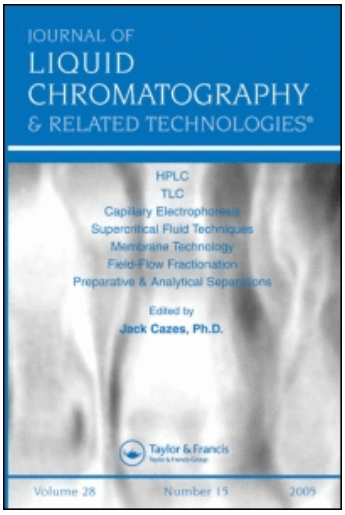

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

HPLC Analysis of Oxidation Hair Dyes in Permanent Hair Colorants

V. Andrisano[a]; R. Gotti[a]; A. M. Di Pietra[a]; V. Cavrini[a]
[a] Department of Pharmaceutical Sciences, Bologna, Italy

To cite this Article Andrisano, V. , Gotti, R. , Pietra, A. M. Di and Cavrini, V.(1994) 'HPLC Analysis of Oxidation Hair Dyes in Permanent Hair Colorants', Journal of Liquid Chromatography & Related Technologies, 17: 13, 2919 — 2937
To link to this Article: DOI: 10.1080/10826079408013510
URL: http://dx.doi.org/10.1080/10826079408013510

JOURNAL OF LIQUID CHROMATOGRAPHY, 17(13), 2919-2937 (1994)

HPLC ANALYSIS OF OXIDATION HAIR DYES IN PERMANENT HAIR COLORANTS

V. ANDRISANO, R. GOTTI,
A. M. DI PIETRA, AND V. CAVRINI*
Department of Pharmaceutical Sciences
Via Belmeloro 6
40126 Bologna, Italy

ABSTRACT

The reversed-phase liquid chromatographic separation of several hair dyes (diamines, aminophenols, phenols, etc.), using mobile phases containing 1,8-diaminoctane as new amine modifier and sodium heptansulfonate, is described. The combined effect of the amine and of the alkylsulfonate enabled very good separation of all the dyes studied. The proposed chromatographic system was found to be selective, rugged and therefore suitable for the reliable quality control of commercial permanent colorants.

A preliminary solid phase extraction (SPE) procedure using SCX sorbents, was found useful to enhance detectability of low concentrated dyes and to isolate phenol compounds from the basic dyes.

INTRODUCTION

Oxidation hair dyes are the precursors of permanent colours developed on the hair by their oxidation [1]. In general, dye formation involves slow oxidation of a primary intermediate (generally aromatic p-diamines and p-aminophenols) by hydrogen peroxide to give p-benzoquinone diimine [2,3] which reacts with the

couplers (generally m-diamines, m-aminophenols, resorcinol etc.) to indophenols, indamine or indaniline or for further reaction to trinuclear or polinuclear dyes.

Semipermanent products incorporate amino or hydroxy- nitrobenzenes which readily diffuse into hair, but also diffuse out again over the course of several shampooings.

Temporary dye products generally consist of high molecular weight acid dyes which are deposited on the hair surface to give a coloring effect removable by a single shampoo .

Many of these compounds may present a risk to users, expecially with regard to sensitization [4,14]. In annex III of European Directive (76/768) limitations on the use of several oxidation hair dyes are reported ; besides in annexe II, a list of these compounds are banned for the cosmetic use.

Despite the fact that TLC [5,6], GC [7] and electrophoretic [8] methods have been used to determine oxidation hair dyes, most reports in the literature concern HPLC methods [9-12]. More recently an ion-pairing method for the determination of p-phenylenediamine in hair dyes [13] was developed, besides a cation exchange HPLC column with electrochemical detection was used to determine p-phenylenediamine in the vapour of haidressing salons [14] and a polymeric reversed phase was used to separate o-,m- and p- isomers of aminophenol [15]. Nevertheless, there is a lack of a systematic analysis of all the most common oxidation hair dyes as raw materials or cosmetic preparations. The reported methods deal just with particular aspects of the whole analytical problems connected with this class of compounds and there exists a need for versatile HPLC methods of general application.

The aim of the present work was to offer a selective and reliable RP-HPLC method with photodiode array detection capable of identifing and determining

most of the oxidation dyes in commercial formulations with improved resolution, reproducibility and sensitivity. To this end an isocratic ion-pairing method, involving the use of a new amine modifier to the mobile phase (1,8-diamminoctane), was developed. When compared to the other amine modifiers (triethylamine, octylamine) 1,8- diaminoctane led to a better performance in terms of resolution, selectivity and reproducibility. The method allowed several dyes to be separated under the same chromatographic system just by modifying the percentage of the organic modifier in the mobile phase, according to the lipophilicity of the analysed dyes. Furthermore, to increase detection sensitivity for hair dyes in cosmetic samples, a solid phase extraction (SPE) method with strong cation exchanger (SCX) sorbent was performed . Through this extraction step, basic dyes can be selectively extracted and separated from phenolic compounds (resorcinol, 1-naphtol, pyrogallol, 4-hydroxy-1-naphtalenesulfonic acid sodium salt) and concentrated with satisfactory recovery and precision.

The proposed method was therefore successfully applied to the analysis of commercial professional hair dye products of complex composition (paste), containing different association of oxidation hair dyes.

EXPERIMENTAL

Materials

All the oxidation dyes (TABLE 1) were obtained from Intercosmo Spa (Bologna , Italy) and used as received.

1,8-diaminoctane (DAO), n-octylamine and triethylamine were from Aldrich (USA); heptansulfonic acid sodium salt was purchased from Janssen (Belgium); urea and sodium dihydrogen phosphate were obtained from Fluka (Switzerland); sodium chloride, ortophosphoric acid and sodium sulfite were from Merck (FRG).

TABLE 1 - Oxidation hair dyes examined by the described RP-HPLC method

Compounds	Abr.	Peak
2-Aminophenol	o-AP	1
3-Aminophenol	m-AP	2
4-Aminophenol	p-AP	3
4-Amino-o-cresol	p-AOC	4
2-Amino-4,6-dinitrophenol (picramic acid)	PA	5
N,N-Dimethyl-1,4-phenylen-diamine	DMPDA	6
2-Ethoxy-1,4-phenylen-diamine	ETPDA	7
4-Methylamino-phenol	p-MAP	8
2-Nitro-1,4-phenylendiamine	NPDA	9
1,4-Phenylendiamine	p-PDA	10
1,3-Phenylendiamine	m-PDA	11
1,2-Phenylendiamine	o-PDA	12
1-Naphtol		
Resorcinol		13
2-Methylresorcinol		
4-Hydroxy-1-naphtalenesulfonic acid, sodium salt	HNSA	14

All the reagents were of analytical grade. Acetonitrile was HPLC grade from Promochem (FRG); water double distilled and filtered through 0.45 μm filter was used to prepare all solutions and buffers .

For the solid phase extraction (SPE) 2.8 ml (500 mg) SCX Analitichem Bond-Elut cartridges were used ; the extraction was carried out using the Baker 10-SPE system connected to a water aspirator. The cartridge was previously conditioned with 3 ml of methanol, followed by 3 ml of 0.85% orthophosphoric acid solution with 0.5% sodium sulfite.

Solutions

Diammoniumoctane heptansulfonate solution (pH 4.5) was prepared by dissolving 1,8-diaminoctane (DAO) (5 mmoles) and heptansulfonic acid sodium salt (20 mmoles) in bidistilled water (1000 ml), adjusting the pH to 4.5 with 8.5% orthophosphoric acid. The dye standard and stock solutions, as well as the sample solutions, were prepared in 0.85% orthophosphoric acid solution containing sodium sulfite (0.5%).

The standard solutions were prepared in 0.025 M phosphate buffer (pH 3.0) containing 1M sodium chloride , 0.5 % sodium sulfite and 5M urea, when the HPLC analysis involved the SPE step. The analyte elution from the SPE column was then performed with the same solvent system but a pH 8.0 was used.

The internal standard(NPDA and DMPDA) solutions were prepared in the same solvent system used for the sample preparation.

Apparatus

The solvent delivery system was a quaternary HP 1050 Ti series Pump, equipped with a Reodyne Model 7125 injector with a 20 μl sample loop . The

eluents were monitored by a Multiwavelenght HP 1050 Detector connected to a 3396 series HP integrator . A photodiode array detector 1040 A(HP) was also used. For routine analyses the detector wavelenght was set at 220-240-275-290 nm, with the integrator attenuation at 0-1-3-8, depending on the dye nature and concentration in the analysed commercial sample.

Chromatographic conditions

Routine analyses were carried out isocratically at ambient temperature on a 10 μm reversed phase Phenomenex Bondclone C18 (300x3.9 I.D.). As mobile phase binary mixtures of acetonitrile with a buffer solution (pH 4.5) containing DAO (0.005 M) and sodium heptansulfonate (0.020 M), were used. The acetonitrile content was comprised between 5 and 30%. The flow rate varied between 1-1.3 ml min^{-1} .

Calibration curves

Standard solutions of the pure dyes (conc. in Table 2) in 8.5% orthophosphoric acid with 0.5% sodium sulfite , containing 15 μg ml^{-1} of nitro p-phenylendiamine as internal standard, were injected in triplicate in the chromatograph. The ratios of analyte area to internal standard area were plotted against the corresponding analyte concentration to obtain the calibration graphs.

Analysis of commercial hair dyes

Four commercial professional cosmetic samples (paste) representative of the various dye compositions were analysed .

Direct Analysis. A 0.2 g aliquot of commercial paste was dispersed with magnetic stirring in 0.85% orthophosphoric acid, containing 0.5% sodium sulfite,

TABLE 2 - Data for the calibration graphs (n=6) in the HPLC determination of selected oxidation hair dyes.

Compounds	Slope	Intercept	Correlation coefficient	Concentration range($\mu g\ ml^{-1}$)
m-AP	0.0692	-0.0108	0.9992	1.0-20.0
p-AP	0.0758	0.0230	0.9990	1.0-23.0
p-PDA	0.0481	-0.0110	0.9990	1.5-25.0
p-AOC	0.0704	0.0180	0.9980	1.5-12.0
ETPDA	0.1045	-0.0210	0.9990	0.5-10.0
p-MAP	0.0832	-0.0153	0.9985	1.5-15.0
mPDA	0.0704	0.0120	0.9980	1.5-15.0

in a 100 ml volumetric flask. Sample 1 and 2 solutions were directly analysed; therefore, 5 ml of the internal standard solution was added before adjusting the volume with 0.85% orthophosphoric acid. NPDA (18 $\mu g\ ml^{-1}$) was the internal standard for the analysis of sample 2; DMPDA (30 $\mu g\ ml^{-1}$) was utilised for the sample 1. The sample suspensions were all filtered through a 0.45 μm Cameo filter and injected into the chromatograph.

Solid phase extraction. Clear solutions from the sample 3 and 4 were prepared, without the internal standard, as above described (filtration through 0.45 mm Cameo filter) and aliquots (12 and 15 ml respectively for the samples 3 and 4) were applied to a SPE SCX cartridge . The subsequent wash step consisted of 3 ml

of water. The dyes retained on the SPE column were then eluted with a solution consisting of 0.025 M potassium phosphate buffer (pH 8.0), 1M NaCl ,5M urea and 0.5 % sodium sulfite, using 3.8 ml for the sample 3 and 2.8 ml for the sample 4.

The eluates from the SPE cartridge were acidified with 200 µl of 17% orthophosphoric acid ; internal standard was added (200 µl of a 140 µg ml^{-1} solution of NPDA for sample 3; 400 µl of a 16 µg ml^{-1} solution of NPDA for sample 4) and 20 µl of each solution were injected in triplicate into the chromatograph . The basic dye contents in each cosmetic sample was calculated by comparison to an appropriate standard solution.

In order to determine the phenolic compounds, after being applied through the cartridge, the sample solutions and the washings were collected together in a 20 ml volumetric flask, the volume adjusted with 0.85% orthphosphoric acid and the solution direcly injected in triplicate into the chromatograph .The phenolic compounds content in each cosmetic sample was calculated by comparison to an appropriate standard solution.

RESULTS AND DISCUSSION

Chromatographic conditions.

According to the basic properties of the hair dyes examined, a reversed-phase liquid chromatographic (RP-HPLC) method, involving the use of an amine modifier in the mobile phase was chosen. Amine modifiers play an important role in RP-HPLC of basic compounds to suppress the adverse silanol effect responsible for severe peak tailing and band broadening [16-21]. In the present work 1,8-diaminoctane (DAO) proved to be a new , useful amine modifier, able to improve the peak shape and the resolution of the basic hair dyes.

The chromatographic analyses were performed on a Bondclone 10 ODS column (300x3.9 mm I.D.) at ambient temperature ,using, as mobile phase, a binary mixture consisting of acetonitrile - DAO heptansulfonate buffer (pH 4.5). The organic phase percentage ranged between 5-30% depending on the lipophilicity of the dyes to be analysed. In order properly to condition the chromatographic system , the mobile phase was allowed to flow through the column for about one hour.

Figures 1 and 2 show two typical chromatographic separations of basic dyes under isocratic conditions. p-PDA, p-AP, m-AP, m-PDA, p-MAP, o-PDA, oAP, DMPDA were separated using a mobile phase consisting of acetonitrile-pH 4.5 DAO Heptansulfonate buffer (5+95), while p-PDA, NPDA, PMAP, DMPDA, ETPDA, PA, p-AOC were separated with lower retention times, using a mobile phase with an increased acetonitrile content (15+85). When compared to other reported methods, the chromatographic system described appears to supply a better selectivity and resolution . Isocratic elution had to be used, because a too long riequilibration time was necessary to perform gradient elutions.

Various DAO\heptansulfonate ratios were experimented on a rapresentative mixture of 4 dyes . As shown in Figures 3 , 5 mM DAO and 20 mM heptansulfonate were found to be the best conditions for a good resolution and peak symmetry. Higher concentrations of heptansulfonate did not increase the analyte retention and therefore did not improve their resolution.

The influence of other amine modifiers, was investigated : octylamine and TEA were used at the same concentration as DAO, with the same amount of heptansulfonate and at the same pH but worse separations were obtained . Higher contents of aqueous phase resulted in longer analysis times without significant resolution improvements.

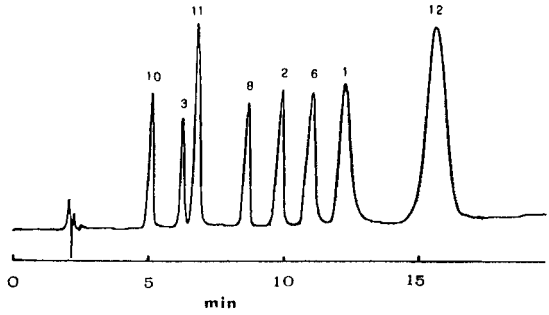

Figure 1-Representative HPLC separation of oxidation hair dyes. Column: Phenomenex Bondclone C-18 (10 μm); mobile phase:acetonitrile-aqueous 5mM 1,8-diaminoctane and 20 mM sodium heptansulfonate solution (pH 4.5) (5+95) at a flow rate of 1,3 ml $min.^{-1}$. Detection at 275 nm. Peaks: Table 1.

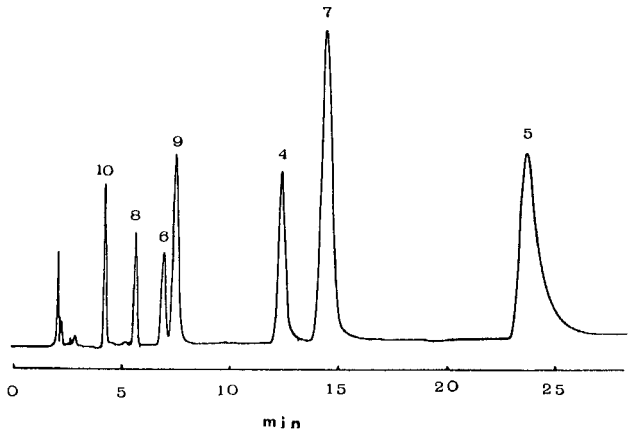

Figure 2- Representative HPLC separation of oxidation hair dyes. Column: Phenomenex Bondclone C-18 (10 μm); mobile phase: acetonitrile-aqueous 5mM 1,8-diaminoctane and 20mM sodium heptansulfonate (pH 4.5), (15+85) at a flow rate of 1.3 ml $min.^{-1}$. Detection at 275 nm. Peaks: Table 1.

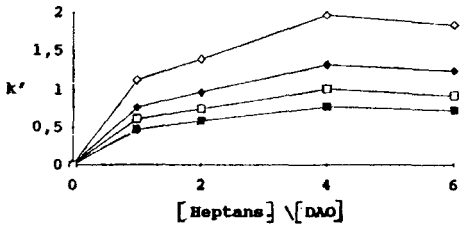

Figure 3- Effect of [heptansulfonate]\[1,8 diaminoctane] molar ratio on the capacity factors (k') for p-PDA(■), m-PDA(□), p-MAP (♦) and ETPDA (◊).

When this study first began, a buffer containing just DAO was employed to suppress the adverse silanol interactions; symmetric peaks were obtained , but an increasing loss of resolution was noticed over time. Therefore, heptansulfonate was added to the mobile phase: increased retention times with improved resolution were obtained and better reproducibility of the chromatographic parameters was attained. This effect was consistent with previously reported studies [21]. More than 1000 injections were performed on the same column under the described conditions without considerable reduction in the column efficiency .On account of the good results obtained with the selected column (Bondclone 10 ODS), a limited number of stationary phases were investigated; among these a Supelco pkb-100 (50x4.5 mm I.D.) column for basic compounds was also used, but, in all the various experimental conditions tried, unsatisfactory separations were obtained.

Sodium Dodecyl sulfate was also assessed as an ion pairing agent, but it was found to be not compatible with DAO because of the poor solubility of the resulting ion pair. On the other hand sodium dodecyl sulfate alone , without amine modifier, provided a useful, but less selective chromatographic system .

Concerning the effect of the pH on the resolution, experiments showed that the range between pH 3.0 and 4.5 is appropriate. Besides, changing from pH 4.5 to

pH 3.0, the system selectivity is slightly modified, with a resulting retention time inversion of some analytes (e.g. p-PDA, p-AP).

Analysis of commercial formulations

The sample pretreatment constituted an important and critical part of the analysis . Because of the poor stability of the basic hair dyes in neutral and basic media, a rapid extractive procedure in acidic medium was developed.

The extraction of the dyes from the cosmetic matrix was performed with 0.85% orthophosphoric acid containing 0.5% sodium sulfite as antioxidant . The resulting suspension was then filtered through a 0.45 mm Cameo filter which is supplied with a prefilter to avoid pores blocking. Care has to be taken in the weighed sample amount, because samples exceeding 0.3 g\100 ml were found to be difficult to filter. The filtered solution was then directly injected into the chromatograph . In Figures 4 and 5, the chromatograms of two representative sample solutions are reported .

When the dyes content in the sample solution was very low (<0.05 mg ml^{-1}), the sample solution was submitted to a solid phase extraction (SPE) procedure which allowed the dyes to be concentrated , enhancing their detectability. Moreover, the SPE step enabled the basic dyes to be separated from the neutral and acidic components, providing simplified chromatograms. In fact, the basic dyes in their protonated form are selectively extracted from the sample solution and retained on the strong cation exchanger, while the phenolic compounds (Resorcinol, 1-naphtol, HNSA) unretained are collected in the filtrate. The subsequent wash step allowed the complete recovery of the phenolic compounds and the washing was therefore added to the filtrate in the same volumetric flask. The volume was adjusted with 0.85% orthophosphoric acid solution and the resulting solution was subjected to the HPLC analysis.

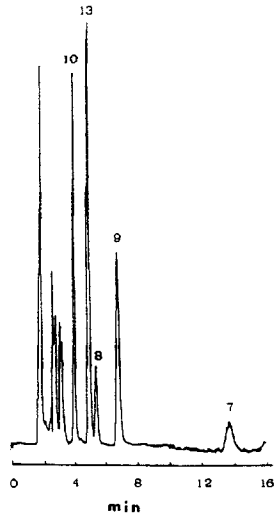

Figure 4- HPLC chromatogram obtained from a commercial hair colorant (sample n°1). Chromatographic conditions as in Fig. 2. UV detection at 275-290 nm. Peaks : Table 1.

The basic dyes retained on the SPE column were eluted with a phosphate buffer (pH 8.0) solution consisting of 1 M sodium chloride and 5 M Urea; this buffer solution, capable of deprotonising and desorpting the basic dyes from the matrix provided an enhanced analyte concentration The eluate obtained was quickly acidified with 0.85 % orthophosphoric acid and, after addition of the internal standard, was subjected to the HPLC analysis. In Figure 6 the chromatograms from sample 3 before and after the SPE procedure are reported .

The same solvent system (acetonitrile-DAO heptansulfonate) proved to be suitable for the HPLC analysis of basic dyes and phenolic compounds. HNSA and Resorcinol (sample 3) were separated using a mobile phase consisting of acetonitrile-pH 4.5 DAO heptansulfonate (5+95) , at a flow rate of 1.3 ml min^{-1}

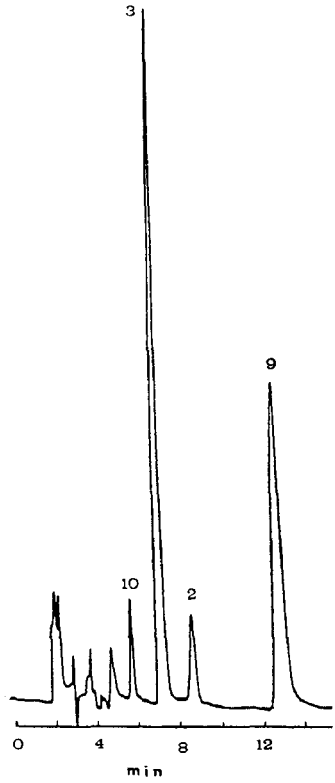

Figure 5- HPLC chromatogram obtained from a commercial hair colorant (sample 2) .Chromatographic conditions and detection as in Figure 1. Peaks: Table 1.

(UV detection at 275 nm)(Figure 6 c), while 1- naphtol required higher percentage of acetonitrile (30%) to obtain a convenient retention time (25 min.)

The identity of the analyte peaks was confirmed by the UV spectra registered by a photo diode array detector.

For quantitative applications linear relationships between the peak area ratios (analyte to internal standard) and analyte concentration were obtained (Table 2)

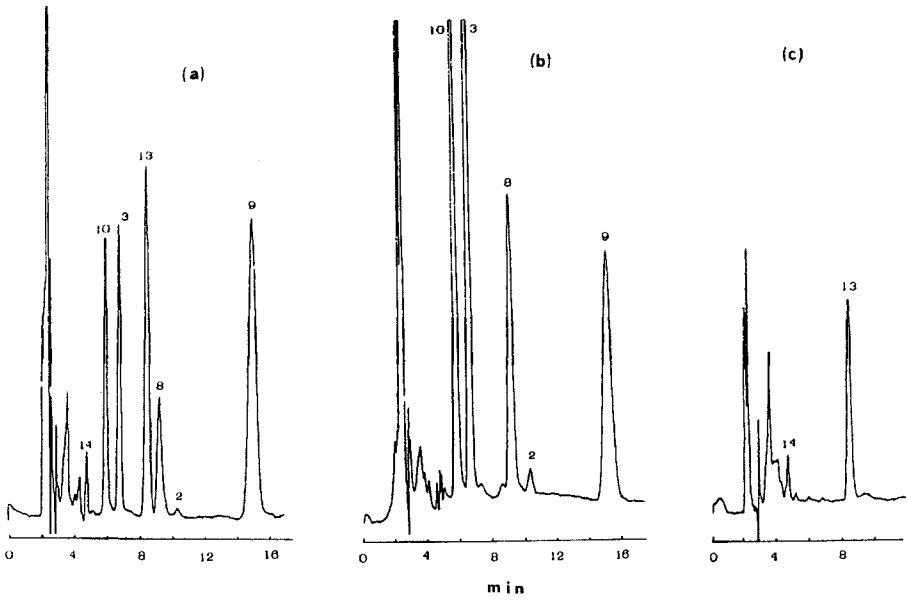

Figure 6-HPLC chromatogram of a) solution of sample n°3 before SPE procedure b) same solution after SPE and c) filtrate through the SCX cartridge . Chromatographic conditions and detection as in Figure 1. Peaks: Table I.

with good precision (RSD% = 0.53-0.96). In the present study our attention was mainly directed to the determination of basic dyes, while just preliminary trials, confirming the suitability of the proposed method, were performed for the assay of phenolic compounds. Four commercial professional products were analysed selecting an appropriate measurement wavelength for each analyte in order to properly modulate the sensitivity. The results obtained are summarised in Table 3. As can be seen, the assay results were in satisfactory agreement with the content declared; the Relative Standard Deviation was between 2-5.6%, with the higher values for m-AP, p-AOC and ETPDA present in the commercial formulations at very low levels (0.0024%,0.0078%,0.034%).

TABLE 3 - Assay results for the HPLC determination of oxidation hair dyes in commercial hair colorants. The results are the average of five determinations and are expressed as a percentage of the content declared by the manufacturer.

Sample	analytes	λ	Found	RSD%	Recovery	RSD%
1[a)]	p-PDA	275	105.50	5.15	100.44	5.09
	p-MAP	275	98.38	2.00	101.80	2.00
	ETPDA	290	95.22	2.53	98.39	3.10
2[a)]	p-PDA	275	99.57	2.31		
	p-AP	275	101.18	2.34	100.60	1.80
	m-AP	275	98.60	5.33	99.50	3.20
3[b)]	p-PDA	275	99.06	4.64	80.08	4.24
	p-AP	275	97.47	4.90	86.82	4.88
	p-MAP	275	94.55	3.84	82.58	1.47
	m-AP	275	91.13	5.60	103.30	5.50
4[b)]	p-PDA	240	103.46	4.23	82.00	3.50
	p-MAP	275	100.20	4.50	80.20	2.40
	p-AOC	220	99.67	4.91	98.00	2.15
	p-PDA[a)]	275	102.25	3.59		

a) The direct method of analysis was used.

b) The method involved the SPE step. The results are related to the effective recovery value

The accuracy of the method was verified by analysing the blank spiked with known quantities of the examined hair dyes . As shown in Table 3, good recovery values were obtained when the direct analysis was performed , while a lower recovery was found when SPE step was necessary to increase the analysis sensitivity. In any case, however, the precision of the method was satisfactory.

CONCLUSION

The proposed reversed phase (C18) HPLC method, involving the use of 1,8-diaminoctane as amine modifier in association with sodium heptansulfonate, provided adequate selectivity for the separation of all the most important oxidation hair dyes. The chromatographic system (isocratic conditions) proved to be rugged enough for routine quality control, because no particular decay of the column (Phenomenex Bondclone 10 mm C18) life was observed . A simplified sample pretreatment can usually be adopted; if necessary, a preliminary SPE on SCX material offers the opportunity for the analyte concentration and the separation of the basic dyes from the other formulation components (phenols).

ACKNOWLEDGEMENTS

This work was supported in part by a grant from Intercosmo S.p.A. (Bologna, Italy). Thanks are due to misses Angela Pelliconi and Annalisa Comastri for their valuable technical assistance.

REFERENCES

1. M.S. Balsam & E. Sagarin , in Cosmetic, Science and Technology, John Wiley § Sons, New York, 1974,vol. II, p.300.

2. J.F. Corbett, J.Soc.Cosmet.Chem., **35**, 297 (1984).

3. K.C.Brown, J.Soc.Cosmet.Chem., **33**, 375 (1982).

4. K.P.N. Viswanathan, V.Gupta, V.Misra, Int. J. Cosmet. Sc., 7, 213 (1985).

5. H.Gottschalck, R. Machens, J.Soc.Cosmet.Chem., **33**, 97 (1982).

6. Italian Gazz. Uff. Suppl. No 7, Jan. 23rd, 1987, 32.

7. N.Goetz, P.Lasserre, P.Borè, G.Kalopissis, Int. J. Cosmet. Sc., **10**, 63 (1988).

8. S.Fanali, J. Chromatogr., **470**, 123 (1989).

9. N.Goetz, J.Mavro, L.Bouleau, A.de Labbey, in Cosmetic Analysis, Cosmetic Science and Tecnology Series, Vol.4, ed. Borè, P., Dekker, M., Inc. New York, 1985, p.245.

10. D.H.Liemand, J.Rooselaar, Mitt.Geb.Lebensmittelunters Hyg., **72**,164 (1981).

11. K.Tashiro, A.Kojima, Y.Okuda, J.Soc.Cosmet.Chem.,**16**, 125 (1983) (Chem.Abstr. 98:221605 b).

12. G.Hoogewiss, D.L. Massart, J.Pharm.Belg., **38**, 76 (1983).

13. M.C.Gennaro, P.L.Bertolo, E.Marengo, J. Chromatogr., **518**, 149 (1990).

14. L.Gagliardi, M. Ambroso, J. Mavro, F.Furno, G.Discalzi. Int.J.Cosmet.Sc., **14**, 19 (1992).

15. C.J.Dowleand, A.P.Malyan, A.M.Matheson, Analyst, **115**, 105 (1990)

16. D.C.Leach, M.A.Stadelius, J.S.Berns, L.R.Snyder, LC-GC Int., **1**, 22 (1988).

17. R.W.Ross, C.A. Lan Cam, J.Chromatogr., **370**, 406 (1986).

18. R.K.Gilpin, S.S.Yang, G.Werner, J.Chromatogr.Sci., **26**, 388 (1988).

19. A.M.Di Pietra , V.Cavrini, V. Andrisano, R.Gatti, J. Pharm. Biomed. Anal., **10**, 873 (1992).

20. G.Stoev,D. Uzunov, J.Liq.Chromatogr., **15**, 3097 (1992).

21. J.A.De Schutter, W. Van Den Bossche, P. De Moerloose, J. Pharm. Biomed. Anal., **4**, 559 (1987).

Received: September 1, 1993
Accepted: March 17, 1994