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学位論文題目	Development of silica-based materials for chromatographic separations in capillary liquid chromatography (キャピラリー液体クロマトグラフィーにおけるクロマトグラフィー分離のためのシリカ系材料の開発)		
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論文内容の要旨

Modern society today is specifically interested in the art technologies in search of solutions to the wide range of issues including industrial waste water management, food quality control, screening of criminal investigations and environmental pollutants. Chromatography has been one of the most extensively used analytical techniques for the analysis of these problems and has been seen to offer satisfactory results. Since its discovery in 1903 by Tswett, fellow scientists have greatly developed it into liquid chromatography (LC), gas chromatography (GC), *etc.* This was due to the need for better samples separation with reduced time and solvent consumption. In the late 1980s, LC packing materials were downsized ($< 10 \mu\text{m}$) with the packing being done at high pressure using slurry techniques. These packed columns were further improved to monolithic columns that have sponge-like structures, which supposedly offered shorter diffusion distances and several solute dispersion paths. The high backpressures experienced in the packed columns were overcome by using monolithic columns. Nevertheless, silica-based packed columns still dominate in the market due to their good chromatographic performance, ease of modification, strong mechanical strength and availability.

Capillary columns were used for the present study in order to achieve satisfactory results with reduced analysis time, sample concentration and eluent consumption. The synthesized silica-based stationary phases were packed into capillary columns and were used to investigate the retention mechanisms under different eluent conditions. One of the synthesized materials in this study was silica based chromium metal-organic framework (MOF) materials, which was able to address a major problem of producing a homogenous surface for the chromatographic evaluation. The Si-Cr column was found capable of separating mix aromatic compounds within 15 minutes. The retention order was found to be from less non-polar (phenol) to highly non-polar compound (diethyl phthalate). However, there was an observed peak broadening on peaks which were due to the interaction of the given compounds (slightly polar) with the Cr open sites. Such drawback could be fixed by replacement of the given ligands with rigid aromatic multi-dentate ligands containing both O⁻ and N⁻ electron rich surfaces, so as to form stable complexes with Cr, effectively closing all the open Cr sites.

Click modified silica column was also synthesized on a need to make a homogenous and a novel stationary phase. According to the FT-IR sample characterization results, the IR spectra on bare silica modification with 3-isocyanatopropyl-triethoxysilane and propargyl bromide, displayed an increase of absorptions intensities at due to C-H stretching indicating a largely ordered structure of the hydrocarbon chains. These spectral changes were clear proofs of a successful reaction. FT-IR spectra of the silica alkyne groups disappeared as observed on the FT-IR spectra of the click-silica alkylazide, which indicated that the intermediate azide group was almost exhausted in the final immobilization procedure. The prepared click alkyl-azide silica bonded stationary phase was achieved through the reaction of alkyne silica and azido-octadecane in presence of Cu catalyst to produce a triazole ring. This ring could serve as ion

exchange site as it is considered to be a basic aromatic heterocycle. On protonation of this ring, this would have resulted to formation of ion exchange sites, responsible for the retention of inorganic anions. These anions were separated in the order of iodate, bromate, bromide, nitrate, iodide, and thiocyanate, which is typical order in common ion chromatography (IC) columns. The analyte anions retention in the column decreased with increase in sodium chloride concentration.

A 4-amino butyric acid silica packing column was also synthesized and used to separate common anions by using sodium chloride as the eluent. It was suggested that the expected mode of inorganic anions separation was due to the secondary amine group's protonation, on the modified silica surface, which may have acted as cationic site interacting with the inorganic anions through electrostatic interaction, for the effective separation. The elution order was in the order of iodate, bromate, nitrite, bromide, nitrate and iodide and the retention mechanism was deduced to be ion-exchange mechanism. This elution order was observed to be similar to that of common IC. As the NaCl concentration was increased, the anions' retention was observed to be decreased. The prepared column's repeatability was assessed with repeated chromatographic runs, excellent repeatability with RSD value of less than 2% was obtained.

The pH of the eluent also affected the retention of the anion. The anions were more retained in the column under acidic condition, and less retained on the stationary phase under neutral condition. This meant that the prepared stationary was protonated at a lower pH, while had less charge at a neutral pH. Thus, the prepared stationary phase worked as an anion-exchange stationary phase at a lower pH. The same behavior was also observed with the synthesized 7-amino heptanoic acid modified column. Moreover, with the increased flow rates, the elution strength was increased and hence the observed reduced retention times. Comparison between the analytes retention results obtained for both the 4-amino butyric acid modified and 7-amino heptanoic acid silica gel, both the chemical stability and the reproducibility of 7-amino heptanoic acid modified silica was better than 4-amino butyric acid. This can be explained by the fact that 7-amino heptanoic acid modified silica formed stable, homogenous, smooth surface unlike 4-amino butyric acid modified silica.

論文審査結果の要旨

液体クロマトグラフィー (LC) 用の固定相として、優れた分離能と機械的強度を持つシリカゲルやその化学修飾体が汎用されているが、シリカ系固定相は酸や塩基性溶媒に弱い。本論文では、シリカゲル担当を化学的安定性の高い修飾法・合成法の開発に成功している。ポリエチレングリコールとクロムを結合した固定相では、順相クロマトグラフィーの保持挙動を示し、様々な芳香族化合物の分離に成功している。また、クリック反応を用い結合した窒素分子を有する固定相では、イオン交換モードでの分離が可能になり、中性移動相で6種類の無機陰イオンの分離を達成し、実サンプルへの応用に適している。さらに、4-アミノ酪酸と7-アミノヘプタン酸を共有結合した固定相では、陰イオンに対して非常に高い分離選択性を持ち、6種類の無機陰イオンの高性能分離を達成し、海水等の分析に応用している。アミノ酸結合固定相は、双性型固定相でもあり、陽イオン交換、陰イオン交換、さらに親水性相互作用クロマトグラフィーでの分離が期待できる。

最終試験結果の要旨

3名で構成する学位審査委員会は、本論文および論文の基礎となる発表論文（査読付論文2編；投稿中・審査中の論文3編）の内容を確認し、2月10日（月）に開催された最終試験（公聴会）における申請者との質疑応答・口頭試問等に基づき慎重に審査した結果、合格と判定した。

発表論文（論文名、著者、掲載誌名、巻号、ページ）

1. Development of silica-based chromium metal organic framework materials for chromatographic separations, Esther Wamaitha Maina, Lee Wah Lim, Toyohide Takeuchi, GP Globalize Research Journal of Chemistry (Accepted)
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