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Separation of Three Monosaccharides Using Amino Ionic Liquid-Based Silica

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An amino-imidazolium ionic liquid was coated on commercial silica and the resulting ionic liquid-based particles were used as special sorbents of solid-phase. The mobile phase of acetonitrile/water from 90:10 to 70:30 (v/v) could separate the monosaccharides. Good linearity was obtained from 1 to 10 mg/mL with a RSD < 3.4 %. The sorbent produced reproducible results and performed stably, highlighting its potential as a separation material.

Keywords: Ionic liquid-based silica, Monosaccharides, Solid-phase extraction, High-performance liquid chromatography.

INTRODUCTION

Monosaccharides and more complex carbohydrates are often analyzed by liquid chromatography[1]. Stationary phases for the separation of monosaccharides can be based on octadecylsilane, amino groups (-NH_2) and ion-exchange resins[2-4]. A typical separation medium for ion-exchange chromatography is sulfonated cross-linked styrene divinyl benzene cation exchange resin and is used most commonly in industrial separation[5,6]. A solid-phase extraction (SPE) with a new stationary phase is one of the most convenient and high-performing technologies for separation. In this case, sorbent selection is essential; it affects the amount adsorbed, selectivity of the adsorbent and its affinity to the adsorbates[7,8].

Ionic liquids contain bulky organic cations (such as *N*-alkylpyridinium or 1-alkyl-3-methylimidazolium), which are combined with inorganic or organic anions. These liquids have attracted considerable attention in many fields of analytical chemistry[9], such as sample preparation, organic synthesis, liquid-phase extraction and chromatographic separations, because they are high-tech, green reaction media with excellent chemical properties[10]. Ionic liquid-modified silica has been used successfully in separation because of its characteristic cations and anions. Some studies have been conducted on the application of these particles as a sorbent to separate some familiar organic compounds and to the extract active components from natural plants[11,12].

This paper reports the preparation of amino ionic liquid-based silica. The modified silica was then packed into a HPLC column and used in the separation of three monosaccharides (Fig. 1).

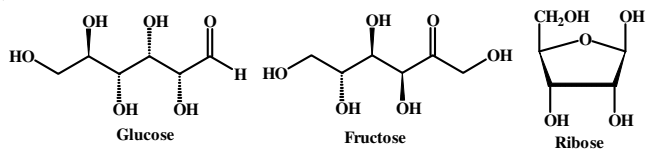

Fig. 1. Chemical structures of monosaccharides

EXPERIMENTAL

(3-Aminopropyl)trimethoxysilane (97 %, Aldrich, Germany), 3-chloropropionyl chloride (> 98 %, Tokyo Chemical Industry CO., Ltd. Japan) and imidazole (= 99.5 %, Sigma-Aldrich, Germany) were used to synthesize a ionic liquid. Monosaccharides were from aldrich (Milwaukee, USA). Methanol, acetonitrile, chloroform (HPLC grade), toluene, methylene chloride, *n*-hexane (extra pure) and triethylamine (first grade) were purchased from Duksan Pure Chemical. Co., Ltd. (Korea). Water was twice distilled and filtered (FH-0.45 μm, Advantec MFS, Inc., Japan) using a decompressing pump (Division of Millipore, Waters, USA).

HPLC analysis: The LC system comprised a M930 solvent delivery pump (Young Lin Co. Korea), a RI detector (Younglin Co., Korea) and an integrated data system (Autochrowin. Ver. 1.42, Younglin Co., Korea). Acetonitrile/water (90/10, v/v) as the mobile phase was used to determine the compounds by a static method.

Preparation of ionic liquid-based silica: Commercial silica (LiChrospher Si 60, 15 mm) was purchased from MERCK (Darmstadt, Germany) and activated using the following procedure. First, silica was stirred with nitric acid/water (50:50, v/v) for 24 h. The activated silica was then filtered and washed

thoroughly with distilled water and ethanol. This pretreatment was performed to enhance the content of silanol groups on the silica surface and eliminate any metal oxide and nitrogenous impurities.

The activated silica was dried at 120 °C for 12 h. Silica (5 g) and an excess of 3-chloropropyltrimethoxysilane (5 mL) were stirred and heated in 100 mL of dry toluene under reflux. After 24 h, the powder was cooled to room temperature and washed with ethanol. The chloropropyl silica (SilCl) obtained was dried under vacuum at 80 °C. Subsequently, 4 g of imidazole was used to modify the surface of SilCl (5 g) in 100 mL of toluene. The imidazole-based silica (SilIm) was obtained after heating the mixture under reflux for 10 h. The SilIm was washed completely with ethanol and dried. Finally, SilIm (5 g) and 3-bromopropylamine hydrobromide (4 g) were stirred and heated in 100 mL ethanol under reflux for 24 h. After the reaction was complete, a pale yellow powder was obtained, which was then washed and dried. The amino IL-based silica ($SilImNH_2$) was obtained (Fig. 2).

Characteristic analysis: Fourier transform infrared (FT-IR) spectroscopy was performed (Vertex 80V, Bruker, Billerica, MA, USA) on KBr pellet over the wavenumber range, 4000-400 cm^{-1}, at a scan rate of 20 scans min^{-1}. The carbon, hydrogen and nitrogen contents were determined by elemental analysis (EA1112, Thermo, Italy). Thermogravimetric analysis (TGA, SCINCO thermal gravimeter S-1000, Seoul, Korea) was performed at a heating rate of 10 °C/min under nitrogen.

Procedure of solid-phase extraction: 0.2 g of $SilImNH_2$ were packed into 3.0 mL empty polypropylene cartridges (Ø 0.9 cm, Alltech, Deerfield, IL, USA) and preconditioned with 5 mL of methanol. After solid-phase extraction separation with different solvents, the filtrates were analyzed with HPLC.

RESULTS AND DISCUSSION

SilCl showed a conspicuous peak at 700 cm^{-1}, which is the finger print region of the C-Cl group. In $SilImNH_2$, the C-Cl peak disappeared and a new peak emerged at 1575 cm^{-1}. The characteristic region of the amide bands ranged from 1500 to 1600 cm^{-1}, indicating the replacement of C-Cl groups with imidazole groups. These results show that silica had been modified successfully with ionic liquid-containing amino groups.

Thermogravimetric analysis can determine the thermal stability of the modifier on the silica surfaces. The weight losses observed were attributed to the loss of organic groups. From 200 to 600 °C, 16.5 % mass losses were observed for $SilImNH_2$, (Fig. 3). $SilNH_2$ showed higher mass loss due to the extra combination of amino groups and bromine, indicating the successful immobilization of amino groups on silica.

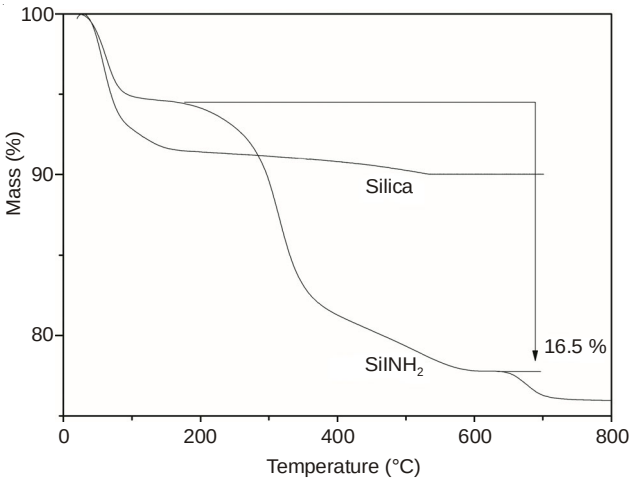

Fig. 3. Thermogravimetric analysis curves of silica and $SilImNH_2$

Validation of the proposed methods: Calibration curves were constructed using the chromatographic peak areas measured at increasing concentrations, ranging from 1 to 10 mg mL^{-1}. Good linearity was obtained with linear correlation equations of $y = 1129x + 0.5$ ($r^2 = 0.999$) for ribose, $y = 147256x + 3.98$ ($r^2 = 0.999$) for fructose and $y = 131254x-3.24$ ($r^2 = 0.999$) for glucose (y is the peak area and x is the concentration of the target compounds).

Separation of monosaccharides: A mixture of monosaccharides (10 mg/mL) was prepared in water and 1 mL of the aqueous solvent was loaded into commercial NH_2 and $SilImNH_2$ solid-phase extraction cartridges. According to the

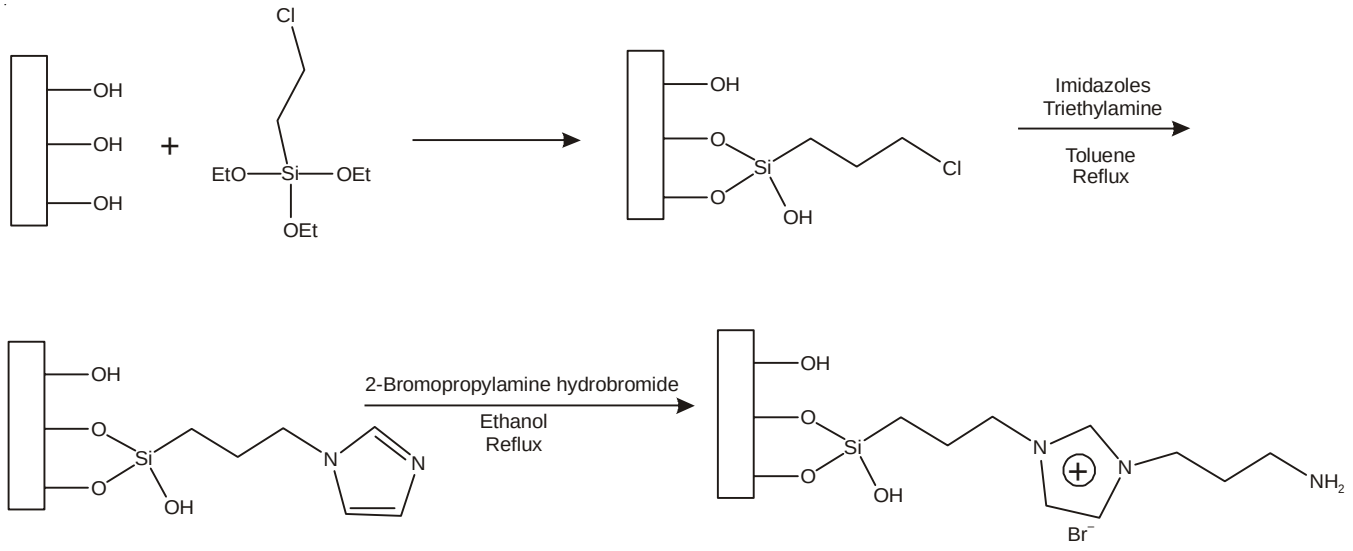

Fig. 2. Preparation scheme of amino ionic liquid-based silica

component of the mobile phase, acetonitrile and water were selected as the elution solvents. Initially, pure acetonitrile was used. After elution with 1 mL, no monosaccharide was detected in the filtrate from the $SilImNH_2$ solid-phase extraction cartridges but all the monosaccharides were eluted from commercial NH_2 solid-phase extraction cartridges. In addition, no more compounds were eluted out with more acetonitrile. This shows that the interaction of $SilImNH_2$ with the monosaccharides was higher than the commercial NH_2 sorbent.

Water was added to acetonitrile to increase the elution ability because of the hydrophilicity of monosaccharides. 1 mL of different components of acetonitrile/water (v/v) were used to elute the monosaccharides from the $SilImNH_2$ solid-phase extraction cartridge. When the component of water was increased to 10 %, ribose was eluted (Fig. 4 (A)). Fructose and glucose were eluted out when the water content was increased to 30 % (Fig. 4 (B)). Pure water was used to determine the elution efficiency. No target compounds remained on the sorbent after 1 mL of the mobile phase had eluted. The solid-phase extraction separation depended on the hydrophobic interaction from the ionic liquid groups on the polymer surface and the hydrogen-bonding interaction from -NH_2 groups. Fructose and glucose contained more -OH groups and higher hydrophobicity than ribose. Therefore, the monosaccharides can be separated by increasing the component of water in acetonitrile.

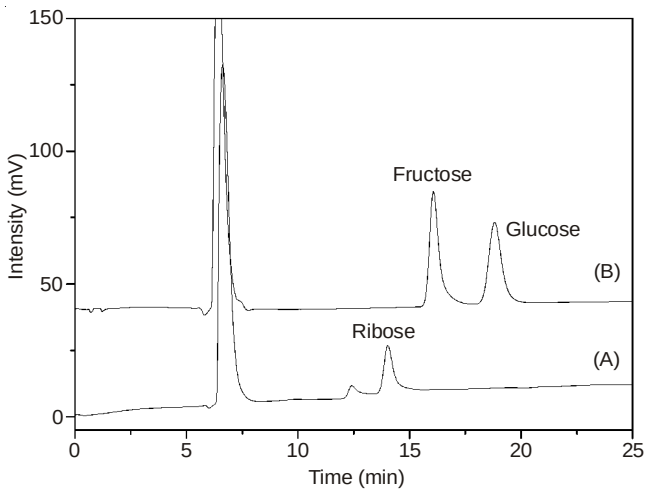

Fig. 4. Chromatograms of SPE separation; (A) $SilImNH_2$ cartridge with acetonitrile/water (90:10, v/v) as mobile phase; (B) $SilImNH_2$ cartridge with acetonitrile/water (70:30, v/v) as mobile phase

Validation of the analytical method and recycling of $SilImNH_2$ in solid-phase extraction: Repeatability assays conducted by five injections of the standard solutions of the monosaccharides after solid-phase extraction over a five-day period. RSDs were < 3.4 % for the standard solutions. Validation of the analytical method and recycling of the sorbent in the solid-phase extraction cartridge were investigated simultaneously. The errors in the concentrations detected were less than 4.12 %, highlighting the stability of the sorbent.

Conclusion

The high stability of ionic liquid-based silica with high concentrations of amino ionic liquid groups was developed for solid-phase extraction. Good linearity was obtained from 1 to 10 mg/mL with a RSD < 3.4 %. The monosaccharides were separated under optimized solid-phase extraction conditions with a low deviation error, highlighting the stability of the sorbent and its potential applicability in solid-phase extraction.

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