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DETERMINATION OF DYE INTERMEDIATES IN OXIDATIVE HAIR DYES BY FUSED-SILICA CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

A fused-silica capillary gas chromatographic method is described for the determination of dye intermediates in oxidative hair dyes. An appropriate amount of hair dye sample is dissolved in 10 ml of methanol containing 0.25 g of ammonium thioglycolate and an appropriate amount of 2-amino-4-methylphenol as an internal standard. This solution is directly injected into a gas chromatograph. A fused-silica capillary column with cross-linked methyl silicone OV-1 or SE-54 as a liquid phase yields excellent resolution of dye intermediates. Some factors affecting the quantitation of dye intermediates are discussed. The proposed method gave good recoveries and reproducibilities, and permits simultaneous determination of various types of dye intermediates without any pretreatment. The use of a nitrogen–phosphorus detector allows the selective detection of nitrogen-containing dye intermediates. This simple and versatile method is applicable for the determination of dye intermediates in commercial hair dyes.

INTRODUCTION

Hair dyes have become one of the most important products in toiletry and cosmetics since modern hair dyeing methodology was established in the 1950s. Various types of hair dyes are now commercially available, among which oxidative hair dyes are most widely used because of their high fastness. A commercial oxidative hair dye commonly contains several kinds of dye intermediates in the wide range of 0.01 to several per cent. Most of these dye intermediates can be classified into five types: diamines, aminophenols, polyphenols, nitro compounds and their salts, whose structures are illustrated in Fig. 1. The content and composition of dye intermediates in a hair dye greatly affect the colour developed by dyeing. Therefore, a reliable and simple method for the determination of dye intermediates is required for quality control in the manufacturing process and performance evaluation.

Various methods have been reported for the determination of dye intermediates in hair dyes. Kijima *et al.*[1], Yamada *et al.*[2] and Tashiro *et al.*[3] reported high-performance liquid chromatographic (HPLC) methods, however these often required several chromatographic conditions in order to analyze commercial hair dyes. Thin-

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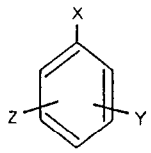

Dye intermediates	X	Y	Z
Aromatic amines	NH_2	NH_2	H,CH_3,OCH_3
Aminophenols	NH_2	OH	H,CH_3
Polyphenols	OH	OH	H,OH
Nitro compounds	NH_2	NH_2,OH	NO_2

Fig. 1. Typical dye intermediates.

layer chromatography[4] has also been applied, however satisfactory quantitation has not been demonstrated. Gas chromatography (GC) with packed columns has been used by many workers[5–7]. This method has the disadvantages of poor resolution and quantitation, and also requires several chromatographic conditions. Our preliminary investigation on the separation of dye intermediates by using conventional packed columns also gave unsatisfactory results.

Recent progress in GC technology is remarkable. In particular, fused-silica capillary GC has been extensively employed for various analyses which cannot be performed on packed columns, and has the advantages of chemical inertness and higher resolving power. This led us to investigate the analysis of dye intermediates by means of fused-silica capillary GC.

The present paper deals with the factors affecting the separation and quantitation of dye intermediates and also deals with a simple and versatile method for their determination in commercial hair dyes.

EXPERIMENTAL

Gas chromatography

All experiments were carried out using Hewlett-Packard Model 5880A and 5890A gas chromatographs equipped with nitrogen–phosphorus detection (NPD), flame ionization detection (FID) and a split/splitless injection system. The fused-silica capillary columns used are summarized in Table I. The oven temperature was set at 140, 200 or 250°C, the injection temperature at 250°C. The detector temperature was 250°C and 300°C for FID and NPD, respectively. Helium was used as a carrier gas at a linear velocity of 35 cm/s. A split injection technique was used with a splitting ratio of 70:1 in all analyses. All samples were automatically injected into a gas chromatography by a Hewlett-Packard Model 7671A automatic sampler. The chromatograms and peak areas were recorded on a terminal attached to the 5880A gas chromatograph or on an Hewlett-Packard Model 3392A integrator attached to the 5890A gas chromatograph.

TABLE I

FUSED-SILICA CAPILLARY COLUMNS USED

Name	Ultra 1	Ultra 2	Supelcowax 10
Liquid phase	OV-1	SE-54	PEG 20M
Length (m)	50	50	30
Diameter (mm)	0.32	0.32	0.25
Film thickness (μm)	0.52	0.52	0.25
Phase ratio	150	150	250
Source	H-P*	H-P	SP**

* Hewlett-Packard.
** Supelco.

TABLE II

ABBREVIATIONS OF DYE INTERMEDIATES USED

Intermediate	*Abbreviation*
o-Phenylenediamine	OPDA
m-Phenylenediamine	MPDA
p-Phenylenediamine	PPDA
Toluene-3,4-diamine	OTDA
Toluene-2,4-diamine	MTDA
Toluene-2,5-diamine	PTDA
2,6-Diaminopyridine	2,6DAPy
o-Aminophenol	OAP
m-Aminophenol	MAP
p-Aminophenol	PAP
p-Amino-*o*-cresol	PAOC
p-Amino-*m*-cresol	PAMC
p-Methylaminophenol	PMAP
Catechol	Cat
Resorcinol	Res
Hydroquinone	Hydro
Methylhydroquinone	M-Hydro
α-Naphthol	αN
β-Naphthol	βN
2,4-Diaminophenol	Amido
1,5-Dihydroxynaphthalene	1,5DHN
Diphenylamine	DPA
p-Aminodiphenylamine	PADPA
p-Nitro-*o*-phenylenediamine	PNOPDA
p-Nitro-*m*-phenylenediamine	PNMPDA
o-Nitro-*p*-phenylenediamine	ONPPDA
4-Amino-2-nitrophenol	4A2NP
2-Amino-4-nitrophenol	2A4NP
2-Amino-5-nitrophenol	2A5NP

Reagents and chemicals

Table II lists 29 dye intermediates and their abbreviations. These compounds, isopropyl benzoate (IPB), 2-amino-4-methylphenol (2A4MP) and N,N-dimethyl-*p*-phenylenediamine (N,N-DMPPDA) were purchased from Tokyo Chemical Industry (Tokyo, Japan) and Wako (Tokyo, Japan), and were used without further purification. Ammonium thioglycolate (50% aqueous solution) was obtained from Denki-kagakukogyo (Tokyo, Japan). All other reagents were of reagent grade. All samples and standard solutions were prepared by using methanol. A model hair dye was prepared by mixing seven kinds of dye intermediates (Cat, OAP, Res, MAP, MPDA, PAOC and PTDA; 5 mg of each) with 1 g of the model base shown in Table III.

Procedures

A hair dye sample containing 0.2–10 mg of each dye intermediate was placed in a 30-ml erlenmeyer flask with a ground stopper, and 0.25 g of ammonium thioglycolate and 10 ml of methanol containing a known amount of 2A4MP (0.5–5.0 mg) as an internal standard were added. The sample solution was shaken vigorously for about 30 s and allowed to stand for 5 min. A 1-μl volume of the supernatant was injected into a gas chromatograph with an automatic sampler. The analysis was performed within 10 h of the sample preparation.

RESULTS AND DISCUSSION

Optimization of the separation

The effect of the liquid phase on the elution behaviour of various dye intermediates was first investigated. As shown in Fig. 2, a Supelcowax 10 column with a bonded polyethylene glycol gave broad peaks for most of the nine dye intermediates. Cat did not produce a clear peak and OAP and MPDA overlapped. On the other hand, symmetrical peaks and excellent separation were obtained by using an Ultra 1 column with a cross-linked methyl silicone. Similar results were obtained with an Ultra 2 column. Therefore, the Ultra 1 and 2 columns were used in the subsequent studies.

TABLE III

COMPOSITION OF THE HAIR DYE BASE USED

Ingredient	*Content (%)*
Propylene glycol	10.0
Ethanol	10.0
Oleic acid	10.0
Lauric acid diethanolamide	15.0
Cetyl alcohol	5.0
Polyoxyethylenenonylphenyl ether ($\bar{p}$ = 13)	15.0
Tetrasodium salt of EDTA	0.5
Ammonium thioglycolate (50% aqueous solution)	4.0
Ammonia (25% aqueous solution)	20.0
Deionized water	10.5

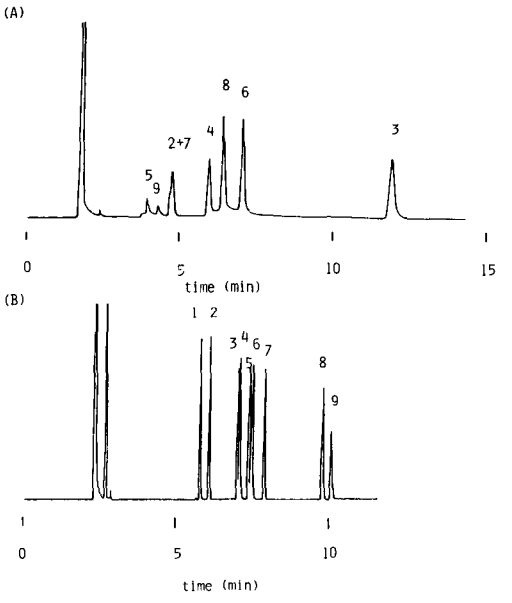

Fig. 2. Comparison of the separation of several dye intermediates on two types of fused-silica capillary columns. (A) Supelcowax 10; oven temperature, 250°C; linear velocity, 30 cm/s. (B), Ultra 1; oven temperature, 140°C; linear velocity, 35 cm/s. Peaks: 1 = Cat; 2 = OAP; 3 = Res; 4 = PAP; 5 = PPDA; 6 = MAP; 7 = MPDA; 8 = PAOC; 9 = PTDA.

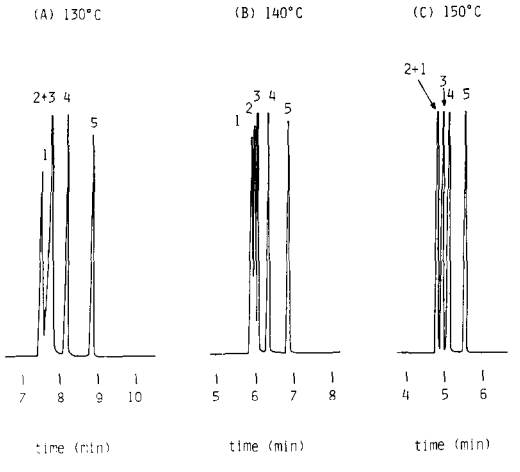

Fig. 3. Influence of oven temperature on the separation of dye intermediates. Column: Ultra 2. Oven temperature: (A) 130°C; (B) 140°C; (C) 150°C. Peaks: 1 = PAP; 2 = Res; 3 = PPDA; 4 = MAP; 5 = MPDA.

Fig. 3 illustrates the effect of the column temperature on the elution behaviour of some dye intermediates using an Ultra 2 column, in terms of the separation of Res, PAP and PPDA which is the most difficult in the present study. Res and PPDA could not be separated at 130°C. However, satisfactory separation of the three dye intermediates was achieved at 140°C. Column temperatures higher than 150°C afforded insufficient separation of Res and PAP. The same tendency was obtained by using the Ultra 1 column. Thus, the column temperature was set at 140°C. Since the linear velocity of the carrier gas did not affect the retention behaviour, it was set at 35 cm/s in terms of the column efficiency.

Based on the results described above and the investigation of other factors such as the film thickness of the liquid phase, column length, etc., the optimum GC conditions for the separation of dye intermediates could be established as shown in the Experimental section. Under these conditions, eighteen dye intermediates could be separated within 25 min as shown in Fig. 4, and all dye intermediates gave symmetrical peaks without the need for derivatization. Such an excellent separation has not hitherto been accomplished. The Ultra 1 column gave similar results to the Ultra 2, except for the overlapping of PAP and Hydro.

On the other hand, diphenylamines and nitro dyes could not be analyzed under the conditions described above because of their high polarity and large molecular weight. However, an increase in the column temperature enabled their direct analyses, as shown in Fig. 5.

Stabilization of oxidative dyes in sample solutions

It is well known that dye intermediates are extremely unstable and are oxidatively polymerized by oxygen in air. Therefore, in order to stabilize dye intermediates in sample solutions, ammonium thioglycolate was chosen as an antioxidant because of its high solubility in methanol. The effect of the concentration of ammonium thioglycolate on the stability of the dye intermediates was investigated using

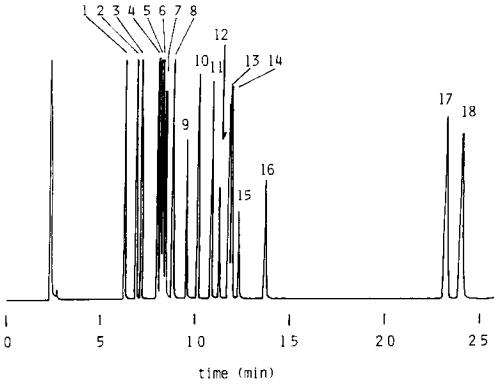

Fig. 4. Typical chromatogram of a standard mixture of eighteen dye intermediates. Column: Ultra 2. Oven temperature; 140°C. Injection temperature: 250°C. Carrier gas (helium) linear velocity: 35 cm/s. Splitting ratio: 70:1. Peaks: 1 = Cat; 2 = OAP; 3 = OPDA; 4 = Hydro; 5 = PAP; 6 = Res; 7 = PPDA; 8 = MAP; 9 = MPDA; 10 = OTDA; 11 = M-Hydro; 12 = PMAP; 13 = PAOC; 14 = PAMC; 15 = PTDA; 16 = MTDA; 17 = αN; 18 = βN.

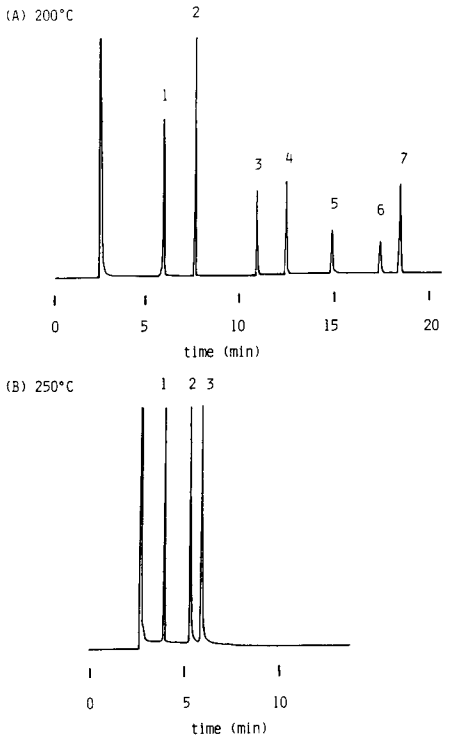

Fig. 5. Typical chromatograms of standard mixtures of diphenylamines and nitro dyes. (A) Oven temperature: 200°C. Peaks: 1 = amido; 2 = DPA; 3 = ONPPDA; 4 = 1,5DHN; 5 = PNOPDA; 6 = PNMPDA; 7 = PADPA. (B) Oven temperature; 250°C. Peaks: 1 = 4A2NP; 2 = 2A4NP; 3 = 2A5NP. Other GC conditions as in Fig. 4.

MPDA, which is the most unstable of all the dye intermediates investigated, and 2A4MP was added as an internal standard. As shown in Fig. 6, the peak area ratio of MPDA to 2A4MP gradually decreased in the absence of ammonium thioglycolate. However, in the presence of greater than 2.5% ammonium thioglycolate, no variation of the peak-area ratio was observed during 10 h. Thus, the concentration of ammonium thioglycolate chosen was 2.5%.

Selection of the internal standard

Since a commercial hair dye usually contains several kinds of dye intermediates such as diamines, aminophenols and polyphenols, it is important to select the most suitable internal standard for their determination. Fig. 7 shows the effect of internal standards with different chemical structures on the precision and accuracy of the determination of three typical dye intermediates. IPB gave poor reproducibilities for all dye intermediates. Both M-Hydro and N,N-DMPPDA gave good reproducibilities only in the determination of dye intermediates of the same structural type. On the contrary, 2A4MP having an amino and a phenolic hydroxyl group gave satisfactory recoveries and reproducibilities for all dye intermediates. On the basis of

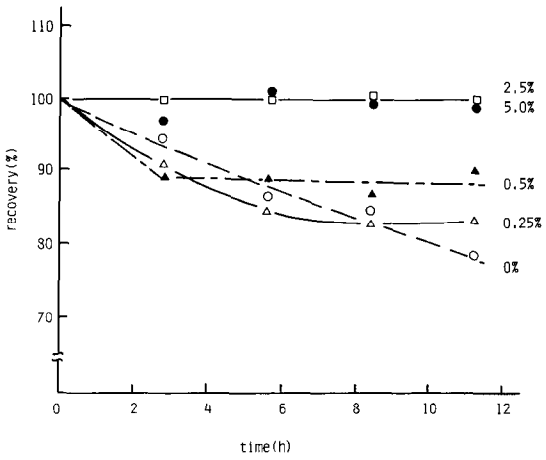

Fig. 6. Effect of the concentration of ammonium thioglycolate in sample solutions on the stability of dye intermediates.

these results, 2A4MP was chosen as an internal standard for the determination of dye intermediates.

Effect of ammonia content

Commercial hair dyes are kept under mild alkaline conditions by use of ammonia. Under these conditions, the phenolic hydroxyl groups of the dye intermediates dissociate to form phenolate anions, which suggests a decrease in the recovery of the dye intermediates. However, as shown in Fig. 8, the recoveries of three dye intermediates were almost constant in the ammonia concentration range of 1–30%. These results indicate that ammonia does not interfere with the determination of dye intermediates.

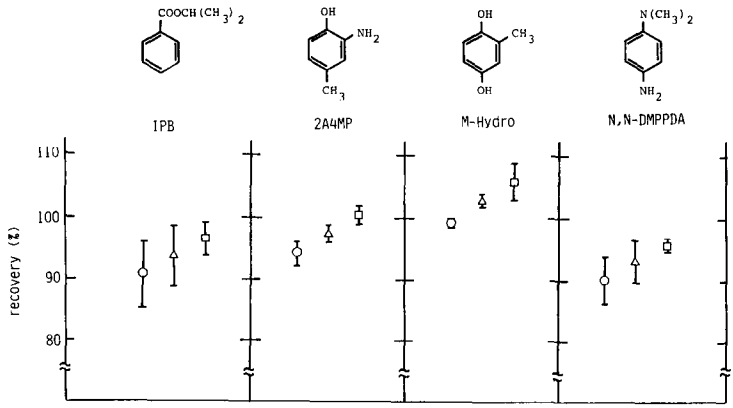

Fig. 7. Effect of internal standards with different chemical structures on the precision and accuracy of the determination of Res (○), MAP (△) and MPDA (□).

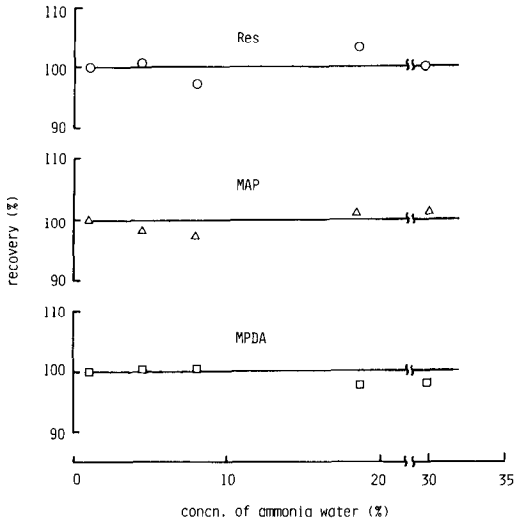

Fig. 8. Effect of the ammonia content on recoveries of dye intermediates.

Recovery and reproducibility

The precision and accuracy of the proposed method were tested by adding known amounts of dye intermediates to the model hair dye prepared as described in the Experimental section. The recoveries of the various dye intermediates were 94.7–108.1%, and the reproducibilities in five replicate analyses were within 2% as shown in Table IV. These results are comparable to those of HPLC methods and suggest that the proposed method permits the direct and simultaneous determination of a variety of dye intermediates in commercial hair dyes.

Application

The determination of dye intermediates in commercial hair dyes was carried out by the proposed method. Fig. 9 shows a typical gas chromatogram for the analy-

TABLE IV

RECOVERY AND REPRODUCIBILITY IN THE ANALYSIS OF THE MODEL HAIR DYE BY THE PROPOSED METHOD

Dye intermediate	*Added (mg)*	*Found (mg)*	*Recovery (%)*	*Coefficient of variation (%)*
Cat	5.00	4.93	98.5	0.45
OAP	5.00	5.02	100.4	1.02
Res	5.00	5.19	103.7	1.95
MAP	5.00	4.94	98.8	1.15
MPDA	5.00	4.74	94.7	0.94
PAOC	5.00	5.06	101.1	1.83
PTDA	5.00	5.41	108.1	2.16

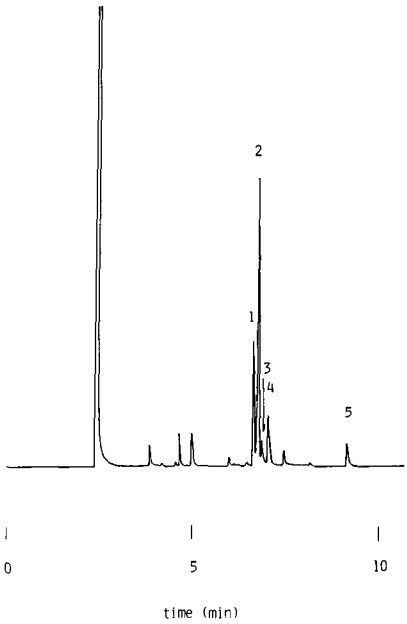

Fig. 9. Typical chromatogram for the analysis of a commercial hair dye. Column: Ultra 1. Other GC conditions as in Fig. 4. Peaks: 1 = PAP; 2 = PPDA; 3 = Res; 4 = MAP; 5 = PAOC.

sis of a commercial hair dye. Five dye intermediates (Res, PAP, MAP, PPDA and PAOC) could be simultaneously analyzed within 10 min without any interference. Table V shows the results of the determination of dye intermediates in five commercial hair dyes. Dye intermediates in the wide concentration range of 0.03–1.81% could be directly determined without any pretreatment.

Use of nitrogen–phosphorus detection

Most commercial hair dyes were successfully analyzed as described above. However, the analysis of a few of them was difficult because of the presence of a large number of interfering peaks. This led us to use nitrogen–phosphorus detection

TABLE V

DETERMINATION OF DYE INTERMEDIATES IN COMMERCIAL HAIR DYES

Commercial hair dye	*Dye intermediates (%, w/w)*							
	MAP	*PAP*	*PAOC*	*PTDA*	*PPDA*	*MPDA*	*2,6DAPy*	*Res*
A	0.36	0.57	–	1.81	–	–	–	0.98
B	0.12	0.25	0.06	–	0.57	0.07	–	–
C	0.03	0.23	–	–	0.22	–	–	0.12
D	–	–	–	–	0.99	0.68	0.31	–
E	0.04	–	–	0.65	–	–	–	0.38

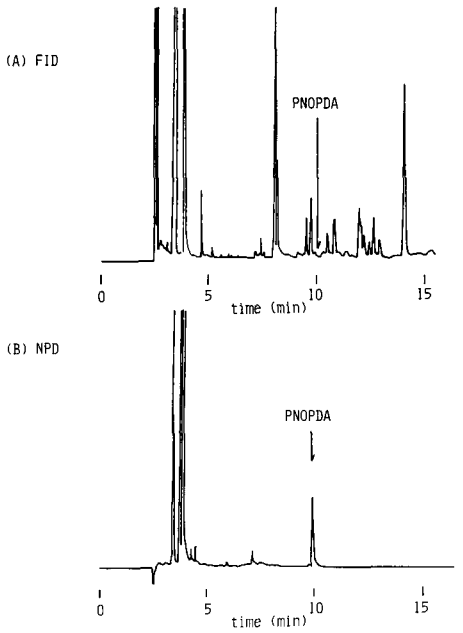

Fig. 10. Application of nitrogen–phosphorus detection for the analysis of a commercial hair dye. Column: Ultra 1. Oven temperature: 200°C. Detection: (A) FID; (B) NPD. Detector temperatures; (A) 250°C; (B) 300°C. Other GC conditions as in Fig. 4.

(NPD), which specifically responds to phosphorus- or nitrogen-containing compounds. Fig. 10 shows an example of the analysis of nitrophenylenediamines in a commercial hair dye, and also shows the selectivity of NPD compared with FID. NPD detected only PNOPDA without any interfering peak, while FID detected a large number of peaks derived from the ingredients of the hair dye. In the present study, quantitation was not carried out using NPD, however this would be possible if an internal standard were used.

CONCLUSION

A simple and versatile method has been developed for the determination of dye intermediates in oxidative hair dyes. It is based on the use of a fused-silica capillary column, which permits the direct and simultaneous determination of various types of dye intermediates without any pretreatment. In spite of the complicated formulation of hair dyes, the present method was applicable to the analysis of dye intermediates in various commercial hair dyes.

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