



Simultaneous determination of phenylenediamines derivatized with 5-(4, 6-dichlorotriazinyl) aminofluorescein by capillary electrophoresis

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Abstract:

Phenylenediamines were ingredients that were used as permanent hair dyes. These compounds were reported to cause allergic dermatitis and have genotoxicity and carcinogenicity. The fluorescent derivatization strategy and micellar electrokinetic chromatography with laser-induced fluorescence detector (MEKC-LIF) were established to analyze o-phenylenediamine (OPD), m-phenylenediamine (MPD), p-phenylenediamine (PPD) and toluene-2,5-diamine (PTD) in hair dye products, hair samples and percutaneous absorption experiment. 5-(4,6-dichlorotriazinyl) aminofluorescein (DTAF) was used as a fluorescent reagent and derived at amino groups of phenylenediamines and underwent nucleophilic substitution reaction. The derivatization condition reacted at 90°C for 10 minutes in alkaline conditions. The derivatives were analyzed by MEKC equipped with LIF detection. The limit of detections (S/N=3) for MPD, PTD, PPD and OPD were 25, 25, 50 and 100 nM, respectively. Comparing to previous studies, the sensitivity enhancements were 30-81-fold. The high sensitive MEKC-LIF method was successfully established and applied to determine the content of phenylenediamines in commercial hair dye products, hair and percutaneous absorption samples.

The higher the concentration of borate buffer solution in derivatization conditions, the lower peak height and wider peak width of the analytes were observed. While the borate buffer concentration was set at 10 mM, MPD and OPD peak height were 2-3 times lower compared with a 20-mM borate buffer. However, OPD derivative overlaps with other

interferences. Ultimately, a 20-mM borate buffer was chosen for further derivatization conditions.

To prevent the aqueous solutions from forming DTAF hydrolyzate, methanol was selected as the solvent in the derivatization reaction by adjusting the proportions of methanol (20%, 50%, 75% and 100%, v/v) throughout the derivatized solution. The results showed that the peaks were broadened when 20% methanol was added. When increasing the proportion of methanol in the derivatized solution, the peak shape of PDs was improved, and the peak height also increased. When 75% methanol is added, four PDs can reach the baseline separation. However, when 100% methanol was added to the derivatized solution, the peaks of the analytes were not observed. The reason was that the pH value of derivatized solution was close to neutral and decreased the nucleophilic ability of PDs. Finally, 75% methanol was chosen as the optimum derivatization condition.

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