



Separation of transition and heavy metals using stationary phase gradients and thin layer chromatography



Stacy L. Stegall^a, Kayesh M. Ashraf^a, Julie R. Moye^a, Daniel A. Higgins^b,
Maryanne M. Collinson^{a,*}

^a Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284-2006, United States

^b Department of Chemistry, Kansas State University, Manhattan, KS 66506-0401, United States

ARTICLE INFO

Article history:

Received 6 January 2016

Received in revised form 28 March 2016

Accepted 2 April 2016

Available online 6 April 2016

Keywords:

Chelation ion chromatography

Planar chromatography

Gradients

Aminosilanes

Organoalkoxysilanes

Sol-gel

ABSTRACT

Stationary phase gradients for chelation thin layer chromatography (TLC) have been investigated as a tool to separate a mixture of metal ions. The gradient stationary phases were prepared using controlled rate infusion (CRI) from precursors containing mono-, bi-, and tri-dentate ligands, specifically 3-aminopropyltriethoxysilane, N-[3-(trimethoxysilyl)propyl] ethylenediamine, and N-[3-(trimethoxysilyl)propyl] diethylenetriamine. The presence and the extent of gradient formation were confirmed using N1s X-ray photoelectron spectroscopy (XPS). XPS results showed that the degree of modification was dependent on the aminosilane precursor, its concentration, and the rate of infusion. The separation of four transition and heavy metals (Co^{2+} , Pb^{2+} , Cu^{2+} , and Fe^{3+}) on gradient and uniformly modified plates was compared using a mobile phase containing a stronger chelating agent, ethylenediaminetetraacetic acid (EDTA). The retention of the metal ions was manipulated by varying the surface concentration of the chelating ligands. The order of retention on unmodified plates and on plates modified with a monodentate ligand was $\text{Fe}^{3+} > \text{Cu}^{2+} \sim \text{Pb}^{2+} \sim \text{Co}^{2+}$, while the order of retention on plates modified with bi- and tri-dentate ligands was $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Pb}^{2+} \sim \text{Co}^{2+}$. Fe^{3+} and Cu^{2+} were much more sensitive to the concentration of chelating ligand on the surface (displaying lower R_f values with increasing ligand concentration) than Pb^{2+} and Co^{2+} . Complete separation was achieved using a high concentration of the tridentate ligand coupled with a longer time for modification, yielding a retention order of $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Pb}^{2+}$.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Gradient surfaces [1–3] are potentially useful in separation science because they provide a means to vary the concentration of functional groups along the length of the surface and influence retention and the separation of complex mixtures [4–9]. In general, two approaches have been used to make gradient surfaces for chromatography. The first involves serially connecting columns each containing a different stationary phase [6–9] and the second involves gradually changing the functional group(s) on a single column [4,5]. The former are examples of discontinuous gradients, while the latter are examples of continuous gradients. Retention factors and thus separation can be manipulated by changing the steepness of the gradient, the functional group(s), and in the case of planar chromatography, the direction of the gradient(s) [4,5]. An

advantage that a continuous stationary phase gradient, as opposed to discontinuous one, has is that it provides an avenue for synergistic (cooperative) interactions between neighboring functional groups in the stationary phase to take place.

Recently, we developed a relatively simple and inexpensive method to create a continuous gradient on surfaces suitable for chromatography known as controlled-rate infusion (CRI) [10]. In this method, a silica-coated substrate, e.g., a thin layer chromatography (TLC) plate, is exposed to functionalized organoalkoxysilane precursors in a time-dependent fashion; condensation takes place between the hydrolyzed precursors and surface silanol groups forming a modified silica surface whose degree of functionality changes in a predefined fashion from one end to the other [10]. Aminoalkoxysilanes are particularly useful in CRI because they react quickly with surface silanol groups due to the self-catalyzing ability of the amine group [11]. In recent work, we prepared single-component gradients from 3-aminopropyltriethoxysilane to separate a mixture of four weak acids and bases, as well as three commonly used over-the-counter drugs [4]. Building on this work,

* Corresponding author.

E-mail address: mmcollinson@vcu.edu (M.M. Collinson).

aligned and opposed multi-component gradients were prepared from 3-aminopropyltriethoxysilane and phenyltrimethoxysilane and used to separate a mixture of water- and fat-soluble vitamins [5].

The focus of the present study is on the development of gradient stationary phases suitable for metal ion separation. The separation and quantification of transition and heavy metals, particularly those that are toxic, is of utmost importance. Many separations utilize silica gel supports and focus on manipulating the composition of the mobile phase to improve the separation, which is not always practical [12–14]. Others have modified the inorganic support with chelating ligands [15–23] and/or utilized chelation ion chromatography (CIC) to separate and quantify mixtures containing transition and heavy metals [24–29]. CIC relies on the competition between an immobilized chelating ligand, such as iminodiacetic acid, a β -diketone, or an amine, in the stationary phase and another chelating agent, such as picolinic or dipicolinic acid or trifluoroacetylacetone, in the mobile phase [24,25]. The principles of CIC have also been applied to TLC [15–18]. Using silica gel TLC plates modified with amines or β -diketones and a mobile phase such as salicylaldehyde or trifluoroacetylacetone in acetone, mixtures of four to six metal ions have been separated [16,18].

In this work, we couple gradient stationary phase technology with CIC as a means to control the retention of metal ions and thus influence their separation. Specifically, gradient stationary phases were prepared with either 3-aminopropyltriethoxysilane, N-[3-(trimethoxysilyl)propyl] ethylenediamine, or N-[3-(trimethoxysilyl)propyl] diethylenetriamine using CRI on a TLC plate. The surface density of the ligands on the stationary phase and hence the strength of the chelation, changes along the length of the support. By using ethylenediaminetetraacetic acid (EDTA) in the mobile phase, a competition is created between the chelating ligands on the stationary phase and a stronger chelating agent in the mobile phase. We demonstrate how changing the aminoalkoxysilane concentration, infusion time, or the number of amine groups can be used to affect the retention factor (R_f) of the selected metal ions and influence separation. We also show how the retention can be changed depending on whether or not a stationary phase gradient is used.

2. Experimental

2.1. Reagents

N-[3-(trimethoxysilyl)propyl] ethylenediamine (97%, referred to as diamine) and N-[3-(trimethoxysilyl)propyl] diethylenetriamine (97%, referred to as triamine) were purchased from Acros Organics. 3-Aminopropyltriethoxysilane (98%, referred to as amine) and isobutyltrimethoxysilane (97%, referred to as isobutyl) were obtained from Alfa Aesar. Cobalt (II) acetate, lead (II) acetate, and copper (II) acetate were obtained from Fisher Scientific; iron (III) perchlorate was obtained from GFS Chemicals. Ethylenediaminetetraacetic acid (EDTA), disodium salt, was purchased from Fisher Scientific. Ethanol (200 proof, USP/ACS grade) was obtained from Pharmaco-Aaper. The TLC plates used in this work were silica gel 60 F₂₅₄ from Sigma Aldrich; the plates were 20 × 20 cm with a 250 μ m layer thickness.

2.2. Preparation of stationary phase

The 20 × 20 cm TLC plates were cut into pieces of the approximate size of 8 cm × 1.7 cm using a glass cutter, cleaned by soaking in ethanol for ~5 min, and dried by heating in an oven (~160° C) for 30 min. The plates were then cooled to room temperature before use. Plates used were (1) as-received (no modification),

Table 1

Aminosilanes, volumes, infusion rates, and infusion times for gradient preparation.

Aminosilane	Volume of Aminosilane (mL)	Infusion Rate (mL/min)	Infusion Time (min)
Triamine	0.08	1.0	15
		1.0	5
	0.50	3.0	15
		1.0	15
		0.5	30
Diamine	0.08	1.0	15
	0.12		
	0.50		
Amine	0.08	1.0	15

(2) uniformly modified, or (3) gradient plates prepared using CRI. Before modification, the plates were soaked in an ethanol solution for ~10 min. Both uniformly modified and gradient plates were exposed to a triamine, diamine, or amine solution prepared from 20: x: 0.004 v/v/v of ethanol: aminosilane: DI H₂O, where x is 0.08, 0.12, or 0.50. The uniformly modified plates were simply soaked in an aminosilane solution for a set period of time. For the gradient plates, the plates were placed upright in a graduated cylinder, and the aminosilane solution was infused into the graduated cylinder using a syringe pump (Harvard Apparatus PHD 2000 Infusion) at a set rate over a given period of time. The exact parameters required for gradient deposition are determined by the kinetics of precursor reaction with the surface, as has been previously explored in detail for aminosilane gradients [10,30]. The volumes of aminosilane, infusion rate, and infusion time employed in the present studies are given in Table 1. All of the plates were rinsed thoroughly with ethanol after being removed from the aminosilane solution.

2.3. Reduction in residual silanol groups

To reduce the number of residual silanol groups on the TLC plates and thus the streaking of metal ions, the plates were exposed to an isobutyl solution (20: 0.25: 0.50: 0.50 v/v/v/v ethanol: isobutyltrimethoxysilane: 0.02 M HCl: 0.01 M KOH) for 12 min after modification with triamine, diamine, or amine. To prepare the isobutyl solution, the ethanol, isobutyltrimethoxysilane, and 0.02 M HCl were stirred for 30 min to hydrolyze the isobutyl. Then, 0.01 M KOH was added, and the solution was stirred for an additional 30 min. This two-step process [31,32] afforded efficient hydrolysis (acid) and condensation (base) of the precursors. After soaking, the plates were air dried and placed in the oven at 160° C for 1 h.

2.4. Separation of metal ions

The metal salts (Co(C₂H₃O₂)₂), Pb(C₂H₃O₂)₂, Cu(C₂H₃O₂)₂, and Fe(ClO₄)₂) were dissolved in 0.1 M HCl at a concentration of 5 mg/mL. A mixture of the four metal ions was prepared by dissolving 5 mg of each of the metal salts in 1 mL of 0.1 M HCl. The metal ion solutions and the mixture were spotted on unmodified, uniformly modified, and gradient plates 1 cm above the bottom of the plate. The gradient plates were spotted on either the low amine end (so that they faced an increasing gradient, termed GPLA) or the high amine end (so they faced a decreasing gradient, termed GPHA). After spotting, the plates were allowed to dry for ~5 min before being placed in a pre-saturated mobile phase chamber. The mobile phase was an EDTA solution prepared using 0.1 M EDTA/0.1 M K₂HPO₄ (pH ≈ 6.5): acetone (50: 50 v/v). The solvent front was allowed to reach 1 cm from the top of the plate. Once the plates were completely dry, they were visualized under UV light at

Download English Version:

<https://daneshyari.com/en/article/1198514>

Download Persian Version:

<https://daneshyari.com/article/1198514>

[Daneshyari.com](https://daneshyari.com)