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HARMFUL EFFECT OF HAIR DYE AND DIFFERENT ANALYTICAL TECHNIQUES TO DETECT HAZARDOUS ELEMENTS IN HAIR DYE

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ABSTRACT

This report provides a concise overview of hair coloring practices, focusing on the types of dyes used, including metallic, natural, temporary, semi-permanent, and permanent dyes. Emphasis is placed on the mechanism of permanent dyes, highlighting key components like dye precursors, oxidizing agents, and ammonia. Safety considerations, such as the need for patch tests due to allergenic potential, are discussed. Analytical techniques for quantifying dye components and detecting heavy metals are explored. The report aims to enhance understanding of hair dye chemistry, safety measures, and health implications within the context of hair coloring practices.

INTRODUCTION

Hair Dye Overview

Hair coloring, whether to cover grays or for a new look, involves various types of dyes, including metallic, natural, temporary, semi-permanent, and permanent. Each type works differently and has its own set of ingredients and application methods.

1. Permanent Hair Dye

Permanent dyes use oxidation to change hair color permanently. They contain colorless dye precursors like PPD, oxidizing agents like hydrogen peroxide, ammonia, and couplers. These dyes penetrate deep into the hair shaft, bleach the natural color, and deposit new color. Common examples include L'Oreal Excellence Cream, Revlon Color Silk, etc.

2. Demi-Permanent Hair Dye

Demi-permanent dyes are milder than permanent ones as they lack ammonia and have lower hydrogen peroxide concentrations. They deposit color molecules on the cuticle and penetrate into the hair cortex. Examples include L'Oreal Casting Cream Gloss, Just for Men, etc.

3. Semi-Permanent Hair Dye

Semi-permanent dyes contain no ammonia or hydrogen peroxide. They only deposit color on the hair's outer layer, the cuticle. They can be synthetic or natural, with examples like Garnier Herbal Shine and Henna. Natural options like Henna generally do not contain harmful chemicals like PPD.

4. Temporary Hair Dye

Temporary dyes consist of large molecules that sit on the hair surface and wash out quickly, typically within one shampoo. They do not penetrate the hair shaft.

- Harmful Chemicals

Heavy metals like Cobalt, Nickel, Chrome, Arsenic, Mercury, Cadmium, Antimony, and Lead are sometimes present in hair dyes. These can be absorbed through the skin and cause various health issues. Monitoring heavy metal content in hair dyes is essential for public health.

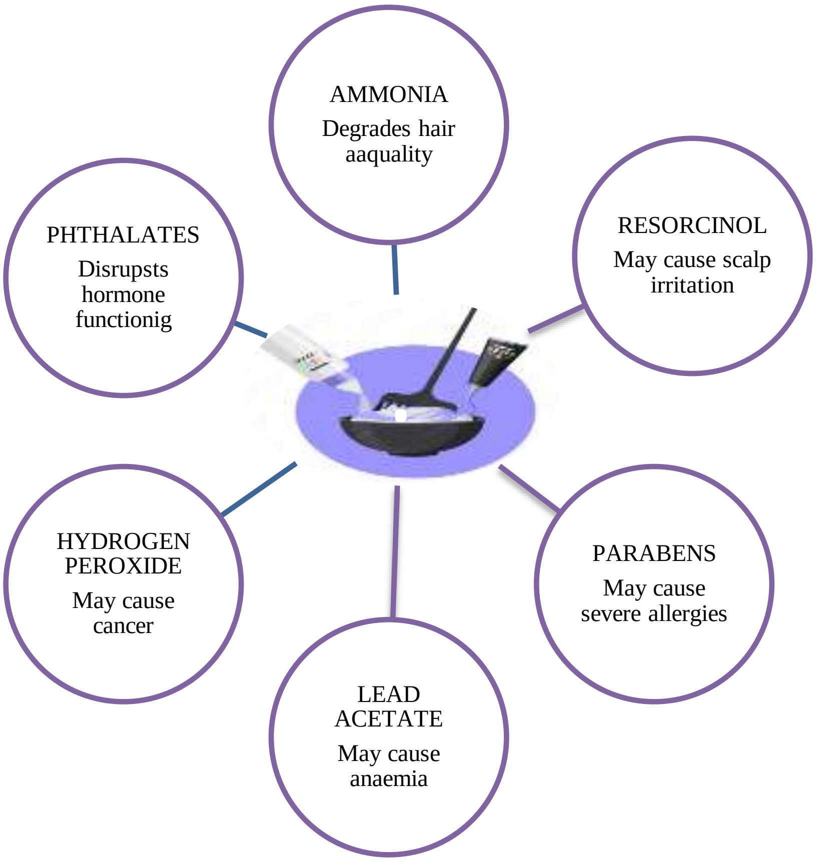

Fig: Toxic ingredients in Hair Dye

Ammonia
- Alkali used to raise hair pH for color deposition.
- Inhalation causes irritation to mucous membranes and can lead to suffocation.
- Skin contact results in blisters, redness, and potential lung problems.
- Prolonged use may disrupt liver function.

Resorcinol
- Reacts with peroxide for permanent hair color.
- Toxic in higher doses, affecting the central nervous system and respiratory function.
- Disrupts thyroid function, potentially causing goitre.
- Acute irritant to eyes; toxic if orally consumed.

Parabens
- Synthetic preservatives for shelf life extension.
- Easily absorbed through skin and metabolized.
- Can cause scalp drying, irritation, color fading, and hair loss.
- Mimics estrogen, linked to hormone disruption and cancer growth.
- Associated with fertility problems and preterm births.

Lead Acetate
- Present in dark-colored hair dyes, potentially carcinogenic.
- Prolonged exposure leads to brain and nerve damage.
- Hairstylists also at risk due to daily exposure.

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Hydrogen Peroxide

- Bleaching agent to remove natural hair pigment.
- Incorrect usage may cause rashes, allergic reactions, hair loss, and scalp burns.

Phthalates

- Hormone-disrupting chemicals used in hair products.
- Disrupt hormonal balance by blocking or mimicking hormones.
- Affect body's natural hormone actions.

Table 1: Major Hair Dye Chemicals & its toxicity

Compound	Toxicity
N,N-bis(hydroxyethyl)-p-phenylenediamine 5 sulphate salt:	Reduced body weight, Darkened thyroid glands, Decreased serum iron concentration, Delayed hypersensitivity, Allergic contact dermatitis.
N-phenyl-p-phenylenediamine 4, N-phenyl-p-phenylenediamine HCl:	Reduced body weight, Degenerated seminiferous tubules, Skeletal malformations, Skin irritation.
Hydroxypropyl bis (N-hydroxyethyl-p-phenylenediamine) 6 HCl	Reduced body weight, Alteration in serum glucose and total protein levels, Reproductive and developmental toxicity.
Methoxy-m-phenylenediamine 8, 4-methoxy-m-phenylenediamine sulphate salt, 4-methoxy-m-phenylenediamine HCl	Skin irritation, Mutagenicity.
2-chloro-p-phenylenediamine 7, 2-chloro-p-phenylenediamine sulphate salt	Skin irritation, Reduced body weight, Ocular irritation.
2-methyl-5-hydroxyethylaminophenol	Skin irritation, Mutagenicity, Allergic contact dermatitis.
p-methylaminophenol sulphate salt	Increased formation of methemoglobin, Skin irritation.
2,4-diaminophenol dihydrochloride salt	Skin irritation,Severe ocular irritation, Mutagenicity.
Hydroquinone	Nephrotoxicity, Cytotoxicity, Skin irritation and sensitization, Mutagenicity, Skin depigmentation.
t-butyl hydroquinone	Reduced body weight, Mutagenicity.
Toluene-2,5-diamine sulphate salt	Skin irritation and sensitization, Ocular irritation, Reproductive toxicity, Skeletal malformation.
Toluene-3,4-diamine	Duodenal lesions, Genotoxicity, Skin sensitization.

Hair Dyes and Cancer Risk

Researcher Study

Researchers investigate the potential link between hair dye use and cancer through lab studies and studies in people. Lab studies show certain ingredients in hair dyes can cause cancer in animals when given in large doses over time. Studies in people focus on bladder cancer, blood cancers (leukaemia and lymphoma), and breast cancer.
Personal hair dye use before and after 1980 is often distinguished due to changes in dye formulations.

Lab Studies

Some hair dye ingredients, including aromatic amines, have shown carcinogenic properties in animals, but the relevance to human exposure is unclear.

Studies in People

Hairdressers and barbers exposed at work show a slight increase in bladder cancer risk, but this link is inconsistent in those who dye their hair personally.

Mixed results regarding blood cancer risks, with some studies indicating increased risks, particularly with early or darker dye use.
Conflicting findings on the association between personal hair dye use and breast cancer risk, with some recent studies suggesting a possible link.

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Expert Agency Evaluation
The International Agency for Research on Cancer (IARC) classifies workplace exposure in hairdressing as "probably carcinogenic to humans" for bladder cancer, but personal hair dye use is "not classifiable" for cancer risk.
The US National Toxicology Program (NTP) has not classified hair dyes' potential to cause cancer but identified some dye chemicals as "Reasonably Anticipated to be Human Carcinogens."

ANALYTICAL METHODS

1. Atomic Absorption Spectrometry (AAS)

Principle
Atomic absorption spectroscopy (AAS) is a technique in analytical chemistry that quantitatively measures the concentration of chemical elements by detecting the absorption of light by free atoms in a gaseous state. It relies on the absorption of light by metallic ions and utilizes the atomic absorption spectrum of a sample to determine the concentration of specific elements. AAS requires known standards to establish a relationship between absorbance and element concentration, following the Beer-Lambert law.

Applications

- Detected heavy metals in hair dyes, indicating potential health risks.
- Used for quantifying toxic substances like chromium in hair dyes.

2. Ultraviolet Visible Spectroscopy (UV-Vis)

Principle
When ultraviolet radiation is absorbed, it causes electrons to move from their ground state to a higher energy state. The ease of electron excitation determines the wavelength of light absorbed. Chemical compounds absorbing ultraviolet light generate a unique spectrum, facilitating compound identification.

Applications

- Developed methods for detecting p-phenylenediamine (PPD) in hair dyes.
- Provided quantitative analysis of hair dye components.

3. Laser-Induced Breakdown Spectroscopy (LIBS)

Principle:
Uses high-power laser pulses to create plasma for elemental analysis. Plasma temperatures surpass 10,000 K, exciting electrons in outer orbitals. As the plasma cools, excited electrons emit photons with wavelengths related to their energy differences. Multiple excited states result in diverse emitted wavelengths for each element. Molecules within the plasma also emit photons, adding to the LIBS spectrum.

Applications

- Developed sensitive detectors to quantify chromium in hair dyes.
- Used for trace elemental analysis in synthetic hair dyes.

4. Energy Dispersive X-ray Spectrometry (EDS)

Principle
When an incident beam excites an electron in an inner shell, it can be ejected, leaving behind an electron hole. Subsequently, an electron from an outer, higher-energy shell fills this hole, emitting X-rays due to the energy difference between the two shells. An energy-dispersive spectrometer can measure the number and energy of these X-rays. The energy of the X-rays is characteristic of the difference in energy between the two shells and the atomic structure of the emitting element, enabling the measurement of the specimen's elemental composition.

Applications

- Detected elements in hair dye samples, showing presence of sulphur and other elements.
- Quantified heavy metals in hair dyes using gas chromatography/mass spectrometry (GC/MS) and EDS.

5. Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Principle
The fundamental principle involves applying plasma energy externally to a sample, exciting its constituent elements. As the excited atoms return to lower energy states, emission rays are released. A spectrometer determines the emission rays corresponding to specific photon wavelengths. The element type is identified based on the position of the photon rays, while

Applications
- Determined heavy metal concentrations in hair dyes, assessing health risks.
- Detected arsenic, chromium, nickel, and lead in hair dye samples.

6. Inductive Coupled Plasma Mass Spectrometry (ICP-MS)
Principle
Inductively coupled plasma mass spectrometry (ICP-MS) is a highly sensitive analytical technique capable of detecting metals and non-metals at concentrations below one part per trillion (ppt). It combines an inductively coupled plasma (ICP) for ionization with a mass spectrometer for ion separation and detection. Typically, Argon is used as a carrier gas to generate the plasma. The sample ions are directed through a series of small cones into the vacuum chamber of the mass spectrometer for analysis.

Applications
- Detected heavy metals like lead, cadmium, copper, and chromium in hair dyes.
- Evaluated heavy metal content in natural pigments-based products.

7. Gas Chromatography/Mass Spectrometry (GC/MS)
Principle
Gas chromatography (GC) operates on the principle of separating a mixture into individual substances through heating. The heated gases, carried by an inert gas like helium, pass through a column. As the separated substances exit the column, they enter the mass spectrometer (MS). Mass spectrometry identifies compounds by their molecular mass. A computer stores a library of known mass spectra for comparison, aiding in compound identification. GC-MS is recognized as a definitive analytical detection method.

Applications
- Detected PPD in hair dyes, providing quantitative analysis.
- Characterized hair dye components for potential toxicity.

8. Liquid Chromatography - Mass Spectroscopy (LC-MS)
Principle
LC-MS technology involves separating components in a mixture using HPLC, followed by ionization and mass/charge ratio-based ion separation. A detector quantifies ions, with the ion source playing a vital role in efficient ion generation. Common ion sources include APCI and ESI, chosen based on the analyte's chemical nature.

Applications
- Identified dyes in hair coloring products, ensuring compliance with regulations.
- Detected and quantified hair dye components, offering a rapid and accurate method.

9. High Performance Liquid Chromatography (HPLC)
Principle
In HPLC, the sample is injected into the mobile phase flow using a syringe. Components migrate through the column at different rates due to interactions with the stationary phase. Detected substances are then analyzed by a detector, and the resulting signal is sent to the HPLC software. The software generates a chromatogram, facilitating identification and quantification of different substances.

Applications
- Estimated Bandrowski's Base in henna-based hair colors, ensuring safety.
- Developed methods for separating and quantifying dye intermediates in hair dyes.

10. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)
Principle
An attenuated total reflection accessory measures changes in an infrared beam when it interacts with a sample. The beam is directed onto an optically dense crystal, creating an evanescent wave that extends into the sample. Changes in the wave indicate sample absorption. The attenuated energy is detected, generating an infrared spectrum.

Applications
- Identified and characterized various dyes, providing valuable information without extraction.
- Determined cationic, azo, and nitroso dyes without extraction, aiding in rapid determination.

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TABLE 2: Summary of analytical methods

Heavy Metal /Harmful chem.	AAS	UV	LIBS	EDS	ICP-OES	ICP-MS	GC/MS	HPLC
Cd	✓				✓	✓		
Cr			✓		✓	✓		
Pd	✓				✓	✓		
Co	✓							
Zn	✓					✓		
Fe	✓							
Ni					✓			
Co					✓			
Cu						✓		
Ba						✓		
As						✓		
PPD		✓		✓			✓	✓

CONCLUSION

Hair dyes, containing potentially harmful components like ammonia and resorcinol, raise health concerns due to inconsistent standardization. Analytical methods, including AAS, LIBS, UV, EDX, ICP-OES, ICP-MS, GC/MS, LC-MS, HPLC, and ATR-FTIR spectroscopy, are crucial for assessing product safety. Notably, HPLC offers a cost-effective and rapid analysis, while ICP-MS ensures accuracy in toxic element assessment. These methods play a vital role in quantifying and identifying harmful components, thus safeguarding consumer health amidst rising hair dye usage. Continued research and application of these techniques remain essential for ensuring product safety.

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