parabens are often used in combination since they have synergetic effects in a wide variety of products such as cosmetics, ointments and suspensions, which allows the use of lower levels while increasing preservative activity [47,48].

For the last few years, parabens have been the topic of controversies among scientists and consumers. Long-term studies indicated that the use of these compounds could result in potential health risks [49-54]. Oishi reported that PP adversely affects hormonal secretion and decreases male reproductive potential [51]. MP has a pronounced estrogenic effect and its constant use is associated with causes of breast cancer, ovarian cancer and endometriosis. According to the Cosmetic Directive in Europe, the maximum allowable concentration of such compounds in cosmetic formulations in the final product is 0.4 wt.% for a single ester and 0.8 wt.% for ester mixtures, expressed as PHBA [55].

A few electroanalytical methods have been reported for the determination of parabens in cosmetics [48,56-61]. Electrochemical quantification of MP was successfully performed using sensors based on: GCE modified with graphene oxide and ruthenium nanoparticles [56], MWCNTs coupled with Nafion-modified GCE [60], gold electrodes modified with Layer-by-Layer (LbL) films of magnetite nanoparticles and polypyrrole [57], pencil graphite electrode modified by molecularly imprinted polymer [61]. Electroanalytical detection of PP using gold nanoparticles-electrodeposited onto indium-tinoxide electrode (AuNP-ITO) functionalized with PEI (poly(ethylene imine)) and NiTsPc (nickel(II) phthalocyanine tetrasulfonate) in the film (ITO-AuNPs-(PEI/NiTsPc)$_3$ was described by de Lima *et al.* [58].

A new approach to the study and simultaneous determination of MP and PP based on electrochemical and chemometric methods has been reported by Behpour *et al.* [48]. The selective and reliable electrochemical method based on molecularly imprinted polymers (MIPs) with dual templates was developed by Wang *et al*. in order to determine the total content of parabens in cosmetics [59]. Rapid response of the MIPs sensor was obtained within 1 min. MIPs sensor was used to determine the total content of parabens in cosmetic samples with recoveries between 98.7 and 101.8 %.

8-hydroxyquinoline

8-hydroxyquinoline (8-HQ), also known as oxine or 8-quinolinol, is an excellent antiseptic, preservative, bactericide and disinfector. 8-HQ is widely used in the production and preservation of cosmetic products due to its strong antimicrobial properties.

Guo *et al*., 2011 fabricated a modified electrode by dropping a supernatant of MWCNTs/Nafion on a GCE and, for the first time, reported the determination of trace 8-HQ in cosmetics by electroanalytical method [62]. As a voltammetric sensor, MWCNTs/Nafion/GCE shows excellent electrocatalytic activity towards the oxidation of 8-HQ because of the synergistic effect of MWCNTs and Nafion – extremely low detection limit (9.0 nM) and high electrode sensitivity in the concentration range from 2×10^{-8} to 10^{-5} M. The results from the interference experiments showed that general concomitant substance in cosmetic products, such as 300-fold coconut oil propylbetaine, sodium lauryl sulfacid, glycerol, citric acid, vitamin C, and vitamin E, did not interfere with the determination of 8-HQ. These data demonstrated that the MWNT/Nafion/GCE voltammetric sensor possessed high selectivity for 8-HQ in cosmetic formulations. The analytical results obtained in the shampoo sample proved the practical applicability of the proposed method.

A modified electrode, obtained by the electrodeposition of 1-amino-2-naphthol-4-sulfonic acid (ANSA) on the surface of GCE, for the rapid and inexpensive determination of 8-HQ in cosmetic samples, was reported by Calam *et al.* [63]. ANSA/GCE is a reliable sensor for the SWV detection of 8-HQ in a wide linear range of 5×10^{-7} to 1.4×10^{-5} M with a detection limit of 1.6×10^{-7} M. The voltammetric analysis using the ANSA/GCE provided excellent reproducibility (RSD = 4.45 %, n = 10), repeatability (RSD = 2.26 %, n = 10) and selectivity: the results showed that 100-fold excess concentrations of NaCl, NaOH, KOH, and ascorbic acid; 30-fold excess concentrations of phosphoric acid, citric acid, alanine, and lysine; and 10-fold concentration of $Al(OH)_3$, glycerin, and benzyl alcohol did not significantly influence the peak current height, with variations of less than 5 %. The long-term storage stability of the electrode was also reasonable – a reduction of 9.56 % in the peak current was observed after 15 days. The real sample analysis reveals the applicability of the sensor for 8-HQ detection in blush cosmetic products.

Recently, Gao and co-authors [64] have established an electrochemical senor for the determination of 8-HQ developed by electropolymerization of tannic acid (TA) on GCE [64]. The modified electrode (PTA/GCE) showed a strong electrocatalytic activity toward the oxidation of 8-HQ due to the enhanced surface area and abundant functional groups that exhibit affinity to 8-HQ. Using DPV, PTA/GCE shows two linear plots with 8-HQ concentrations from 0.5 to 5 µM and 5 to 50 µM (LOD = 36 nM). The electrochemical senor was applied in the quantitative determination of 8-HQ in hair conditioner samples with a satisfactory result.

Triclosan

Triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol, TCS) as an antibacterial and an antifungal agent has been used in various cosmetic, healthcare, and personal care products, such as mouthwashes, toothpaste, soaps, dish-washing liquids, and antibacterial creams [65]. The European Community Cosmetic Directive approved TCS usage as a preservative in cosmetics and toiletries up to 0.3 wt.% [66]. Literature and related studies have shown inflammatory skin conditions and endocrine disruption after exposure to TCS. It was also reported that TCS is toxic to aquatic living organisms. Once in the aquatic environment, TCS can undergo a series of transformation reactions to produce chlorophenols, chloroform and dioxin-type derivatives classified as human carcinogens [65,67]. Therefore, the safety of TCS has been questioned in regard to environmental and human health. A review article presented by Sri *et al.* describes the progress made in the use of nanostructured particles as active electrode materials for the electrochemical sensing of TCS in environmental samples [68].

To the best of our knowledge, there are only a few reports on electrochemical sensors for TCS successfully applied in cosmetic samples [65,67,69-73]. Table 2 presents a comparison of the analytical parameters of these sensors used for the determination of TCS in cosmetics and cleaning products.

Table 2. *Comparison of the analytical parameters of electrochemical sensors for the determination of triclosan (TCS) in cosmetics and cleaning products*

Electrode material	Method	Linear range	LOD	Real sample	Ref.
GCE[1]	DPV[7]	10 – 600 μg L^{-1} 1 – 8 mg L^{-1}	5 μg L^{-1}	toothpaste, hand gel, liquid soap	[65]
Fe_3O_4@Au-PPy/GO/GCE[2]	DPV[7]	10 nM – 1 μM	2.5 nM	toothpaste, shampoo, liquid soap	[67]
SPCE[3]	DPV[7]	1.2 μM – 1 mM	–	toothpaste, mouthwash	[69]
MWCNTs/GCE	DPV[7]	50 μg L^{-1} – 1.75 mg L^{-1}	16.5 μg L^{-1}	toothpaste	[70]
CNDs-CS/GCE[4]	LSV[8]	10 nM – 1 mM	9.2 nM	toothpaste, mouthwash, hand sanitizer	[71]
LS11-ODA-AuNPs/GCE[5]	DPV[7]	0.01 – 0.5 μM	0.005 μM	toothpaste, liquid soap	[72]
ZIF-11/HRAC/GCE[6]	DPV[7]	0.1 – 8 μM	0.076 μM	lipstick, skin cream, cleansers	[73]

[1]GCE: glassy carbon electrode; [2]PPy: polypyrrole, GO: graphene oxide; [3]SPCE: screen-printed carbon electrode; [4]CNDs-CS: composite film based on chitosan and carbon nanodots; [5]LS11-ODA-AuNPs: core-shell structure of bacteriochlorin-supported AuNPs; [6]ZIF-11/HRAC/GCE: composite of zeolite imidazolate framework-11 and activated carbon derived from rice husks; [7]DPV: differential pulse voltammetry; [8]LSV: linear sweep voltammetry.

The extremely low detection limit of 2.5 nM was reported recently by Saljooqi *et al.* [67]. The electroanalysis of TCS was demonstrated by the use of Fe_3O_4@AuPPy/GO-nanocomposite modified GCE. Nanocomposites consisting of conducting polymers and nanomaterials have received great attention. The appropriate combination of different nanoscaled materials with the conductive polymer may open a new vista for utilizing novel enhanced electrochemical sensing platforms with high performance. The combination of carbon nanomaterials with metal nanoparticles and/or polymers to form composites could increase surface active sites to readily accumulate TCS into the hybrid films. Iron oxide magnetic nanoparticles (Fe_3O_4NPs) were frequently applied in electrochemical sensors because of their great surface-to-volume ratio, fast electron transfer, and strong adsorption ability. In particular, if Fe_3O_4 surface is loaded or coated with noble metal nanoparticles like Au, the transfer of electrons and conductivity increase significantly. To evaluate the applicability of the present methodology on real samples, the authors performed experiments in toothpaste, shampoo, liquid soap, and urine. The results showed that the Fe_3O_4@Au-PPy/GO nanocomposite displays an acceptable recovery and can be utilized for TCS sensing with the purpose of pharmacokinetics investigations and quality control.

Zinc pyrithione

Zinc pyrithione (bis[(2-pyridyl-1-oxo)-thio]zinc) is a broad-spectrum antimicrobial agent that has been used for more than 60 years to treat dandruff and seborrheic dermatitis. Its effective bactericide, fungicide and algaecide functions are utilized in most daily hair care products. Zinc pyrithione (ZPT) has been established as one of the most effective antidandruff ingredients for use in shampoo, conditioner, rinse and hairdressing formulations. Being subject to several safety evaluations, ZPT was previously found safe as an antidandruff agent in rinse-off hair care products at a maximum concentration of 2.0 %. On the 4th March 2020, the Scientific Committee on

Consumer Safety concluded that ZPT is safe when used in a concentration of maximum 1 % [74]. ZPT is currently regulated as a preservative in rinse-off products (with the exception of oral hygiene products) in a concentration of up to 0.5 % in general products and up to 1.0 % in hair products [75].

ZPT is substantially insoluble in water and is present in aqueous-based products as a dispersion of fine solid particles. The electrochemical oxidation of ZPT using a metal oxide-modified carbon paste electrode (M_xO_y/CPE) has been investigated in various alkaline solutions and the optimum experimental conditions for the determination of ZPT containing cosmetic samples were describe-ed [76]. The higher catalytic activities among ten metal oxides dispersed on CPE are shown at SnO_2, ZrO_2 and Bi_2O_3. The authors also have presented the results of a comparative study of various pH and supporting electrolytes. The height of the ZPT wave in solutions of 0.1 M tetrabutylammonium hydroxide (Bu_4NOH) was found to be higher. The calibration plot of SnO_2/CPE obtained by plotting the peak current at 0.620 V (vs. SCE) against the concentration of ZPT shows linearity over the range of 1.6 to 32 mg L^{-1}. The direct determination of the concentration of ZPT in commercial products (shampoo, conditioner, rinse and hairdressing products) was successfully accomplished by means of DPV using the same modified electrode.

A disposable type of cobalt phthalocyanine-modified screen-printed carbon electrode (CoPc/SPE) in a couple with FIA was developed for the analysis of ZPT in commercial hair care products [77]. The presented method shows several advantages for ZPT detection over the SnO_2/CPE-based DPV assay, such as lower over-potential, the limit of detection and working volume. Under the optimized hydrodynamic flow injection parameters, the CoPc/SPE yielded a linear calibration plot in the window of 6 to 576 µM with a detection limit of 0.9 µM in 0.1 M KOH solution at an applied potential of 0.3 V (*vs.* Ag/AgCl). The authors demonstrated that the CoPc/SPE is effective and selective for the ZPT analysis in commercial shampoos.

Both commented studies offer rapid, easy, selective and inexpensive approaches for direct routine ZPT analysis in hair care products. The electrochemical procedures described above do not have the drawbacks of classical methods, namely trans-chelation at HPLC analysis (the need for preceding formation of the Cu(II) complex), photodegradation of ZPT at thin-layer chromatography, a lack of selectivity of titrimetric methods, *etc*.

UV filters in sunscreen products

Sunscreens have been recommended by dermatologists for a long time as a protective measure against excessive amounts of sunlight to prevent UV-induced erythema. Moreover, numerous studies show that the regular use of sunscreens contributes to the prevention of skin cancer and photoaging [78,79]. UV filters can be classified into two groups according to their nature: i) the inorganic UV filters (physical UV filters) principally work by reflecting and scattering the UV radiation; ii) the organic UV filters (chemical UV filters) absorb ultraviolet radiation. Chemical UV filters are organic compounds with high molar absorptivity in the UV range and usually possess single or multiple aromatic structures, sometimes conjugated with C=C double bonds and/or carbonyl moieties [80].

Cosmetics containing organic UV filters are most commonly used, despite causing different side effects. The adverse reactions to sunscreens include subjective irritation (stinging, burning), contact dermatitis and comedogenicity. The potential adverse effects induced by UV filters in experimental animals include reproductive/developmental toxicity and disturbance of hypothalamic–pituitary–thyroid axis (HPT) [81,82].

Organic chemicals that absorb UV radiation are added to sunscreen products in concentrations of up to 10 % for skin protection. Some of these compounds are also included in other cosmetics, such as skin lotions, beauty creams, lipsticks, hair sprays, *etc*. The level and quality of UV protection provided by sunscreen products has improved significantly during the last three decades. Nowadays, the trend toward cosmetic products with higher protective effects and screening efficiency against both UVB (290 – 320 nm) and UVA (320 – 400 nm) wavelengths has led to the extensive development of formulations containing combinations of various organic UV filters at different concentrations. Modern sunscreens should provide broad-spectrum UV protection because this ensures that the natural spectrum of sunlight is attenuated without compromising its quality. For example, octyl-methoxycinammate (OMC), benzophenone-3 (BZ3) and 4-methylbenzylidene camphor (4-MBC) are UV filters usually combined in sunscreen formulations because their UV spectra have overlapping bands and the mixture allows a good sun protection factor (SPF) in the whole range of UVB and UVA radiation [83].

There are positive lists for sunscreen agents in the three main legislations regarding cosmetic products, that is, those in force in EU, USA and Japan (in the USA they are considered as OTC drugs) where the maximum authorized contents are stipulated [80]. However, until today there are no official analytical methods. Methods based on HPLC are the most widely employed for the separation and determination of sunscreen agents [84].

To the best of our knowledge, there are a limited number of published articles dealing with the determination of sunscreen agents in cosmetics by means of electrochemical techniques. Differential pulse voltammetry using a carbon-epoxy composite electrode in non-aqueous solvents [85] or mercury film electrode in strongly alkaline media [86] have been successfully applied to determine different UV filters in sunscreen products. Square wave voltammetry using GCE is fast and sufficiently sensitive to ensure octocrylene (OCR) quantification at low concentrations [87]. OCR was reduced at a potential of -0.97 V (*vs.* Ag/AgCl) on a GCE using a mixture of 0.04 M Britton-Robinson buffer and ethanol (7:3, v/v) as a supporting electrolyte. The results reveal satisfactory precision and accuracy, demonstrating that the proposed method is an acceptable alternative for the analytical determination of OCR in cosmetic preparations.

Cardoso *et al.,* 2007 studied the voltammetric behavior of 4-MBC by square wave voltammetry (SWV) using mercury electrode in Britton-Robinson buffer and cationic surfactant, cetyltrimethylammoniun bromide (CTAB) [83]. A single peak of 4-MBC reduction was observed at -1.21 V (*vs.* Ag/AgCl), the calculated LOD was 2.99 nM and the LOQ was 9.98 nM. Authors applied the developed methodology to determine 4-MBC in commercial sunscreen SPF 15, 20 and 30 and for the simultaneous determination when other protection agents were associated, such as BZ3 or OMC. Subsequently, the research group published the first study dealing with the simultaneous determination of the three UV filters using surfactant and polarography [88]. A method based on electrochemical reduction for the simultaneous determination of three sunscreen agents (4-MBC, BZ3 and OMC) by differential-pulse polarography (DPP) was proposed. The authors validated the methodology using four commercial sunscreen preparations and the results showed high recovery rates.

Lopes Neves *et al*. [89] developed a new analytical methodology for the determination of BZ3, 4-MBC and OMC in cosmetics samples by SWV using a mercury film modified gold electrode as an alternative to dropping mercury electrode, contributing to the generation of less toxic residues, a safer process for the analyst, and a low cost in terms of analysis.

Hair-waiving agents

Thioglycolic acid

Thioglycolic acid (TGA) is an organic compound containing both a thiol and a carboxylic acid functional groups. TGA and its salts are frequently used in hair-waving and depilatory products. The chemistry of hair-waving is based on the cleavage of hair disulfide bonds by the thiol groups of the TGA. Here, it should be noted that skin contact with low-molecular-weight organic acids can lead to severe pain and burns, which can heal slowly with the formation of scar tissue. TGA, even in dilute solutions, may cause conjunctival hyperemia and corneal injury. In this regard, the EU Cosmetics Directive has limited the maximum permissible concentration of TGA and its salts, calculated as TGA, to 11.0 % at pH 7.0 to 9.5 [90].

The voltammetric behavior of TGA at a carbon paste electrode modified with cobalt phthalocyanine (CoPc) was studied by Shahrokhian *et al*. [91]. The CoPc/CPE shows high electrocatalytic activity toward oxidation of TGA, substantially lowering the overpotential of an anodic reaction. The results of these studies were used to develop a potentiometric method for determining TGA and its salts in hair-treatment products. However, the authors note that other compounds with reducing properties and redox potentials close to TGA, such as hydrogen sulfide, sulfite and mercaptoethanol, may interfere if they are present in the sample. This issue has been resolved by Zen and co-authors, who developed a sensitive and selective method combining HPLC with electrochemical detection for the quantitative determination of TGA [92]. In this study, HPLC was used to eliminate interference from the matrix of real samples, and preanodized screen-printed carbon electrodes (SPCEs*) were used to determine TGA. SPCEs* have the advantages of being inexpensive, easy to handle, disposable, flexible and stable. Under optimized conditions, the linear range for TGA is up to 20 ppm with a detection limit of 0.042 ppm. The practical application of the proposed method was demonstrated by the determination of TGA in commercial hair-waving products. The authors stated that the new method offers a viable alternative to previous approaches used in the routine determination of TGA.

Sulfites

Sulfites are commonly used as preservatives/antioxidants in the food and cosmetic industry. Sodium sulfite is a reducing agent that alters the structure of hair; including sulfite in hair setting products, hair curvature or straightening can be regulated. In addition, to use as a hair-waiving/straightening agent, it can also function as a preservative in various cosmetic formulations [93]. Exposure to sulfites has been reported to induce a range of adverse clinical effects in sensitive individuals, ranging from allergic contact dermatitis, urticaria, flushing, and life-threatening anaphylactic and asthmatic reactions [94]. Scientific Committee on Cosmetic Products and Non-Food Products (SCCNFP) has suggested that the sulfite concentration added to cosmetic products has to be lower than 6.7 % to maintain the safety of hair settings and skin care products [95].

Conventional methods applied in industry for sulfite analysis are Monier–Williams and iodometric methods. At present, only one publication is available on the development of an electrochemical method for the analysis of sulfites in cosmetics. Chen *et al.* developed an oxygen-incorporated gold electrode by depositing gold particles on a screen-printed electrode in an aqueous solution [96]. The detection sensitivity of dissolved sulfite at the oxygen-rich gold electrode (AuOSPE) and that at oxygen-poor gold electrodes was studied by an FIA in a 0.1 M PBS (pH 6.0) at an applied potential of 0.3 V (*vs.* Ag/AgCl). Bisulfite is the active species in this system according to its various forms at different pH solutions. The results showed that oxygen-incorporated atoms play an important role in improving the sensitivity of the new gold electrode. The practical applicability of developed electrode material coupled with FIA (AuOSPE/FIA) to detect selectively sulfite content in cosmetics was tested in two hair-waving products and satisfactory results were obtained.

Coloring agents in hair dyes

Commercial oxidative dye products form the permanent color *in situ* by a coupling reaction and oxidation. Permanent hair dyes are generally composed of three constituents: a precursor agent (*p*-phenylenediamine, PPD), a coupling agent (electron-donating group substituted aromatic compounds, for example, resorcin) and an alkaline medium-based oxidizer (*e.g.,* H_2O_2 – ammonia mixture) [97]. Black henna, used to color the hair or skin, also contains PPD as a chromophoric constituent. At the same time, PPD is the most frequent contact sensitizer, and thus a primary patch test is recommended before using any hair dyes/henna containing PPD. The clinical findings of hair dye allergy vary and include contact dermatitis, lichen simplex chronicus, non-specific eczema and dermographism on the hair dye-exposed area or/and extended area [98]. Several experiments have shown a significant association between the use of products containing PPD and mutagenicity, according to the Scientific Committee on Consumer Products (SCCP) [99]. A safe limit for PPD in hair dye products that can provide desirable coloring with minimum body exposure to PPD needs to be carefully defined [100]. European Union Cosmetic Directive Regulation has banned PPD in topical products intended for superficial purposes while allowing PPD inclusion in cosmetic products marketed as oxidizing coloring agents with a maximum concentration of 4 % (free base). Specifically, the permitted concentration is 2 % (free base) when mixing PPD with H_2O_2 following the preparation protocol of hair dyeing products [101,102]. The risk associated with using PPD has motivated researchers to develop new strategies and reliable analytical techniques to detect and quantify this chemical in cosmetic products to guarantee legislative requirements and ensure their safety.

Due to their similar structural and chemical characteristics for phenylenediamine isomers and dihydroxybenzenes isomers, there are few reports on detection using the electrochemical method alone. A review article that discusses the sources and toxic effects of PPD, and makes a critical comparison between conventional and electrochemical methods (reported from 1935 to 2021) to detect and quantify PPD in various samples, was presented by Singh *et al.* [97]. Table 3 summarizes the electrochemical sensors applicable in the analysis of PPD in hair dyes.

Table 3. *Comparison of the analytical parameters of electrochemical sensors for analysis of p-phenylenediamine (PPD) in hair dyes*

Electrode material	Method	Linear range	LOD	Ref.
β-MnO_2/CS/GCE[1]	Amp.[5]	0.2 – 150 µM	50 nM	[103]
PSC82/GCE[2]	Amp.[5]	0.5 – 2900 µM 2900 – 10400 µM	0.17 µM	[104]
PANI/ZnO-starch-rGO/GCE[3]	DPV[6]	1 – 180 µM	0.1 µM	[105]
IL-GO@Cu-Ag/GCE[4]	DPV[6]	0.018 – 22 µM	3.96 nM	[106]

[1]β-MnO_2/CS/GCE: glassy carbon electrode modified with β-MnO_2 nanowires/chitosan hydrogel; [2]PSC82/GCE: Sr-doped perovskite oxide with the composition of $Pr_{1-x}Sr_xCoO_{3-\delta}$(x = 0.2); [3]PANI/ZnO-starch-rGO/GCE: glassy carbon electrode modified with nanocomposite „polyaniline/ZnO-anchored bio-reduced graphene oxide“; [4]IL-GO@Cu-Ag/GCE: glassy carbon electrode modified with bimetallic nanocomposite „ionic liquid functionalized graphene oxide wrapped Cu-Ag nanoalloy particles”; [5]Amp.: amperometry; [6]DPV: differential pulse voltammetry.

Recently, Singh and co-authors [106] reported an efficient electrochemical sensor based on a novel bimetallic nanocomposite „ionic liquid functionalized graphene oxide wrapped Cu-Ag nanoalloy particles” modified glassy carbon electrode (IL-GO@Cu-Ag/GCE). The synergism between ionic liquid functionalized graphene oxide and Cu-Ag nanoalloy facilitated the electron transfer and increased surface area, and therefore, excellent performance was explored with good storage stability, high sensitivity, the negligible influence of common interferents and the best limit of detection as compared to other reported works. The sensor demonstrated a high electrocatalytic effect on the oxidation of PPD at a potential of 0.21 V (*vs.* Ag/AgCl) in a linear concentration range of 0.018 to 22 µM and LOD of 3.96 nM. The fabricated electrode showed good selectivity towards PPD in the presence of *o*-phenylenediamine, *m*-phenylenediamine, hydroquinone, resorcinol, ammonia and H_2O_2. Real sample analysis in spiked dye and water samples exhibited good recovery results, which established the prepared nanocomposite as an alternative for the development of an efficient electrochemical tool for PPD detection.

Aluminium

Aluminium compounds are often used in personal care products, including antiperspirants, lipsticks and toothpastes. In particular, the most extensively used aluminium compound in cosmetic products as an antiperspirant is aluminium chlorohydrate ($Al_2(OH)_5Cl\times 2H_2O$) in various cosmetic application forms, such as aerosols, liquid/powder roll-ons, solid sticks, gels, and creams. Here, it should be noted that aluminium chlorohydrate is a cosmetic ingredient not regulated in Cosmetic Regulation 1223/2009. Other aluminium salts, such as aluminium zirconium chloride hydroxide complexes and aluminium zirconium chloride hydroxide glycine complexes, are covered by entry 50 in Annex III of the Cosmetic Regulation for use as antiperspirants with specific conditions of use.

There is convincing evidence that the use of aluminium salts-based antiperspirant products continues to increase worldwide. Recent reports indicated that continuous usage of the aluminium chlorohydrate-containing cosmetic products allows transdermal absorption of cutaneous generated hormones and pheromones and as a link to breast and prostate cancers [107]. Frequent application of aluminium salts to the underarm as an antiperspirant adds a high additional exposure directly to the local area of the human breast. Coincidentally the upper outer quadrant of the breast is where there is also a disproportionately high incidence of breast cysts and breast cancer. Aluminium has been measured in human breast tissues/fluids at higher levels than in blood, and experimental evidence suggests that at physiologically relevant concentrations, aluminium can adversely impact human breast epithelial cell biology [108].

The examination revealed that the number of published electrochemical sensors for the analysis of aluminium in cosmetics is limited. A new flow injection analysis (FIA) based electrochemical measurement using built-in three-in-one screen-printed silver electrode (SPAgE) suitable for rapid, low cost and low working volume detection of aluminium chlorohydrate has been introduced by Chiu *et al.* [109]. SPAgE configuration of Ag-working, Ag-counter and Ag/Ag_xO (silver oxides) pseudo-reference electrodes was developed for sensitive and selective electroanalysis of aluminum chlorohydrate present in antiperspirants, through the free Cl^- ion liberated from aluminum chlorohydrate in aqueous medium, as a redox signal at Ag-working electrode. The calibration graph was linear in the concentration range of 1 to 200 ppm and the limit of detection was 295 ppb aluminum chlorohydrate. The detection limit obtained is about ten times lower than that of previous work on aluminum chlorohydrate detection by linear sweep voltammetry approach (3.03 ppm) [110]. Finally, four real antiperspirant samples (in the form of roll-on liquid and lotion) assays were successfully demonstrated, with recovery values lying in the potential window of 98 to 106 %.

Heavy metals

Bocca *et al.* [111] reviewed the concentration of metals in different types of cosmetics manufactured and sold worldwide and the data on metals' dermal penetration and systemic toxicology. Next year, a review article focused on the problems related to the presence of heavy metals in cosmetics, including their sources, concentrations and law regulations, as well as the danger to the health of these products users was presented by Borowska *et al.* [1]. Studies have shown that low-dose but long-term exposure to heavy metals in the human body can cause chronic poisoning, causing irreversible adverse effects on human organs and seriously threatening human health. Consequently, developing effective methods that are sensitive, highly selective and affordable for heavy metal ions detection is indispensable in the quality control of cosmetics.

Mercury (Hg) has a long history of use as a whitening agent in cosmetic products. Mercury suppresses melanin production and eliminates dead skin cells, resulting in a stereotyped slate-grey skin color [112]. Inorganic mercury can be absorbed via the sweat glands, sebaceous glands, and hair follicles, and after absorption, it is distributed to all tissues. Repeated topical applications can result in systemic toxicity, neurological disorders and kidney dysfunction. Recently, a case of mercury intoxication caused by daily-use whitening cosmetics was reported by Wang *et al.* [113].

Japan strictly prohibits the use of mercury in cosmetics. In Europe and China, the maximum concentration of mercury in cosmetic products for eyes and lips is 0.07 ppm. The Food and Drug Administration (FDA) limits the amount of mercury in cosmetics to trace amounts under 1 ppm. Nevertheless, many cosmetics contain mercury above 1000 ppm to increase the whitening effect [114]. Many studies were carried out to identify and quantify mercury in cosmetic products and detected too high mercury levels [115]. Additionally, mercury is not always listed as an ingredient in mercury-containing products; in many cosmetics, the concentration of mercury is specifically hidden in their product labels [116,117]. Monitoring the mercury ion levels in cosmetic products is therefore of fundamental importance.

Suherman *et al.* [118] presented a review article focused on recent advances in voltammetric techniques to detect ultra-trace levels of inorganic Hg^{2+} in an aqueous solution, providing an overview and a critical evaluation. It is well known that the preconcentration time required to detect trace or ultra-trace levels of Hg^{2+}, can affect analysis sensitivity and sampling frequency. Thus, an important improvement in the voltammetric analysis is decreasing the accumulation time without compromising the sensitivity, selectivity and linear range of the response.

Zen *et al.* [116] reported the determination of mercury in cosmetics using an in-built screen-printed three electrodes containing partially crosslinked poly(4-vinlylpyridine) (pcPVP) modified carbon working, carbon-counter, and Ag^+-quasireference electrodes (SPE/pcPVP) by means of square wave anodic stripping voltammetric (SWASV) technique. The preconcentration was performed at a fixed applied potential of -0.5 V (*vs*. Ag/AgCl) for 60 s. The calibration graph was linear in the window of 100 to 1000 ppb with a detection limit of 69.5 ppb. Two unbranded skin-lightening lotions were tested in parallel with inductively coupled plasma-optical emission spectroscopic (ICP-OES) measurements. Calculated recovery values were 94.29 and 98.07 %, respectively. The authors concluded that the analytical methodology is suitable for rapid and easy single-use mercury detection in cosmetic products.

A new method for selective determination of trace mercury by linear scan voltammetry using silver ink screen-printed electrode (AgSPE) in the presence of KI dissolved 0.05 M H_2SO_4 solution has been demonstrated [117]. Electrooxidation of iodide at AgSPE showed a systematic increase in inhibitory current against the mercury concentration at 0 V (*vs.* Ag/AgCl). The linear dynamic range of 500 to 4500 ppb was established; LOD and LOQ were found to be 98 and 318 ppb, respectively. The method was considered appropriate for constructing a new detection technique without any preconcentration. Such an approach is suitable for constructing a new detection technique without any interference from arsenic, cadmium, and lead ions.

Chemically modified MWCNTs paste electrode with chloroplatinum(II) complex for the determination of mercury using square wave stripping voltammetry was presented [119]. Under optimal conditions, the linear range was from 5.0 µM to 0.1 mM with a LOD of 3.7 µM. The recovery values were between 98.9 and 101.1 %, indicating that the modified electrode was capable of the quantification of Hg^{2+} in the skin-lightening cosmetics.

PANI/MWCNTs/AuNP-modified ITO electrode was developed via direct electrodeposition of PANI, MWCNTs and AuNPs on a film-coated ITO electrode and applied to analyze mercury in cosmetic products [112]. The optimum conditions for mercury detection using the modified ITO electrode were of Tris-HCl buffer (pH 7.0) in the presence of 1 mM methylene blue (MB) as a redox indicator. The sensor response was linear from 0.01 to 10.0 ppm (LOD = 0.03 ppm), which gave a platform for the sensitive detection of mercury in real samples. However, the interference studies are inconclusive. The concentrations of mercury and the tested common substances in cosmetics are not specified. The presented graph clearly shows that some electrochemically active substances have significant interference. So the selectivity of this sensing platform remains questionable.

Lead (Pb) and cadmium (Cd) are two potentially harmful heavy metals that cause considerable concern. Lead can impair almost all the organs of the human body and causes physical and mental impairments. Lead affects the neurological, reproductive, and renal systems. Symptoms may include headaches, memory problems, reduced fertility, *etc.* [120]. Lead and its compounds are banned in the European Union according to Regulation (EC) No 1123/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetics products under Annex II: List of Substances Prohibited in Cosmetic Products [121]. A compound of lead, lead acetate, is allowed as a colorant only in hair dyeing at concentrations lower than 0.6 % in ASEAN countries under ASEAN Cosmetics Directory (ACD) Annex III [122]. Cadmium is classified as a group I carcinogen; it can accumulate in various organs and tissues, but mostly in the kidney cortex [123]. Cadmium and its compounds are listed as substances that must not form part of the composition of cosmetic products [124].

Among cosmetic products, lipstick and eye cosmetics are most commonly used. They are produced by adding pigments that may contain heavy metals as impurities in the pigment formulation. An important non-dietary Pb exposure pathway for women is the mouthing or ingesting lip products such as lipsticks and lip glosses. Zhao and co-authors identified $PbCrO_4$ as the dominant Pb species in lip products with extremely high Pb concentrations [125]. Feizi *et al.* [123] analyzed by ICP-OES 60 samples of lipstick and eye pencil of different brands (produced by China, France, Turkey, Germany, and Korea). Mean concentrations of Pb and Cd in all the brands studied were 41.86 and 53.42 µg g^{-1}, respectively. The overall results showed that in all brands and colors of lipsticks, only 33 % had Pb content less than the FDA limit (20 µg g^{-1}) [126], and 44 % of all samples among lipsticks had Cd content less than the FDA limit of 3 µg g^{-1}. In eye pencils, 100 % of samples had Cd content above the recommended value of 3 µg g^{-1}.

In particular, kohl (also known as surma or kajal) is extensively used as traditional eye cosmetics in different countries of Africa and South Asia [127]. Kohl is applied to the conjunctival surfaces rather than to the outside of the eyelids and can cause eye damage or long-term health problems because it contains lead (galena stone, PbS) and antimony (stibnite, Sb_2S_3). Lead is mainly responsible for kohl's toxic effects, being associated with high concentrations of this element in blood samples from regular cosmetic users. Several studies have demonstrated that Pb levels are extremely high in this product and its use has been associated with the development of plumbism. Although Pb is the main component of kohl, Sb also promotes pathological dysfunctions, and dermal and DNA strand lesions [128].

Swetha *et al.* [129] reported a novel electrochemical sensor approach based on a high-index facets (HIF)-silver nanoflower modified GCE (AgNF@GCE) for anodic stripping voltammetric detection of Pb^{2+} in cosmetics and human blood serum. Unlike the conventional AgNPs, this platform displayed remarkable activity for sensitive and selective electrochemical analysis of Pb^{2+} because it provides a highly crystalline and large surface area with HIFs {422} and {111}. The newly developed AgNF@ GCE system can effectively determine Pb^{2+} in the presence of other common interfering metal ions, such as Cu^{2+}, Fe^{2+}, Mg^{2+}, Ni^{2+}, K^+, and Na^+. The method is defined as a promising approach for the rapid, sensitive detection of Pb^{2+} without any complicated offline preparation of real samples.

Coated wire ion selective electrode (CW-ISE) [130], composite cork–graphite sensor (Figure 4) [131], disposable screen-printed non-single crystal silver electrode (AgSPE) [132], gold nanoparticle (AuNP)/hexaammineruthenium(III) ($[Ru(NH_3)_6]^{3+}$)/Nafion modified GCE [133], and carbon black-modified carbon paste (CB-CP) electrode [134], were fabricated and used as working electrodes in the determination of Pb^{2+} in various commercial cosmetics.

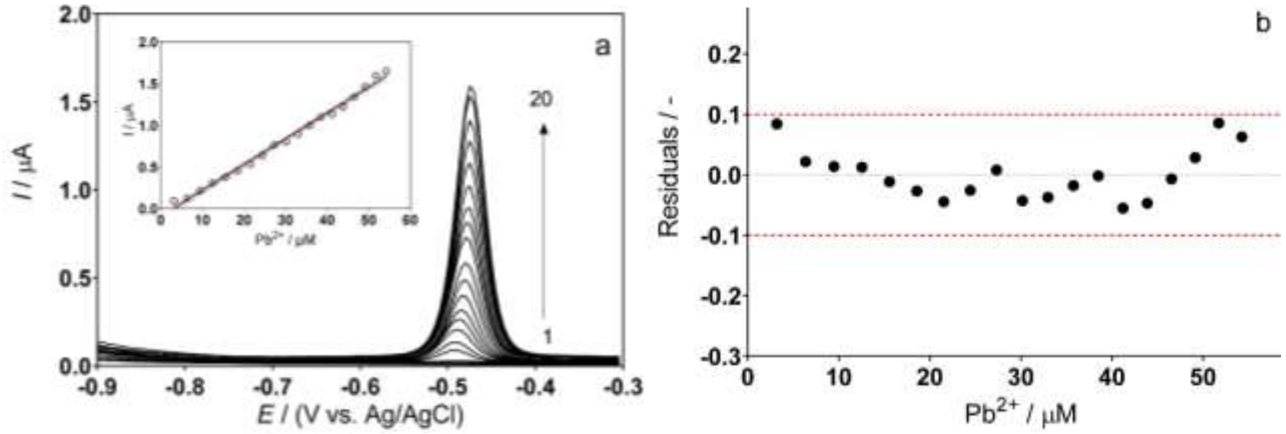

Figure 4. *DPSV responses for the determination of Pb(II) using the cork–graphite sensor. (**a**) DPSV curves recorded for different concentrations of Pb(II) in 0.1M acetate buffer (pH 4.5): (1) 0, supporting electrolyte; (2) 3.19; (3) 6.35; (4) 9.46; (5) 12.53; (6) 15.57; (7) 18.56; (8) 21.51; (9) 24.43; (10) 27.31; (11) 30.16; (12) 32.92; (13) 35.75; (14) 38.49; (15) 41.19; (16) 43.87; (17) 46.51; (18) 49.13; (19) 51.70 and (20) 54.26 µM. Inset: Plot of the electrochemical response, in terms of current, as a function of lead concentration. (**b**) Graphical representation of the residuals behavior, which confirms the linearity of the calibration curve. Reproduced from Ref. [131]. Licensee MDPI, Basel, Switzerland (2022)*

A comprehensive elucidation of the recent developments in the electrochemical detection of Cd^{2+} was presented by Yi *et al.* [135]. The determination of Cd^{2+} at trace and ultra-trace levels in environmental water samples by means of electrochemical methods was discussed in details. However, there hasn't yet been a published electroanalytical method for Cd^{2+} alone in cosmetics.

It is a challenging task to simultaneously, reliably and conveniently measure heavy metal ions in complex samples, such as cosmetics. New strategies were presented by de Furtado *et al.* [136] for the simultaneous voltammetric quantification of Pb^{2+} and Zn^{2+} in hair cosmetics (color wash lotion and anti-dandruff shampoo) employing chemically modified composite electrodes. Two methods for simultaneous determination of Pb^{2+}, Zn^{2+} and Cd^{2+}, with a cheap and easy to fabricate graphite-epoxy composite electrode, were developed. One method uses an *in situ* bismuth film modification and the other uses an *ex situ* organic film modification via diazonium salt reduction. Determinations were carried out in acetate buffer (pH 6.0) with a deposition potential of -1.4 V (applied during 120 s), followed by SWV measurements and subsequent cleaning with an application of 0.3 V potential. Detection limits of 0.07, 0.05 and 0.06 µM were achieved for Pb^{2+}, Cd^{2+} and Zn^{2+}, respectively. The data were compared to those found by applying flame atomic absorption spectrometry (FAAS), being considered statistically equivalent. The results are remarkable, considering that the cosmetic samples tested are quite complex, especially due to the greasy content and high concentration of surfactants. In summary, a comparison of various sensors applied to the electroanalysis of heavy metals in cosmetics is shown in Table 4.

Table 4. *Comparison of the analytical parameters of the electrochemical sensors for the determination of Hg^{2+} and Pb^{2+} in cosmetics*

Analyte	Electrode material	Method	Linear range	LOD	Real sample	Ref.
Hg^{2+}	SPE/pcPVP[1]	SWASV[7]	100 – 1000 ppb	69.5 ppb	skin-lightening cosmetics	[116]
	AgSPE[2]	LSV[8]	500 – 4500 ppb	98 ppb		[117]
	CPC/MWCNTs/PE[3]	SWASV[7]	5.0 μM – 0.1 mM	3.7 μM		[119]
Pb^{2+}	AgNF@GCE[4]	ASV[9]	10 – 700 ppb	0.74 ppb	eyeliner, lipstick	[129]
	CW-ISE[5]	Pot.[10]	10 – 100 μM	8.0 μM	lipstick	[130]
	Cork-graphite	DPSV[11]	3.19 – 54.26 μM	1.06 μM	hair dyes	[131]
	AgSPE	SWV[12]	0.06 – 0.79 μM	0.31 nM		[132]
	AuNPs([Ru(NH$_3$)$_6$]$^{3+}$)Nafion/GCE	ASV[9]	0.3 – 0.75 ppm	0.045 ppm		[133]
	CB-CP[6]	DPV[13]	0.04 – 3.2 μg	4 ng		[134]

[1] SPE/pcPVP: an in-built screen-printed three electrodes containing partially crosslinked poly(4-vinylpyridine) modified carbon working, carbon-counter, and Ag$^+$-quasireference electrodes; [2] AgSPE: silver ink screen-printed electrode; [3] CPC/MWCNTs/PE: chloroplatinum (II) complex-modified MWCNTs paste electrode; [4] AgNF@GCE: silver nanoflower modified glassy carbon electrode; [5] CW-ISE: coated wire ion selective electrode; [6] CB-CP: carbon black-modified carbon paste; [7] SWASV: square wave anodic stripping voltammetry; [8] LSV: linear scan voltammetry; [9] ASV: anodic stripping voltammetry; [10] Pot.: potentiometry; [11] DPSV: differential pulse stripping voltammetry; [12] SWV: square wave voltammetry; [13] DPV: differential pulse voltammetry.

Wang *et al*. [137]reported the first simultaneous analysis of mercury, lead, and arsenic (As) in cosmetics based on the electrochemical method. A disposable cost-effective gold-sputtered plastic electrode was used for the simultaneous detection of Pb^{2+}, As^{3+}, and Hg^{2+} in cosmetics based on differential pulse stripping voltammetry (DPSV). Under the optimized conditions, the DPSV peaks of these three metal ions could be well and reproducibly separated with satisfactory linear range and low detection limits of 2, 5 and 0.5 μg L^{-1} for Pb^{2+}, As^{3+}, and Hg^{2+}, respectively. The method was successfully applied for the simultaneous determination of three target ions in real cosmetic samples (eye shadow, skin lotion and talcum powder) with satisfactory results. Noting the low cost and convenient fabrication of the plastic-based sensors, the authors concluded that this approach might serve as an attractive alternative to conventional methods in routine analysis of those trace heavy metal ions in cosmetics.

Conclusion remarks

Considering that the use of cosmetic and personal care products in daily life has increased globally, it is important for researchers to keep on improving the performance of existing analytical methodologies, as well as developing innovative solutions. As the demand for cost-effective, rapid, highly selective and ultrasensitive quantification of various cosmetics ingredients rapidly increases, the electroanalytical methods provide a feasible path toward the next generation of reliable sensing devices (Figure 5).

Figure 5. *Cosmetic ingredients considered for electrochemical analysis*

The miniaturization potential of electrochemical systems attracts increasing research attention because electronic measurements can be integrated in hand-held devices and smartphones, which would allow fast, accurate, and on-site detection.

Perspectives

The large number of applications discussed in the present article clearly demonstrates the feasibility and utility of electrochemical sensors for analyzing ingredients in real cosmetics samples. After a thorough critical review of previous research studies, the following challenges were identified as priorities for the development of new advanced electroanalytical devices for the quality control of cosmetics.

- Considering the high matrix complexity of cosmetic samples, effective approaches should be developed to suppress the non-specific adsorption of interfering species.
- Currently, nanotechnology in the field of electrochemical sensors has been a crucial strategy for constructing reliable monitoring systems for cosmetic products safety. Future developments in electrochemical design will inevitably focus on the technology of new nanomaterials to improve the selectivity, reproducibility and operational stability of the sensor systems.
- Using easy and low-cost fabrication methods for mass production while maintaining the accuracy and precision achieved within a laboratory environment.
- The review showed that mainly single analyte methods had been proposed. Regarding the variety of ingredients considered for analytical control, the multianalyte arrays will be much more useful in real cosmetic analysis. Such sensor systems provide a simple, simultaneous multianalyte assay with a short analytical time.
- Producing portable and commercially available electroanalytical devices in order to extend their applications in extra-laboratory areas.

Conflicts of interest: The authors declare no conflict of interest.

References

[1] S. Borowska, M.M. Brzóska, Metals in cosmetics: implications for human health, *Journal of Applied Toxicology* **35** (2015) 551-572. https://doi.org/10.1002/jat.3129
[2] A. Salvador, A. Chisvert, *Analysis of Cosmetic Products*, Elsevier, Amsterdam, The Netherlands, 2017. https://doi.org/10.1016/B978-0-444-63508-2.00016-3

[3] H. Karimi-Maleh, R. Darabi, M. Shabani-Nooshabadi, M. Baghayeri, F. Karimi, J. Rouhi, M. Alizadeh, O. Karaman, Y. Vasseghian, C. Karaman, Determination of D&C Red 33 and Patent Blue V Azo dyes using an impressive electrochemical sensor based on carbon paste electrode modified with ZIF-8/g-C_3N_4/Co and ionic liquid in mouthwash and toothpaste as real samples, *Food and Chemical Toxicology* **162** (2022) 112907. https://doi.org/10.1016/j.fct.2022.112907

[4] M. Lores, M. Llompart, G. Alvarez-Rivera, E. Guerra, M. Vila, M. Celeiro, J.P. Lamas, C. Garcia-Jares, Positive lists of cosmetic ingredients: Analytical methodology for regulatory and safety controls—A review, *Analytica Chimica Acta* **915** (2016) 1-26. https://doi.org/10.1016/j.aca.2016.02.033

[5] H. Karimi-Maleh, H. Beitollahi, P. Senthil Kumar, S. Tajik, P. M. Jahani, F. Karimi, C. Karaman, Y. Vasseghian, M. Baghayeri, J. Rouhi, P. L. Show, S. Rajendran, L. Fu, N. Zare, Recent advances in carbon nanomaterials-based electrochemical sensors for food azo dyes detection, *Food and Chemical Toxicology* **164** (2022) 112961. https://doi.org/10.1016/j.fct.2022.112961

[6] Y. Feng, Y. Li, Y. Tong, C. Cui, X. Li, B.-C. Ye, Simultaneous determination of dihydroxybenzene isomers in cosmetics by synthesis of nitrogen-doped nickel carbide spheres and construction of ultrasensitive electrochemical sensor, *Analytica Chimica Acta* **1176** (2021) 338768. https://doi.org/10.1016/j.aca.2021.338768

[7] B. S. Lynch, E. S. Delzell, D. H. Bechtel, Toxicology review and risk assessment of resorcinol: Thyroid effects, *Regulatory Toxicology and Pharmacology* **36** (2002) 198-210. https://doi.org/10.1006/rtph.2002.1585

[8] Regulation (EC) No 1223/2009 of the European Parliament and of the Council, of 30 November 2009, on Cosmetic Products. *Off. J. Eur. Union* 2009. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009R1223 (Accessed on August 30, 2022).

[9] S. Cotchim, K. Promsuwan, M. Dueramae, S. Duerama, A. Dueraning, P. Thavarungkul, P. Kanatharana, W. Limbut, Development and Application of an Electrochemical Sensor for Hydroquinone in Pharmaceutical Products, *Journal of The Electrochemical Society*, **167** (2020) 155528. https://doi.org/10.1149/1945-7111/abd0cd

[10] Y. Olumide, A. Akinkugbe, D. Altraide, T. Tahir, N. Ahamefule, S. Ayanlowo, C. Onyekonwu, N. Essen, Complications of chronic use of skin lightening cosmetics, *International Journal of Dermatology* **47** (2008) 344-53. https://doi.org/10.1111/j.1365-4632.2008.02719.x

[11] S. Aydar, D. E. Bayraktepe, H. Filik, Z. Yazan, A Nano-Sepiolite Clay Electrochemical Sensor for the Rapid Electro–Catalytic Detection of Hydroquinone in Cosmetic Products, *Acta Chimica Slovenica* **65** (2018) 946-954. http://dx.doi.org/10.17344/acsi.2018.4615

[12] A. Ferrari, S. Rowley-Neale, C. Banks, Screen-printed electrodes: Transitioning the laboratory in-to-the field, *Talanta Open* **3** (2021) 100032. https://doi.org/10.1016/j.talo.2021.100032

[13] S. Cinti, F. Arduini, Graphene-based screen-printed electrochemical (bio)sensors and their applications: Efforts and criticisms, *Biosensors and Bioelectronics* **89** (2017) 107-122. https://doi.org/10.1016/j.bios.2016.07.005

[14] W. Duekhuntod, C. Karuwan, A. Tuantranont, D. Nacapricha, S. Teerasong, A Screen Printed Graphene Based Electrochemical Sensor for Single Drop Analysis of Hydroquinone in Cosmetic Products, *International Journal of Electrochemical Science* **14** (2019) 7631-7642. https://doi.org/10.20964/2019.08.94

[15] H.-H. Yang, H.-H.Ting, Y. Shih, Self-validated detection of hydroquinone in medicated cosmetic products using a preanodized screen-printed ring disk carbon electrode, *Analytical Methods*, **8** (2016) 5495-5502. https://doi.org/10.1039/C6AY01000H

[16] M. Harsini, U. Untari, E. Fitriany, A. N. Farida, M. Z. Fahmi, S.C.W. Sakti, G. Pari, Voltammetric analysis of hydroquinone in skin whitening cosmetic using ferrocene modified carbon paste electrode, *Rasayan Journal of Chemistry* **12** (2019) 2296-2305. http://dx.doi.org/10.31788/RJC.2019.1245479

[17] G. Manasa, A. K. Bhakta, Z. Mekhalif, R. J. Mascarenhas, Voltammetric Study and Rapid Quantification of Resorcinol in Hair Dye and Biological Samples Using Ultrasensitive Maghemite/MWCNT Modified Carbon Paste Electrode, *Electroanalysis* **31** (2019) 1363. https://doi.org/10.1002/elan.201900143

[18] N. M. M. A. Edris, Y. Sulaiman, Ultrasensitive voltammetric detection of benzenediol isomers using reduced graphene oxide-azo dye decorated with gold nanoparticles, *Ecotoxicology and Environmental Safety* **203** (2020) 111026. https://doi.org/10.1016/j.ecoenv.2020.111026

[19] N. Butwong, S. Srijaranai, J. D. Glennon, J. H. T. Luong, Cysteamine Capped Silver Nanoparticles and Single-walled Carbon Nanotubes Composite Coated on Glassy Carbon Electrode for Simultaneous Analysis of Hydroquinone and Catechol, *Electroanalysis* **30** (2018) 962-968. https://doi.org/10.1002/elan.201700704

[20] T. Dodevska, D. Hadzhiev, I. Shterev, Y. Lazarova, Application of biosynthesized metal nanoparticles in electrochemical sensors: Review, *Journal of the Serbian Chemical Society* **87** (2022) 401-435. https://doi.org/10.2298/JSC200521077D

[21] J. A. Buledi, S. Ameen, N. H. Khand, A. R. Solangi, I. H. Taqvi, M. H. Agheem, Z. Wajdan, CuO Nanostructures Based Electrochemical Sensor for Simultaneous Determination of Hydroquinone and Ascorbic Acid, *Electroanalysis* **32** (2020) 1600. https://doi.org/10.1002/elan.202000083

[22] A. Domínguez-Aragón, R. B. Dominguez, E. A. Zaragoza-Contreras, Simultaneous Detection of Dihydroxybenzene Isomers Using Electrochemically Reduced Graphene Oxide-Carboxylated Carbon Nanotubes/Gold Nanoparticles Nanocomposite, *Biosensors* **11** (2021) 321. https://doi.org/10.3390/bios11090321

[23] K. Saha, S. S. Agasti, C. Kim, X. Li, V. M. Rotello, Gold Nanoparticles in Chemical and Biological Sensing, *Chemical Reviews* **112** (2012) 2739-2779. https://doi.org/10.1021/cr2001178

[24] S. A. Shahamirifard, M. Ghaedi, A new electrochemical sensor for simultaneous determination of arbutin and vitamin C based on hydroxyapatite-ZnO-Pd nanoparticles modified carbon paste electrode, *Biosensors and Bioelectronics* **141** (2019) 111474. https://doi.org/10.1016/j.bios.2019.111474

[25] S.A. Barutçu, D.E. Bayraktepe, Z. Yazan, K. Polat, F. Hayati, Investigation of electrochemical oxidation mechanism, rapid and low-level determination for whitening cosmetic: arbutin in aqueous solution by nano sepiolite clay, *Chemical Papers* **75** (2021) 3483-3491. https://doi.org/10.1007/s11696-021-01581-3

[26] J.-M. Zen, H.-H. Yang, M.-H. Chiu, C.-H. Yang, Y. Shih, Selective Determination of Arbutin in Cosmetic Products Through Online Derivatization Followed by Disposable Electrochemical Sensor, *Journal of AOAC International* **94** (2011) 985-990. https://doi.org/10.1093/jaoac/94.3.985

[27] A. Khatoon, J.A. Syed, J.A. Buledi, S. Shakeel, A. Mallah, A.R. Solangi, Sirajuddin, S.T.H. Sherazi, M.R. Shah, Bio-green fabrication of bell pepper mediated silver nanoparticles: an efficient material for electrochemical sensing of arbutin in cosmetics, *Journal of the Iranian Chemical Society* **19** (2022) 3659-3672. https://doi.org/10.1007/s13738-022-02558-z

[28] Scientific Committee on Safety (SCCS). Opinion on oxidative hair dye substances and hydrogen peroxide used in products to colour eyelashes. Brussels, Belgium, European Commission. 2012. Report No. SCCS/1475/12. pp. 1-21. http://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_111.pdf

[29] A. Müller, S. Sachse, M. Decker, F.-M. Matysik, W. Vonau, Comparison of H_2O_2 screen-printed sensors with different Prussian blue nanoparticles as electrode material, *Journal of Electrochemical Science and Engineering* **10** (2020) 199-207. https://doi.org/10.5599/jese.719

[30] S. Chen, R. Yuan, Y. Chai, F. Hu, Electrochemical sensing of hydrogen peroxide using metal nanoparticles, *Microchimica Acta* **180** (2013) 15-32. https://doi.org/10.1007/s00604-012-0904-4

[31] K. Dhara, D. R. Mahapatra, Recent advances in electrochemical nonenzymatic hydrogen peroxide sensors based on nanomaterials: a review, *Journal of Materials Science* **54** (2019) 12319-12357. https://doi.org/10.1007/s10853-019-03750-y

[32] H. Shamkhalichenar, J.-W. Choi. Review—Non-Enzymatic Hydrogen Peroxide Electrochemical Sensors Based on Reduced Graphene Oxide, *Journal of the Electrochemical Society* 167 (2020) 037531. https://doi.org/10.1149/1945-7111/ab644a

[33] M. A. Riaz, Y. Chen, Electrodes and electrocatalysts for electrochemical hydrogen peroxide sensors: a review of design strategies, *Nanoscale Horizons* **7** (2022) 463-479. https://doi.org/10.1039/D2NH00006G

[34] K. Atacan, M. Özacar. Construction of a non-enzymatic electrochemical sensor based on CuO/g-C_3N_4 composite for selective detection of hydrogen peroxide, *Materials Chemistry and Physics* **266** (2021) 124527. https://doi.org/10.1016/j.matchemphys.2021.124527

[35] M.-H. Chiu, A. S. Kumar, S. Sornambikai, P.-Y. Chen, Y. Shih, J.-M. Zen, Cosmetic Hydrogen Peroxide Detection Using Nano Bismuth Species Deposited Built-in Three-in-One Screen-Printed Silver Electrode, *International Journal of Electrochemical Science* **6** (2011) 2352-2365. http://www.electrochemsci.org/papers/vol6/6072352.pdf

[36] A. Benvidi, M. T. Nafar, S. Jahanbani, M. D. Tezerjani, M. Rezaeinasab, S. Dalirnasab, Developing an electrochemical sensor based on a carbon paste electrode modified with nano-composite of reduced graphene oxide and $CuFe_2O_4$ nanoparticles for determination of hydrogen peroxide, *Materials Science and Engineering C* **75** (2017) 1435-1447. https://doi.org/10.1016/j.msec.2017.03.062

[37] I. Mihailova, V. Gerbreders, M. Krasovska, E. Sledevskis, V. Mizers, A. Bulanovs, A. Ogurcovs, A non-enzymatic electrochemical hydrogen peroxide sensor based on copper oxide nanostructures, *Beilstein Journal of Nanotechnology* **13** (2022) 424-436. https://doi.org/10.3762/bjnano.13.35

[38] V. Katic, P. L. dos Santos, M. F. dos Santos, B. M. Pires, H. C. Loureiro, A. P. Lima, J. C. M. Queiroz, R. Landers, R. A. A. Muñoz, J. A. Bonacin, 3D Printed Graphene Electrodes Modified with Prussian Blue: Emerging Electrochemical Sensing Platform for Peroxide Detection, *ACS Applied Materials and Interfaces* **11** (2019) 35068-35078. https://doi.org/10.1021/acsami.9b09305

[39] D. Ye, Y. Xu, L. Luo, Y. Ding, Y. Wang, X. Liu, L. Xing, J. Peng, A novel non-enzymatic hydrogen peroxide sensor based on $LaNi_{0.5}Ti_{0.5}O_3/CoFe_2O_4$ modified electrode, *Colloids and Surfaces B* **89** (2012) 10-14. https://doi.org/10.1016/j.colsurfb.2011.08.014

[40] G. L. Luque, N. F. Ferreyra, A. G. Leyva, G. A. Rivas, Characterization of carbon paste electrodes modified with manganese based perovskites-type oxides from the amperometric determination of hydrogen peroxide, *Sensors and Actuators B* **142** (2009) 331-336. https://doi.org/10.1016/j.snb.2009.07.038

[41] Z. Zhang, S. Gu, Y. Ding, J. Jin, A novel nonenzymatic sensor based on $LaNi_{0.6}Co_{0.4}O_3$ modified electrode for hydrogen peroxide and glucose, *Analytica Chimica Acta* **745** (2012) 112-117. https://doi.org/10.1016/j.aca.2012.07.039

[42] D. Xu, L. Li, Y. Ding, S. Cui, Electrochemical hydrogen peroxide sensors based on electrospun $La_{0.7}Sr_{0.3}Mn_{0.75}Co_{0.25}O_3$ nanofiber modified electrodes, *Analytical Methods* **7** (2015) 6083-6088. https://doi.org/10.1039/c5ay01131k

[43] S. Michalkiewicz, A. Skorupa, M. Jakubczyk, Carbon Materials in Electroanalysis of Preservatives, *Materials* **14** (2021) 7630-7653. https://doi.org/10.3390/ma14247630

[44] F. Z. Kashani, S. M. Ghoreishi, A. Khoobi, Experimental and statistical analysis on a nanostructured sensor for determination of p-hydroxybenzoic acid in cosmetics, *Materials Science and Engineering: C* **94** (2019) 45-55. https://doi.org/10.1016/j.msec.2018.08.068

[45] F. Z. Kashani, S. M. Ghoreishi, A. Khoobi, M. Enhessari, A carbon paste electrode modified with a nickel titanate nanoceramic for simultaneous voltammetric determination of *ortho*- and *para*-hydroxybenzoic acids, *Microchimica Acta* **186** (2019) 12. https://doi.org/10.1007/s00604-018-3113-y

[46] K. Charoenkitamorn, W. Siangproh, O. Chailapakul, M. Oyama, S. Chaneam, Simple Portable Voltammetric Sensor Using Anodized Screen-Printed Graphene Electrode for the Quantitative Analysis of *p*-Hydroxybenzoic Acid in Cosmetics, *ACS Omega* **7** (2022) 16116-16126. https://doi.org/10.1021/acsomega.2c01434

[47] K. M. Naik, S.T. Nandibewoor, Electroanalytical method for the determination of methylparaben, *Sensors and Actuators A* **212** (2014) 127-132. https://doi.org/10.1016/j.sna.2014.03.033

[48] M. Behpour, S. Masoum, A. Lalifar, A. Khoobi, A novel method based on electrochemical approaches andmultivariate calibrations for study and determination of methylparaben in the presence of unexpected interferencein cosmetics, *Sensors and Actuators B* **214** (2015) 10-19. http://dx.doi.org/10.1016/j.snb.2015.03.003

[49] P. D. Darbre, Underarm cosmetics and breast cancer, *Journal of Applied Toxicology* **23** (2003) 89-95. https://doi.org/10.1002/jat.899

[50] P. Harvey, Parabens, oestrogenicity, underarm cosmetics and breast cancer: a perspective on a hypothesis, *Journal of Applied Toxicology* **23** (2003) 285-288. https://doi.org/10.1002/jat.946

[51] S. Oishi, Effects of propyl paraben on the male reproductive system, *Food and Chemical Toxicology* **40** (2002) 1807-1813. https://doi.org/10.1016/s0278-6915(02)00204-1

[52] J. J. Prusakiewicz, H. M. Harville, Y. H. Zhang, C. Ackermann, R. L. Voorman, Parabens inhibit human skin estrogen sulfotransferase activity: possible link to paraben estrogenic effects, *Toxicology* **232** (2007) 248-256. https://doi.org/10.1016/j.to x.2007.01.010

[53] R. S. Tavares, F. C. Martins, P. J. Oliveira, J. Santosa, F. P. Peixoto, Parabens in male infertility-is there a mitochondrial connection, *Reproductive Toxicology* **27** (2009) 1-7. https://doi.org/10.1016/j.reprotox.2008.10.002

[54] Y. Okamoto, T. Hayashi, S. Matsunami, K. Ueda, N. Kojima N. Combined activation of methyl paraben by light irradiation and esterase metabolism toward oxidative DNA damage, *Chemical Research in Toxicology* **21** (2008) 1594-1603. https://doi.org/10.1021/tx800066u

[55] Regulation (EC). No 1223/2009 of the European Parliament and of the Council, of 30 November 2009, on Cosmetic Products. Off. J. Eur. Union 2009. ANNEX V, p. 136. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009R1223 (Acessed on August 30, 2022).

[56] C. D. Mendonça, T. M. Prado, F. H. Cincotto, R. T. Verbinnen, S. A. S. Machadop, Methylparaben Quantification Via Electrochemical Sensor Based On Reduced Graphene Oxide Decorated With Ruthenium Nanoparticles, *Sensors and Actuators B* **251** (2017) 739-745. http://dx.doi.org/10.1016/j.snb.2017.05.083

[57] L. F. de Lima, M. D. Cristiane, M. M. Celina, A. P. Elisabete, F. Marystela, Layer-by-Layer nanostructured films of magnetite nanoparticles and polypyrrole towards synergistic effect on methylparaben electrochemical detection, *Applied Surface Science* **505** (2020) 144278. https://doi.org/10.1016/j.apsusc.2019.144278

[58] L. F. de Lima, E. A. Pereira, M. Ferreira, Electrochemical sensor for propylparaben using hybrid Layer-by-Layer films composed of gold nanoparticles, poly(ethylene imine) and nickel(II) phthalocyanine tetrasulfonate, *Sensors and Actuators B* **310** (2020) 127893. https://doi.org/10.1016/j.snb.2020.127893

[59] Y. Wang, Y. Cao, C. Fang, Q. Gong, Electrochemical sensor for parabens based on molecular imprinting polymers with dual-templates, *Analytica Chimica Acta* **673** (2010) 145-150 https://doi.org/10.1016/j.aca.2010.05.039

[60] P. Luo, J. Liu, Y. Li, Y. Miao, B. Ye, Voltammetric Determination of Methylparaban in Cosmetics Using a Multi-Wall Carbon Nanotubes/Nafion Composite Modified Glassy Carbon Electrode, *Analytical Letters* **45** (2012) 2445-2454. https://doi.org/10.1080/00032719.2012.691589

[61] M. Soysal, An Electrochemical Sensor Based on Molecularly Imprinted Polymer for Methyl Paraben Recognition and Detection, *Journal of Analytical Chemistry* **76** (2021) 381-389. https://doi.org/10.1134/S1061934821030114

[62] S. Guo, X. Wu, J. Zhou, J. Wang, B. Yang, B. Ye, MWNT/Nafion Composite Modified Glassy Carbon Electrode as the Voltammetric Sensor for Sensitive Determination of 8-Hydroxyquinoline in Cosmetic, *Journal of Electroanalytical Chemistry* **656** (2011) 45-49. https://doi.org/10.1016/j.jelechem.2011.02.010

[63] T. T. Calam, E. B. Yılmaz, Electrochemical determination of 8-hydroxyquinoline in a cosmetic product on a glassy carbon electrode modified with 1-amino-2-naphthol-4-sulphonic acid, *Instrumentation Science and Technology* **49** (2021) 1-20. https://doi.org/10.1080/10739149.2020.1765175

[64] Z. Gao, Q. Zeng, M. Wang, L. Wang, Sensitive Detection of 8-Hydroxyquinoline in Cosmetics by Using a Poly(tannic acid)-Modified Glassy Carbon Electrode, *ChemistrySelect* **7** (2022) e202200257. https://doi.org/10.1002/slct.202200257

[65] L. Fotouhi, H. R. Shahbaazi, A. Fatehi, M. M. Heravi, Voltammetric Determination of Triclosan in Waste Water and Personal Care Products*, International Journal of Electrochemical Science* **5** (2010) 1390-1398. http://www.electrochemsci.org/papers/vol5/5091390.pdf

[66] Regulation (EC). No 1223/2009 of the European Parliament and of the Council, of 30 November 2009, on Cosmetic Products. Off. J. Eur. Union 2009. ANNEX V, p. 138. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009R1223 (Accessed on August 30, 2022).

[67] A. Saljooqi, T. Shamspur, A. Mostafavi, A Sensitive Electrochemical Sensor Based on Graphene Oxide Nanosheets Decorated by Fe_3O_4@AuNanostructure Stabilized on Polypyrrole for Efficient Triclosan Sensing, *Electroanalysis* **32** (2020) 1297-1303. https://doi.org/10.1002/elan.201900634

[68] V. R. Sri, R. Shwetharani, J. Mohammed, A. Mabkhoot, R. G. Balakrishna, F. A. Harraz, Review on Electrochemical Sensing of Triclosan using Nanostructured Semiconductor Materials, *ChemElectroChem* **9** (2022) e202101664. https://doi.org/10.1002/celc.202101664

[69] R. M. Pemberton, J. P. Hart, Electrochemical behaviour of triclosan at a screen-printed carbon electrode and its voltammetric determination in toothpaste and mouthrinse products, *Analytica Chimica* Acta **390** (1999) 107-115. https://doi.org/10.1016/s0003-2670(99)00194-4

[70] J. Yang, P. Wang, X. Zhang, K. Wu, Electrochemical sensor for rapid detection of triclosan using a multiwall carbon nanotube film, *Journal of Agricultural and Food Chemistry* **57** (2009) 9403-9407. https://doi.org/10.1021/jf902721r

[71] H. Dai, G. Xu, L. Gong, C. Yang, Y. Lin, Y. Tong, J. Chen, G. Chen, Electrochemical detection of triclosan at a glassy carbon electrode modifies with carbon nanodots and chitosan, *Electrochimica Acta* **80** (2012) 362-367. https://doi.org/10.1016/j.electacta.2012.07.032

[72] Y. L. Su, H. C. You, S. H. Cheng, C. Y. Lin, Fabrication of bacteriochlorin shell/gold core nanoparticles for the sensitive determination of trichlosan using differential pulse voltammetry, *Analytica Chimica Acta* **1123** (2020) 44-55. https://doi.org/10.1016/j.aca.2020.04.070

[73] N. D. Luyen, T. T. T. Toan, H. T. Trang, V. T. Nguyen, L. V. T. Son, T. S. Thanh, N. M. Thanh, P. T. Quy, D. Q. Khieu, D. T. Nguyen, Electrochemical Determination of Triclosan Using ZIF-11/Activated Carbon Derived from the Rice Husk Modified Electrode, *Journal of Nanomaterials* (2021) 8486962. https://doi.org/10.1155/2021/8486962

[74] Scientific Committee on Consumer Safety SCCS OPINION ON Zinc Pyrithione (ZPT) (CAS No 13463-41-7) - Submission III, p. 25. https://ec.europa.eu/health/document/download/aa535110-c020-4924-8507-5f867adc9972_en

[75] Regulation (EC). No 1223/2009 of the European Parliament and of the Council, of 30 November 2009, on Cosmetic Products. Off. J. Eur. Union 2009. ANNEX V, p. 135. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009R1223 (Accessed on August 30, 2022).

[76] L. H. Wang, Determination of Zinc Pyrithione in Hair Care Products on Metal Oxides Modified Carbon Electrodes, *Electroanalysis* **12** (2000) 227-232. https://doi.org/10.1002/(sici)1521-4109(200002)12:3<227::aid-elan227>3.0.co;2-i

[77] Y. Shih, Flow injection analysis of zinc pyrithione in hair care products on a cobalt phthalocyanine modified screen-printed carbon electrode, *Talanta* **6** (2004) 912-917. https://doi.org/10.1016/j.talanta.2003.10.039

[78] L. R. Gaspar, P. M. B. G. Maia Campos, Evaluation of the photostability of different UV filters associations in a sunscreen. *International Journal of Pharmaceutics* **307** (2006) 123-128. https://doi.org/10.1016/j.ijpharm.2005.08.029

[79] S. Seité, A. Fourtanier, D. Moyal, A. R. Young, Photodamage to human skin by suberythemal exposure to solar ultraviolet radiation can be attenuated by sunscreens, *British Journal of Dermatology* **163** (2010) 903-914. https://doi.org/10.1111/j.1365-2133.2010.10018.x

[80] A. Chisvert, A. Salvador, UV Filters in Sunscreens and other Cosmetics. Regulatory Aspects and Analytical Methods. *Analysis of Cosmetic Products* (2007) 83-120. https://doi.org/10.1016/b978-044452260-3/50028-0

[81] M. Krause, A. Klit, M. Blomberg Jensen, T. Søeborg, H. Frederiksen, M. Schlumpf, W. Lichtensteiger, N.E. Skakkebaek, K.T. Drzewiecki, Sunscreens: are they beneficial for health? An overview of endocrine disrupting properties of UV-filters, *International Journal of Andrology* **35** (2012) 424-436. https://doi.org/10.1111/j.1365-2605.2012.01280.x

[82] M. Ghazipura, R. McGowan, A. Arslan, T. Hossain, Exposure to benzophenone-3 and reproductive toxicity: A systematic review of human and animal studies, *Reproductive Toxicology* **73** (2017) 175-183. https://doi.org/10.1016/j.reprotox.2017.08.015

[83] J. C. Cardoso, B. M. L. Armondes, T. A. de Araújo, J. L. Raposo, N. R. Poppi, V. S. Ferreira, Determination of 4-methylbenzilidene camphor in sunscreen by square wave voltammetry in media of cationic surfactant, *Microchemical Journal* **85** (2007) 301-307. https://doi.org/10.1016/j.microc.2006.07.006

[84] I. Narloch G. Wejnerowska, An Overview of the Analytical Methods for the Determination of Organic Ultraviolet Filters in Cosmetic Products and Human Samples, *Molecules* **26** (2021) 4780-4807. https://doi.org/10.3390/molecules26164780

[85] M.-L. Chang, C.-M. Chang, Voltammetric determination of sunscreen by convenient epoxy-carbon composite electrodes, *Journal of Food and Drug Analysis* **9** (2001) 199-206 https://doi.org/10.38212/2224-6614.2783

[86] L. H. Wang, Voltammetric Behavior of Sunscreen Agents at Mercury Film Electrode, *Electroanalysis* **14** (2002) 773-781. https://doi.org/10.1002/1521-4109(200206)14:11<773::AID-ELAN773>3.0.CO;2-A

[87] J. B. G. Júnior, T. A. Araujo, M. A. G. Trindade, V. S. Ferreira, Electroanalytical determination of the sunscreen agent octocrylene in cosmetic products, *International Journal of Cosmetic Science* **34** (2011) 91-96. https://doi.org/10.1111/j.1468-2494.2011.00686.x

[88] J. C. Cardoso, B. M. L. Armondes, J.B.G.eV. Ferreira, Simultaneous electrochemical determination of three sunscreens using cetyltrimethylammonium bromide, *Colloids and Surfaces B* **63** (2008) 34-40. https://doi.org/10.1016/j.colsurfb.2007.11.001

[89] R. A. Lopes Neves, F. Moreira Araujo, F. Siqueira Pacheco, G. Chevitarese Azevedo, M. A. Costa Matos, R. Camargo Matos, Electrochemical Determination of Sunscreens Agents in Cosmetic Using Square Wave Voltammetry, *Electroanalysis* **313** (2018) 496-503. https://doi.org/10.1002/elan.201800747

[90] Regulation (EC). No 1223/2009 of the European Parliament and of the Council, of 30 November 2009, on Cosmetic Products. Off. J. Eur. Union 2009. ANNEX III, p. 71. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009R1223 (Accessed on August 30, 2022).

[91] S. Shahrokhian, Y. Javad, Electrocatalytic oxidation of thioglycolic acid at carbon paste electrode modified with cobalt phthalocyanine: application as a potentiometric sensor, *Electrochimica Acta* **48** (2003) 4143-4148. https://doi.org/10.1016/S0013-4686(03)00582-6

[92] J. M. Zen, H. H. Yang, M. H. Chiu, Y. J. Chen, Y. Shih, Determination of Thioglycolic Acid in Hair-Waving Products by Disposable Electrochemical Sensor Coupled with High-Performance Liquid Chromatography, *Journal of AOAC International* **92** (2009) 574-579. https://doi.org/10.1093/jaoac/92.2.574

[93] B. Nair, A. R. Elmore, Cosmetic Ingredients Review Expert Panel. Final report on the safety assessment of sodium sulfite, potassium sulfite, ammonium sulfite, sodium bisulfite, ammonium bisulfite, sodium metabisulfite and potassium metabisulfite, *International Journal of Toxicology* **22** (2003) 63-88. https://doi.org/10.1080/10915810305077x

[94] H. Vally, N. L. Misso, Adverse reactions to the sulphite additives, *Gastroenterol Hepatol Bed Bench* **5** (2012) 16-23 http://www.ncbi.nlm.nih.gov/pmc/articles/pmc4017440/

[95] The Scientific Committee on Cosmetic Products and Non Food Products intended for consumers, Evaluation and Opinion on: Inorganic Sulfites and Bisulfites, 23rd Plenary Meeting of the SCCNFP, 18 March, 2003 https://ec.europa.eu/health/ph_risk/committees/sccp/documents/out_200.pdf

[96] P. Y. Chen, C. C. Huang, M. C. Chen, J. C. Hsu, Y. Shih, Determination of Sulfite in Hair Waving Products Using Oxygen-Incorporated Gold-Modified Screen-Printed Electrodes. *Electroanalysis* **24** (2012) 2267-2272. https://doi.org/10.1002/elan.201200126

[97] M. Singh, S. R. Bhardiya, A. Rai, V. K. Rai, Electrochemical approach for recognition and quantification of p-phenylenediamine: a review, *Sensors and Diagnostics* **1** (2022) 376-386. https://doi.org/10.1039/d1sd00070e

[98] H. J. Han, H. J. Lee, C. H. Bang, J. H. Lee, Y. M. Park, J. Y. Lee, P-Phenylenediamine Hair Dye Allergy and Its Clinical Characteristics, *Annals of Dermatology* **30** (2018) 316-321. https://doi.org/10.5021/ad.2018.30.3.316

[99] Scientific Committee on Consumer Products (SCCP). Opinion on Exposure to Reactants and Reaction Products of Oxidative Hair Dye Formulations; European Commission, Health & Consumer Protection Directorate-General: Luxembourg, 2005. https://ec.europa.eu/health/ph_risk/committees/04_sccp/docs/sccp_o_032.pdf

[100] M. H. Al-Enezi, F. S. Aldawsari, Study of P-Phenylenediamine (PPD) Concentrations after Hair Dye Mixing: A Call for Safety Reassessment, *Cosmetics* **9** (2022) 41-57. https://doi.org/10.3390/cosmetics9020041

[101] A. Chisvert, P. Miralles, A. Salvador. Chapter 8 - Hair Dyes in Cosmetics: Regulatory Aspects and Analytical Methods. In Analysis of Cosmetic Products, 2nd ed.; A. Salvador, A. Chisvert, Eds.; Elsevier: Boston, MA, USA, 2018; pp. 159-173 https://doi.org/10.1016/B978-0-444-63508-2.00008-4

[102] O. J. X. Morel, R. M. Christie, Current Trends in the Chemistry of Permanent Hair Dyeing, *Chemical Reviews* **111** (2011) 2537-2561. https://doi.org/10.1021/cr1000145

[103] Y. H. Bai, J. Y. Li, Y. Zhu, J. J. Xu, H. J. Chen, Selective Detection of *p*-Phenylenediamine in Hair Dyes Based on a Special CE Mechanism Using MnO_2 Nanowires, *Electroanalysis* **22** (2010) 1239-1247. https://doi.org/10.1002/elan.200900576

[104] J. He, J. Sunarso, J. Miao, H. Sun, J. Dai, C. Zhang, W. Zhou, Z. Shao, A highly sensitive perovskite oxide sensor for detection of p-phenylenediamine in hair dyes, *Journal of Hazardous Materials* **369** (2019) 699-706 https://doi.org/10.1016/j.jhazmat.2019.02.070

[105] M. Singh, A. Sahu, S. Mahata, P. Shukla, A. Rai, V. K. Rai, Efficient electrocatalytic oxidation of p-phenylenediamine using a novel PANI/ZnO anchored bio-reduced graphene oxide nanocomposite, *New Journal of Chemistry* **43** (2019) 6500-6506. https://doi.org/10.1039/c9nj00837c

[106] M. Singh, S. R. Bhardiya, A. Asati, H. Sheshma, V.K. Rai, A. Rai, Sensitive electrocatalytic determination of p-phenylenediamine using bimetallic nanocomposite of Cu-Ag nanoalloy and ionic liquid-graphene oxide, *Journal of Electroanalytical Chemistry* **894** (2021) 115360. https://doi.org/10.1016/j.jelechem.2021.115360

[107] K. G. McGrath, Apocrine sweat gland obstruction by antiperspirants allowing transdermal absorption of cutaneous generated hormones and pheromones as a link to the observed incidence rates of breast and prostate cancer in the 20th century, *Medical Hypotheses* **72** (2009) 665-674. https://doi.org/10.1016/j.mehy.2009.01.025

[108] P. D. Darbre, Aluminium and the human breast, *Morphologie* **100** (2016) 65-74. https://doi.org/10.1016/j.morpho.2016.02.001

[109] M. H. Chiu, A. S. Kumar, S. Sornambikai, J. M. Zen, Y. Shih, Flow Injection Analysis of Aluminum Chlorohydrate in Antiperspirant Deodorants Using a Built-in Three-in-one Screen-Printed Silver Electrode, *Electroanalysis* **22** (2010) 2421-2427. https://doi.org/10.1002/elan.200900635

[110] J. M. Zen, T. H. Yang, A. Kumar, Y. J. Chen, J. C. Hsu, Y. Shih, Detection of Aluminum Chlorohydrate Content in Antiperspirant Deodorants Using Screen-Printed Silver Electrodes by One Drop Analysis, *Electroanalysis* **21** (2009) 2272-2276. https://doi.org/10.1002/elan.200904670

[111] B. Bocca, A. Pino, A. Alimonti, G. Forte, Toxic metals contained in cosmetics: a status report, *Regulatory Toxicology and Pharmacology* **68** (2014) 447-467. https://doi.org/10.1016/j.yrtph.2014.02.003

[112] N. A. Bohari, S. Siddiquee, S. Saallah, M. Misson, S. E. Arshad, Optimization and Analytical Behavior of Electrochemical Sensors Based on the Modification of Indium Tin Oxide (ITO) Using PANI/MWCNTs/AuNPs for Mercury Detection, *Sensors* **20** (2020) 6502. https://doi.org/10.3390/s20226502

[113] Z. Wang X. Fang, Chronic Mercury Poisoning from Daily Cosmetics: Case Report and Brief Literature Review, *Cureus* **13** (2021) e19916. https://doi.org/10.7759/cureus.19916

[114] G. F. Sun, W. T. Hu, Z. H. Yuan, B. A. Zhang, H. Lu, Characteristics of mercury intoxication induced by skin-lightening products, *Chinese Medical Journal* **130** (2017) 3003-3004. https://doi.org/10.4103/0366-6999.220312

[115] N. M. Hepp, W. R. Mindak, J. W. Gasper, C. B. Thompson, J. N. Barrows, Survey of cosmetics for arsenic, cadmium, chromium, cobalt, lead, mercury, and nickel content, *Journal of Cosmetic Science* **65** (2014) 125-145 https://pubmed.ncbi.nlm.nih.gov/25043485/

[116] J. M. Zen, A. S. Kumar, S. C. Lee, Y. Shih, Microliter Volume Determination of Cosmetic Mercury with a Partially Crosslinked Poly(4-vinylpyridine) Modified Screen-Printed Three-Electrode Portable Assembly, *Electroanalysis* **19** (2007) 2369-2374. https://doi.org/10.1002/elan.200703990

[117] M. H. Chiu, J. M. Zen, A. S. Kumar, D. Vasu, Y. Shih, Selective Cosmetic Mercury Analysis Using a Silver Ink Screen-Printed Electrode with Potassium Iodide Solution, *Electroanalysis* **20** (2008). 2265-2270. https://doi.org/10.1002/elan.200804307

[118] A. L. Suherman, E. E. L. Tanner, R.G. Compton, Recent developments in inorganic Hg^{2+} detection by voltammetry, *TrAC Trends in Analytical Chemistry* **94** (2017) 161-172. https://doi.org/10.1016/j.trac.2017.07.020

[119] I. M. Isaa, M. I. Saidin, M. Ahmad, N. Hashim, S. A. Bakar, N. M. Ali, S. M. Si, Chloroplatinum(II) complex-modified MWCNTs paste electrode for electrochemical determination of mercury in skin lightening cosmetics, *Electrochimica Acta* **253** (2017) 463-471. http://dx.doi.org/10.1016/j.electacta.2017.09.092

[120] A. L. Wani, A. Ara, J. A. Usmani, Lead toxicity: a review, *Interdisciplinary Toxicol*ogy **8** (2015) 55-64. http://dx.doi.org/10.1515/intox-2015-0009

[121] Regulation (EC). No 1223/2009 of the European Parliament and of the Council, of 30 November 2009, on Cosmetic Products. Off. J. Eur. Union 2009. ANNEX II, p. 32. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009R1223 (Accessed on August 30, 2022)

[122] ASEAN definition of cosmetics and illustrative list by category of cosmetic products. https://www.aseancosmetics.org/docdocs/technical.pdf (Accessed on August 30, 2022)

[123] R. Feizi, N. Jaafarzadeh, H. Akbari, S. Jorfi, Evaluation of lead and cadmium concentrations in lipstick and eye pencil cosmetics, *Environmental Health Engineering and Management Journal* **6** (2019) 277-282. http://dx.doi.org/10.15171/EHEM.2019.31

[124] Regulation (EC). No 1223/2009 of the European Parliament and of the Council, of 30. 11. 2009, on Cosmetic Products. Off. J. Eur. Union 2009. ANNEX II, p. 26. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009R1223 (Accessed on August 30, 2022).

[125] D. Zhao, J. Li, C. Li, A.L. Juhasz, K.G. Scheckel, J. Luo, H.B. Li, L.Q. Ma, Lead relative bioavailability in lip products and their potential health risk to women, *Environmental Science and Technology* **50** (2016) 6036-6043. http://dx.doi.org/10.1021/acs.est.6b01425

[126] FDA. Lipstick and Lead: Questions and Answers. U.S. Food and Drug Administration (FDA) (2011) http://www.fda.gov/cosmetics/productsingredients/products/ucm137224.htm

[127] K. Goswami, Eye cosmetic 'surma': hidden threats of lead poisoning, *Indian Journal of Clinical Biochemistry* **28** (2013) 71-73. http://dx.doi.org/10.1007/s12291-012-0235-6

[128] E. Navarro-Tapia, M. Serra-Delgado, L. Fernández-López, M. Meseguer-Gilabert, M. Falcón, G. Sebastiani, S. Sailer, O. Garcia-Algar, V. Andreu-Fernández, Toxic Elements in Traditional Kohl-Based Eye Cosmetics in Spanish and German Markets, *International Journal of Environmental Research and Public Health* **18** (2021) 6109-6125. https://doi.org/10.3390/ijerph18116109

[129] P. Swetha, J. Chen, A. S. Kumar, S. P. Feng, High index facets-Ag nanoflower enabled efficient electrochemical detection of lead in blood serum and cosmetics, *Journal of*

Electroanalytical Chemistry **878** (2020) 114657. http://dx.doi.org/10.1016/j.jelechem.2020.114657

[130] Q. Fardiyah, B. Rumhayati, I. Rosemiyani, Determination of lead in cosmetic sampels using coated wire lead(II) ion selective electrode based on phyropillite, *UNEJ e-Proceeding* (2017) 270-272. https://jurnal.unej.ac.id/index.php/prosiding/article/view/4239

[131] T. M. Barros, D. M. de Araújo, A. T. L. de Melo, C. A. Martínez-Huitle, M. Vocciante, S. Ferro, E.V. dos Santos, An Electroanalytical Solution for the Determination of Pb^{2+} in Progressive Hair Dyes Using the Cork–Graphite Sensor, *Sensors* **22** (2022) 1466. https://doi.org/10.3390/s22041466

[132] Y. Shih, J. M. Zen, A. S. Kumar, Y. C. Lee, H. R. Huang, Determination of the toxic lead level in cosmetic-hair dye formulations using a screen-printed silver electrode, *Bulletin of the Chemical Society of Japan* **77** (2004) 311-312 https://doi.org/10.1246/bcsj.77.311

[133] S. Palisoc, A. M. Causing, M. Natividad, Gold nanoparticle/hexaammineruthenium/Nafion® modified glassy carbon electrodes for trace heavy metal detection in commercial hair dyes, *Analytical Methods* **9** (2017) 4240-4246 https://doi.org/10.1039/c7ay01114h

[134] J. V. Maciel, G. D. da Silveira, A. M. M. Durigon, O. Fatibello-Filho, D. Dias, Use of carbon black based electrode as sensor for solid-state electrochemical studies and voltammetric determination of solid residues of lead, *Talanta* **236** (2022) 122881. https://doi.org/10.1016/j.talanta.2021.122881

[135] Y. Yi, Y. Zhao, Z. Zhang, Y. Wu, G. Zhu, Recent developments in electrochemical detection of cadmium, *Trends in Environmental Analytical Chemistry* **33** (2022) e00152. https://doi.org/10.1016/j.teac.2021.e00152

[136] L. A. De Furtado, I. O. de Lucena, J. O. de Fernandes, F. G. Lepri, D. L. de Martins, F. S. Semaan, New strategies for the simultaneous voltammetric quantification of Pb and Zn in hair cosmetics samples employing chemically modified composite electrodes, *Journal of the International Measurement Confederation* **125** (2018) 651-658. https://doi.org/10.1016/j.measurement.2018.05.042

[137] W. Wang, N. Bao, W. Yuan, N. Si, H. Bai, Haiyu Li, Q. Zhang, Simultaneous determination of lead, arsenic, and mercury in cosmetics using a plastic based disposable electrochemical sensor, *Microchemical Journal* **148** (2019) 240-247. https://doi.org/10.1016/j.microc.2019.05.011