



Preparation of decarboxylic-functionalized weak cation exchanger and application for simultaneous separation of alkali, alkaline earth and transition metals



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ARTICLE INFO

Article history:

Received 19 January 2016

Received in revised form

23 February 2016

Accepted 2 March 2016

Available online 3 March 2016

Keywords:

Click chemistry

Weak cation exchanger

Mercaptosuccinic acid

Ion chromatography

Stationary phase

ABSTRACT

A novel weak cation exchanger (WCX) with dicarboxyl groups functionalized has been developed by clicking mercaptosuccinic acid onto silica gel. The simple synthesis starts with modification of silica gel with triethoxyvinylsilane, followed by efficient coupling vinyl-bonded silica with mercaptosuccinic acid via a “thiol-ene” click reaction. The obtained WCX demonstrated good separation and high selectivity towards common metals. Simultaneous separation of 10 alkali, alkaline earth and transition metals was achieved within 12 min. Ion exchange and complex mechanism dominates the separation process. Its utility was demonstrated for determination of metals in tap water.

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1. Introduction

Although atomic spectrometry-based techniques dominate the determination of metals presently [1,2], ion chromatography method still has some merits such as simultaneous detection of multiple metals per injection and easy use. Silica-based cation exchanger combined with unsuppressed conductimetric detection has found many applications for simultaneous determination of metal cations [3–5]. Although bare silica gel itself can serve as a cation exchanger owing to the silanol groups on the surface of silica gel [6], direct use of bare silica as cation exchanger lacks enough selectivity and capacity for separation of metals. Moreover, it is also restricted by difference of silica gels from different companies or different batches. Thus doping or chemical modification of silica gel to introduce functional groups is always required. Ohta et al. proposed a way to dope aluminum or zirconium in silica gel to behave cation exchanger and successful separation of alkali and alkali earth metals was achieved in 2001 [7,8]. By physically coating poly(butadiene-maleic acid) onto silica gel, Kolla et al. described a carboxyl-functionalized weak cation exchanger (WCX) in 1987, which demonstrated effective separation of alkali and alkali earth metals [9] and even transition metals [3].

Some chemical modification approaches [5,10,11] such as nucleophilic silanization [5] or co-condensation of polymer [11] were also reported. One of potential drawback of these approaches is unwanted side reaction products existing [12,13].

Since introduced in 2001 by Kolb et al. [14], Click chemistry has become a modular synthetic approach towards the assembly of new molecule by efficiently coupling small units together [15,16]. Such way has many advantages, including simplicity, high efficiency and high selectivity, high yield and mild conditions [17]. By Clicking cysteine [18] and arginine [19] onto silica gel, two kinds of amino acid-based stationary phases were described for hydrophilic interaction chromatography (HILIC) in our previous work. In addition, Zhao et al. reported a WCX (or stationary phase) prepared by Clicking alkyne-carboxylic acids onto silica gel for separation of proteins in 2012 [20]. Another WCX was also reported for HILIC by clicking thioglycolic acid with vinyl-bonded silica gel via “thiol-ene” click chemistry [21]. It demonstrated excellent hydrophilic property towards the model polar analytes.

It was noted that the clicked molecules used previously for preparation of WCX contain sole carboxyl group per functional molecule and a possible problem is low capacity or low selectivity for metal cations. If the functional molecule contains two or more carboxyl groups, it may be a better choice for preparation of WCX since strong metal complex interaction may be involved, similar to common metal strong complex reagent like ethylenediaminetetraacetic acid (EDTA) and iminodiacetic acid (IDA). Based on such

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consideration, herein we described a decarboxyl-functionalized stationary phase via “thiol-ene” click chemistry and it demonstrated for simultaneous separation of alkali, alkaline earth and transition metals using a sole eluent.

2. Experimental

2.1. Materials and reagents

Spherical silica was from Fuji (5 μm dia., 10 nm pore size; 300 m^2/g surface area, Fuji Silysia Chemical Ltd., Japan). Triethoxyvinylsilane, mercaptosuccinic acid, acrylic acid and azobisisobutyronitrile (AIBN) were obtained from Aladdin Co. (Shanghai, China). (3-Mercaptopropyl) trimethoxysilane (3-MPTS) was obtained from Silicone New Material Corp. (Wuhan, China). Oxalic acid, pyridine, potassium hydroxide, hydrochloric acid, toluene, methanol, tartaric acid and the model analytes for chromatographic evaluation were purchased from Lingfeng Chemical Reagent Corp. (Shanghai, China). The chemicals are analytical grade unless otherwise stated. Pure water was provided by a Milli-R04 purification system (Millipore, Germany). Unless otherwise stated, pure water was used for solution preparation throughout.

2.2. Instrumentation

An IC system (CIC-100, Shenhan Chromatography Technology Corp., Qingdao, China) was used to perform chromatographic experiments. It consists of a PEEK pump and 5-electrode conductivity detector. Oxalic acid was used as the eluent and the separations were performed under non-suppressed mode.

An ultrasonic cleaning machine with working frequency of 40 kHz and power of 200 W was purchased from Hechuang Ultrasonic Instrument Corp. (KH5200B, Kunshan, China). Elemental analysis was carried out on a Varil EL III elemental analyzer (Elementar, Germany).

2.3. Preparation of Click-MA and column packing

The synthetic route of Click-MA is outlined in Fig. 1. Silica gel was initially activated by refluxing method in 1 mol/L hydrochloric acid for 6 h. After filtration, the residue was washed with water to reach neutral and then dried at 80 $^{\circ}\text{C}$ overnight to remove the adsorbed water of silica gel. 3 g of activated silica gel was placed in a flask, followed by the addition of 30 mL anhydrous toluene and then 4 mL triethoxyvinylsilane along with 6 mL pyridine as catalyst. The mixture was refluxed under nitrogen for 24 h with stirring at 250 r/min. The silanized silica gel was filtered and washed with acetone, water and methanol successively. The residue was then dried at 50 $^{\circ}\text{C}$ for 12 h. The vinyl-modified silica was then clicked with 3 g mercaptosuccinic acid in 45 mL MeOH/H₂O (1/2, v/v) in the presence of 60 mg AIBN at 65 $^{\circ}\text{C}$ for 24 h. The resulting solution was filtered, washed with dichloromethane, water and MeOH in turn and dried at 60 $^{\circ}\text{C}$ for 12 h to yield Click-MA.

To highlight the advantage of decarboxylic-functionalized WCX, a WCX with sole carboxyl functional group was also prepared by clicking acrylic acid onto 3-MPTS-bonded silica gel (Click-AA). The general synthesis route was provided in [Support information \(SI\)-Fig. 1](#).

Click-MA (or Click-AA) (2.5 g) was in slurry packed into a stainless steel tube (4.6 mm i.d. \times 150 mm length) under 7000 psi of pressure with MeOH as the slurry and propulsion solvent.

3. Results and discussion

3.1. Characterization of Click-MA

The vinyl-silica and Click-MA were characterized by elemental analysis (data shown in [SI-Table 1](#)). Obvious increases of carbon content was observed for vinyl-silica (3.09%), indicating that vinyl groups were successfully introduced onto silica gel. Relative to vinyl-silica, $\sim 0.92\%$ increase of carbon content of Click-MA was calculated, resulting from the successful bonding of mercaptosuccinic acid onto vinyl-silica. The surface coverage of mercaptosuccinic acid was calculated to be ~ 0.19 mmol/g, thus the apparent capacity of carboxyl groups was ~ 0.38 mmol/g, which is comparable to those of some commercial available weak exchange columns.

3.2. Chromatographic evaluation of Click-MA under IC mode

Rich decarboxyl groups associated with Click-MA offer possibility of separating metals. More important, dicarboxyl moieties may favor analysis of divalent metal ions relative to monocarboxylic group owing to easy chelation interaction between decarboxyl groups and metal besides ion exchange interaction (similar to metal complex reagent such as EDTA and IDA). To confirm such suspect, the comparison of Click-MA (with decarboxyl groups) and Click-AA (with sole carboxyl group) was made, as provided in [Fig. 2](#). Under the same condition, Click-MA showed much stronger retention and effective separation towards model metals relative to Click-AA. For Click-AA, co-elution occurred for Ni^{2+} and Na^+ , Cd^{2+} , Mg^{2+} and Ca^{2+} .

Under unsuppressed conductimetric detection mode, the use of acid eluent is a better choice for lowering limit of detection since the largest equivalent mobility of hydronium, leading to larger conductivity difference and then higher sensitivity. In comparison, the use of organic acid eluent is superior to inorganic acid since the equivalent mobility of counterion of hydronium is usually lower than that of inorganic counterparts, which can result in lower background and then lower noise level. More important, organic acids have complex ability to metals which helps to enhance elution strength (details will be discussed below). Thus several kinds of organic acid eluents were tested for five model transition metals, including oxalic acid, citric acid and tartaric acid and oxalic acid-tartaric acid. The data (not shown) indicated that oxalic acid behaved best in terms of peak shape, short retention time and separation resolution. This probably resulted from higher

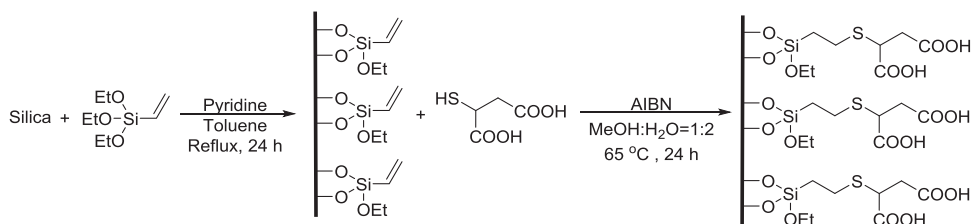


Fig. 1. The preparation of Click-MA.

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