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Research on the Mechanism of Hair Dyeing Agents and Strategies for Health Risks Reduction

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Abstract. Hair dye is a type of special-purpose cosmetic designed to alter hair color and is classified as a special-purpose cosmetic. Its core function is to impart color to hair via chemical or physical mechanisms. In a broad sense, all products aimed at changing hair color fall under the category of hair dye. Analyses and experiments on hair dyes of different brands, colors, and types can be conducted to assess their potential harm to the human body. Such harm includes sensitization and carcinogenicity. Overall, the adverse effects of hair dyes on the human body are not inevitable and vary with individual physiological constitution. This study aims to explore the allergenicity and harmfulness of hair dyes by investigating scenarios in daily life.

Keywords: Hair dye, Sensitization, para-phenylenediamine (PPD), ImmuSkin-MT

1. Introduction

Hair dyes are special-purpose cosmetics used to change hair color. The hair color modificates through chemical or physical mechanisms. However, para-phenylenediamine (PPD) in permanent hair dyesand other ingredients have been proven to be closely related to potential health risks, including skin contact allergies, asthma, and lung function damage [1,2]. Human hair, as a human excretory tissue, has its detection technology applied in the study of heavy metal absorption and drug metabolism, providing a technical path for the in vivo exposure analysis of hair dye ingredients [1]. Although existing studies have revealed the toxicity of PPD and different types of hair dyes, there are still research gaps in the analysis of risk assessment based on new detection technology.

Against this backdrop, this study attempts to elucidate the typical application mechanisms of existing hair dyes and explores safe protection measures for hair dyeing using SERS technology and the ImmuSkin-MT model as examples. It aims to fill the existing gaps in research on hair dye mechanisms and risk assessment, providing theoretical and practical support for industry transformation and safe consumer use.

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2. Literature review

2.1. Health risk research on the core ingredients

Current research on hair dyes has established a link between their core components and potential health risks. PPD, as shown in Figure 1, which is commonly present in permanent hair dyes, has a strong protein binding ability and can cause skin contact allergies, asthma and lung function damage. PPD is a key component, which may cause skin contact allergies, asthma and impaired lung function. This substance has an extremely strong protein-binding ability and can deeply penetrate the interior of hair strands. In addition, this substance exhibits high toxicity. Both topical contact and oral ingestion can lead to toxic side effects, with the severity of harm primarily dependent on the exposure dose [2].

Studies on PPD exposure populations have focused on black and white hair from native Asian populations. Some scholars have studied PPD Asian native hair and white hair were prepared. By studying the population. From biochemical tests, hematological tests and pulmonary function tests, etc. Tests were conducted to compare different groups in terms of demographic characteristics and other factors. Ultimately, the study population was divided into three groups based on different PPD exposure concentrations. Compared with the medium and low exposure groups, the workers in the high exposure group exhibited higher levels of neutrophils and hemoglobin. The conclusion is that workers exposed to high-concentration crystalline silica have reduced lung function indices and a decline in health-related quality of life [2].

2.2. Study on different types of hair dyes

Among the types of semi-permanent hair dyes, basic hair dyes are a type of hair dye containing cationic basic pigments. Basic hair dyes are direct dyes. Notably, they do not require PPD, hydrogen peroxide, or alkaline agents to achieve dyeing effects. Instead, they directly attach alkaline pigments to the hair surface in a colored form, thus avoiding oxidative damage to hair and skin while featuring a straightforward application process [3]. Three types of basic hair dyes, namely cationic basic hair dye (CBD), nonionic basic hair dye (NBD), and anionic basic hair dye (ABD) have been investigated. Both white hair (WH) and black hair (BH) were dyed with the three basic hair dyes.Visually, the color of the white hair dyed with the three basic hair dyes was lighter than that of the black hair dyed with the same dye. The color of the hair varied depending on the type of basic hair dye, and this variation was more pronounced in white hair. Regardless of hair type, NBD resulted in the darkest color, while ABD produced the lightest color [4].

As shown in Figure 1, detection technologies (GC-MS, LC-MS, and TXRF) are applied to studies on heavy metal absorption and drug delivery, providing a basis for tracking hair dye ingredients. However, existing research still needs further exploration in using novel analytical techniques to elucidate the interaction mechanisms between hair dye ingredients and hair, and in assessing the sensitization of hair dye products through in vitro skin models.

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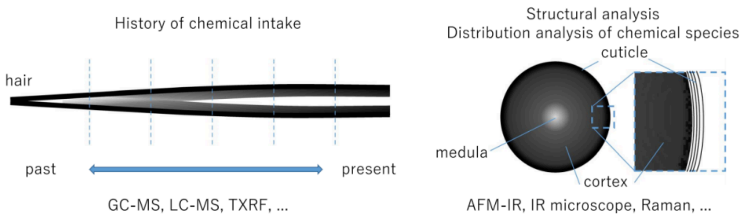

Figure 1. Hair detection technologies for chemical intake history and structural analysis(2024) [1]

3. The chemical mechanism of hair dye

The chemical principle of hair dye is that alkaline substances open the cuticles of hair, enabling dye precursors and oxidants to undergo oxidative polymerization within the hair shaft to form macromolecular pigments, thereby altering the color of the hair. The active ingredients, typically ammonia, hydrogen peroxide, and dye precursors such as PPD, each perform distinct roles at the molecular level.

3.1. Mechanism of action of hair dye

Permanent hair dyes mainly refer to those that use dye intermediates and dyes.Under the action of oxidants, the mixture undergoes coupling reactions to form large-molecule dyes. The main components of dye intermediates include phenol- or aniline-based compounds such as para-phenylenediamine and para-aminophenol [5].

The epidermis (outermost layer of hair fibers) is covered with numerous cuticles, which consist of scale-like or tile-like cells and protect the inner structure of the hair. The cortex layer is closely wrapped around the medulla and is the main component of hair fibers. The amount of cortex fibers directly determines the thickness of the hair [5].

When the alkaline agent interacts with hair, after the alkaline agent comes into contact with the hair, it creates alkaline conditions to open hair cuticles. Hydrogen peroxide, dye precursors, and other small molecules in the dye penetrates the cortex and medulla. The oxidant (typically hydrogen peroxide) undergoes a chemical reaction with the chromogenic agent (such as para-phenylenediamine, etc.) in the cortex layer. After a series of reactions such as oxidation, coupling, and condensation, colored macromolecular dye molecules are formed. Once the reaction is complete, the residual components of the hair dye on the hair surface are rinsed off, and the pH of the hair strands returns to a normal range. The cuticles will close again, and at this point, the dye macromolecules will be firmly entrapped in the hair, causing it to display different colors. It is precisely because the cuticles on the hair open during the hair dyeing process that small molecules enter the interior of the hair strands and undergo coupling reactions to form large molecules. These large molecules are not easy to pass through the cuticles, making the dyed hair less likely to fade [5].

3.2. Characteristics of different types of hair dyes

As the average individual loses approximately 100 hairs per day,which given the high prevalence of regular hair dye use, confirmatory analysis of hair dyes of highly valuable in forensic investigations of hair evidence [6]. However, most of the current methods for hair dye analysis are invasive, destructive or unreliable.

Plant-derived hair dyes are generally categorized into two types: dye bases and metal ion-containing bases. The main components of dye matrices include surfactant solvents, natural plant

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dyes, antioxidants, thickeners, inhibitors, chelating agents and fragrances, etc. The most critical component in dye matrices is natural plant dyes. Currently, in industrial production, the primary extraction techniques for natural plant dyes include water immersion extraction, organic solvent extraction, ultrasonic-assisted extraction, and microbial fermentation [5].

Biological dyes can be directly adhered to hair for coloring. Under typical conditions, they are formulated with antioxidants, thickeners, inhibitors, chelating agents, preservatives and fragrances [5]. However, given consumer preference for easy-to-use, fast-coloring products, the current research focuses on integrating biological dyes with shampoos or conditioners to develop multifunctional hair dye products that possess both shampooing and hair care capabilities.

3.3. Hair dye testing technology

3.3.1. ImmuSkin-MT in vitro sensitization test model

Based on this skin replacement model (RHS) generated from hair follicle cells, a co-culture system is developed which called ImmuSkin-MT model. It combines with two key immune cell types - Langerhans cells and T lymphocytes, using hair follicle cells as seed cells, a skin substitute model (encompassing the epidermis and dermis) was constructed in vitro. The classification of sensitizers (e.g., extreme, strong) and their grouping criteria grouping and basis of sensitizers, such as extremely strong and strong, are helpful for eliminating interference.

RHS is placed on the gel containing MoLCs to form a three-layer structure comprising the epidermis, dermis and immune layer. Exogenous substances with varying skin sensitization potentials are topically applied to the skin model. 5 micromoles of 2, 4-dinitrochlorobenzene (DNCB) and 10 micromoles of para-phenylenediamine were used as extreme skin sensitizers, 300 micromoles of isoeugenol as a strong sensitizer, and 250 micromoles of resorcinol as a moderate sensitizer. 500 micromoles of glycerol are used as a non-sensitizing agent, and 0.1% dimethyl sulfoxide (DMSO) was used as the solvent for the negative control [7].

Since the ImmuSkin-MT construct mimics the essential characteristics of the skin immune system, such as the dendritic cell layer and the interaction ability between antigen-presenting cells and T lymphocytes, researchers investigates whether this model could also recognize skin allergens.The model successfully simulates type IV hypersensitivity reactions that occur after contact with allergens, with typical symptoms including itching, erythema, blisters and desquamation [7].

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3.3.2. SERS

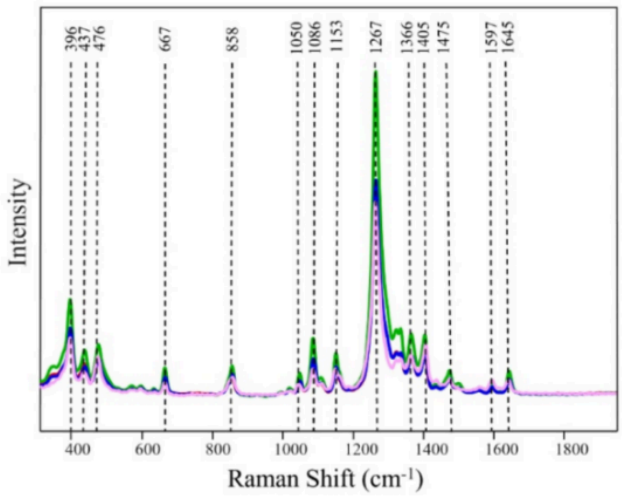

Figure 2. For single-color and dual-color dyes applied to hair: normalized and baseline-corrected surface-enhanced Raman spectra (2023) [6]. X-axis: Raman Shift (cm^{-1}); Y-axis: Intensity

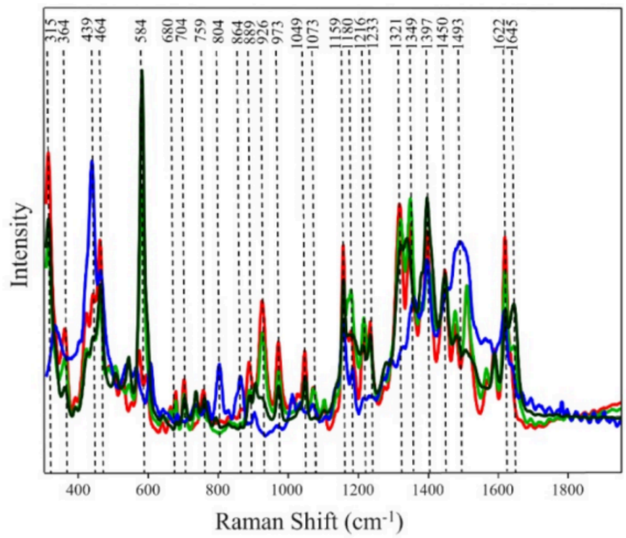

Figure 3. Normalized and benchmarked surface-enhanced Raman spectra of monochromatic and dichromatic hair dyes of different brands, types and colors.(2023) [6]. X-axis: Raman Shift(cm-1)Y-axis: Y-axis: Intensity

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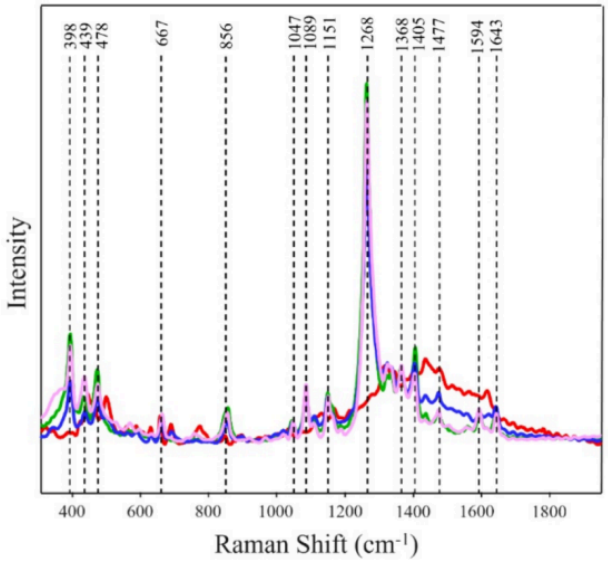

Figure 4. Normalized and baseline-corrected surface-enhanced Raman spectroscopy (SERS) spectra of single-color and dual-color hair dyes from different brands on hair.(2023) [6]. X-axis: Raman Shift(cm-1) Y-axis: Intensity

Surface-enhanced Raman spectroscopy (SERS) is a minimally invasive, rapid and highly accurate technique that can be used to identify hair dyes on hair. SERS can achieve nearly 100% accuracy in identifying hair dyes of different colors. The same accuracy is also observed for different brands and types of hair dyes [7].

The SERS spectra of different dyes exhibit unique characteristic vibration peaks (i.e., 'spectral fingerprints'). It can reveal the order of application of two hair dyes, and can trace the complete dyeing history even if the hair has been dyed with multiple hair dyes (Figure 2, Figure 3) [6]. The characteristic peaks of ISPu are concentrated at 16 wavenumber positions such as 364, 437, and 531 (Figure 4). The WSPu shows distinct signals at 10 wavenumbers such as 395, 475, and 667. Figure 4 shows the surface-enhanced Raman spectra (SERS) of these four hair samples.

Spectral analysis has been widely applied and widely trusted in forensic toxicology, geology and pathology. One method that has begun to attract the attention of forensic professionals is high-throughput, non-destructive and non-invasive ERS. Surface-enhanced Raman spectroscopy is a technique that can amplify Raman spectral signals [8]. SERS can reveal the history of hair dyeing, including the color, brand and type of hair dye used. The study also found that the spectral fingerprints of re-dyed hair largely correspond to one of the two hair dyes used. This can be explained by the fact that the Raman cross-sections of the dyes in such hair dye pairs differ. Therefore, in the SERS spectra of hair containing two dyes, the dye with the larger Raman cross-section dominates the signal. It can be expected that the above SERS-based method will require a library of hair dyes containing two and three dyes simultaneously present on the hair in forensic applications to achieve reliable and accurate determination of the hair dyeing history [6].

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4. Health effects of hair dye

4.1. Direct health risk of sensitization damage

PPD is a common ingredient in hair dyes, which can cause skin contact allergies and asthma, accompanied by impaired lung function. Occupational exposure to para-phenylenediamine may be associated with impaired lung function, reduced health-related quality of life, and subjective pruritus in workers [2].

4.2. Exposure-specific risks in the occupational population

Occupational exposure to para-phenylenediamine (PPD) may cause health problems such as skin allergies and alterations in lung function. However, most previous studies have focused on the general population or emergency cases, while studies on the occupational population have been limited to individual case reports of hairdressers [2].

4.3. Properties and risks of surfactants and hair dyes

The expriement has proved that hair dyes are associated with a certain increase in the risk of cancer and allergies [4]. Hair dyes can be categorized into permanent and semi-permanent types. The degree of hair damage varies. Their chemical components exhibit significant differences in the mechanisms and extent of damage to the hair cuticle and cortex, permanent hair dyes, containing oxidizing agents (such as hydrogen peroxide) and aromatic amines (such as p-phenylenediamine), pose a relatively higher risk of damaging hair structure.

5. Discussion

Hair dyes typically contain PPD, and this compound is associated with various adverse health outcomes. And it will also cause damage to the hair itself. Nowadays, many stores will first apply some scalp protection spray to customers prior to dyeing. To mitigate these risks, scalp protectants are sprayed on consumers before dyeing to physically block the penetration of chemicals into the scalp. And the barber will also wear gloves to provide physical protection against chemical exposure. They wear protective gloves and masks to avoid direct skin contact and inhalation of volatile components, thus establishing a basic physical protection system.

Meanwhile, the optimization and upgrading of hair dye formulations becomes a trend in the industry. The environmentally friendly, low-irritant raw materials have gradually become the core research topics, which reduce the potential health risks and environmental impacts of traditional hair dyes, providing technical support for the safe use of hair dyes.

6. Conclusion

Bioenzymatic catalysis technology is gradually replacing traditional ammonia-based components in hair dyes, enabling simultaneous dyeing and hair care. The demand for trendy hair colors among Generation Z has driven explosive growth in new products, including temporary hair dyes and highlight sprays. The adoption rate of degradable packaging materials has significantly increased. Technological iteration is driving the industry to transform from traditional chemical-based products to natural and intelligent alternatives. It should also promote green and sustainable development, rendering hair dyes more biocompatible and less harmful to the human body. Bleaching hair is more

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damaging to hair quality than dyeing it. So it can be said that future development will undoubtedly be more hair-friendly.

The study also has limitations. It focuses on primary models without considering economic, customer preferences and other factors. Future studies should combine in vitro models with population-based empirical research, integrate economic and market factors, and focus on environmental impacts and individual differences to promote the hair dye industry's green and safe development.

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