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Effect of the temperature and mobile phase composition on the retention behavior of nitroanilines on ligand-exchange stationary phase

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Abstract

This paper deals with the separation of isomers of nitroaniline by liquid chromatography using the ligand-exchange technique. The chromatographic separations were performed on the ligand-exchanger sporopollenin. The sporopollenin used as support of stationary phase was modified with carboxylated-ethylenediamine matrix and was loaded with cobalt(II) ions. Using the column packed with cobalt(II) loaded carboxylated diaminoethyl sporopollenin [Co(II)-CDAE-S], the retention behavior of 3- and 4-nitroanilines was investigated. The mobile phase used, was a mixture of 0.05 M NH_4OH in ethanol–water. The resolution was strongly affected by the presence of ammonium hydroxide in the mobile phase and a concentration of 0.05 M was shown to be necessary for the separation of analytes. To study the effects of temperature on the resolution, column runs were also performed at various temperatures (15–60 °C). With increasing temperature, a decreased interaction between the solutes and the ligand-exchanger was observed. Consequently, the best results were obtained using a mixture of 0.05 M NH_4OH in ethanol–water (10:90, v/v) as the mobile phase at a column temperature of 35 °C. Ligand-exchange chromatography on the Co(II)-CDAE-S could be a useful alternative method for the separation of nitroaniline.

Keywords: Ligand-exchange choromatography; Sporopollenin; Nitroaniline

1. Introduction

Nitroanilines are important pollutants in water because of their wide use in many industrial processes such as the manufacture of pharmaceuticals, dyes and synthetical colours [1]. Furthermore, they are of great environmental concern because of their high toxicity to living things [2]. For this reason, nitroanilines are chemical species that need monitoring, so the separation of their positional isomers is very important. In view of the importance of these compounds, a rapid and sensitive method of analysis is needed for their detection in the environment.

Nowadays, technique of ligand-exchange is preferable for the separation of neutral compounds in environmental samples due to its high selectivity. So far, the analysis of such neutral compounds has been widely performed by gas chromatography and high performance liquid chromatography. However, positional isomer separation is one of the most complicating areas of separation science because of their similar physical and chemical properties. Ligand-exchange chromatography, among other methods, has become more and more important for the separation of isomers. It utilizes the reversible formation of complex to separate neutral compounds which can coordinate the attached metal ions onto a solid support matrix [3,4]. Ligand-exchange technique has been employed for compounds coordinating with transition metal ions that form complexes of different stabilities [5]. Solvent molecules holding coordination sites on the matrix are exchanged with the ligands in sample. Briefly, ligand-exchange is based on the formation of metal complexes between the central metal and the analytes. Ligand-exchange is a process first described by Helfferich, and evaluated from the fundamental works of Walton and Stokes [6,7]. Since then, ligand-exchange technique has been widely applied to the separation of a large number of ligands such as proteins, amino acid, purin and pyrimidine bases [8–11] and numerous researches dealing with different applications of ligand-exchange have appeared [12–14].

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Packing materials for chromatographic separation of ligands have been continuously improved. In general, a solid phase support includes two aspects: the base support and the stationary phase that is chemically or physically immobilised onto a solid support and carries out the necessary functions. The base support plays a dominant role in the mechanical, chemical and thermal stability of packing materials. One of such materials is sporopollenin which possesses a high content of functional groups available for modification. This material may be successfully used at high temperatures, since it has a constant chemical structure that is stable under high temperature and in the presence of concentrated acids [15–18]. In this work, sporopollenin, whose surface has previously been chemically modified with a cobalt(II)-carboxylated-ethylenediamine matrix, was employed as stationary phase for the separation of nitroanilines. Ethylenediamine complexes possess a very stable structure, with a very minor dissociation tendency as well as having suitable functional groups for a ligand-exchange matrix [19–21]. In recent years, studies with ligands and modified sporopollenin have generated enhanced interest in the potential of sporopollenin as a support material; however there are very limited records on sporopollenin resin interaction with ligands. Up to date, there has been no investigation on the effect of temperature and mobile phases on the uptake of ligands by pretreated sporopollenin [22–24]. Adjusting the composition of the mobile phase and the temperature of column are the most widely used tools for controlling the separation of analytes in column chromatography. We therefore considered the effect of temperature and mobile phase on the separation of nitroanilines by Co(II)-CDAE-S resin. The aim of our study was to establish the most suitable conditions for the selective separation of 3- and 4-nitroaniline by Co(II)-CDAE-S.

2. Experimental

2.1. Material

Sporopollenin (20 μm mesh, BDH Chemicals) which has been used as stationary phase was modified as ligand-exchanger using ethylenediamine, bromoacetic acid and $CoCl_2$ as we have previously reported [25]. Modification of sporopollenin and ligand-exchange of nitroanilines are illustrated in Fig. 1. Nitroanilines and all other chemicals were purchased from Merck Chemical Company and were of reagent grade. Deionized water was used in the preparation of the mobile phase.

2.2. Chromatographic runs

The ligand-exchange stationary phase was packed into a glass column by the conventional slurry packing method. The Co(II)-CDAE-S column was flushed with deionized water until the effluent was free of cobalt(II) ions and then equilibrated for 30 min with the mobile phase before analytes were injected. The chromatographic system used in the present study is a peristaltic pump (Alitea S2) and a UV–vis spectrophotometer (Shimadzu 160A) connected to the chromatographic column. The column temperature was controlled using a water jacket connected to a thermostated circulator within a deviation of ±0.1 °C and a heat exchanger was used for preheating the mobile phase before it reaches the column. Sample solutions were prepared by dissolving 1.0×10^{-2} mol of each analyte in 10 ml of mobile phase solution. The column was eluted with 0.05 M NH_4OH throughout the whole range (5–95% ethanol in water) of mobile phase, and elution behavior of analytes was investigated at various temperatures (15–60 °C) by means of their capacity factors and resolution. The capacity factor (k) was

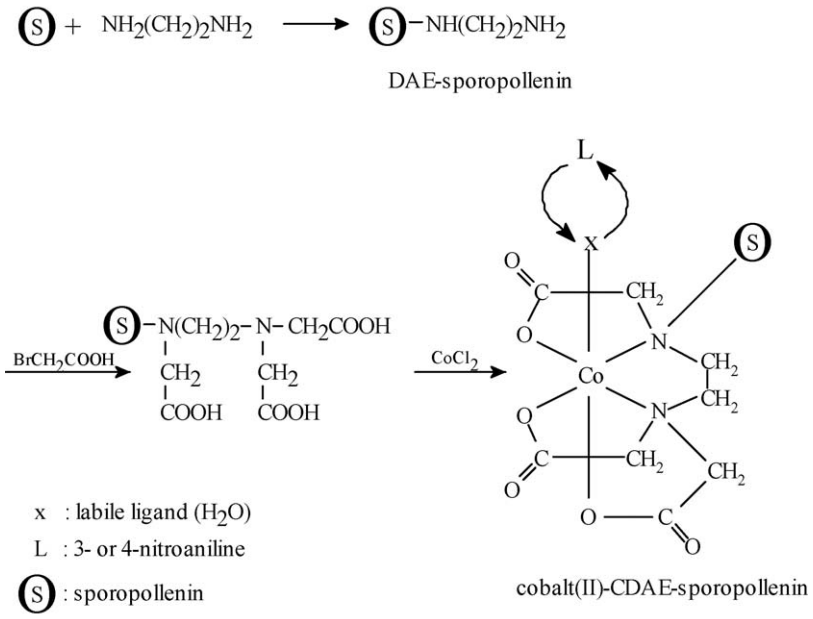

Fig. 1. Modification of sporopollenin as ligand-exchanger.