

Liquid chromatography–mass spectrometry analysis of dyes formed by in situ oxidative methods then purified by absorption and extraction from hair wefts

Journal of Chemical Research
May–June 2021: 450–461
© The Author(s) 2020
Article reuse guidelines:
sagepub.com/journals-permissions
DOI: 10.1177/1747519820978621
journals.sagepub.com/home/chl



M John Plater  and Andrea Raab

Abstract

The dye mixtures formed from three commercial hair colour formers were purified by absorption onto human hair wefts, washed and dried, extracted with dichloromethane:trifluoroacetic acid (75:25) and then analysed by liquid chromatography–mass spectrometry. Only 1–2 dyes were identified from each complex mixture of commercial aromatic amines along with a broad UV absorption mainly consisting of mixtures of quaternary ammonium salts from shampoos and some surfactants. Mecetronium ethyl sulfate and didecylidimethylammonium chloride were the main ammonium salts.

Keywords

hair wefts, hydrogen peroxide, phthalate, *p*-phenylenediamine, quaternary salt

Date received: 14 August 2020; accepted: 16 November 2020

Introduction

Hair colouration is a popular fashion¹ with different colours sought after.² Modern products can be divided into two types, oxidative^{3–5} and nonoxidative,⁶ depending upon the type of chemistry that is used.¹ Permanent or oxidative hair dyeing requires three main components (Figures 1 and 2). The first is an easily oxidised electron rich aromatic amine such as *p*-phenylenediamine **1** or *p*-aminophenol **7** which is called a primary intermediate or developer.^{7–9} The second is called a coupler such as *m*-aminophenol **3**, resorcinol **5** or 4-amino-2-hydroxy toluene **10**. The electron rich groups are *meta* to each other and are not conjugated so these compounds are much less easily oxidised compared to the primary intermediate in which the electron rich groups are *para* to each other and are conjugated. The third component is an oxidant which is typically aqH₂O₂. The oxidant serves to oxidise the primary intermediates and in combination with aqNH₃, to lighten the natural hair colour.¹ Permanent hair colour formers come in two components. The first of these contains the primary intermediates with couplers in aqNH₃, and the second contains stabilised aqH₂O₂. A mixture of precursors is used, typically from four to ten. The solutions are mixed to give a suspension of pH 9.5 which is then pasted onto the hair and left for 30 min, followed by thorough washing which removes non-absorbed dye. The nature of the oxidised species formed from the primary intermediates has been considered,^{6,9–12} followed by their

electrophilic aromatic substitution with a coupler leading to the dyes. The mixtures of primary intermediates and couplers used suggest that a mixture of dyes will be formed, but this does not give information about the composition of the dyes absorbed onto hair. Here, we report our studies on the liquid chromatography–mass spectrometry (LC–MS) analysis of the dyes which have been purified by absorption onto human hair wefts and then extracted with dichloromethane:trifluoroacetic acid (75:25).

Discussion

The dyes formed from three commercial hair colour formers were analysed and a control was performed using pure *p*-phenylenediamine **1**. Commercial stabilised aqH₂O₂ in a hair packet was used for all the oxidations. These colour formers are called Honey Blonde, Light Brown Warm and Dark Brown named after the hair colours they give. Table 1 lists the different primary intermediates and the couplers present in these colour formers. Each colour former

Department of Chemistry, University of Aberdeen, Aberdeen, UK

Corresponding author:

M John Plater, Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, UK.
Email: m.j.plater@abdn.ac.uk



Creative Commons CC BY: This article is distributed under the terms of the Creative Commons Attribution 4.0 License (<https://creativecommons.org/licenses/by/4.0/>) which permits any use, reproduction and distribution of

the work without further permission provided the original work is attributed as specified on the SAGE and Open Access pages (<https://us.sagepub.com/en-us/nam/open-access-at-sage>).

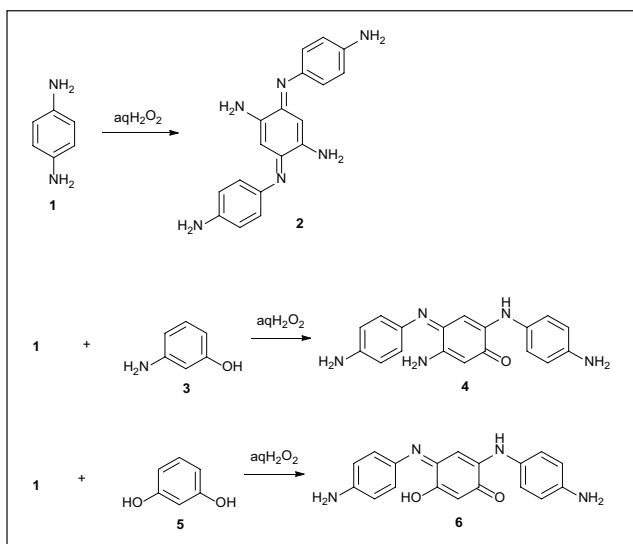


Figure 1. The formation and structure of some common hair dyes **2**,^{5,8} **4**^{5,13} and **6**,^{5,14,15} requiring a primary intermediate only or both a primary intermediate and a coupler.

contains from five to seven precursors. Honey Blonde, Light Brown Warm and Dark Brown each contain two primary intermediates. Clearly, a multiple number of dyes might be produced from these precursors and might be more than necessary or give a range of possible shades. These amines are toxic aromatic amines which some people can have an allergic reaction too and this is an interesting pathway for the industry to have developed. This project provides an understanding of which dyes are selectively absorbing onto the hair wefts so might help influence or simplify the design of the colour former packs.

LC-MS analysis of the dyes extracted from hair wefts dyed from Honey Blonde, Light Brown Warm and Dark Brown commercial colour formers and a control

The experimental method was much the same as that used with the commercial hair colour former packet and is described in the experimental section. *p*-Phenylenediamine **1** or mixtures of commercial amines (Table 1) were mixed with the aqH₂O₂ in a beaker and the hair was mixed in. After washing the hair and drying, it was extracted with dichloromethane:trifluoroacetic acid (75:25) which was allowed to evaporate. The extract was then dissolved in MeOH and prepared in a sample vial. Figure 3 shows the LC-MS chart for the control, and Figures 4–6 show the LC-MS charts for the Honey Blonde, Light Brown Warm and Dark Brown commercial colour former packets, respectively. The LC-MS charts show the UV absorption at 230 nm in black and the horizontal axis is the retention time. The vertical axis has two scales on it. The UV axis is in mAU, and the mass spectral scale is in electro spray mass spectrometer (ES-MS) counts. All the absorption peaks are

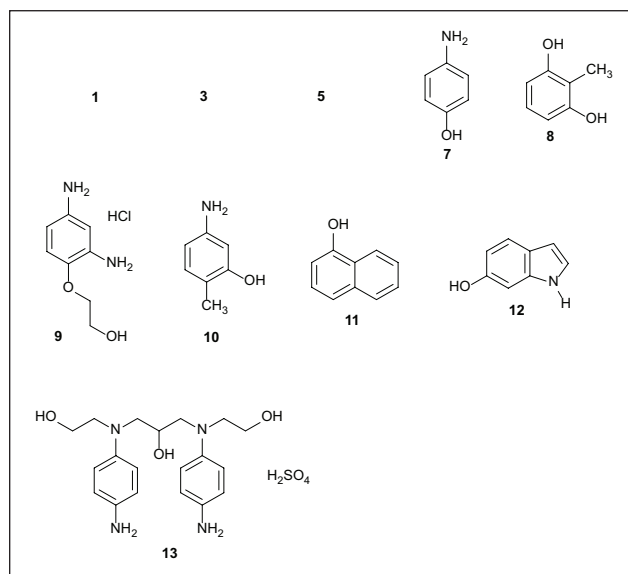


Figure 2. The primary intermediates and couplers present in some different hair colour formers **1**, **3**, **5** and **7–13**.

Table 1. Table of the amines present in each hair colouration pack. The colours are taken from the colours on each hair colour former packet. Compounds **1**, **7** and **13** are primary intermediates and the rest are couplers.

Compound	Honey Blonde	Light Brown Warm	Dark Brown
1	X	X	X
7	X	X	
3	X	X	X
5	X	X	X
8		X	
9			X
10		X	
11		X	
12	X		
13			X

presented as an accurate mass in the mass spectral data. The neutral dyes all appear as (M + H). Figure 3 shows the LC-MS analysis of the hair extract formed from the in situ oxidation of *p*-phenylenediamine **1** with aqH₂O₂. A strong absorption occurs at *m/z* 319.1666 (M + H) (calculated *m/z* 319.1666). This is assigned as compound **2**^{5,8} (Figures 1 and 7). This control experiment is useful as it verifies that the method of oxidation, absorption and extraction is working. In the retention time range 2–12 min, a broad UV absorption is present with no defined or separated absorption peaks. Luckily, the desired dyes elute faster than this complex material and are free from it. This material is analysed shortly.

Figure 4 shows the LC-MS analysis of the hair extract formed from the in situ oxidation of the commercial colour former Honey Blonde with aqH₂O₂. A strong absorption occurs at *m/z* 321.1347 (M + H) (calculated *m/z* 321.1346). This is assigned as the known compound **6**^{5,13,14} (Figure 7).

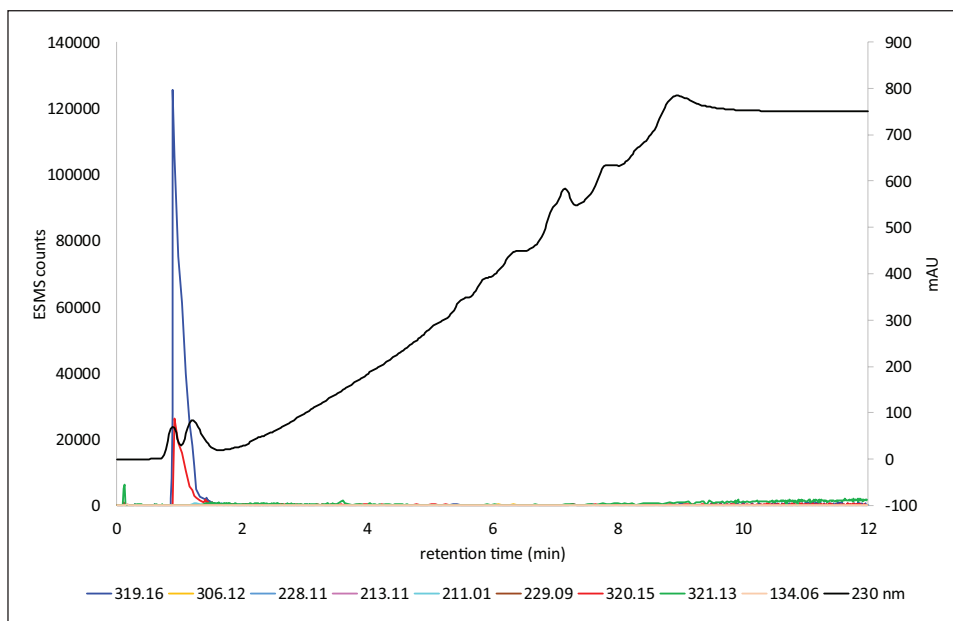


Figure 3. LC-MS gradient 1 chart 1 of dye **2** extracted from hair wefts with dichloromethane:trifluoroacetic acid (75:25). The dye was absorbed onto the hair by the in situ oxidation of *p*-phenylenediamine **1** with commercial hair packet aqH₂O₂ (1:1).

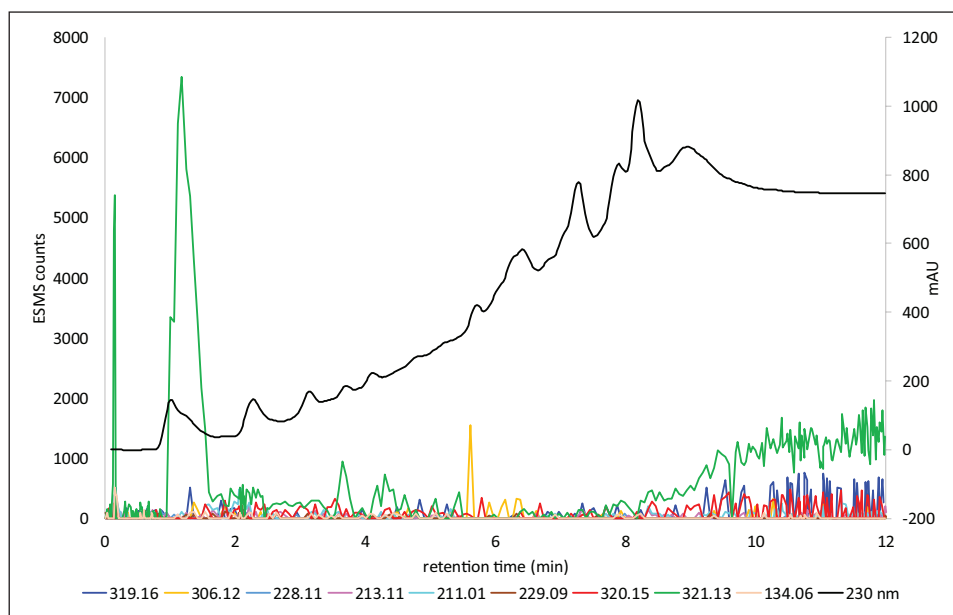


Figure 4. LC-MS gradient 1 chart 1 of dye **6** extracted from hair wefts with dichloromethane:trifluoroacetic acid (75:25). The dye was absorbed to the hair by the in situ oxidation of a commercial Honey Blonde hair colour former with aqH₂O₂ (1:1).

Figure 5 shows the LC-MS analysis of the hair extract formed from the in situ oxidation of the commercial colour former Light Brown Warm with aqH₂O₂. A strong absorption occurs at *m/z* 320.1507 (*M* + *H*) (calculated *m/z* 320.1506) and *m/z* 319.1666 (*M* + *H*) (calculated *m/z* 319.1666). These are assigned as the known compounds **4**^{5,15} and **2**, respectively, (Figure 7).

Figure 6 shows the LC-MS analysis of the hair extract formed from the in situ oxidation of the commercial colour former Dark Brown with aqH₂O₂. A strong absorption occurs at *m/z* 321.1347 (*M* + *H*) (calculated *m/z* 321.1346) and *m/z* 320.1507 (*M* + *H*) (calculated *m/z* 320.1506).

These are assigned as the known compounds **6** and **4**, respectively, (Figure 7).

The dyes observed were weaker in intensity than expected and were swamped out by much stronger chromophores, hence the need to analyse the data in stages. The number of dyes observed, three in total, was much less than expected and many more must surely form. These are the known compounds **2**,^{5,8} **4**^{5,15} and **6**^{5,13,14} shown in Figures 1 and 7. No dye was observed from primary intermediate **13** in the Dark Brown colour packet presumably because it can form a polymeric dye which did not extract or it elutes slowly because of its larger size. Dyes **2**, **4** and **6** must form

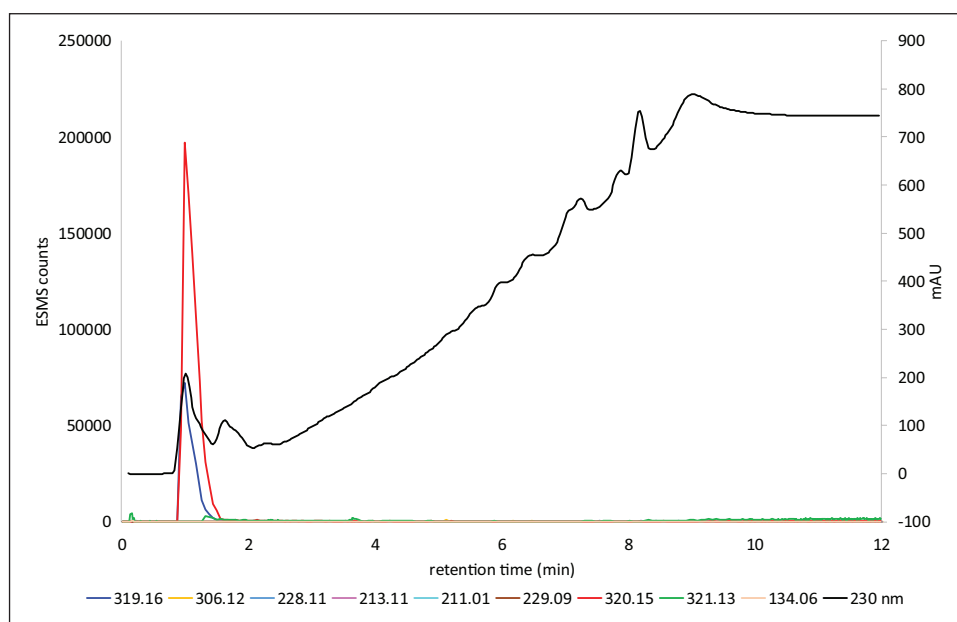


Figure 5. LC-MS gradient 1 chart 1 of dyes 2 and 4 extracted from hair wefts with dichloromethane:trifluoroacetic acid (75:25). The dyes were absorbed to the hair by the in situ oxidation of a commercial Light Brown Warm hair colour former with aqH₂O₂ (1:1).

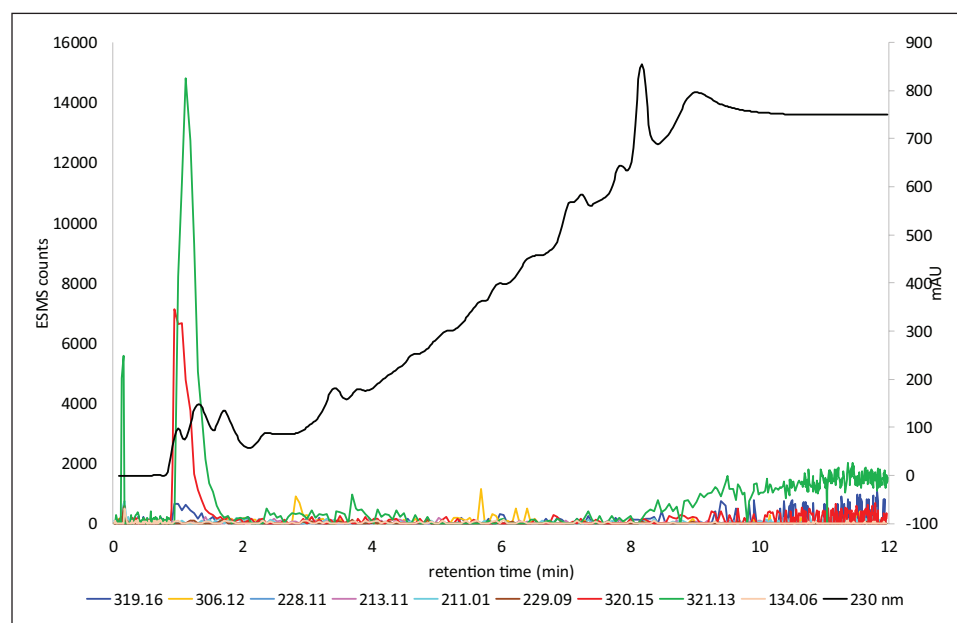


Figure 6. LC-MS gradient 1 chart 1 of dyes 4 and 6 extracted from hair wefts with dichloromethane:trifluoroacetic acid (75:25). The dyes were absorbed to the hair by the in situ oxidation of a commercial Dark Brown hair colour former with aqH₂O₂ (1:1).

efficiently and bind strongly to the hair but they can also be extracted. The extracted hair partially lightens in colour but does not lose all its colour so some compounds will still be bound in the hair. The experiment is easy to perform because the absorption onto hair is a method of purifying the dye mixture leaving behind impurities. It would not be possible to analyse the crude mixture of dyes by LC-MS without a preliminary purification so absorption of the dyes onto hair is meaningful and it provides information about which dyes are binding to the hair. The long hair wefts are easy to work with, to wash and to remove excess dye. The method of extraction of the dyes from the hair using

dichloromethane:trifluoroacetic acid (75:25) is new and also convenient as it is non-aqueous or non-nucleophilic so it will not degrade the hair or the dyes and it is also volatile so evaporates easily after the extraction has been performed. This keeps the sample treatment as simple as possible. After extraction of the hair, the solvent was evaporated at room temperature in the fume hood air flow until dry and the residue was taken up in MeOH ready for analysis in a sample vial.

Figures 8-16 show the gradient 1 LC-MS charts of Honey Blonde, Light Brown Warm and Dark Brown colour former with more information added in stages about

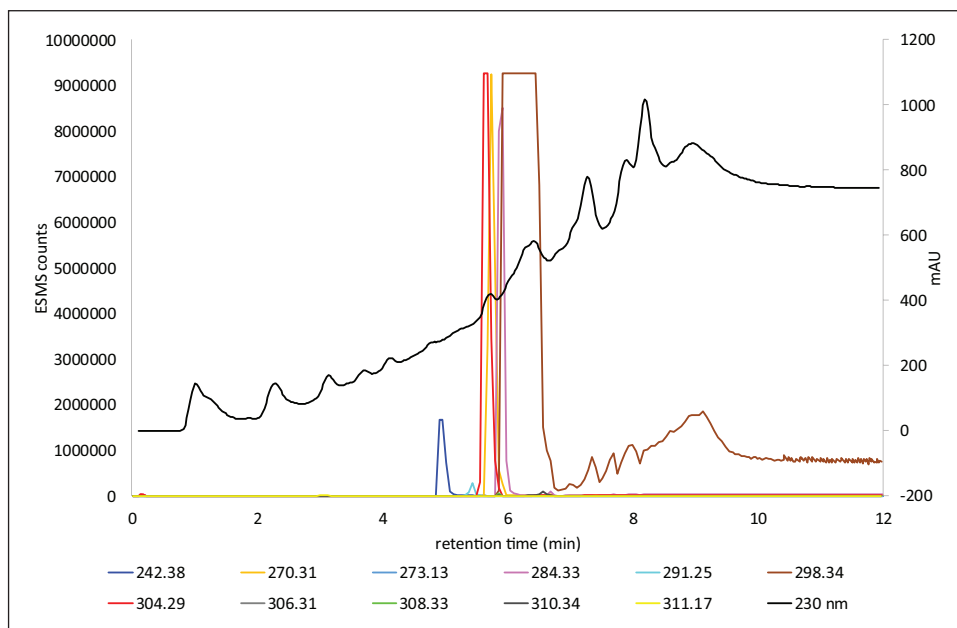


Figure 7. Summary of representative dyes proposed to form in hair colour former packets which were extracted after absorption onto hair wefts.

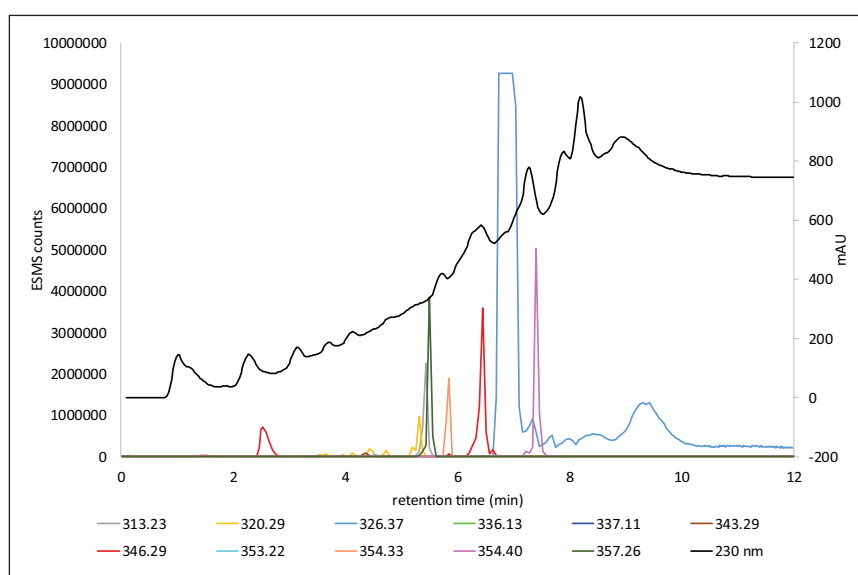


Figure 8. LC-MS gradient 1 chart 2 of Honey Blonde colour former.

the UV absorbing material. File 1 Supplemental Figures 17S–19S gradient 1 and Files 2–5 Supplemental Figures 20S–35S gradient 2 are in the Supplemental. Table 2, compounds **14–15**, shows quaternary ammonium salts identified in the extracts. More examples are in the Supplemental (Supplemental Table 1S, compounds 1S–6S). Table 3, compounds **16–19**, shows decomposition products believed to come from the quaternary ammonium salts. Table 4, compounds **20–22**, shows phthalates and Table 5, compounds **23–26**, shows miscellaneous compounds. In summary, the broad UV absorption of the LC-MS charts is dominated by quaternary ammonium salts **14** and **15** and many other compounds. These have not come from the hair colour formers according to the packet ingredients so must be already absorbed on the long human hair weft from washing with shampoos where

they are included. The absorption peaks are not scaled to ensure fine detail is seen. This work shows that quaternary ammonium salts have a high affinity for hair wefts and the number of them suggests that they absorb permanently over many years from different shampoos. Called ‘quats’ for short, quaternary ammonium compounds are used commonly in hair conditioners, shampoos and lotions to impart a slippery feel to the hair and skin.¹⁶ They allow a little dollop of conditioner to easily glide and be distributed throughout the hair. Different quaternary ammonium salts and surfactants are added to shampoos and it is possible they accumulated over a 10-year period or longer as the hair weft is 15 inches long. Some phthalates are also used in shampoos as are some of the miscellaneous compounds. The dominant quaternary ammonium salt is mecetronium ethyl sulfate **14** which has intense peaks in

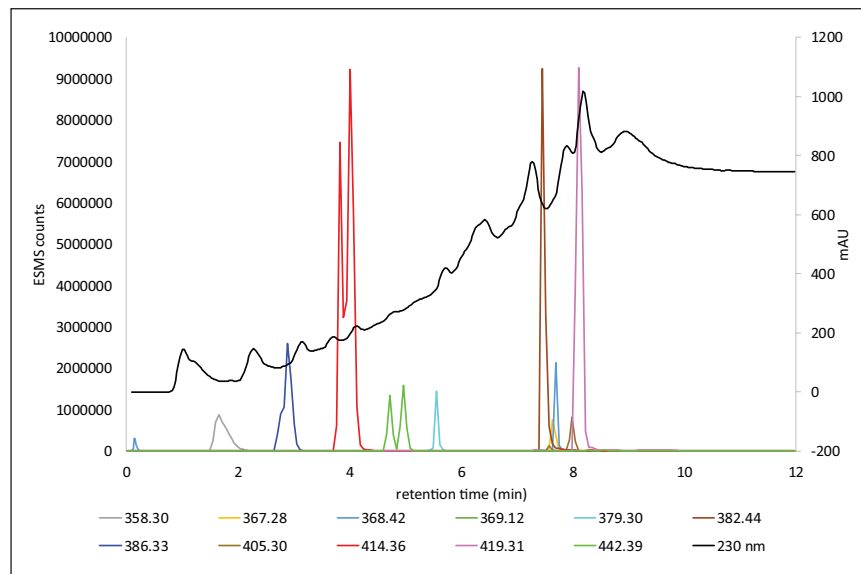


Figure 9. LC-MS gradient I chart 3 of Honey Blonde colour former.

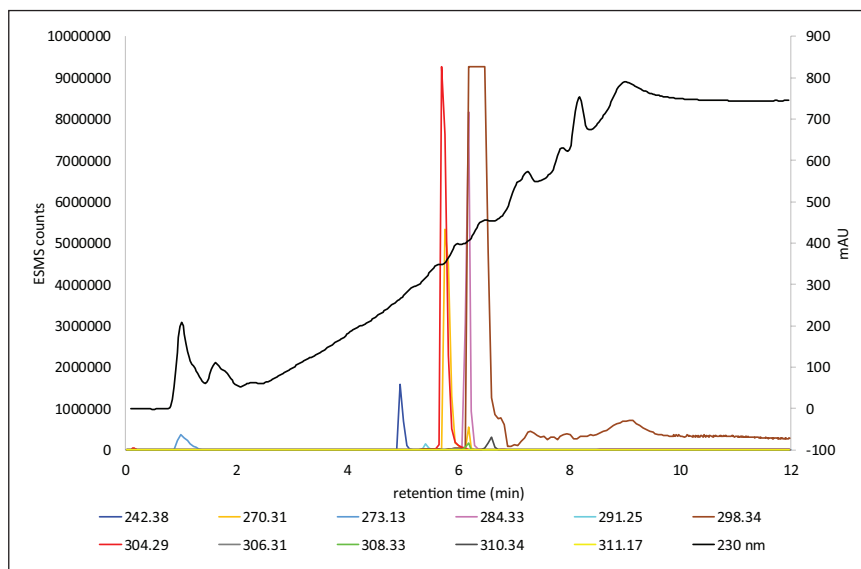


Figure 10. LC-MS gradient I chart 4 of Honey Blonde colour former.

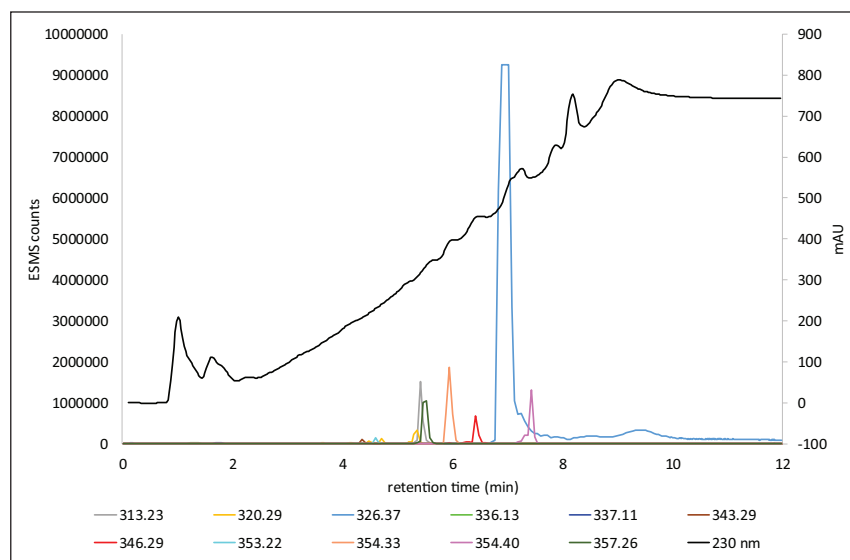


Figure 11. LC-MS gradient I chart 2 of Light Brown Warm colour former.

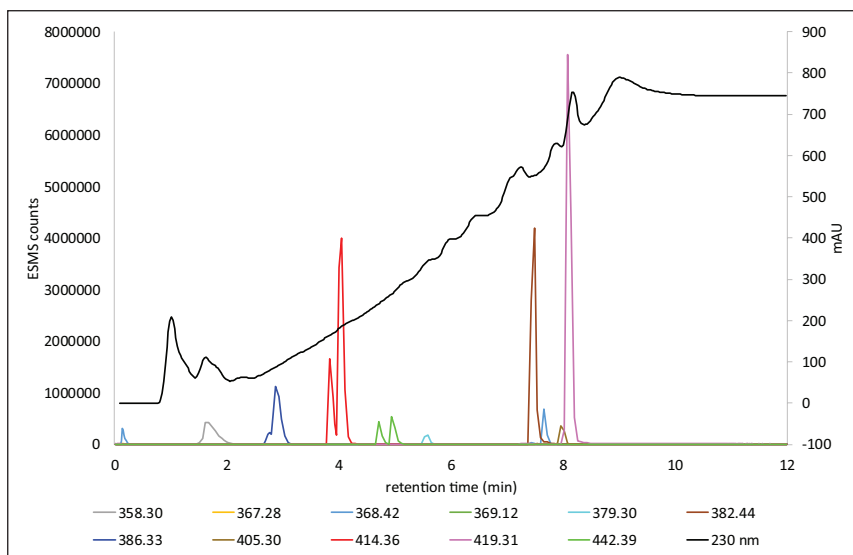


Figure 12. LC-MS gradient I chart 3 of Light Brown Warm colour former.

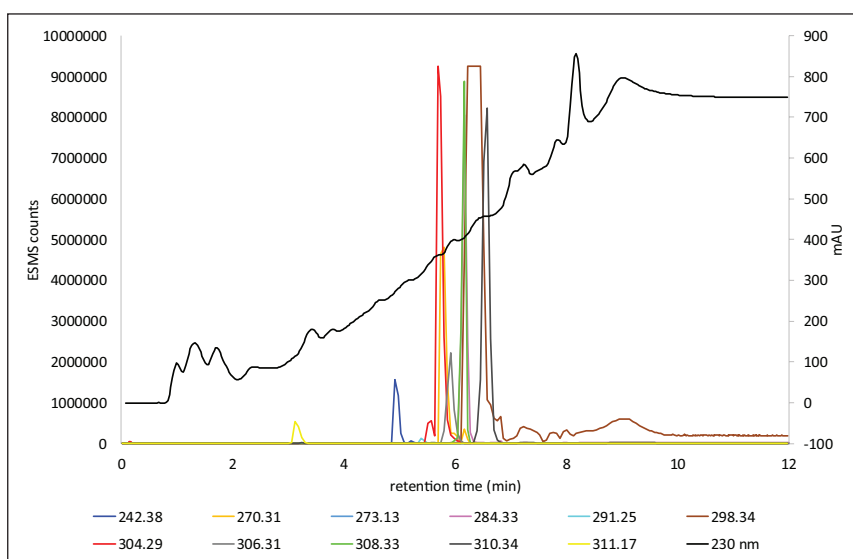


Figure 13. LC-MS gradient I chart 4 of Light Brown Warm colour former.

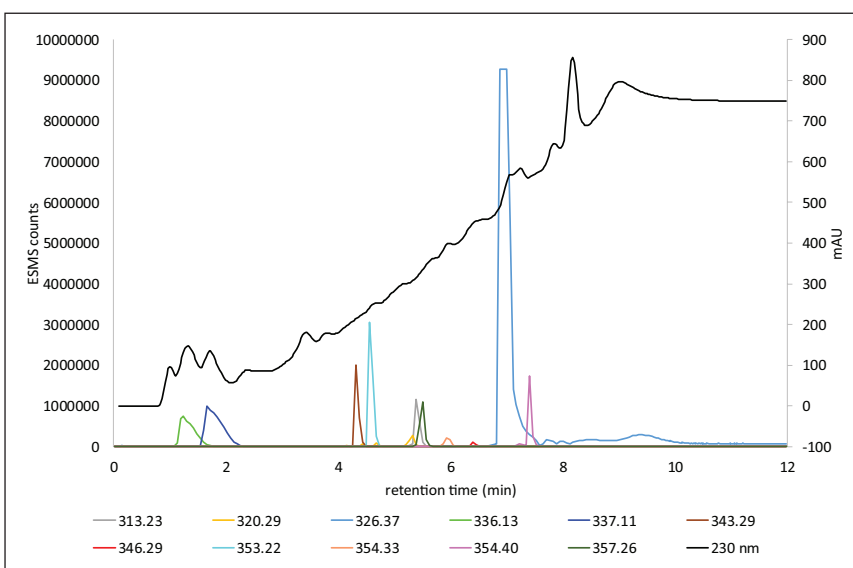


Figure 14. LC-MS gradient I chart 2 of Dark Brown colour former.

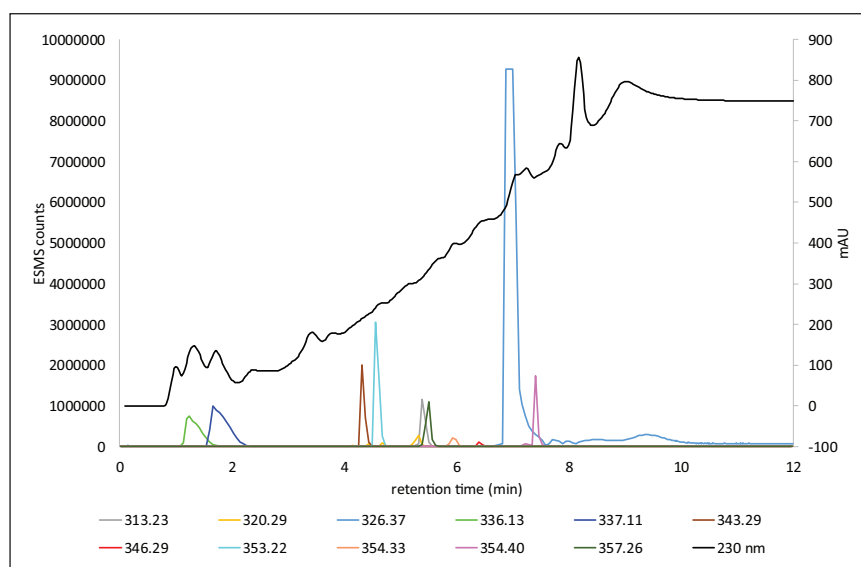


Figure 15. LC–MS gradient I chart 3 of Dark Brown colour former.

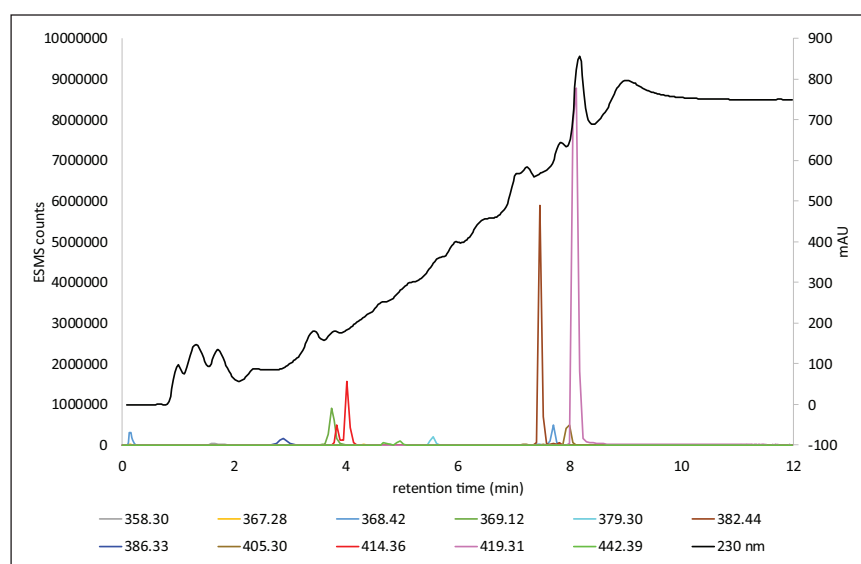


Figure 16. LC–MS gradient I chart 4 of Dark Brown colour former.

Table 2. Quaternary ammonium salts identified by LC–MS analysis of coloured hair wefts extracted with dichloromethane:trifluoroacetic acid (75:25).

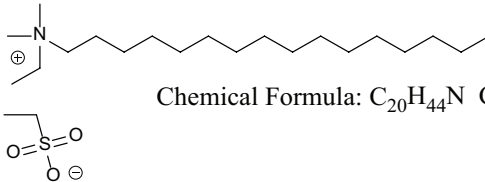
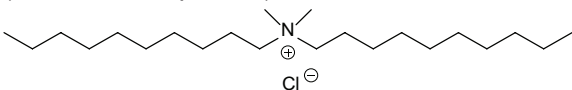
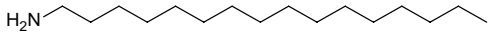
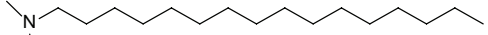
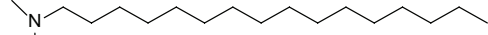
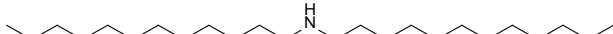
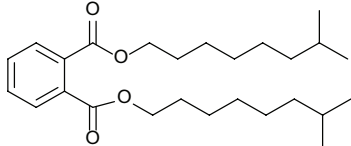
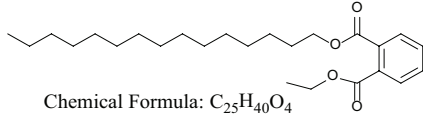
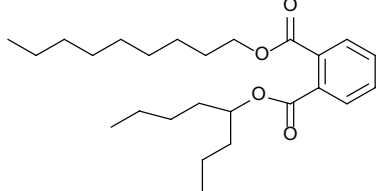
Compound	Quaternary ammonium salts identified from the LC–MS analyses	Accurate mass	Calculated mass
14	 <p>Chemical Formula: $C_{20}H_{44}N^+ C_2H_5SO_3^-$</p> <p>Ethylhexadecyldimethylammonium ethylsulfate (mecetronium ethyl sulfate)</p>	298.3471 (M ⁺)	298.3468 (M ⁺)
15	 <p>Chemical Formula: $C_{22}H_{48}N^+ Cl^-$</p> <p>Didecyldimethylammonium chloride</p>	326.3781 (M ⁺)	326.3781 (M ⁺)

Table 3. Decomposition products of quaternary ammonium salts identified by LC–MS analysis of coloured hair wefts extracted with dichloromethane:trifluoroacetic acid (75:25).

Compound	Decomposition products from quaternary ammonium salts identified from the LC–MS analyses	Accurate mass	Calculated mass
16	 Chemical Formula: C ₁₆ H ₃₅ N Hexadecylamine	242.2844 (M + H)	242.2842 (M + H)
17	 Chemical Formula: C ₁₈ H ₃₉ N Hexadecyldimethylamine	270.3155 (M + H)	270.3155 (M + H)
18	 Chemical Formula: C ₁₉ H ₄₁ N Hexadecylethylmethylamine	284.3313 (M + H)	284.3312 (M + H)
19	 Chemical Formula: C ₂₄ H ₅₁ N Didodecylamine	354.4093 (M + H)	354.4094 (M + H)

LC–MS: liquid chromatography–mass spectrometry.

Table 4. Phthalates identified by LC–MS analysis of coloured hair wefts extracted with dichloromethane:trifluoroacetic acid (75:25).

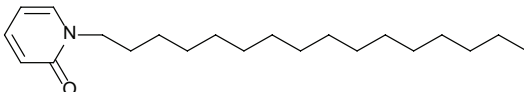
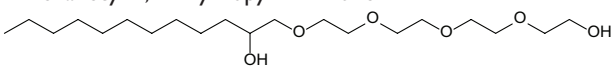
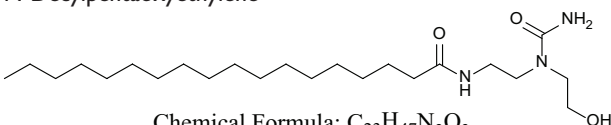
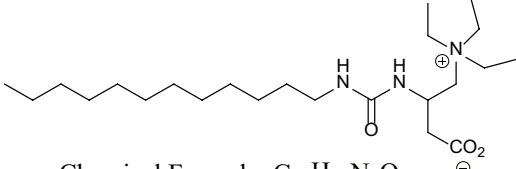
Compound	Phthalates identified from the LC–MS analyses	Accurate mass	Calculated mass
20	 Chemical Formula: C ₂₆ H ₄₂ O ₄ Isononylphthalate	419.3157 (M + H)	419.3156 (M + H)
21	 Chemical Formula: C ₂₅ H ₄₀ O ₄ Phthalic acid, ethyl pentadecyl ester	405.2998 (M + H)	405.2999 (M + H)
22	 Chemical Formula: C ₂₅ H ₄₀ O ₄ Nonyl-4-octanoyl phthalate	405.2998 (M + H)	405.2999 (M + H)

LC–MS: liquid chromatography–mass spectrometry.

Figures 8, 11 and 14 (brown trace) (M + H, 298.3471, calcd 298.3468).^{16,17} The next predominant quaternary ammonium salt is didecyldimethylammonium chloride **15**. This has strong peaks in Figures 9, 12 and 15 (light blue trace) (M + H, 326.3781, calcd 326.3781). The rest can be identified but are present in much smaller amounts and are in the Supplemental.

The strong affinity of quaternary ammonium salts for hair can be exploited for making new colour extenders.^{18,19} The study here verifies that the method has precedent and that a wide variety of quaternary ammonium salts and dyes might be exploited by covalent attachment together. The oxidative in situ formation of dyes, a commercial method which dominates supermarket shelves, remains a method

Table 5. Miscellaneous compounds identified by LC–MS analysis of coloured hair wefts extracted with dichloromethane:trifluoroacetic acid (75:25).

Compound	Miscellaneous compounds identified from the LC–MS analyses	Accurate mass	Calculated mass
23	 <p>Chemical Formula: C₂₁H₃₇NO</p> <p>1-Hexadecyl-1,2-dihydropyridin-2-one</p>	320.2948 (M + H)	320.2948 (M + H)
24	 <p>Chemical Formula: C₂₀H₄₂O₆</p> <p>N-Decylpentaoxyethylene</p>	379.3056 (M + H)	379.3054 (M + H)
25	 <p>Chemical Formula: C₂₃H₄₇N₃O₃</p> <p>N-[2-[(Aminocarbonyl)(2-hydroxyethyl)amino]ethyl]stearamide</p>	414.3691 (M + H)	414.3690 (M + H)
26	 <p>Chemical Formula: C₂₃H₄₇N₃O₃</p> <p>(3R)-3-[(Dodecylcarbamoyl)amino]-4-(triethylazaniumyl)butanoate</p>	414.3691 (M + H)	414.3690 (M + H)

LC–MS: liquid chromatography–mass spectrometry.

with some toxicity owing to the toxicity of aromatic amines and the many by-products that form. Some people experience an unpleasant inflammatory reaction, so alternative cleaner and less toxic methods of fixing dyes to hair are desirable.

The common decomposition products **16–19** in Table 3, of the quaternary ammonium salts, were also unexpected. Hexadecyldimethylamine **17** (Figures 8, 11 and 14) (orange trace) (M + H, 270.3155, calcd 270.3155) and hexadecylethylmethylamine **18** (Figure 11) (pink trace) (M + H, 284.3313, calcd 284.3312) are both decomposition products from the main quaternary ammonium salt mecetronium ethyl sulfate **14** so their occurrence together along with this salt is anticipated. The extractant is strongly acidic but the trifluoroacetate anion is non-nucleophilic and would not be expected to dealkylate the ammonium salt. Hexadecylamine **16** (Figures 8, 11 and 14) (bright blue trace) (M + H, 242.2844, calcd 242.2842) and didodecylamine **19** (Figures 9, 12 and 15) (pink trace) (M + H, 354.4093, calcd 354.4094) are present in minor amounts. Decomposition of the quaternary ammonium salts requires a dealkylation and loss of a methyl or ethyl group or possibly an aerial oxidation. Either mechanism appears to be slow or the products still bind to the hair in lesser amounts.

Phthalates were also identified as some of the components which can also be used in shampoos. Isononylphthalate **20** (Figures 10, 13 and 16) (pink trace) (M + H, 419.3157, calcd, 419.3156) and either phthalic acid ethyl pentadecyl ester **21** (Figures 10, 13 and 16) (brown trace) (M + H, 405.2998, calcd 405.2999) or nonyl-4-octanoyl phthalate

22 (Figures 10, 13 and 16) (M + H, 405.2998, calcd 405.2999) occur together as a pair at about 8.1 min. The stability of the ester to repeated washing is note worthy but the greasy chain may stabilise it, and after hydrolysis, the components may be washed off from the hair.

Miscellaneous compounds 1-hexadecyl-1,2-dihydropyridin-2-one **23** (Figures 9, 12 and 15) (M + H, 320.2948, calcd 320.2948) might be a minor decomposition product from cetylpyridinium chloride **1S** (Supplemental Figures S21, S25, S29 and S33) (red trace) (M + H, 304.2998, calcd 304.2998) because they both occur in the same three extracts in small amounts. N-Decylpentaoxyethylene **24** (Figures 10, 13 and 16) (light blue trace) (M + H, 379.3056, calcd 379.3054), N-[2-[(aminocarbonyl)(2-hydroxyethyl)amino]ethyl]stearamide **25** (Figures 10, 13 and 16) (red trace) (M + H, 414.3691, calcd 414.3690) or isomer (3R)-3-[(dodecylcarbamoyl)amino]-4-(triethylazaniumyl)butanoate **26** are all minor surfactants in the extracts.

Conclusion

The dyes formed from three commercial hair colour formers have been purified by selective absorption on long human hair wefts. After washing and drying, the dyes were extracted with a non-nucleophilic and volatile solvent mixture of dichloromethane and trifluoroacetic acid. After ambient evaporation of the extractant, the extract was taken up in MeOH with no further treatment and analysed by LC–MS. Only one or two dyes, compounds **2**, **4** or **6**, were identified

despite the more complex mixture of aromatic amines present in the starting mixtures (Table 1) which were oxidised with the aqH_2O_2 supplied. This suggests that the complex mixture of toxic aromatic amines²⁰ in cosmetic hair dye which is oxidised might be simplified with the knowledge of which dyes bind efficiently to the hair wefts. A broad overlapping UV absorption was also present which was analysed in stages because of its complexity. The broad UV absorption consisted of a number of quaternary ammonium salts, some amines formed by their decomposition, and some phthalates and miscellaneous surfactants. Health and safety data and further information on these compounds are easily found by searching the molecular formula online. Long Remy human hair wefts must absorb quaternary ammonium salts from shampoos over a number of years building up a mixture of them. Ammonium salts and other compounds bind tightly to hair wefts from shampoos and might be a basis for the development of novel colour extenders^{18,19} like anthraquinones which can disperse and bind tightly on hair wefts and polyacrylonitrile (PAN) fibres.^{21–32}

Methods

For analytical separation, an Agilent 1290 Infinity high-performance liquid chromatography (HPLC) system consisting of a quaternary HPLC pump, cooled auto sampler compartment, column compartment and diode array UV-Vis detector was used. An F5-Kintex C-18 column (2.1 mm × 150 mm, Thermo Scientific, UK) was used for the separation with an acetonitrile/methanol gradient (both 0.1% v/v formic acid) from 40% acetonitrile to 100% in 10 min with 2 min hold and then reset (gradient 1); from 5% acetonitrile to 100% in 10 min with 2 min hold and then reset (gradient 2). Data are shown in the Supplemental section (Supplemental Figures S18–S36). The flow rate was 0.5 mL min⁻¹, the column temperature was 40 °C, and the sample volume was 5 µL. The mass spectrometer (ES-MS) used was a Maxis II UHR-TOF LC-MS System (Bruker UK Ltd, UK) with electrospray ionisation (ESI) source connected to the UV-Vis detector by a short length of PEEK tubing. The ES-MS was operated in positive ion mode with a capillary voltage of 4.5 kV using sodium formate clusters for calibration and methyl stearate as lock mass. Mass spectra were recorded automatically. Long blonde human hair wefts (15 inches) from China were purchased from Remy and were used for dyeing in accordance with the relevant guidelines and regulations of the University of Aberdeen Health and Safety committee.

LC-MS analysis of the dyes extracted from hair wefts dyed from Honey Blonde, Light Brown Warm and Dark Brown commercial colour former packets and a control

The experimental method was much the same as that used with the commercial hair colour former packet. An equal volume of aqH_2O_2 (5 mL), provided, was mixed with an equal volume of the mixture of primary intermediates and couplers (5 mL) in a beaker. For the control, pure *p*-phenylenediamine **1** was oxidised. Tied long extensions from a blonde Remy human hair weft (1 cm in width) were

pasted in the beaker onto the hair with a spatula and left for 30 min. The hair was then rinsed under a water tap and left to dry. It was then immersed in a solvent mixture of dichloromethane:trifluoroacetic acid (75:25) for 5 min in a fume hood with the fan off. If the mixture of hair and solvent goes dry, then more of the solvent mixture was added. The extractant becomes darker but not excessively. The hair was removed from the extractant and left to dry in the fume hood. The beaker was allowed to slowly evaporate without any treatment and then mixed with a small amount of MeOH. This MeOH was placed in a small vial ready for LC-MS analysis (four vials in total). Two different gradients G1 and G2 of MeOH/CH₃CN were used for the analyses (see section ‘Methods’).

Acknowledgements

The authors are grateful to the Development Trust of the University of Aberdeen for funding.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship and/or publication of this article: This work was supported by the Development Trust of the University of Aberdeen.

ORCID iD

M John Plater  <https://orcid.org/0000-0003-0204-9695>

Supplemental material

Supplemental material for this article is available online.

References

1. Morel OJX and Christie RM. *Chem Rev* 2011; 111: 2537.
2. Personal communication, Mokoko Hair Salon, 333 King Street, Aberdeen AB24 5AP.
3. Hofmann AW. *Jahr Chem* 1863; 42.
4. Monnet P. French Patent 158558, 1883.
5. Sousa AC, Fátima M, Piedade MM, et al. *Green Chem* 2016; 18: 6063.
6. Zviak C. *The science of hair care*. New York; Basel: Ed Marcel Dekker, 1986.
7. Corbett JF. *Dyes Pigm* 1999; 41: 127.
8. Corbett JF. *J Soc Cosmet Chem* 1973; 24: 103.
9. Brown KC and Corbett JF. *J Soc Cosmet Chem* 1979; 30: 191.
10. Corbett JF. *J Chem Soc* 1969; (B): 207.
11. Corbett JF. *J Chem Soc* 1969; (B): 213.
12. Robbins CR. *Chemical and physical behavior of human hair*. 4th ed. New York: Springer, 2002.
13. Zhang G, Bailey AD, Bucks ME, et al. *Dyes Pigm* 2018; 149: 167.
14. Bonnet A, Barre G and Gilard P. *J Chim Phys* 1995; 92: 1823.
15. Corbett JF. *J Chem Soc Perkin II* 1972; 539.
16. Nocerino C and Tan-Walker RLB. WIPO 0182891 A1, 2001.
17. Dasher GF, O’Cull KA and Schumper TJ. US3980091, 1976.
18. Lang G and Audoussat M-P. US6503283 B1, 2003.
19. Deneulenaere C. US6045591, 2000.

20. *Home-get the facts-p-phenylenediamine: campaign for safe cosmetics*. San Francisco, CA: Web Link Breast Cancer Prevention Partners (BCPP).
21. Baserga E. CH602863 A5, 1978.
22. Lim M-III, Stasaitis LR and Pan Y-G. CA2175542 A1, 1997.
23. GB939513A, 1963.
24. Gamlen GA, Rattee ID, Vivianstead C, et al. GB958899, 1964.
25. Gamlen GA, Morris C, Scott DF, et al. GB1005240, 1965.
26. Gamlem GA, Morris C, Scott DF, et al. GB1012625, 1965.
27. GB951734A, 1964.
28. Staley JM and Giles RR. US2957010, 1960.
29. Gamlen GA, Morris C, Scott DF, et al. US3116275, 1963.
30. Boyd SN and Salem NJ. US2737517, 1956.
31. GB896972A, 1962.
32. Balsley RB. US4081436, 1978.