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Separation of Transition and Heavy Metals Using Stationary Phase Gradients and Chelation Thin Layer Chromatography / Evaluation of the Effectiveness of POGIL-PCL Workshops

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Separation of Transition and Heavy Metals Using Stationary Phase Gradients and Chelation Thin Layer Chromatography / Evaluation of the Effectiveness of POGIL-PCL Workshops

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University

by

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List of Abbreviations

Part 1

α	Fraction of EDTA in the form Y^{4-}
2D TLC	Two-dimensional thin layer chromatography
Amine	3-aminopropyltriethoxysilane
CIC	Chelation ion chromatography
Co	Cobalt
CRI	Controlled-rate infusion
Cu	Copper
Diamine	N-[3-(trimethoxysilyl)propyl] ethylenediamine
DMG	Dimethylgloxime
EDTA	Ethylenediaminetetraacetic acid
Fe	Iron
GPHA	Gradient plate-high amine
GPLA	Gradient plate-low amine
HAHT	High triamine-high thiol
HALT	High triamine-low thiol
Hg	Mercury
HSAB	Hard-soft acid-base
ICP	Inductively coupled plasma
IDA	Iminodiacetic acid
IDWC	Infusion-withdrawal dip-coating
Isobutyl	Isobutyltrimethoxysilane

K_f	Formation constant
LAHT	Low triamine-high thiol
LALT diagonal	Low triamine-low thiol diagonal
LALT	Low triamine-low thiol
LC	Liquid chromatography
MS	Mass spectrometry
MTMOS	Melthyltrimethoxysilane
Ni	Nickel
PAR	4-(2-pyridylazo) resorcinol
Pb	Lead
R_f	Retention factor
R_{fx}	Retention factor in the x-direction
R_{fy}	Retention factor in the y-direction
SAM	Self-assembled monolayer
Thiol	(3-Mercaptopropyl)trimethoxysilane
TLC	Thin layer chromatography
TMOS	Tetramethoxysilane
Triamine	N-[3-(trimethoxysilyl)propyl] diethylenetriamine
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy
Zn	Zinc
µg/L	Micrograms per liter

Part 2

BCCE	Biennial Conference on Chemical Education
POGIL	Process-Oriented Guided Inquiry Learning
POGIL-PCL	Process-Oriented Guided Inquiry Learning in the Physical Chemistry Laboratory
REDCap	Research Electronic Data Capture
SII	Strengths, Improvements, and Insights

Abstract

Part 1

Gradient surfaces exhibit a variation in chemical or physical properties along the length of the surface. Chemical properties that may be varied include wettability, polarity, charge, or reactivity; physical properties include porosity and surface roughness. Gradients may also be classified as discontinuous, in which materials with varying chemistries are serially connected, or continuous, in which the surface chemistry is varied gradually along the length of the surface. Gradient surfaces have been utilized for a variety of applications such as directed transport, cell adhesion, protein adsorption, and separating mixtures. Gradients are often prepared using silane- or polymer-based methods; commonly known techniques include diffusion, contact printing, dip coating, and self-assembly. One drawback of many methods used to prepare gradients is that they lack the ability to control the steepness. Also, some methods used to prepare gradients are restricted in the types of substrates they can modify.

Controlled-rate infusion (CRI), developed in our group, allows for control over the steepness of the gradients, can be used to modify a variety of substrates, and can be used to create surfaces with a variety of functionalities by simply using an organoalkoxysilane with a different functional group. In CRI, a substrate such as a silicon wafer or thin layer chromatography (TLC) plate is exposed to an organoalkoxysilane in a time dependent fashion. Organoalkoxysilanes are useful in CRI because they react quickly with the hydroxyl groups on a silica surface. The steepness of the gradient can be controlled by varying the concentration of the organoalkoxysilane or the infusion time. The surface chemistry can also be altered by using different organoalkoxysilanes.

In this work, CRI was used to prepare gradients for the purpose of separating transition and heavy metals. The separation, identification, and quantification of transition and heavy metals, some of which are toxic, are particularly important for environmental applications. One method used for separating transition and heavy metals is chelation ion chromatography (CIC), which relies on a competition between a chelating agent in the stationary phase and a chelating agent in the mobile phase. The principles of CIC are applied in this work by utilizing chelating gradients prepared using CRI in the stationary phase and ethylenediaminetetraacetic acid (EDTA) in the mobile phase.

Initial work on this project was focused on controlling the retention of the metal ions by varying the number of amine groups, aminoalkoxysilane concentration, and the infusion time. TLC plates were modified using N-[3-(trimethoxysilyl)propyl]diethylenetriamine (triamine), N-[3-(trimethoxysilyl)propyl]ethylenediamine (diamine), and 3-aminopropyltrimethoxysilane (amine). The gradient profiles were characterized using X-ray photoelectron spectroscopy (XPS). The retention factors of the four metal ions, Co^{2+}, Pb^{2+}, Cu^{2+}, and Fe^{3+}, varied predictably with increasing number of amine groups, increasing aminoalkoxysilane concentration, and increasing infusion time, producing small but useful changes in the retention factors.

The continuation of this project involved the preparation of two-dimensional multi-component gradients on TLC plates. Multi-component gradients were prepared using triamine and 3-mercaptopropyltrimethoxysilane (thiol). CRI was used to prepare aligned, opposed, and orthogonal 2D gradients. The 2D multi-component gradients were used to separate six transition and heavy metals (Co^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+} and Hg^{2+}). On the aligned and opposed gradients, the metal ions faced uniform modification in the first dimension (x-direction) and a gradient in the second dimension (y-direction). On the orthogonal gradients, the metal ions faced a gradient in both dimensions. The retention, and thus the separation, was affected by the presence or absence of a gradient in the first dimension and the direction of the gradient.

Part 2

Workshops are commonly used as a means of promoting the implementation of new teaching methods and materials. Workshops may be conducted only once, or they may be part of a series. Recently, learning communities have been developed to support faculty who wish to implement new teaching methods. Studies on workshop effectiveness often focus on rates of implementation and on perceived barriers to implementation. There are several models used to describe the process that occurs as instructors change their teaching methods. Lewin and Rogers both describe multistage processes which involve learning about and considering new teaching methods and deciding whether to adopt new teaching methods. Another model, situational learning, describes the process of learning part of a community of practitioners.

This work focused on understanding the factors that motivated instructors in the early and late stages in the process of change. Instructors who attended the POGIL-PCL (Process-Oriented Guided Inquiry Learning in the Physical Chemistry Laboratory) workshops were asked to complete an online survey. The goals of the survey were to understand the factors that initially interested instructors in POGIL-PCL, to determine if instructors enter the implementation stage, and to understand the factors that affect how instructors implement POGIL-PCL.

Later surveys were designed to explore the development of the POGIL-PCL network and assess whether implementation is sustained over time. The follow-up surveys were designed to evaluate the growth of the POGIL-PCL network, to characterize the strength of the participants' ties to the network, and to determine how instructors implement POGIL-PCL. This work is based on theories of network development described by Kezar and Rogers. A common theme in the theories on network development and related research is the importance of communication with peers or colleagues; this idea is also emphasized in our work. Networks can be characterized based on the frequency of interaction and the nature of the communication (formal vs. informal, hierarchical v.s two-way, and social/friendly vs. professional). The second part of this work focuses on characterizing the POGIL-PCL network using theories of network development, just described.

Part 1: Separation of Transition and Heavy Metals Using Stationary Phase Gradients and Chelation Thin Layer Chromatography

Chapter 1: Introduction (Part 1)

1.1 Abstract

The main focus of this work is the application of stationary phase gradients to the separation of transition and heavy metals. Gradient surfaces have been prepared using both continuous and discontinuous methods. However, these methods are sometimes complicated or tedious, and they do not allow for control over the gradient profile. More recently, our group developed a method known as controlled-rate infusion (CRI), which allows the gradient profile to be modified in a time-dependent fashion using silane chemistry. CRI can also be used to prepare chelation gradients for the complexation and separation of transition and heavy metals. In this chapter, various methods used to prepare gradient surfaces will be discussed. Later, the separation of transition and heavy metals using stationary phases modified with chelating ligands is discussed. Finally, the use of multidimensional thin layer chromatography for the separation of complex mixtures is presented.

1.2 Gradient surfaces

Gradient surfaces exhibit a variation in surface chemistry along the length of the substrate.[1-5] Gradients may be chemical, varying characteristics such as wettability or polarity, or physical, varying characteristics such as surface roughness or porosity.[2, 3, 5] Gradients can also be single-component, meaning they are modified with one functionality, or multi-component, meaning they are modified with two or more functionalities.[1, 6] Gradients have been applied to the study of many phenomena such as directing liquid transport and studying rates of adsorption or reaction.[2, 3] Genzer and other groups have published extensively on those preparations and application of gradient surfaces.[2, 3, 5, 7] This discussion will focus mainly on chemical gradients and their applications.

1.3 Preparation of gradients

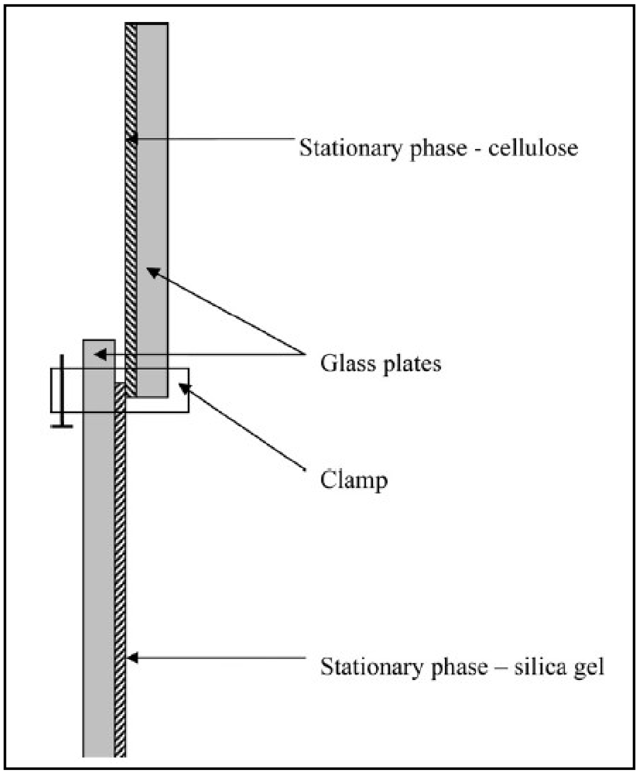
Gradients may be prepared in a variety of ways. Gradient preparation methods may be broadly classified as discontinuous or continuous.[1, 3, 7-9] Discontinuous gradients involve serially connecting materials with varying chemistries;[7, 9] continuous gradients involve gradually changing the surface chemistry along the length of the substrate.[1, 3, 4, 8, 10] Continuous gradients may be prepared using silane chemistry, polymer chemistry, or self-assembled monolayers.[3] Both continuous and discontinuous gradients are discussed in more detail below. An illustration of the two gradient types is show in Figure 1.1.

Figure 1.1 Top: Discontinuous gradient where A, B, C, and D represent different materials connected in series. Bottom: Continuous gradient in which the surface chemistry is varied from a high degree of functionality (left) to a low degree of functionality (right).

1.3.1 Discontinuous gradients

As discussed above, discontinuous gradients are prepared by connecting materials with different surface chemistries in a series. This may be done by connecting different materials such as silica gel, cellulose, alumina, or polyamide.[3, 7] Another way to prepare discontinuous gradients is to connect substrates that are made of the same material but contain varying functionalities.[9] A recent example of the former was prepared by Cimpoiu et al.who connected silica gel plates to cellulose plates to prepare a stationary phase gradient, as shown in Figure 1.2 A.[7] Oda et al. prepared an example of the latter by connecting silica gel columns with varying ratios of octadecylsilane and methylsilane (shown in Figure 1.2 B).[9] Discontinuous gradients have also been prepared using polymeric materials. Currivan et al. prepared discontinuous polymer gradients on monolithic columns by photografting 2-acrylamido-2-methyl-1-propanesulphonic acid onto a monolith and by filling capillary segments with mixtures of the 2-acrylamido-2-methyl-1-propanesulphonic acid and vinyl azlactone monomers (shown in Figure 1.3 A).[11] Maruška et.al. prepared discontinuous polymer gradients for capillary liquid chromatography and capillary electrochromatography by filling capillaries with varying concentrations of nonpolar and polar monomers to create segments with varying hydrophobility, as shown in Figure 1.3 B.[12] Discontinuous gradients are easy to prepare, which is likely why they are popular, particularly in chromatography. However, there are drawbacks to discontinuous gradients. One drawback is that, if the connections between each part of the gradient are not tight, analytes may be lost as they are transferred from one part to another. Another potential drawback is that discontinuous gradients do not allow for synergistic effects between neighboring functional groups.[13]

A)



B)

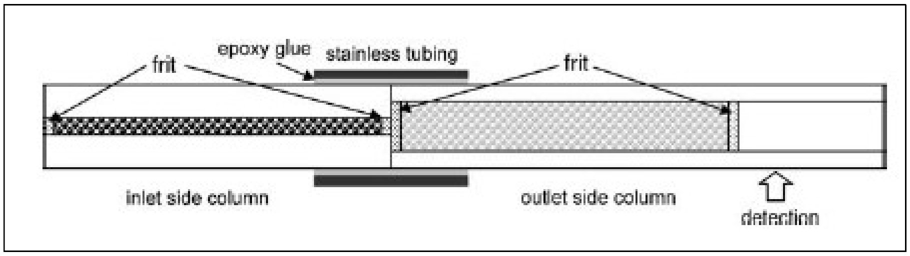
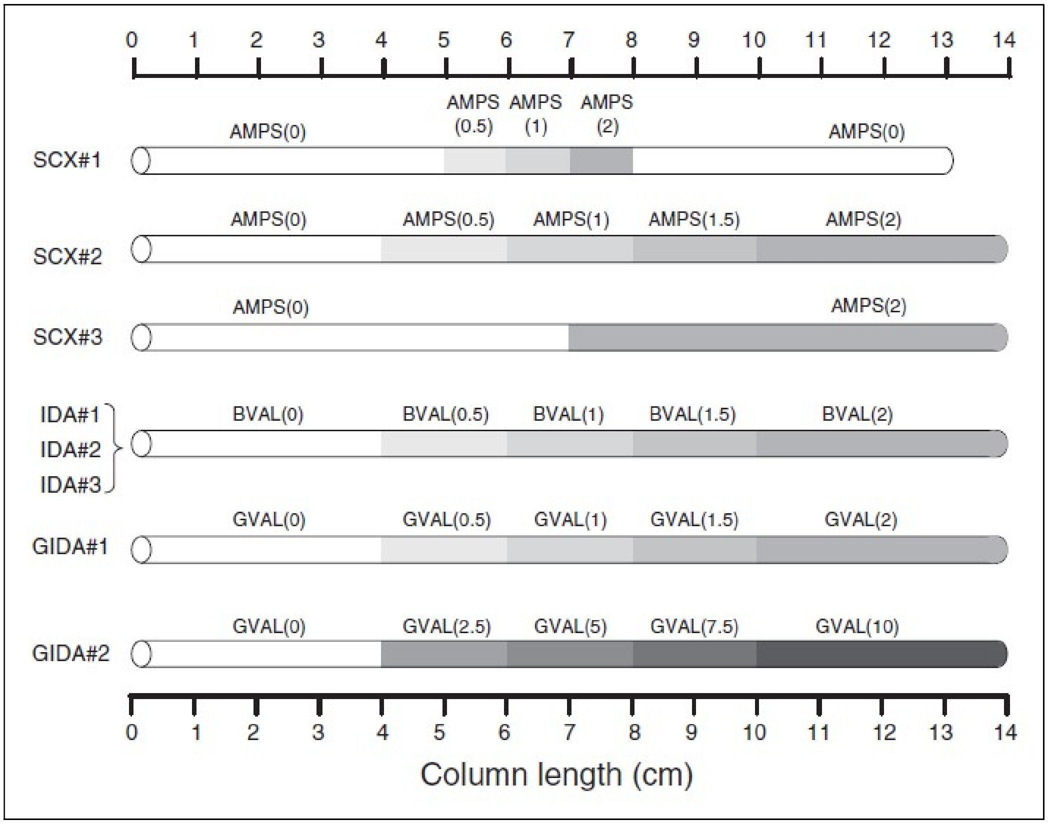


Figure 1.2 A) Discontinuous gradient with a TLC plate. A silica gel stationary phase is clamped to a cellulose stationary phase. B) Discontinuous gradient in liquid chromatography. The pieces have different ratios of octadecylsilane and methylsilane. Reprinted from Ref 7 and 9, respectively, with permission from Elsevier.

A)



B)

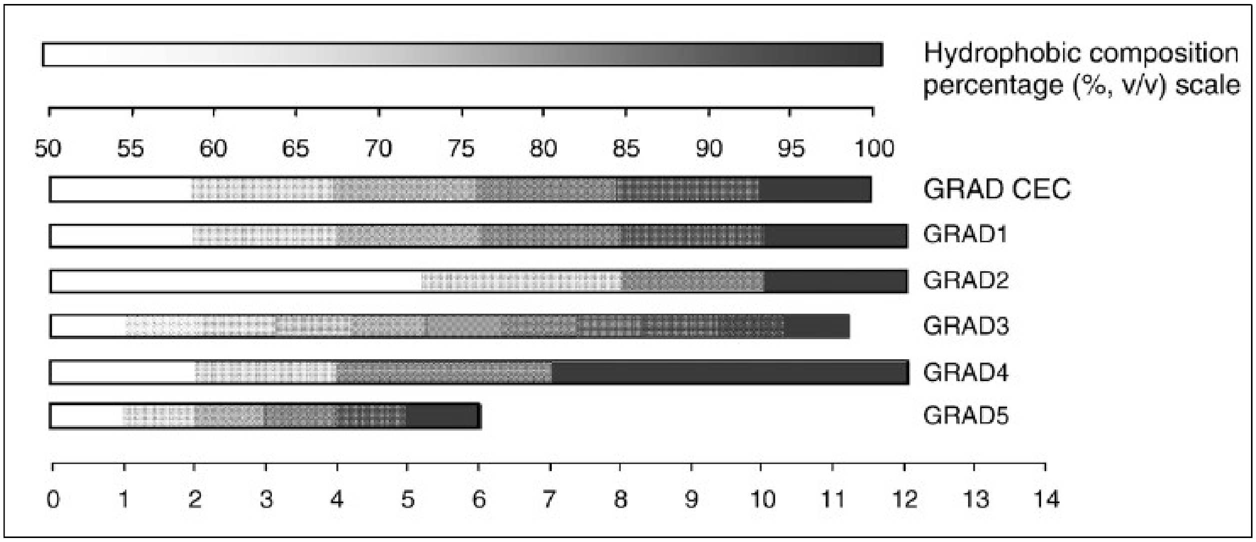


Figure 1.3 A) Discontinuous gradient prepared on monolithic columns by photografting and copolymerization methods. B) Discontinuous gradient prepared with segments of varying hydrophobicity. Reprinted with permission from Ref 11 and 12, respectively.

1.3.2 Continuous gradients

Continuous gradients are prepared by varying the surface chemistry along the length of a single substrate.[1, 3, 4, 8, 10] Many different approaches have been developed to prepare continuous gradients; the most common approaches involve silane chemistry, polymer chemistry, and self-assembled monolayers.

A) Silane chemistry

1) Organoalkoxysilane and chlorosilane reactions

The general structure of an organoalkoxysilane is shown below,

$$\mathbf{R_{4-x}Si(OR')_x}$$

where R is a functional group such as an amine, thiol, cyano, nitrile, phenyl, or other functionality, OR′ is a hydrolyzable group such as a methoxy or ethoxy, and x is one, two, or three. Organoalkoxysilanes can be used as coupling agents in polymer chemistry and as modifiers for a variety of surfaces such as silica, alumina, glass, or quartz.[14-17] Organoalkoxysilanes are particularly useful due to their ability to react with the hydroxyl groups on a silica surface, such as a silicon wafer or thin layer chromatography plate.[4, 14] In solution, organoalkoxysilanes undergo hydrolysis and condensation[14], as shown in Figure 1.4 below.

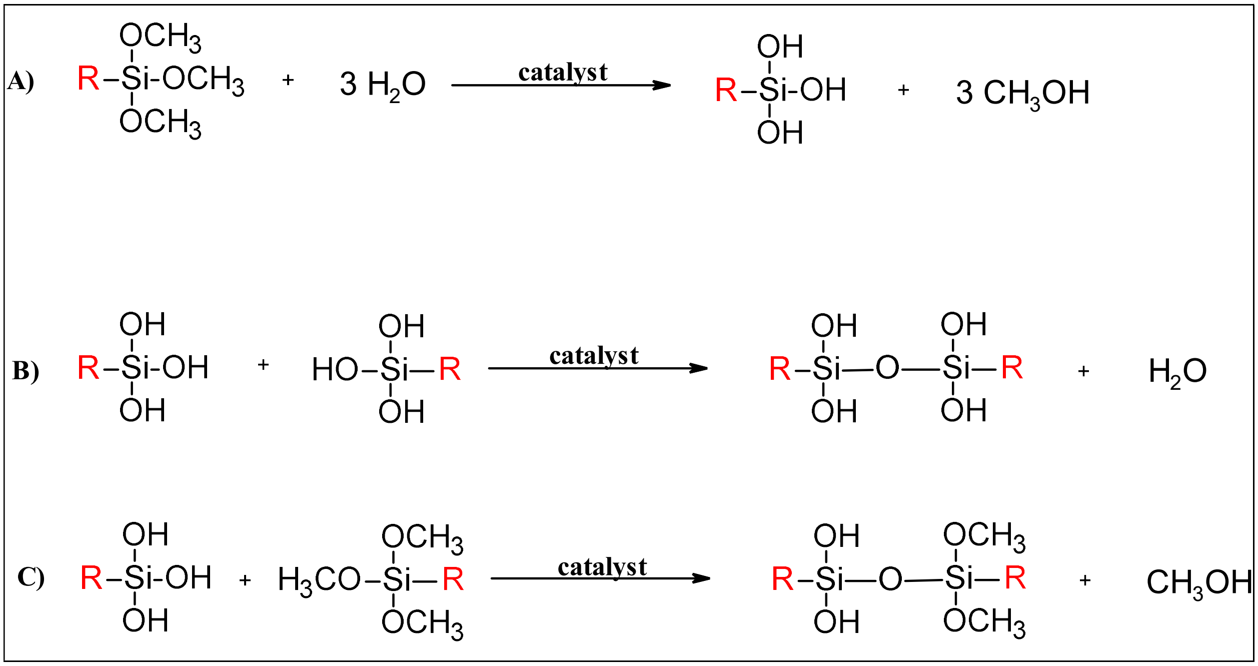


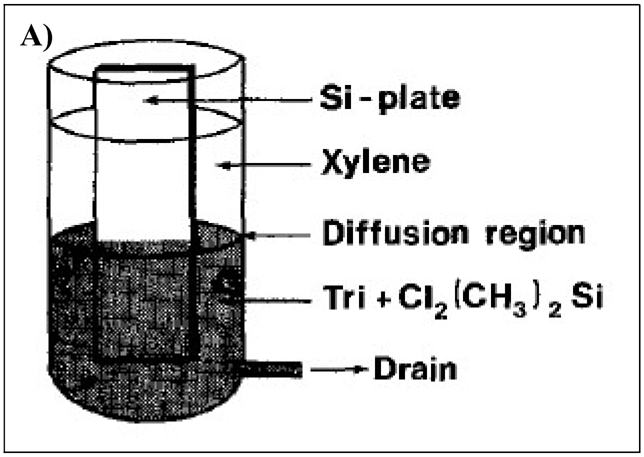
Figure 1.4 **A)** Hydrolysis of an organoalkoxysilane. **B) and C)** Condensation of an organoalkoxysilane where the hydroxyl groups react **(B)** or the hydroxyl group of one silane reacts with the methoxy group of another silane **(C)**.

Water is necessary for hydrolysis; therefore, hydrolysis can occur as a result of exposure to moisture in the atmosphere or on the surface of the substrate. The rates of hydrolysis and condensation are dependent on several factors, including pH, temperature, steric factors, and inductive effects. At lower pH, hydrolysis occurs more quickly, whereas, at higher pH, condensation is faster.[4, 14] The functional group can also affect the rate of reaction; for example, aminoalkoxysilanes are capable of self-catalysis, increasing the rate of reaction.[14, 18]

Chlorosilanes can also be used to modify glass and silica surfaces.[19-21] In the presence of water, chlorosilanes undergo hydrolysis and condensation.[21] The chlorosilanes react with silanol or hydroxyl groups on the surface, forming HCl as a byproduct. Mono-, di-, or tri-chlorosilanes may be used to functionalize the surface with alkyl or organic functional groups.[21]

2) Silane gradients

Two notable approaches to prepare gradients that were developed by Elwing et al. and Chaudhury et. al., respectively, both involve silane chemistry.[19, 20] Elwing et al. used liquid diffusion to prepare methylsilane gradients.[20] As shown in Figure 1.5 A, Elwing and coworkers placed a silicon or glass substrate in a container with two immiscible solvents, one of which contained a reactive chlorosilane (dichlorodimethylsilane). As the dichlorodimethylsilane diffused from the higher-density trichloroethylene into the lower-density xylene, a methyl gradient was formed on the substrate.[20] Later, Chaudhury and Whitesides developed wettability gradients by exposing a substrate to a reactive chlorosilane dissolved in paraffin oil.[19] The substrate was placed next to the drop and exposed to the vapor; the side of the substrate next to the drop contained a higher degree of functionality than the side farthest from the drop.[19] Figure 1.5 B shows the development of a gradient using vapor diffusion and a plot of the water contact angle along the length of the gradient.



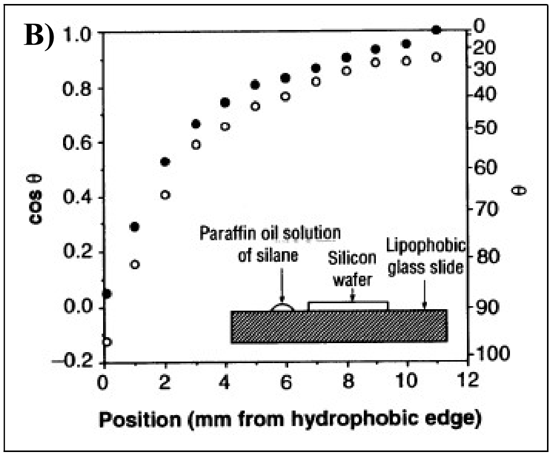


Figure 1.5 A) Preparation of a continuous gradient using liquid diffusion, which was developed by Elwing et.al. B) Preparation of a continuous gradient using vapor diffusion, developed by Chaudhury and Whitesides. (Reprinted from Ref 20 with permission from Elsevier and Ref 19 with permission from AAAS, respectively.)

Other notable attempts to prepare gradients using silane chemistry include contact printing and dip-coating.[3, 22-24] In contact printing, a wedge-shaped stamp saturated with a silane, typically poly(dimethylsiloxane), is applied to the substrate. The concentration of silane adsorbed onto the surface is dependent on the thickness of the stamp, resulting in a lower surface concentration where the stamp is thinner and a higher surface concentration where the stamp is thicker.[3] Kraus et al.used poly(dimethylsiloxane) stamps soaked in hexanethiol to prepare thiol gradients on a gold surface, as shown in Figure 1.6.[24] Contact printing can also be used to prepare gradients with different shapes. For example, Choi and Newby created radial, one-directional, and symmetrical gradients with octadecyltrichlorosilane using contact printing, as shown in Figure 1.7.[23]

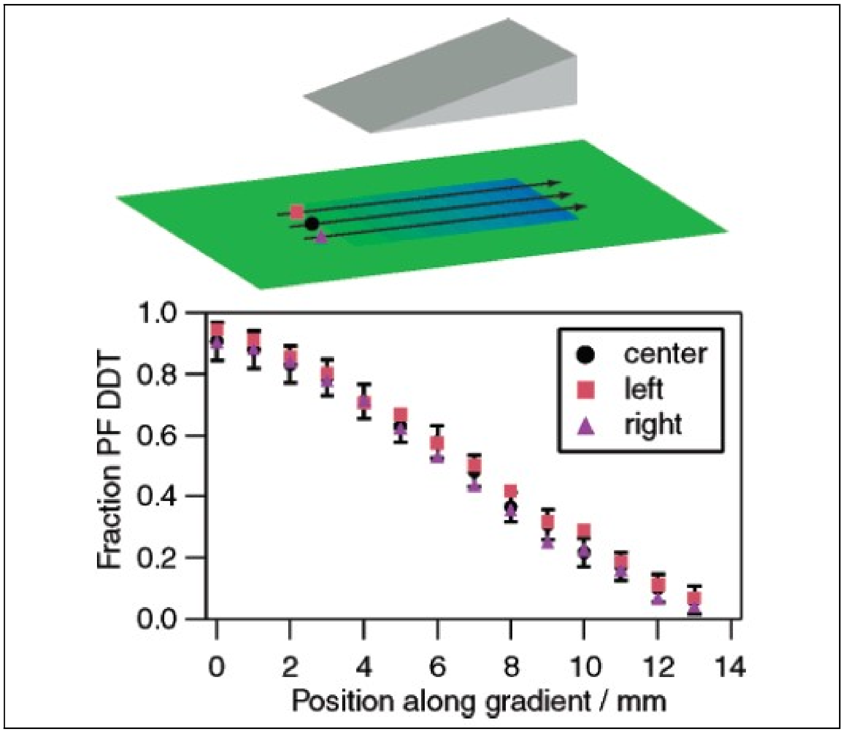


Figure 1.6 Gradient prepared using contact printing. Top: Gradient surface prepared using a wedge-shaped stamp. Bottom: Gradient profile from the left, center, and right of the surface obtained using x-ray photoelectron spectroscopy (XPS). (Reprinted from Ref 24 with permission. Copyright 2005 American Chemical Society.)

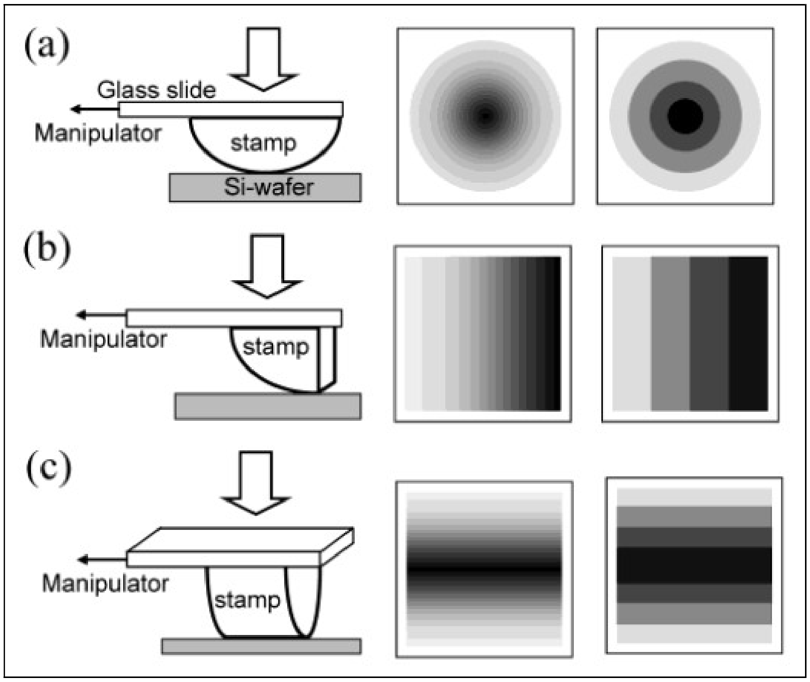


Figure 1.7 Octadecyltrichlorosilane gradients created using contact printing: **(a)** radial, **(b)** one-directional, and **(c)** symmetrical gradients. (Reprinted from Ref 23 with permission. Copyright 2003 American Chemical Society.)

More recently, our collaborators developed a method termed “infusion-withdrawal dip-coating” (IDWC).[25] In IDWC, a silica substrate is placed in a glass reservoir filled with tetramethoxysilane (TMOS). As shown in Figure 1.8, the TMOS is withdrawn on one side as methyltrimethoxysilane (MTMOS) is infused from the other side. The withdrawal of TMOS occurs at a slightly faster rate than the infusion of MTMOS, forming a polarity gradient along the length of the substrate.[25]

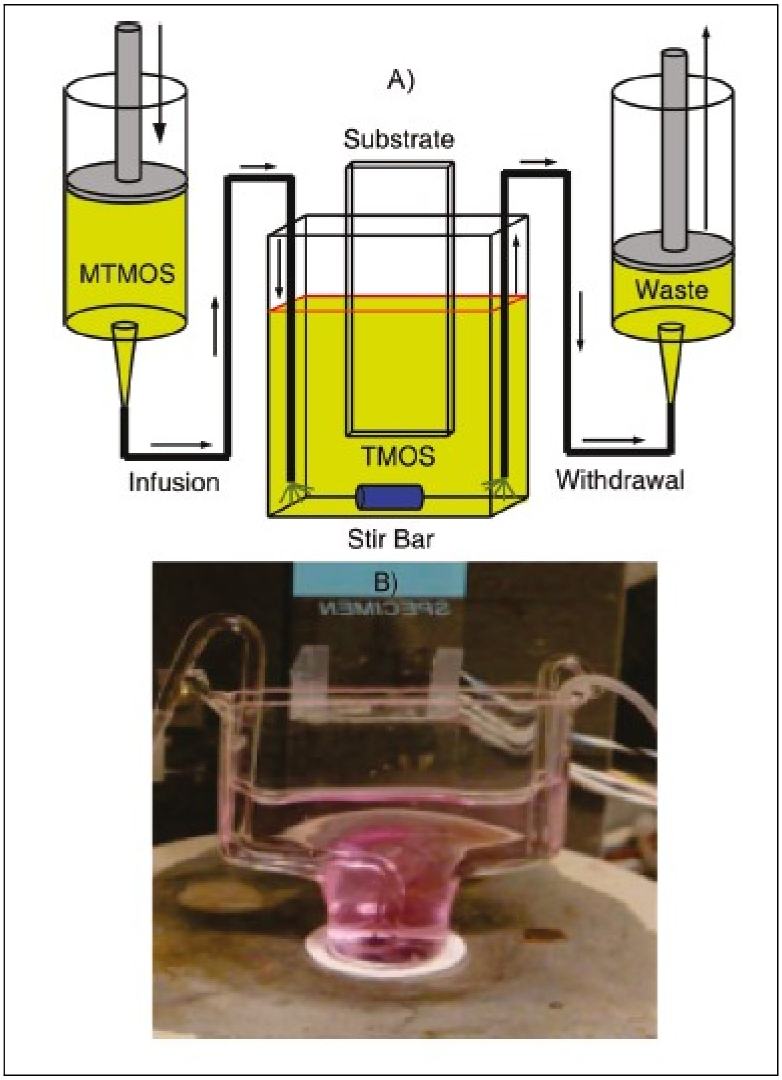


Figure 1.8 A) Diagram of the "infusion-withdrawal dip-coating" apparatus used to prepare polarity gradients. B) Photograph of the apparatus. (Reprinted from Ref 25 with permission. Copyright 2010 American Chemical Society.)

Another recent approach to preparing continuous gradients is controlled-rate infusion (CRI), which was developed by Kannan et al. in the Collinson group.[4] In CRI, a silica-coated substrate, such as a silicon wafer or thin layer chromatography (TLC) plate, is exposed to an organoalkoxysilane in a time-dependent fashion.[1, 4, 6, 8, 13, 18, 26] As shown in Figure 1.9 A, a syringe pump is used to infuse the organoalkoxysilane into a vial containing the substrate at a constant pre-programmed rate. This procedure results in a gradient because the bottom of the plate has been soaking for a longer period of time, resulting in a higher degree of functionality, whereas the top of the plate has been soaking for a shorter period of time, resulting in a lower degree of functionality. The gradient steepness can be controlled by varying the organoalkoxysilane concentration or the infusion time. The ability to control the gradient steepness is the main advantage of CRI.[1, 4, 6, 8, 13, 18, 26] CRI was developed on planar substrates; however, it has been adapted for use on cylindrical substrates such as chromatography columns.[27] CRI has also been used to prepare single-component gradients (i.e., modification with one organoalkoxysilane)[8] and multi-component gradients (i.e., modification with two or more organoalkoxysilanes).[1, 6] Multi-component gradients may be aligned, in which the gradients for each functionality are in the same direction, or opposed, in which the gradients are in opposite directions, as shown in Figure 1.9 B.[1, 6] CRI has been used to prepare both aligned and opposed gradient by simply repeating the infusion. For aligned gradients, the substrate is infused in the same orientation each time; for opposed gradients, the substrate is rotated 180° before the second infusion.[1, 6]

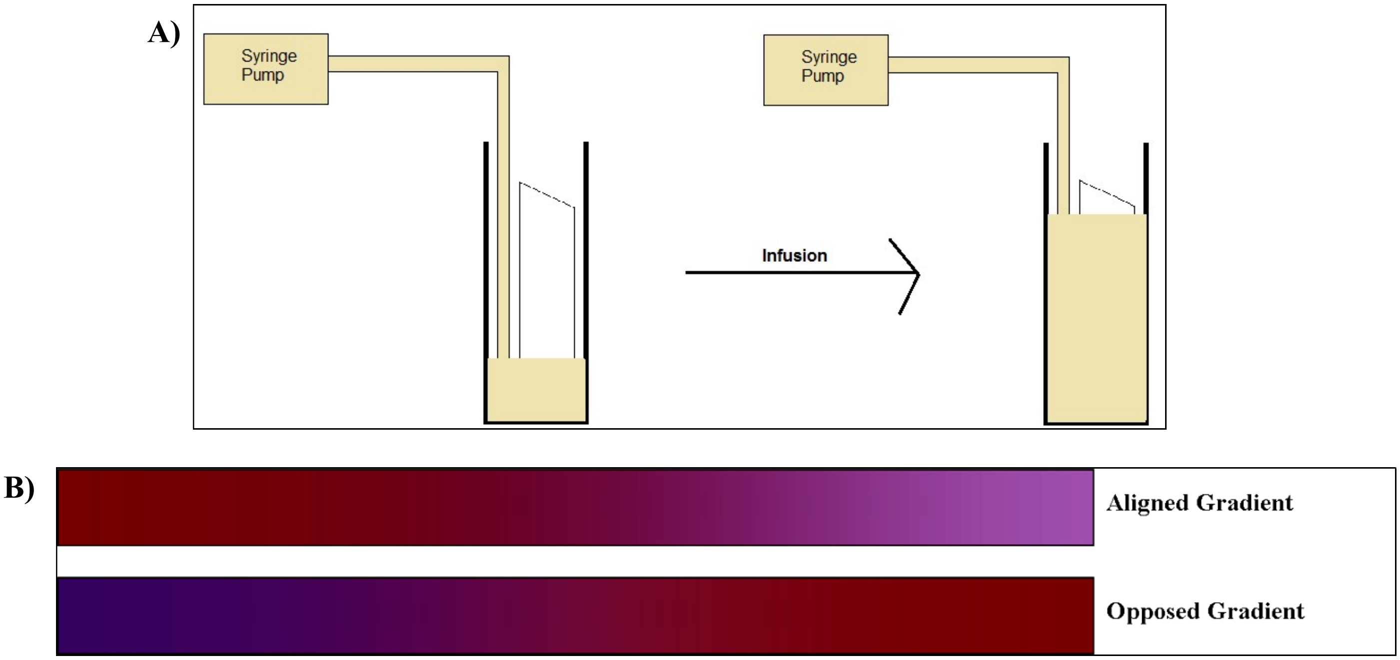


Figure 1.9 A) Schematic illustrating controlled-rate infusion. After infusion, the bottom of the substrate has been soaking for a longer period of time and, therefore, has a higher degree of functionality, whereas the top has been soaking for a shorter period of time and, therefore, has a lower degree of functionality. B) Schematic of aligned (top) and opposed (bottom) gradients.

B) Polymer chemistry

Polymer chemistry is another common means for preparing continuous gradients. Most often, polymer gradients are prepared by chemical grafting or by adsorption of monomers.[2, 3, 5, 28-30] Tomlinson and Genzer created a method in which a substrate containing a chemisorbed initiator is placed in a monomer solution; the solution is slowly drained using a micropump, forming a polymer brush gradient, shown in Figure 1.10.[28] Genzer and coworkers also created two-component orthogonal gradients using the same method by placing a silicon wafer containing chemisorbed [11-(2-bromo-2-methylpropionyloxy)undecyl] trichlorosilane in a monomer solution and slowly draining the monomer solution; the silicon wafer was then rotated orthogonally and reacted with a second monomer solution.[31] .

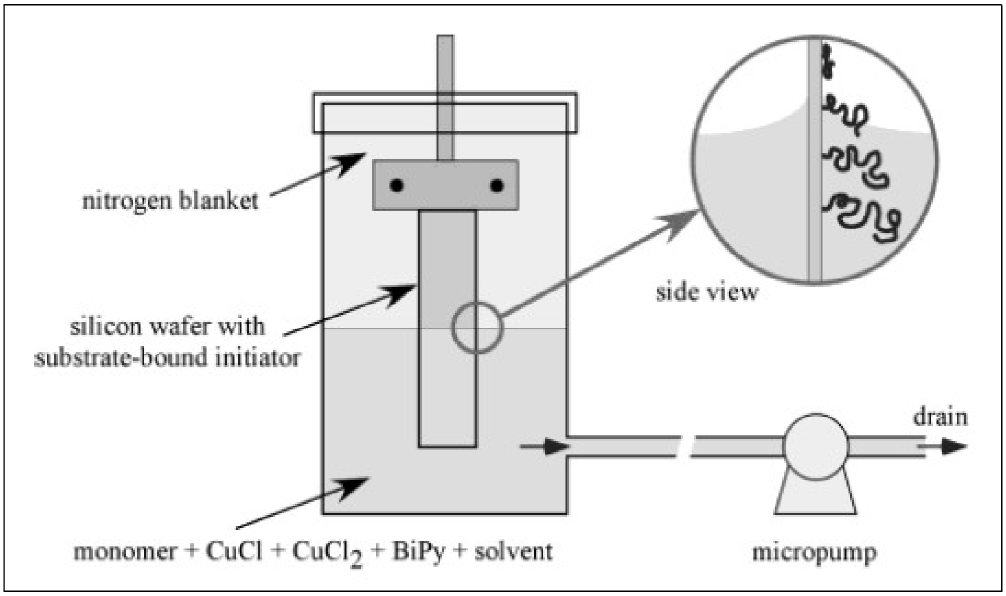


Figure 1.10 Apparatus used by Tomlinson and Genzer to prepare polymer brush gradients. The inset show the polymerization occurring on the substrate as it is exposed to the monomer solution. (Reprinted from Ref 30 with permission. Copyright 2003 American Chemical Society.)

Other commonly used techniques for continuous gradient formation include corona discharge, radio-frequency plasma discharge, and temperature gradients.[3, 5, 29] Corona discharge can be used to prepare polymer gradients by exposing the substrate, which is placed on a on a moveable sample bed, to a steady increase in power from an electrode. The polymer surface is oxidized as it is exposed to power from the electrode, creating a wettability gradient.[29] Lee et al. used corona discharge to prepare gradients on polyethylene sheets, as shown in Figure 1.11 A. The sheets were placed on a moveable bed and exposed to a knife-type electrode which was connected to a radio frequency generator; the power was gradually increased, leading to an increase in oxidation of the surface groups.[32] The advantage of the corona discharge method is that it can be used with various polymers, including polyethylene, polypropylene, polyethylene terephthalate, polymethyl methacrylate, and polystyrene; however, corona discharge may create products that are not stable over long periods of time.[29] Radio-frequency plasma discharge is a similar technique, however, instead of using a movable bed; a moveable mask in placed over the sample and moved at a constant speed. Radio- frequency plasma discharge is usually conducted under vacuum to prevent reaction of the sample with air.[29]

Polymer gradients have also been prepared using gradients in temperature, as shown in Figure 1.11 B.[3, 33] Ionov et al. created polymer gradients by soaking silicon wafers in 3-glycidoxypropyl trimethoxysilane or polyglycidylmethacrylate. An end-functionalized polymer was spin-coated onto the substrate and then exposed to a temperature gradient by placing the substrate onto a stage with heating and cooling elements at opposite ends. The gradients were characterized using ellipsometry.[33]

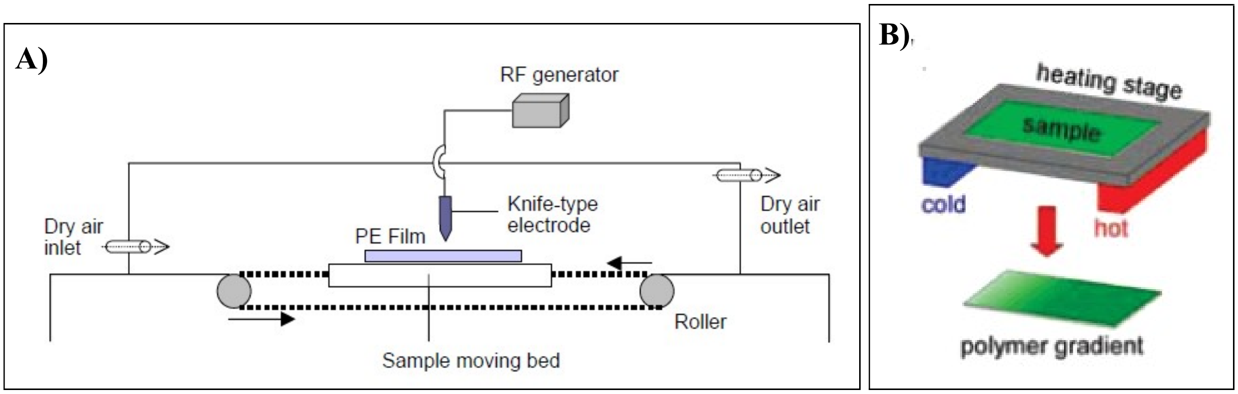


Figure 1.11 A) Preparation of a polymer gradient using corona discharge; the movable bed is moved at constant speed as the power from the radiofrequency generator (RF) is increased.. **B)** Preparation of a polymer gradient using a difference in temperature. (Reprinted from Ref 29 with permission from Elsevier and Ref 2 with permission (Copyright 2008 American Chemical Society.).

C) Self-assembly on gold

Alkanethiol self-assembled monolayers (SAM) have also been used to prepare continuous gradients.[3, 5, 34] Due to electrostatic and van der Waals forces, alkanethiols have a high affinity for gold and silver and form ordered layers on the surface.[34] Several methods have been used to prepare gradient SAMs, including diffusion, desorption and adsorption, gradient immersion, lithography, contact printing, and gradual deposition.[3, 5]

Gradient SAMs may be prepared by allowing the alkanethiol to diffuse over a period of time. Liedberg and Tengvall created gradient SAMs by allowing two different alkanethiols to diffuse across a gold substrate from each end.[35] Two glass frits, each containing a different alkanethiol, were placed at the ends of the substrate, as shown in Figure 1.12; the alkanethiols were allowed to diffuse for several hours. The gradients were characterized using ellipsometry, contact angle measurements, infrared spectroscopy, and X-ray photoelectron spectroscopy (XPS).[35, 36]

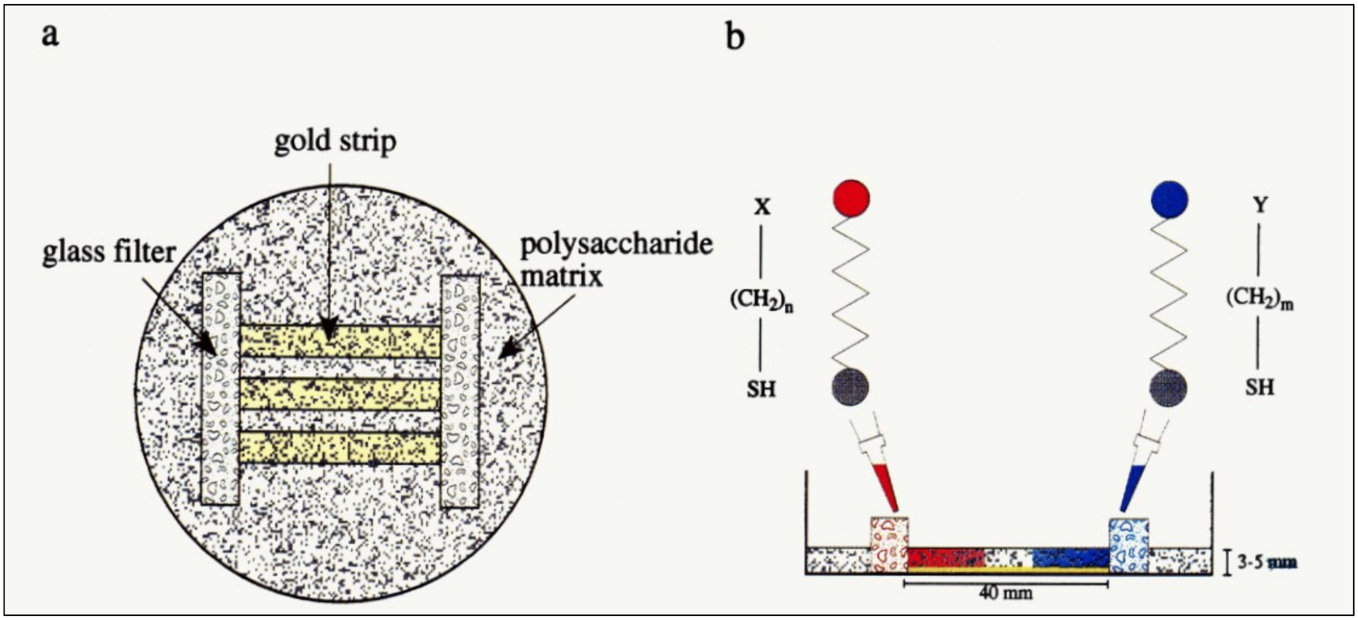


Figure 1.12 Preparation of alkanethiol gradient SAM using diffusion: a) Top view, b) Side view. Reprinted from Ref 35 with permission. Copyright 1995 American Chemical Society.

Most approaches for preparing gradients utilize constructive modification; however, destructive modification has also been utilized.[37, 38] In destructive modification, electrochemical or photochemical desorption is used to remove functional groups from the surface.[37, 38] Terrill et al. prepared thiol gradients by applying a potential to a substrate modified with an alkanethiol;

the slope of the gradient was controlled by varying the applied potential.[38] Plumer and Bohn prepared two-component gradients by using electrochemical desorption to prepare an organothiol gradient and then reacting the substrate with carboxylic acid–modified nanospheres.[37]

Additionally, other desorption routes, such as scanning tunneling microscopy, photocatalytic oxidation, and focused X-ray beams, have been used to prepare gradient SAMs. Fuierer et al. used scanning tunneling microscopy to create an alkanethiol gradient by varying the scan speed.[39] Fuierer and coworkers also created two-component gradients by backfilling with ferrocenyl-undecanethiolate in dodecanethiolate.[39] Blondiaux et al. used photocatalytic lithography to prepare two-component gradients, as shown in Figure 1.13.[40] A substrate modified with an alkanethiol was exposed to UV light through a titanium oxide film; the titanium oxide film had a graytone gradient, creating an oxidation gradient. The substrate was then backfilled using a different alkanethiol.[40]

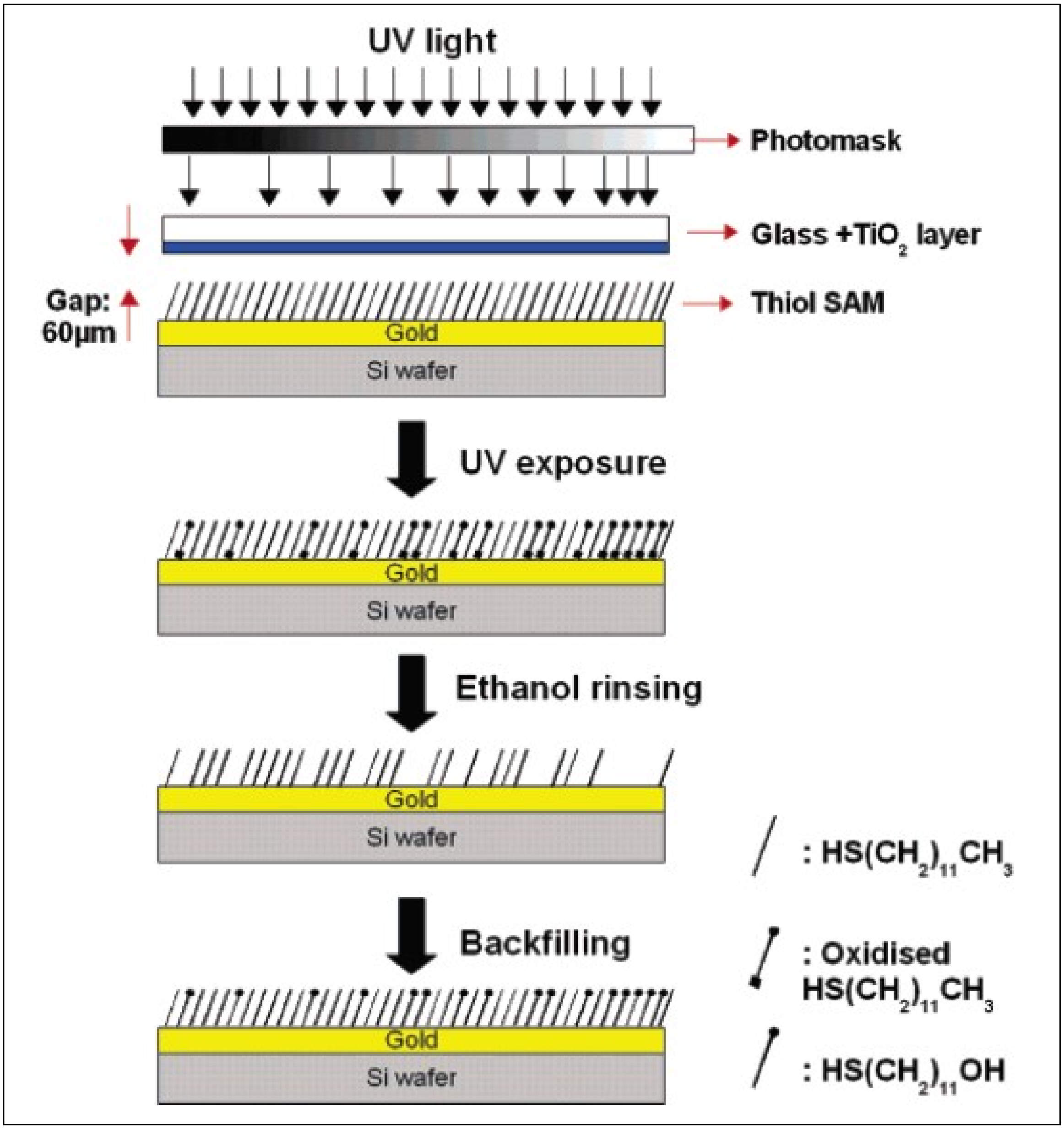


Figure 1.13 Preparation of two-component alkanethiol gradient SAM using photocatalytic lithography. The surface is oxidized using UV light and then backfilled using a different alkanethiol. Reprined from Ref 40 with permission. Copyright 1995 American Chemical Society.

Gradual immersion is another technique for preparing gradient SAMs. The substrate is gradually immersed in an alkanethiol solution, creating a concentration gradient.[5, 41, 42] Morgenthaler et al. used a linear-motion drive to gradually immerse a gold substrate into solutions of methyl- or hydroxyl-terminated thiolates.[41] Morgenthaler et al. also used gradient immersion to prepare two-component gradients.[42] The gold substrates were immersed in a dodecanethiol solution at a rate of 75µm/s; after being rinsed with ethanol and then dried with nitrogen, the substrates were immersed in 11-mercapto-1-undecanethiol or 1-mercapto-undercanonic acid.[42]

Contact printing can be used to prepare gradient SAMs using the same methodology used for silane chemistry.[3, 5] Some researchers have also used inkjet printing to prepare gradients. Pardo et al. used modified commercial inkjet printers to prepare hexadecanethiol, mercaptohexadecanonic acid, and mercaptohexadecanol gradients.[43] Alkanethiol SAMs are advantageous due to their high stability; however, they are limited to metal surfaces, most notably gold, silver, and copper.[5]

1.4 Applications of gradients

Gradient surfaces have been used to direct liquid transport and for recording and screening chemical and physical properties. Gradient surfaces have also been applied to the separation of complex mixtures. Several of these applications will be described below.

1.4.1 Directed transport

Several researchers have used gradients surfaces to direct liquid transport; wettability gradients have often been used to control the motion of water droplets.[19, 20] For example, Chaudbury and Whitesides used n-decyltrichlorosilane gradients to make water travel uphill, as shown in Figure 1.14 A.[19] Similarly, Morgenthaler et al. used alkanethiol gradients to control the motion of water droplets, as shown in Figure 1.14 B.[41] Wettability gradients have found application in condensation heat transfer, microfluidics, and removing debris from inkjet printing.[44, 45]

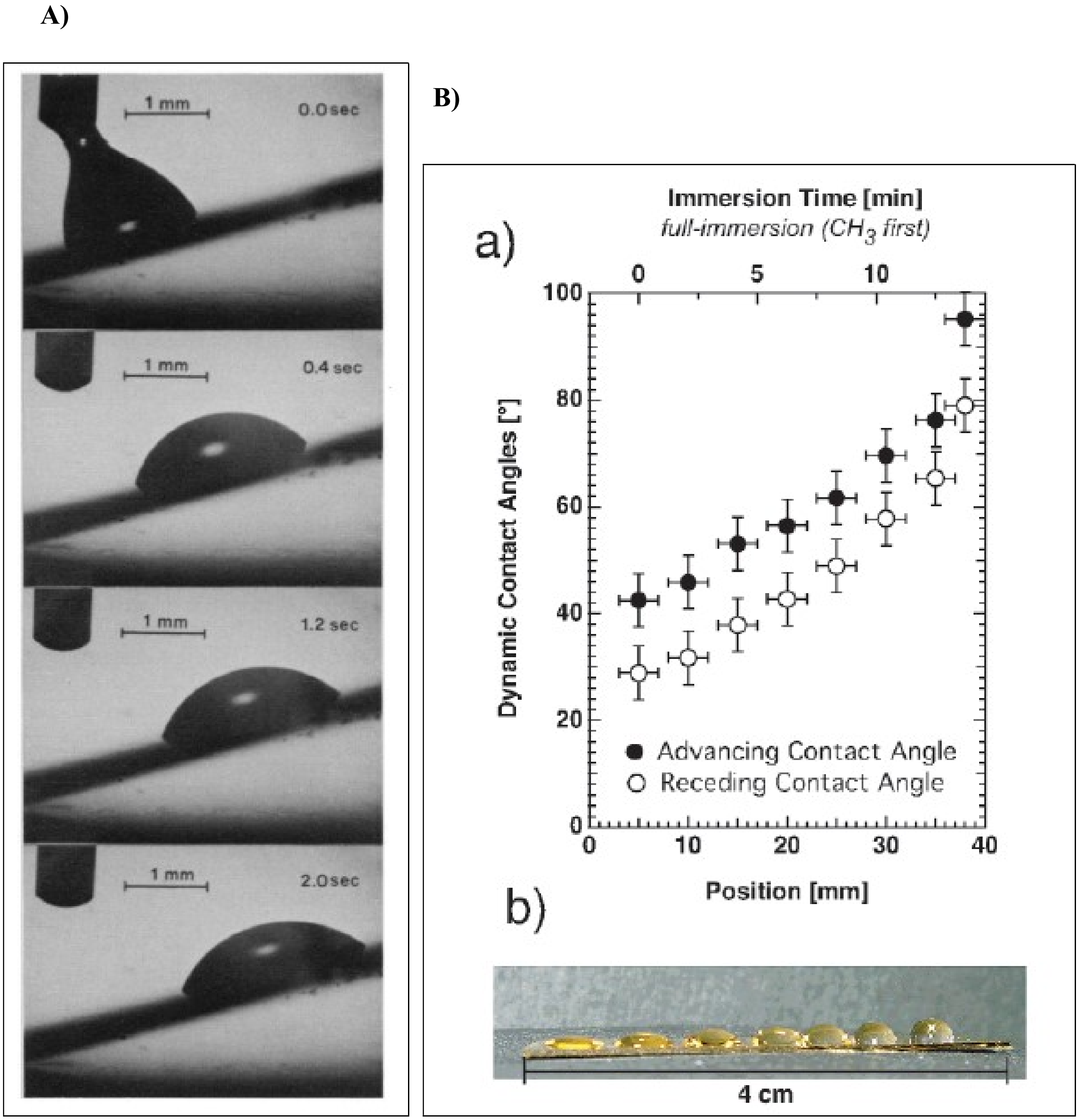


Figure 1.14 A) Water droplet moving uphill on a wettability gradient. B) Wettability gradient: a) Change in contact angle as the immersion time increases. b) Photograph of water droplets on an alkanethiol wettability gradient. Reprined from Ref 19 with permission from AAAS and Ref 40 with permission (Copyright 2003 American Chemical Society).

Gradients have also been used to control the motion of living cells by varying the surface chemistry, electrostatic potential, or mechanical properties.[3] Chang et al. used aldehyde gradients prepared by gradually immersing glass slides in trimethoxysilylalkylaldehyde to control the motion of dendrimers.[46]

1.4.2 Recording phenomena

Gradients have also been used to record and screen properties such as cell and protein adsorption, chemical reactions, and polymerzation.[2, 3, 30] Tomlinson and Genzer used surface gradients to study the polymerization of poly(methyl methacrylate).[30] Such gradients have been utilized to study the kinetics of polymerization and as sensors that are position dependent.[30] Gradient surfaces have also been used to study protein adsorption for biomedical applications.[5]

1.4.3 Separating mixtures

Discontinuous gradients have been used in TLC and liquid chromatography to separate vitamins and alkylbenzenes, respectively.[7, 9] The use of stationary phase gradients allows for more efficient separation of complex mixtures.[7, 8] In some cases such as vitamins, which have structural analogs, it is sometimes difficult to find an optimal combination of stationary and mobile phases. The use of stationary phase gradients with varying functionalites or different mechanisms of separation may be used to improve separation.[7] Stahl and Warren each used continuous pH gradients prepared with a gradient mixer to separate mixtures of dyes.[47, 48] More recently, our group has used continuous stationary phase gradients for separation. Kannan et al. used single component amine gradients to separate mixtures of weak acids and bases and over-the-counter drugs; in both cases, separation was greater on gradient plates than on uniformly-modified plates.[8] Dewoolkar et. al used multi-component amine/phenyl gradients to separate water- and fat-soluble vitamins; the order of retention was found to depend on whether amine or phenyl was applied first, whether the vitamins were spotted on the high or low end of the gradients, and whether the gradients were aligned (in the same direction) or opposed (in the opposite directions).[1] Such separations offer an alternate paradigm to the use of mobile phase gradients for detectors that are sensitive to changes in the mobile phase and for use in TLC, where mobile phase gradients are difficult to implement.[8, 27] Gradient surfaces have also been applied to the study of metal ion binding. Kannan et. al used aminosilane gradients to study the coordination of Cu and Zn to N-containing ligands.[26] This study will be discussed in more detail in section 1.7.

1.5 Chelation ion chromatography (CIC)

The first aspect of this work involves the use of gradient surfaces; the second aspect involves the use of chelating agents for the separation of transition and heavy metals. The second aspect of this work is discussed below.

1.5.1 Chelation

Chelation is the formation of a coordinate bond between a ligand and a metal ion, where the metal ion acts as the central atom.[49] Figure 1.10 shows a schematic of a chelating ligand bound to a metal ion.

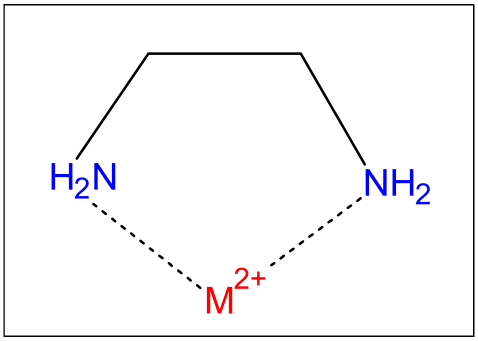


Figure 1.15 Schematic of a chelating ligand (ethylenediamine) bound to a metal ion (represented as M^{2+}).

The chelate effect is the principle that metal complexes formed by multidentate ligands are more stable than metal complexes formed by monodentate ligands.[49] The chelate effect is believed to be due to favorable changes in entropy; however, a recent computational study by Vallet et al. indicates that enthalpy also contributes to the chelate effect.[50]

1.5.2 Attributes of CIC

Numerous studies have utilized chelating ligands immobilized on solid surfaces for the extraction, preconcentration, and separation of metal ions.[51-75] For example, Bois et. al utilized amine ligands for the adsorption of Cu^{2+}, Ni^{2+}, Co^{2+}, and Cr^{6+} and mercapto ligands for the adsorption of Cd^{2+}.[52] Similarly, Soliman utilized mono-, di-, tri-, and tetra-amine modified silica for the extraction of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}.[62]

In chelation ion chromatography (CIC), a competition is created between a chelating agent on a solid support (the stationary phase) and a chelating agent in the mobile phase.[76-78] CIC is used for the separation of transition and heavy metals. In a detailed review, Jones and Nesterenko list the following attributes of CIC:[76]

- Coordinate bonds are formed between the metal ion and the stationary phase functionality.
- Separation is due to both the thermodynamic and kinetic factors involved in the formation of metal complexes.
- Bonding of alkali metals to chelating groups is weak compared to transition and heavy metals, which reduces the effect of alkali metals on the separation.
- Separation is affected by pH due to the effect of pH on conditional stability constants.

The formation of coordinate bonds between metal ions and chelators, such as iminodiacetic acid (IDA), β-diketones, carbamates, amines, and 8-hydroxyquinoline (shown in Figure 1.16), on the stationary phase is a distinguishing feature of CIC.[76, 78]

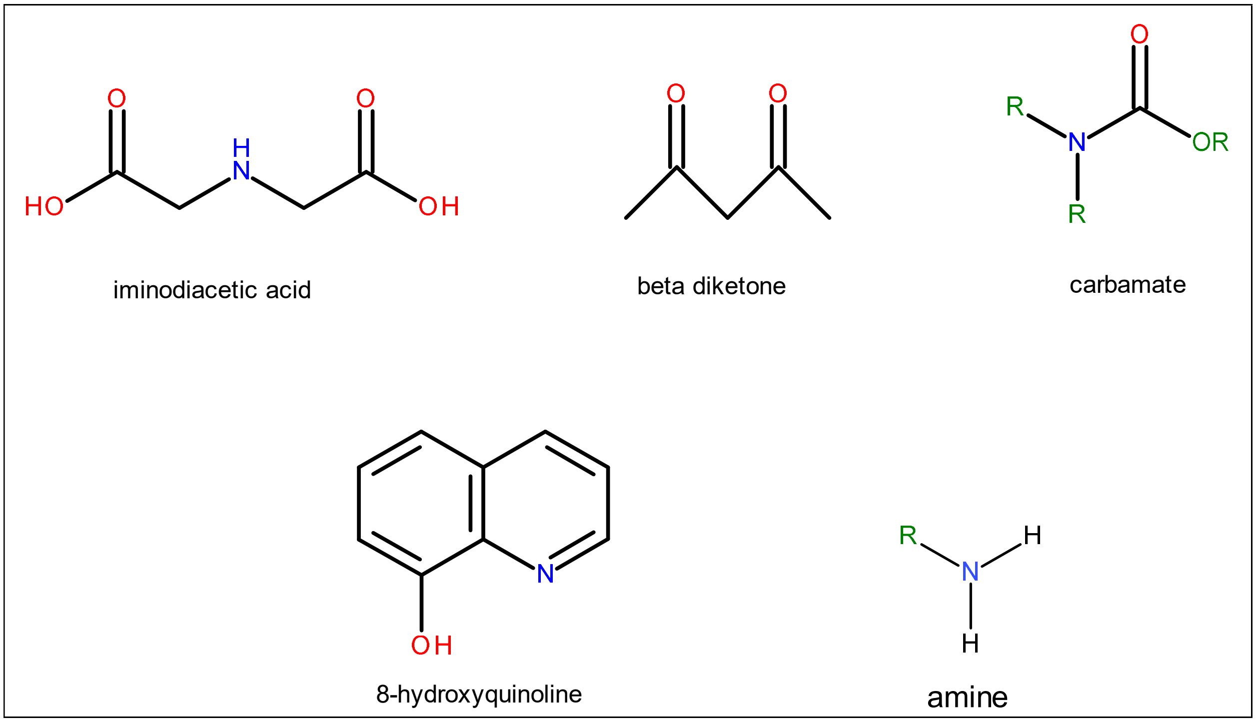


Figure 1.16 Structures of iminodiacetic acid, a β-diketone, carbamate, 8-hydroxyquinoline., and amines.

Other types of chromatography, such as ion-exchange, that are used to separate metals do not involve the formation of new chemical bonds.[76] The use of chelating ligands in the stationary allows for greater control over selectivity through the choice of chelating ligands, the use of chelating ligands in the mobile phase, and the possibility of ion exchange as an additional mechanism.[76]

There have been numerous studies on the separation of transition and heavy metals using CIC.[74, 76, 79-102] While many of these studies have applied the principles to LC,[76, 79-98] some have applied CIC to TLC.[74, 99-102] Both TLC and LC systems with CIC are discussed below.

A. TLC: While there are multiple studies on the separation transition and heavy metals using TLC, many only utilize a chelating agent in the mobile phase, which cannot truly be classified as CIC.[103-111] As an example, Mohammad and Fatima used mobile phases containing varying concentrations of formic acid to separate metal ions on silica gel TLC plates.[105] One drawback of such systems is that separations are often limited to two or three metal ions. A few studies have, however, applied CIC to TLC. Sweet et al. studied the separation of Fe^{3+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} on stationary phases modified with amines, β-diketones, and thiocarbamates.[99] A total of 29 mobile phases, including ethylenediamine, acetylacetone, trifluoroacetylacetone, dimethylgloxime, 8-hydroxyquinoline, and salicyladoxime, in various organic solvents were utilized for the study. The majority of the stationary phase and mobile phase combinations did not give a satisfactory separation, usually only separating one or two of the metal ions from the mixture. Sweet et al. obtained complete separation on a β-diketone stationary phase using a 10% trifluoroacetylacetone mobile phase.[99] In a later study, Sweet et al. studied the effect of the structure of γ-amine on separation. Brush and polymer structures were prepared for the stationary phase by utilizing monoalkoxy and trifunctional trialkoxy silanes, respectively.[101] The polymer structure caused elongated spots that either stayed near the baseline or continued to the solvent front. Separation was improved with the brush structure; however, complete separation was not obtained.[101]

B. Liquid chromatography (LC): The use of CIC in LC systems has been of great interest in the last 30 years, as evidenced by numerous articles and reviews.[76-98] Moyers and Fritz published one of the first studies on CIC in 1977. These authors used a resin modified with propylenediaminetetracetic acid to separate Cu^{2+}, U^{6+}, Th^{4+}, and Zr^{4+}.[97] Since that time, several chelating stationary phases have been developed. To prepare a chelating stationary phase, silica- or polymer-based columns are modified with a chelating agent.[76, 77] In general, there are two approaches to modifying the stationary phase: the chelating agent can be chemically bonded to the stationary phase, or the stationary phase substrate can be coated with the chelator by soaking in a solution.[76] The disadvantage of modifiying the stationary phase by soaking the column is that the adsorbed molecules could come off the column as the mobile phase passes through, resulting in distorted peaks. For silica gel columns, packed columns are commonly used,[76, 79-84, 89, 90, 92, 93, 95, 96, 98] although a few studies have utilized monolithic columns.[77, 78, 87, 88, 94] Common mobile phases include picolinic or dipicolinic acid, trifluoroacetylacetone, formic acid, salicylaldoxime, and ethylenediamine.[76, 78] In order to detect metal ions after separation, UV-detection with post-column conversion using a detection reagent such as 4-(2-pyridylazo) resorcinol (PAR) is often used.[76-78] However, some researchers have used on-line detection such as inductively coupled plasma-mass spectrometry (ICP-MS).[83, 85] For example, Huang et al. used CIC coupled with ICP-MS to separate Mo, V, and W.[83] A few have also utilized amperometry, although the application to transition metals has been limited.[85]

The use of CIC for practical applications has been demonstrated in several studies. Almeida et al. used a C18 packed column modified with sodium hexane-sulfonate and a tartrate mobile phase to separate and detect Cu, Pb, Zn, Ni, Co, Cd, and Mn in human hair.[79] Dias et al. used an IDA-modified packed column to detect transition and heavy metals in ethanol used as a fuel additive.[81] McGillicuddy et al. used monolithic columns modified with N-hydroxyethyliminodiacetic or N-(2-hydroxyethyl)-N-(2-[phosphonomethyl)amino]acetic acid and compared different chelating stationary phases to separate and detect Mn^{2+}, Cd^{2+}, and Zn^{2+} in mussel tissue.[87] Shaw et al. used a packed column modified with 2,6-pyridinedicarboxylic acid, to detect uranium in seawater and in stream sediment.[90] In addition, Hsu, Chang, and Liu demonstrated the use of CIC on a packed column modified with a [24]ane-N6 polymer to detect Cu^{2+}, Cd^{2+}, Co^{2+}, and Zn^{2+} in seawater and oyster tissue.[95]

1.5.3 Advantages of CIC

CIC has been shown to be useful in the separation of transition and heavy metals, as evidenced by multiple journal articles, several reviews, and even a book on the topic.[70, 76-81, 83-94, 96, 97, 112, 113] However, there are existing methodologies for identifying and /or separating metal ions, most notably inductively coupled plasma (ICP) and ion chromatography.[49] ICP is well known as a method for identifying metal ions. The main advantages of ICP are its ability to analyze up to 70 elements at once and the ability to detect ultratrace levels (as low as ppb or ppt).[49] However, ICP is expensive and cannot distinguish between oxidation states.[85, 87, 88] Also, ICP can suffer from spectral and chemical interferences.[49, 85, 87, 88] While ion chromatography is capable of distinguishing between oxidation states and can also analyze multiple elements at once, alkali and alkaline earth metals can swamp the ion exchange sites, which makes it difficult to detect transition and heavy metals and can also degrade the column.[49, 85, 87, 88]

CIC offers several advantages:[76, 78, 85, 87, 88]

- It is possible to distinguish between oxidation states.
- Alkali and alkaline earth metals do not interfere with separation because they do not bind as strongly to chelating ligands compared to transition and heavy metals.
- Transition and heavy metals can be detected at levels of μg/L (ppb).
- The choice of chelating ligands in the stationary phase and mobile phase allows for control over selectivity.
- CIC can be accomplished using existing LC instrumentation.

1.6 Gradients for metal ion chelation

Most studies on metal ion chelation have utilized one or more chelating ligands to optimize metal ion binding to the solid support.[26] Metal ion uptake has been studied via complexiometric titration, atomic absorption spectroscopy, and inductively coupled plasma-atomic emission spectrometry.[26, 51, 52, 55, 60, 63, 64, 67] Changing the ligand density provides another means of optimizing metal ion binding. Typically, this is done by preparing multiple samples with different concentrations of the chelating ligand; however, gradient surfaces allow for optimization using only one sample.[26] Bronstein et al. used poly(acrylic acid) polymer blends to study the interaction of Fe and Ce with the polymer gradients; as the concentration of the polymer increased along the length of the gradient, the concentration of Fe increased as well.[114] In our group, Kannan et al. used amine-functionalized gradient surfaces to study the coordination complexes of Cu^{2+} and Zn^{2+}.[26] Diamine and triamine gradients were prepared on silicon wafers using CRI, and the modified silicon wafers were soaked in metal ion solutions to form coordination complexes, as shown in Figures 1.17 and 1.18.[26]

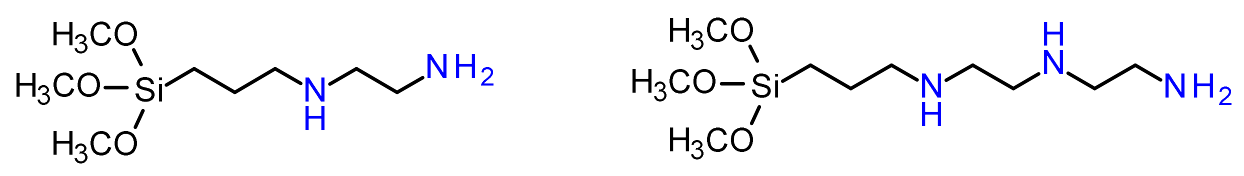


Figure 1.17 Left: structure of N-[3-(trimethoxysilyl)propyl] ethylenediamine (diamine). Right: structure of N-[3- (trimethoxysilyl)propyl] diethylenetriamine (triamine).

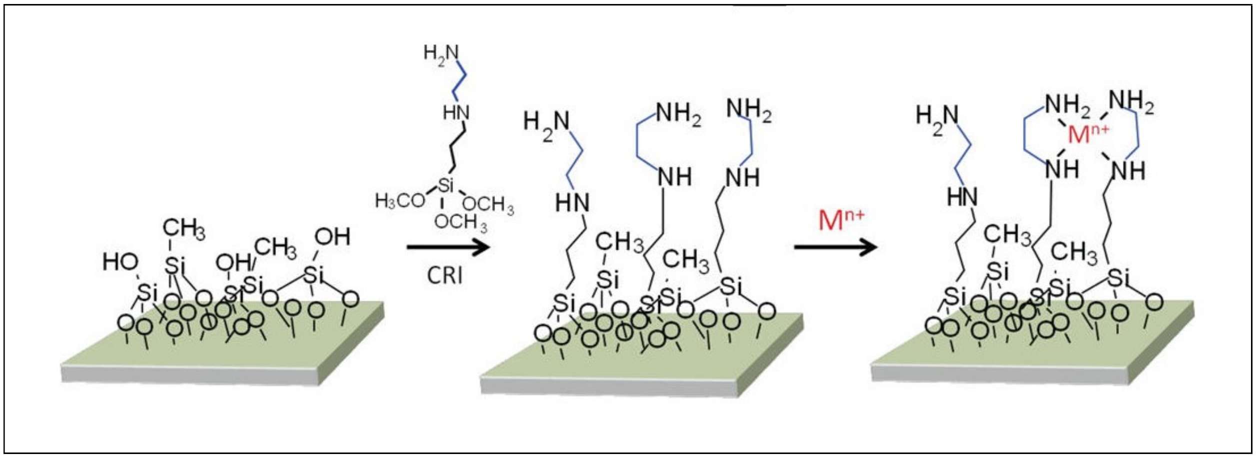


Figure 1.18 Schematic illustrating the modification of a silicon wafer with ethylenediamine using CRI and the subsequent formation of metal coordination complexes by soaking in a metal ion solution. Reprinted from Ref 26 with permission. Copyright 2014 American Chemical Society.

Using x-ray photoelectron spectroscopy (XPS), the nitrogen to metal ion (N/M^{n+}) ratio was determined.[26] For Cu^{2+}, the N/M^{n+} ratio was 8 to 11 for diamine, indicating that there are unbound amine groups on the surface. The N/M^{n+} ratio for triamine to Cu^{2+} was 4, indicating that more of the Cu^{2+} is bound to triamine.[26] Figure 1.19 shows a schematic of Cu^{2+} bound to triamine on a gradient surface. For Zn^{2+}, the N/M^{n+} was 4 to 8 on the diamine surface and 5 to 7 on the triamine surface, indicating that diamine binds Zn^{2+} more tightly than Cu^{2+}.[26] In this work, the differences in metal ion binding to chelating ligands on the surface will be utilized for separation.

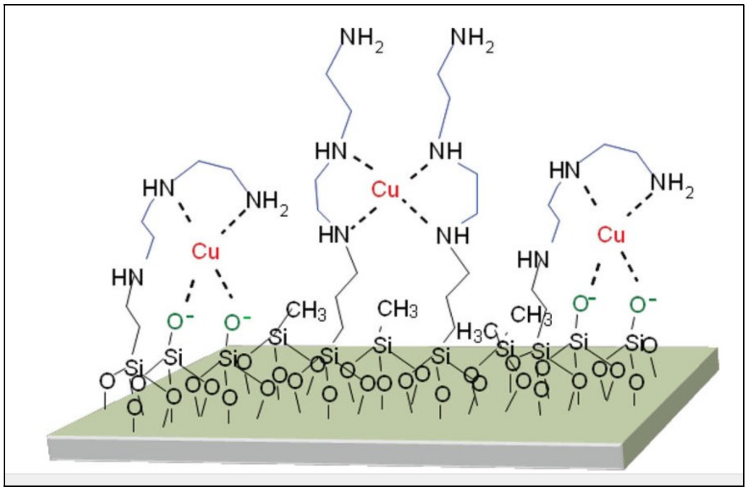


Figure 1.19 Schematic illustrating possible structures of Cu-triamine complexes. Cu^{2+} could be bound to two amine groups and two O from the silanol groups, as shown on the left and right, or to four amine groups, as shown in the middle. Reprinted from Ref 26 with permission. Copyright 2014 American Chemical Society.

1.7 Two-dimensional thin layer chromatography (2D TLC)

TLC, which is utilized in this work, is typically performed by developing the plate in one direction. However, for more complex mixtures, separation may be achieved by developing the plate in two directions that are orthogonal to each other. Nyiredy and Ciesla et al. describe five main types of 2D TLC:[115, 116]

- Comprehensive: the same stationary phase is used with different mobile phases in each dimension, or a bilayer plate is used with the same or different mobile phases in each dimension.
- Targeted or selective: only certain analytes (usually the ones that are not separated in the first dimension) are subjected to separation in the second dimension.
- Modulated: in the first dimension, the plate is developed multiple times with mobile phases of decreasing polarity; in the second dimension, the plate is developed multiple times with mobile phases that have different selectivity.

- Coupled-layer: after development in the first dimension, analytes are grafted onto a different stationary phase.
- Combination: a combination of any of the four methods listed above.

Two-dimensional TLC has been used in the separation of plant extracts, pesticides, and vitamins.[115-120] Horvat et al. also used 2D TLC to separate a mixture of ten transition and heavy metal ions on cellulose plates using an acetonitrile/HCl/water mobile phase in the x-direction and 2-pentanol/acetonitrile/HCl in the y-direction.[121] While 2D TLC can be useful in separating mixtures that are not adequately resolved in the first dimension, there are several disadvantages:[115]

- Only one sample can be applied per plate.
- Nonvolatile solvents are difficult to remove.
- Mobile phases used in the first dimension may modify the stationary phases.

Separation using 2D TLC is further complicated by the difficulty in finding stationary phase and/or mobile phase combinations that are truly orthogonal.[115] The simplest type of 2D TLC, which is not orthogonal, is one in which the same stationary phase and mobile phase is used in both directions. In this case, any improvement in separation is due to the increase in the development distance.[115, 116] In a system that is truly orthogonal, the separation should utilize the entire plate, increasing the number of analytes that can be separated and the distance between the analytes, as shown in Figure 1.20.[115]

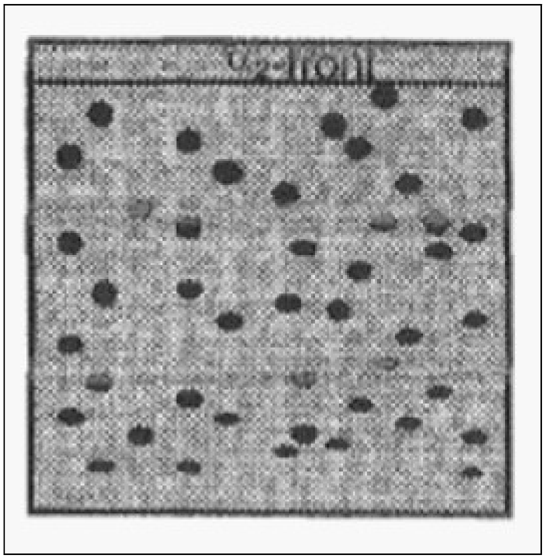


Figure 1.20 Two-dimensional TLC plate in which the separation utilizes the entire plate. Reprinted from Ref 116 with permission.

1.8 Overview of dissertation (Part 1)

The separation and identification of the transition and heavy metals is extremely important. Many transition and heavy metals are toxic, even at low concentrations. Water supplies can be contaminated by transition and heavy metals due to natural sources, such as weathering of rocks and soil or volcanic eruptions, and human causes, such as mining and processing, coal-burning, and manufacturing.[122] Current methods of identifying transition and heavy metals, including ICP and ion chromatography, suffer from problems such as the inability to distinguish between oxidation states and interference from alkali and alkaline earth metals. The ability to distinguish between oxidation states is important because some metal ions can be less toxic in a certain oxidation state, and some are beneficial in one oxidation state but toxic in another. For example, Cr^{3+} is an essential nutrient, as it plays a role in biologically active complexes, serving as glucose tolerance factors; however, Cr^{6+} is a carcinogen.[123, 124] Chelating ion chromatography provides a means of separating transition and heavy metals and distinguishing between oxidation states without interference from alkali and alkaline earth metals. Chelation gradients provide another means of controlling selectivity and achieving separation.

The goal of this work was to use gradient surfaces prepared using CRI, developed by Kannan et. al., to control the retention, and thus the separation of transition and heavy metals.[4, 8, 18, 26] In the first part of this work, chelation gradients were prepared on TLC plates using amine, diamine, and triamine ligands. The stationary phases were characterized using XPS in order to demonstrate the presence and extent of the gradient. The retention, and thus separation, of the metal ions was manipulated by changing the type of ligand and the surface concentration. In the second part of this work, 2D chelation gradients were prepared with the goal of improving the separation achieved in the first part of this work. Aligned, opposed, and orthogonal triamine-thiol gradients were prepared and used to separate six transition and heavy metals. By varying the direction of the gradient, the order of separation could be manipulated. Complete separation of all six metal ions was achieved on the orthogonal gradient.

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Chapter 2: Separation of Transition and Heavy Metals Using Stationary Phase Gradients and Thin Layer Chromatography

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2.1 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 $Fe^{3+} > Cu^{2+} \sim Pb^{2+} \sim Co^{2+}$, while the order of retention on plates modified with bi- and tri-dentate ligands was $Fe^{3+} > Cu^{2+} > Pb^{2+} \sim Co^{2+}$. 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 $Fe^{3+} > Cu^{2+} > Co^{2+} > Pb^{2+}$.

2.2 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).[4] 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.[4] Aminoalkoxysilanes are particularly useful in CRI because they react quickly with surface silanol groups due to the self-catalyzing ability of the amine group.[10] 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, 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.[11-13] Others have modified the inorganic support with chelating ligands[14-22] and/or utilized chelation ion chromatography (CIC) to separate and quantify mixtures containing transition and heavy metals.[23-28] 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.[23, 24] The principles of CIC have also been applied to TLC.[14-17] Using silica gel TLC plates modified with amines or β-diketones and a mobile phase such as salicylaldoxime or trifluoroacetylacetone in acetone, mixtures of four to six metal ions have been separated.[15, 17]

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.

2.3 Experimental

2.3.1 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 F_{254} from Sigma Aldrich; the plates were 20 x 20 cm with a 250 µm layer thickness.

2.3.2 Preparation of stationary phase

The 20 x 20 cm TLC plates were cut into pieces of the approximate size of 8 cm x ~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), (2) uniformly modified, or as (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 H_2O, 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.[4, 29] The volumes of aminosilane, infusion rate, and infusion time employed in the present studies are given in Table 2.1. All of the plates were rinsed thoroughly with ethanol after being removed from the aminosilane solution.

Table 2.1. 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
	0.12	1.0	
	0.50	3.0	5
		1.0	15
		0.5	30
Diamine	0.08	1.0	15
	0.12		
	0.50		
Amine	0.08	1.0	15

2.3.3 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[30, 31] afforded efficient hydrolysis (acid) and condensation (base) of the precursors. After soaking, the plates were air dried and placed in the oven at 160º C for 1 hr.

2.3.4 Separation of metal ions

The metal salts ($Co(C_2H_3O_2)_2$, $Pb(C_2H_3O_2)_2$, $Cu(C_2H_3O_2)_2$, and $Fe(ClO_4)_2$) 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 K_2HPO_4 (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 254 nm and the distance traveled by each metal ion was measured. Photographs of the plates were obtained using a digital camera, examples of which are shown in Figure 2.1 for diamine and triamine.

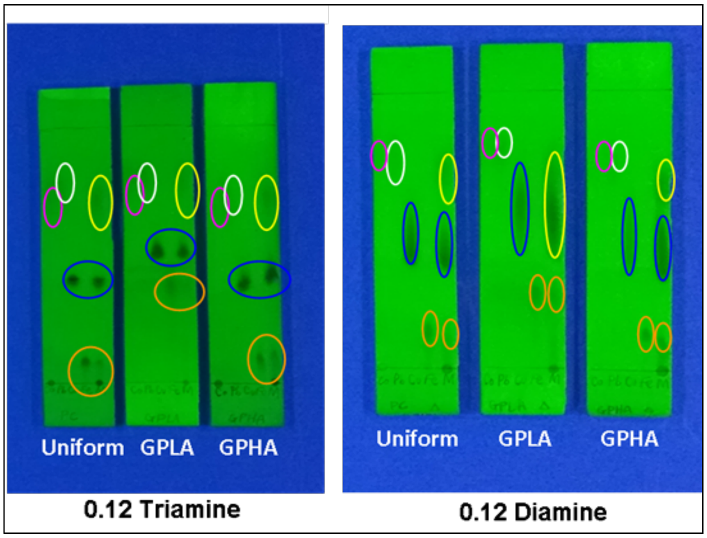

Figure 2.1 Photographs of 0.12 triamine (left) and 0.12 diamine (right) uniformly modified and gradient plates spotted with Co^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, and a mixture of the four metal ions under UV radiation (254 nm). (pink: Co^{2+}, white: Pb^{2+}, blue: Cu^{2+},orange: Fe^{3+}, yellow: mixture of Co^{2+} and Pb^{2+}).

The retention factor (R_f) for each metal ion was calculated using Eq. 1,

$$R_f = \frac{\text{distance traveled by analyte}}{\text{distance traveled by the solvent front}} \tag{1}$$

Since metal ions tend to streak, the R_f values were calculated from the center of the streak. Standard deviations were calculated using R_f values from three plates. Two of the plates were prepared on the same day, and a third plate was prepared the next day to evaluate reproducibility.

2.3.5 Characterization of the TLC plates using XPS

The gradient profiles of the modified plates were characterized using X-ray photoelectron spectroscopy (XPS). The plate was cut into ten pieces, 0.8 cm in length. The silica powder was scraped from every other piece and analyzed using a ThermoFisher ESCAlab 250 imaging X-ray photoelectron spectrometer. For uniformly modified plates, each sample was scanned once. For gradient plates, each sample was scanned at three points and the average value and standard deviation were reported. The binding energies were corrected using the C1s peak as 284.6 eV. Quantification of the N1s peak area was done by commercially available software (Avantage

Version 4.4). For ease of comparison, the area under the N1s peak was divided by 2 and 3 for diamine and triamine, respectively.

2.3.6 Variation of the mobile phase (Early work- umpublished)

To compare the effect of the mobile phase on separation, other chelators were utilized in place of EDTA in the mobile phase. The mobile phases are listed in Table 2.2 below. All mobile phases were prepared 50:50 v/v with acetone. (The concentrations listed in the table are the final concentrations after dilution with acetone.)

Table 2.2. Mobile Phases used with Various Stationary Phases.

Mobile Phase	**Stationary Phase**
0.1 M citric acid 0.5 M citric acid	20 : 0.04 : 0.004 v/v/v of ethanol: diamine: DI H_2O
1 M acetamide	20 : 0.04 : 0.004 v/v/v of ethanol: diamine: DI H_2O
1 M acetic acid	20 : 0.04 : 0.004 v/v/v of ethanol: diamine: DI H_2O 20 : 0.50 : 0.004 v/v/v of ethanol: triamine: DI H_2O
1 M acetylacetone in acetone 1 M acetylacetone in acetone	20 : 0.50 : 0.004 v/v/v of ethanol: triamine: DI H_2O

For the 0.1 M citric acid, 0.5 M citric acid, 1 M acetamide, and 1 M and 2 M acetylacetone in acetone mobile phases, none of the metal ions moved from the baseline. With 1 M acetic acid, the metal ions moved on uniformly modified plates (20 : 0.04 : 0.004 ethanol : diamine : DI H_2O); however, the retention factors did not change with increasing infusion time. When 1 M acetic acid was used with 0.50 triamine plates, none of the metal ions moved. As expected, the chelating agent in the mobile phase needs to be stronger than the chelating agent in the stationary phase in order for the metal ions to move from the baseline.

2.4 Results

The separation of four transition and heavy metal ions, Co^{2+}, Pb^{2+}, Cu^{2+}, and Fe^{3+}, was evaluated on unmodified TLC plates, uniformly modified TLC plates, and gradient plates. On an unmodified TLC plate, three of the four metal ions (Co^{2+}, Pb^{2+}, Cu^{2+}) were not significantly retained (Rf ~ 0.80) and did not separate. Fe^{3+} was retained (Rf ~ 0.47) and separated from the other three metal ions, indicating that it has some affinity for the silica surface, whereas the other metal ions do not. For the gradient plates, the separation was strongly dependent on the spotting end (GPHA vs. GPLA) and the extent at which the plate was modified, which is influenced by the concentration of amine in solution, the infusion time, and the type of chelator. Each of these variables is described in the sections that follow with comparisons made to the uniformly modified plates.

2.4.1 Chelator

The coordination ability of the surface immobilized ligands with the metal ions will be dependent on the number of donor atoms, their orientation on the surface, and their surface density.[32] To more closely examine how the chelator influences separation, gradients were made from three different aminoalkoxysilanes containing one, two, or three donor atoms. The presence of a gradient and how the surface density of chelating groups changes with distance was evaluated by XPS. Figure 2.2 shows representative N1s XPS spectra and corresponding plots of N1s peak area as a function of distance for materials made from amine, diamine, and triamine. Consistent with prior work,[32] the binding energy for the N 1s peak is 399.8 ± 0.1 eV and a small shoulder due to protonated and H-bonded amines can be seen at 401.9 ± 0.1 eV.

The uniformly modified substrates show a near constant amount of nitrogen on the surface with distance, while the gradient samples show a gradual increase in N from top to bottom for each chelator. The surface coverage is slightly higher for the materials prepared from amine and is lowest for the triamine, consistent with steric factors as we have noted in prior work.[29, 32]

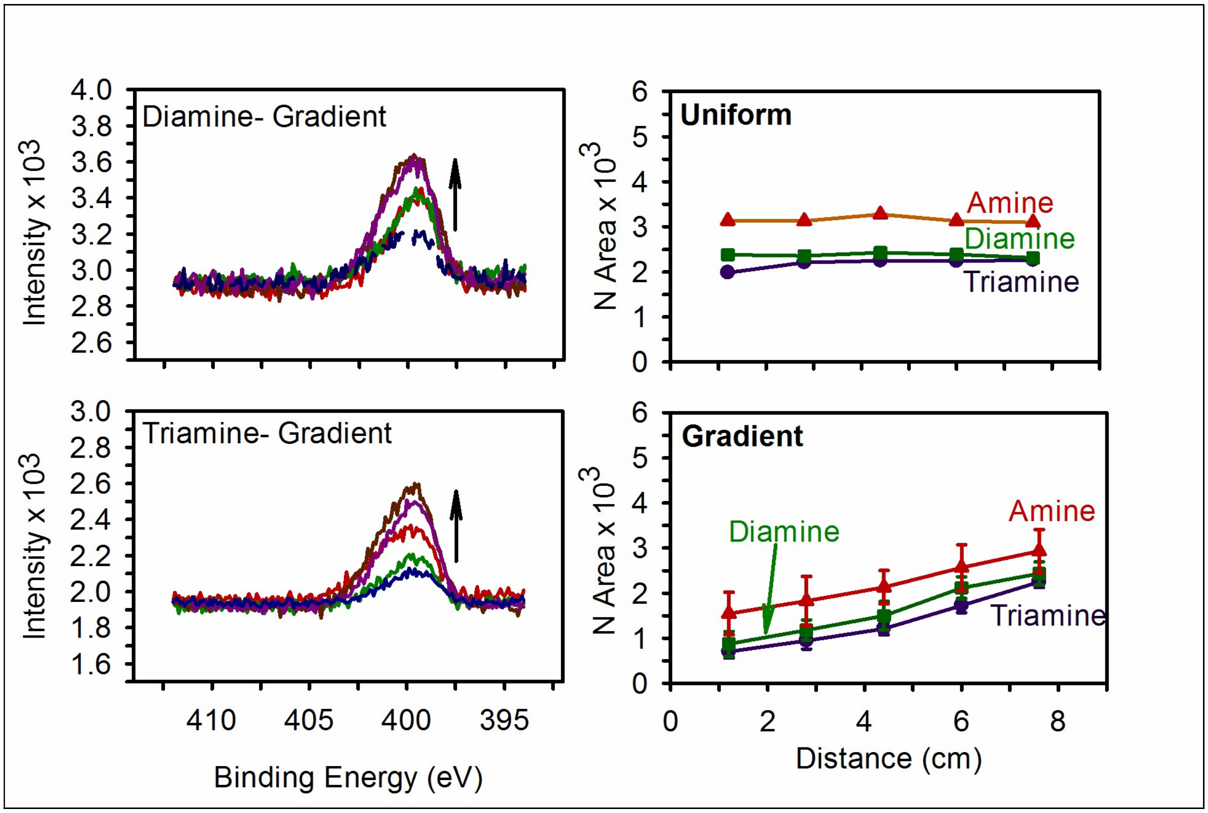

Figure 2.2 Left: N1s spectra from five points along the length of the gradient for diamine (top) and triamine (bottom). The arrow indicates gradient direction from low to high amine. Right: N1s (CPS eV) profiles of the uniformly modified (top) and gradient plates (bottom) for x = 0.08 amine (brown triangles), diamine (green squares), and triamine (purple circles). The N1s area was divided by 2 and 3 for diamine and triamine, respectively.

The effect of the number of N donor atoms on the separation of the metal ions can be seen in Figure 2.3, which shows the R_f values for the four different metal ions on the different TLC plates prepared with x = 0.08 chelator. What can be immediately seen is that the retention factors depend on the number of donor atoms in the chelator, with greater retention noted on the triamine modified plates. This result is not unexpected, as multi-dentate ligands such as diamine and triamine will form more stable complexes with a metal ion compared to a monodentate ligand. Such results were also observed in metal uptake studies.[33] Previous detailed XPS undertaken on similar Cu^{2+}-diamine and Cu^{2+}-triamine chelation gradients prepared on modified silicon wafers revealed a N/Cu ratio of 9-11 for the diamine gradient and 4 for coordination to a triamine gradient.[32] Both mono- and bis-complexes were noted with ratios estimated to be 70:20 for diamine and 60:30 for triamine. For 1:1 complexes, the other two sites were filled with oxygen from neighboring silanol or Si-O-Si groups.[32] The tridentate ligand provides more nitrogen atoms to chelate copper and thus yields a more stable coordination complex.[32]

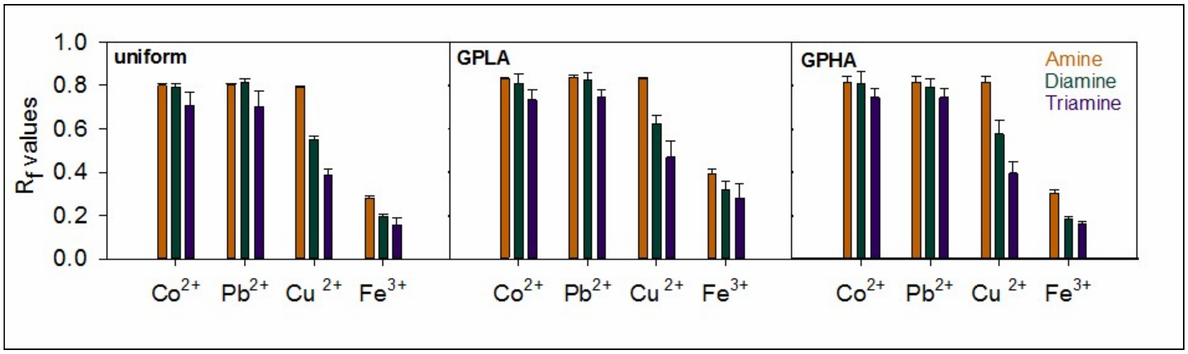

Figure 2.3 Comparison of the effect of varying the number of amine groups on the R_f values of Co^{2+}, Pb^{2+}, Cu^{2+}, and Fe^{3+} on uniformly modified plates, GPLA, and GPHA where x = 0.08. Error bars represent standard deviations obtained from three plates.

Of the four metal ions, Cu^{2+} and Fe^{3+} were the most sensitive to the surface bound chelator. Co^{2+} and Pb^{2+} were less affected by the surface bound chelator, as their R_f values only decrease slightly when the number of amine groups increase from two to three. On the amine modified plate, three of the four metal ions were barely retained indicative of weak bonding and coordination of this monodentate ligand to the metal ions. On the other hand, the bi-and/or tri-coordinate ligands were able to retain the metal ions to a varying degree as described in more detail in later sections. A strong chelating ligand is thus required on the stationary phase to retain the metal ions and produce a separation.

2.4.2 Variation in the Triamine Concentration.

To evaluate the effect of triamine concentration on the separation of the four metal ions, the volume of triamine was increased in the deposition solution from 0.08 to 0.12 to 0.50 mL. The N1s profiles of the uniformly modified and gradient plates obtained from XPS spectra are shown in Figure 2.4**.** Predictably, the area under the N 1s peak increases as the concentration of triamine in the deposition solution increases. The gradient profiles increase steadily from the low amine (~1.2 cm) end of the plate to the high amine (~7.2 cm) end, confirming the presence of a gradient.

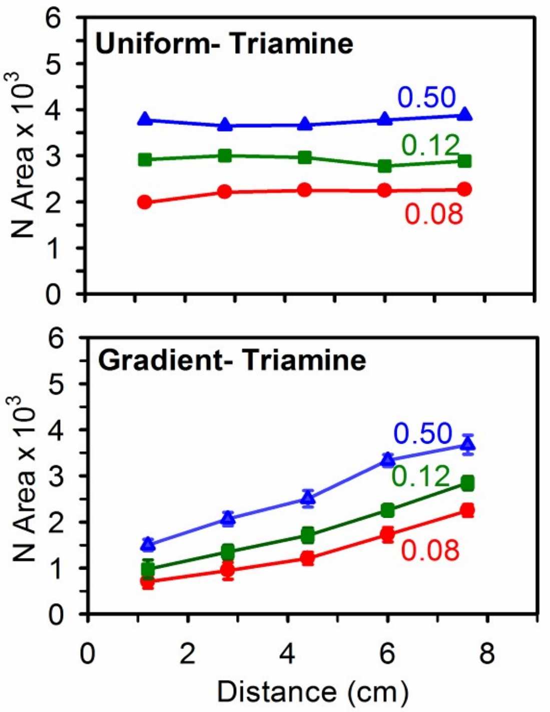

Figure 2.4 N1s area (CPS eV) profiles of uniformly modified (top) and gradient plates (bottom) for x = 0.08 (red circles), 0.12 (green squares), and 0.50 (blue triangles) triamine.

Figure 2.5 shows the effect of increasing triamine concentration on the R_f values of Co^{2+}, Pb^{2+}, Cu^{2+}, and Fe^{3+} spotted on uniformly modified and gradient plates. The R_f factors of Co^{2+} and Pb^{2+} on the uniformly modified plate ($R_f = 0.71 \pm 0.07$) are similar to those obtained on an unmodified plate (0.82 ± 0.04), while for Cu^{2+} and Fe^{3+}, the retention increases. For Cu^{2+}, the R_f decreases from 0.82 ± 0.04 on an unmodified TLC plate to 0.39 ± 0.03 on the 0.08 triamine modified plate. For Fe^{3+}, the R_f decreases from 0.47 ± 0.03 to 0.16 ± 0.04 on unmodified and $x = 0.08$ uniformly modified TLC plates, respectively. The decrease in R_f values indicates that the Cu^{2+} and Fe^{3+} have a much higher affinity for surface bound triamine than Co^{2+} and Pb^{2+}. With the exception of Pb^{2+}, retention of all the metal ions can be increased by increasing the surface concentration of triamine. As the concentration of triamine increases, a greater density of N groups is available to form a strong chelate with the metal ion, thus increasing retention. Of all the metal ions studied, Fe^{3+} is most sensitive to the surface bound triamine as evident by a decrease in the R_f factor by almost three as the concentration in deposition solution increases from $x = 0.08$ to 0.12, while Pb^{2+} is the least sensitive.

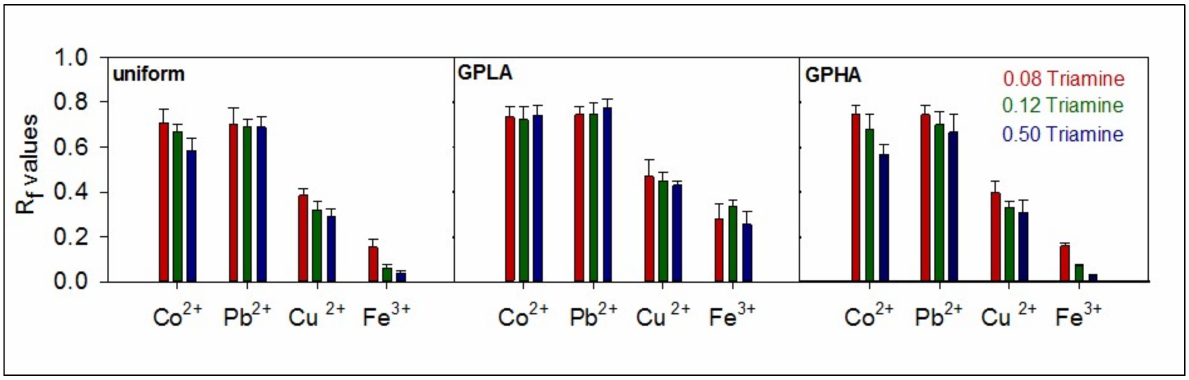

Figure 2.5 Effect of increasing triamine concentration on the R_f values of Co^{2+}, Pb^{2+}, Cu^{2+}, and Fe^{3+} on uniformly modified plates, GPLA, and GPHA. Error bars represent standard deviations obtained from three plates.

On GPHA, the separation of the metal ions is almost identical to that seen on the uniformly modified plates, but very different than on GPLA, indicating the importance of the spotting end. The amount of triamine on the high amine end of GPHA and on the uniformly modified plates is very similar (Figure 2.4). The metal ions are thus strongly chelated to the surface near the spotting end. However, on GPLA, the spotting end contains a much lower amount of bound chelator (~1/3 less as seen in Figure 2.4). As a result, the metal ions are able to travel up the plate before being retained to a significant degree by the increasing concentration of the bound chelator and their R_f factors are larger on GPLA compared to the uniform substrate or GPHA. This observation is most obvious for Fe^{3+}, which is strongly affected by the amount of triamine on the surface. It is also interesting that when the metal ions are spotted on the low amine end (GPLA), the surface concentration of triamine is not as important. The R_f factors for each ion are similar even though the amount of surface bound triamine differs. For GPHA and the uniformly modified substrate, however, the R_f of Fe^{3+} decreases significantly as the amount of triamine on the surface increases. With the addition of triamine to the stationary phase, Cu^{2+}, as well as Fe^{3+}, both are now able to be separated from the mixture. Although Co^{2+} has a lower R_f than Pb^{2+} on the $x = 0.50$ triamine plates, some overlap was observed due to the streaking.

2.4.3 Variation in the Infusion Time.

The rate of infusion is another variable that can be changed to alter the degree of modification, and hence the retention factors and separation of the metal ions on the TLC plate. A lower degree of modification takes place when the infusion time is fast. In this work, the infusion times were changed from 5 to 15 to 30 min, keeping the triamine concentration constant at 20 : 0.50 : 0.004 v/v/v ethanol : triamine : DI H_2O. Figure 2.6 shows the profiles of the 5, 15, and 30 min uniformly modified and gradient plates as evaluated by XPS. As expected, the degree of modification increases with an increase in the exposure time of the TLC plate to the amine. The gradient profiles are very similar with a slightly greater amount of amine on the surface during a 30 min infusion time vs. a 5 min infusion time.

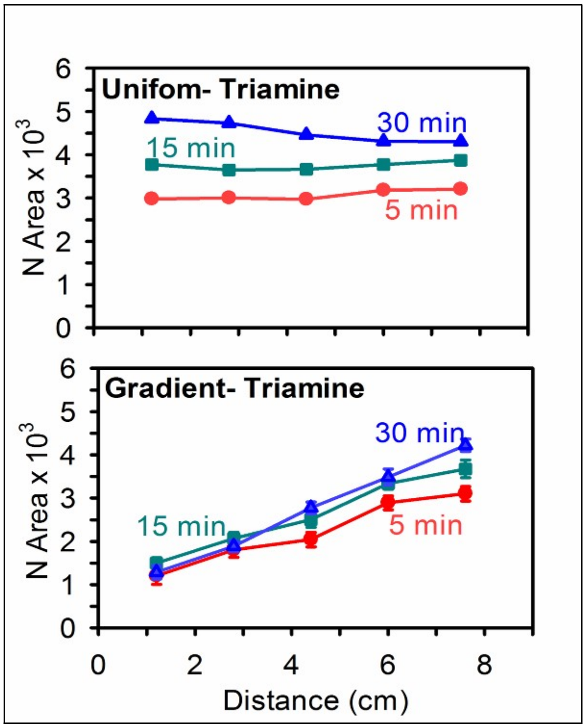

Figure 2.6 Profiles of uniformly modified (top) and gradient plates (bottom) for 5 min (red circles), 15 min (teal squares), and 30 min (blue triangles) exposure to the triamine precursor (x = 0.50).

As can be seen in Figure 2.7, the trends in R_f values are very similar to those seen with changing triamine concentration. Co^{2+}, Cu^{2+}, and Fe^{3+} are sensitive to the amount of triamine on the TLC plate. As the time of infusion increases (degree of modification increases), R_f factors decrease. Pb^{2+} is least sensitive to modification, consistent with the data reported in Figure 2.5 for increasing triamine concentration, while Fe^{3+} barely moves off of the baseline, even when the infusion time was only 5 min. Fe^{3+} has a high affinity for the stationary phase (triamine + surface silanol groups). Once again, the separation on the uniformly modified plates is similar to GPHA, but very different from GPLA. Clearly, spotting end is very important and influences retention factors; again most notably those of Fe^{3+}. On GPLA, Fe^{3+} moves up the plate where it does not to any significant extent on either the uniform plate or GPHA because of the initial presence of a relatively high amount of triamine near the spotting end.

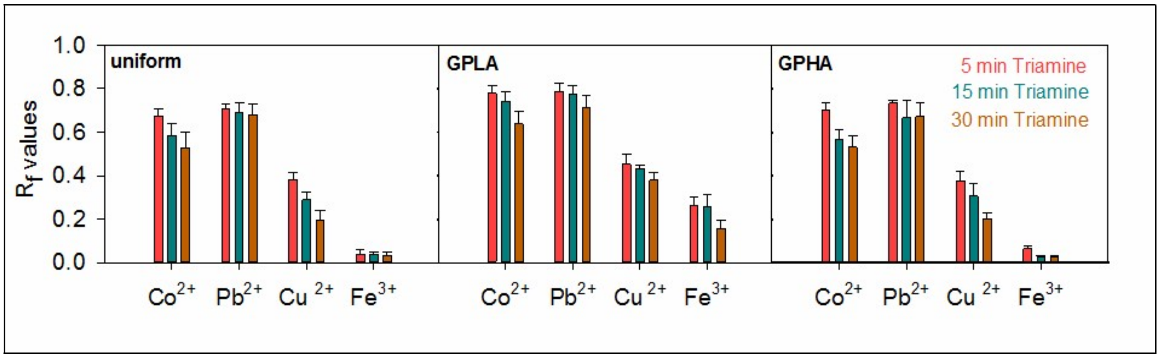

Figure 2.7 Comparison of the effect of varying infusion time on the R_f values of Co^{2+}, Pb^{2+}, Cu^{2+}, and Fe^{3+} on uniformly modified plates, GPLA, and GPHA where x = 0.5. Error bars represent standard deviations obtained from three plates.

Co^{2+} and Pb^{2+} were previously inseparable with a 15 min infusion time; however, with a 30 min infusion time, all four metal ions were separated on the uniformly modified plates and on both gradient plates, as can be seen in the photograph of the TLC plate in Figure 2.8. While the metal ions are separated on a uniformly modified plate and on GPHA, Fe^{3+} does not move from the baseline. On GPLA, the four metal ions are still separated, and Fe^{3+} moves up the plate, providing the advantage that these four metal ions could be separated from contaminants or other metal ions that do not move from the baseline.

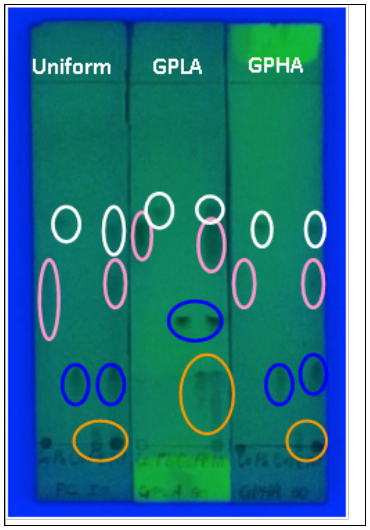

Figure 2.8 Photographs of 30 min triamine (0.50) uniformly modified and gradient plates with Co^{2+} (pink), Pb^{2+} (white), Cu^{2+} (blue), Fe^{3+} (orange), and a mixture of the four metal ions under UV radiation (254 nm).

2.4.4 Varying Diamine Concentration.

Similar experiments were performed with diamine where the volume of diamine in the deposition solution (x) was changed from 0.08 to 0.12 to 0.50 ml. Figure 2.9 shows the profiles for uniformly modified and gradient plates. As expected, the amount of nitrogen on the surfaces increased with increasing concentration and with increasing exposure time (from the low end to the high end of the gradient). However, compared to the triamine profiles, the N 1s peak areas were slightly higher for diamine. This was noted in previous papers and attributed to steric hindrance in the case of triamine, leading to a lower surface concentration of triamine.[29, 32]

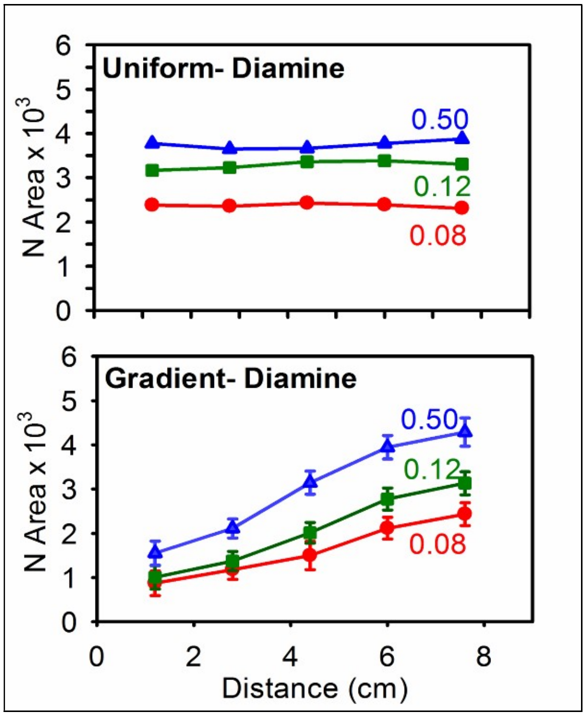

Figure 2.9 Profiles of uniformly modified (top) and gradient plates (bottom) for 0.08 (red circles), 0.12 (green squares), and 0.50 (blue triangles) diamine.

When the metal ions were spotted on the modified plates, streaking was more pronounced with diamine modified plates vs. the triamine modified plates, which can be seen by comparing the two panels in Figure 2.1. The streaking is believed to be due to the interaction with surface silanol groups. The addition of an organoalkoxysilane with terminal -CH_3 groups (in this case, isobutyltrimethoxysilane) helps reduce the streaking by removing some of the excess surface silanol groups. It can also diminish the fluorescence of the TLC plate as noted in the darking of the TLC plates shown in Figure 2.8. Capping all (or most) of the surface silanol groups is not desirable, however, as this would make the plate too hydrophobic and also eliminate remaining coordination sites being filled by surface silanols. Streaking is one of the disadvantages of modifying the TLC plates with diamine, particularly at the low concentrations. Since diamine only has two N atoms per molecule (as opposed to three in triamine), coordination will be weaker, thus metal ion interactions with surface silanols will likely increase.

R_f values for the different metal ions and different plates are depicted in Figure 2.10. As observed for the triamine modified plates, the separation on GPHA and uniform plates are very similar to each other. For Co^{2+} and Pb^{2+}, there is a slight dependence of R_f with concentration whereas Cu^{2+} and Fe^{3+} are more sensitive to amount of modifier on the surface. Fe^{3+} is significantly less retained on the diamine modified plates compared to the triamine modified plates. Again, triamine is a stronger chelator than diamine. Due to the increased streaking, Co^{2+}, Pb^{2+}, Cu^{2+} are not separable at low concentrations of diamine. While the streaking is reduced at higher concentrations of diamine, Co^{2+} and Pb^{2+} are still inseparable.

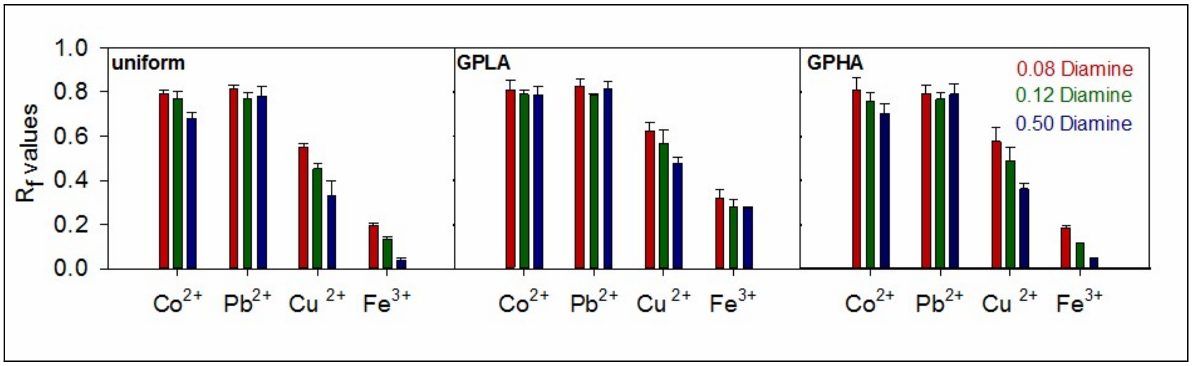

Figure 2.10. Comparison of the effect of increasing diamine concentration on the R_f values of Co^{2+}, Pb^{2+}, Cu^{2+}, and Fe^{3+} on uniformly modified plates, GPLA, and GPHA. Error bars represent standard deviations obtained from 3 plates.

2.5 Discussion

Many factors can impact the separation of metal ions on functionalized silica including sorption and electrostatic interactions and chelating effects.[34] Retention and separation will be influenced by the extent and type of modification of the stationary phase as well as the properties of the mobile phase, most notably pH. Further complications can arise because the TLC plate is not a fully equilibrated system and because differential solvent evaporation from the mixed mobile phase is possible.[35] The difference in the retention and separation of the different metal ions can be explained by their affinities with surface immobilized functionalities and the mobile phase. The metal ions will be displaced in an order consistent with their affinity for the stationary phase compared to the mobile phase.[22] In this work, the pH of the mobile phase was kept constant at pH 6.5, while the type (mono-, bi-, or tri-dentate ligands) and concentration of immobilized chelator varied. Interactions between the metal ions and the silica surface will be relatively weak compared to chelating effects between the immobilized nitrogen containing ligands. [36, 37]

When metal ions are spotted on an amine-modified silica surface with a relatively low density of chelator, they likely form 1:1 and 1:2 metal-ligand complexes with remaining sites filled with oxygen from neighboring silanol and/or Si-O-Si groups.[32] As the surface density of chelating groups changes along the length of the gradient surface, the extent and thus the strength of chelation will inevitably change as we have previously shown in detailed XPS studies.[32] The formation constants are well known for the M-L_x (L = EDTA, Triamine, Diamine) complexes in solution but significantly less known for metals coordinated in various geometries with surface-immobilized ligands.[34]

Fe^{3+} is easily separated from the other three metal ions, even on an unmodified TLC plate. When even a small concentration of a bi- or tri- dentate ligand is added to the surface, the R_f of Fe^{3+} decreases noticeably (going from ~0.5 on an unmodified plate to ~0.2 or lower on plates modified with a bi- or tri-dentate ligand). These results can be understood by considering Pearson's Hard-Soft Acid-Base (HSAB) theory.[38] Fe^{3+} is considered to be a hard acid while nitrogen and oxygen are hard bases.[39] On an unmodified silica TLC plate, Fe^{3+} strongly interacts with the surface and is retained to a much greater extent than the other metal ions in this study.

Furthermore, on the gradient plates that contain both amine and silanol groups, it is very difficult to displace Fe^{3+} since it is tightly bound to the surface.

Co^{2+}, Pb^{2+}, and Cu^{2+} are considered borderline (not hard or soft) acids in Pearson's HSAB theory,[39] explaining why they are not retained as heavily as Fe^{3+}. As a first approximation, differences in their retention can be explained by comparing formation constants (K_f) of solution species (M-EDTA; M-L_x where x = 1),[40-44] Table 2.2. The ratio, K, of their affinity for the stationary phase compared to the mobile phase (EDTA) is given by Eq. 2,

$$K = \frac{K_f \text{ (aminosilane)}}{K_f \text{ (EDTA)}} \tag{2}$$

where K_f (aminosilane) is the formation constant for diamine or triamine and K_f' (EDTA) is the conditional formation constant for the EDTA complex at pH 6.5 ($\alpha = 9.45 \times 10^{-5}$).[44] A higher ratio means the metal ion has a high affinity for the stationary phase compared to the mobile phase; therefore, the R_f for the metal ion will be lower. While the values listed in Table 2.2 were determined in solution, the order of retention predicted by the values of K is consistent with our experimental results. Clearly, Cu^{2+} has a higher affinity for both diamine and triamine than $Co^{2+}$and Pb^{2+}, which have similar values. It can also be seen that all three metal ions have a higher affinity for triamine than for diamine, which is also consistent with the experimental results (lower R_f values on triamine plates compared to diamine plates.)

Table 2.3. Formation Constants and Ratio (K) of Affinities for Diamine, Triamine and EDTA with Co^{2+}, Pb^{2+}, and Cu^{2+}.

Metal Ion	**Log K_f (Diamine)[42, 43]**	**Log K_f (Triamine)[42, 43]**	**Log K_f (EDTA)[44]**	**Ratio K (Diamine)**	**Ratio K (Triamine)**
Co^{2+}	5.60	8.0	16.45	1.5×10^{-7}	3.7×10^{-5}
Pb^{2+}	7.00	8.5	18.0	1.1×10^{-7}	3.3×10^{-6}
Cu^{2+}	10.54	15.9	18.78	6.1×10^{-5}	13.9

On an unmodified surface and on a surface modified with a monodentate ligand, the order of retention (affinity for the stationary phase) is $Fe^{3+} > Cu^{2+} > Pb^{2+} \sim Co^{2+}$. Given that Cu^{2+} and Fe^{3+} have higher affinities for the stationary phase, it is not surprising that their R_f values are influenced by the concentration of aminosilane. Conversely, Co^{2+} and Pb^{2+} have little affinity for the aminosilane stationary phase, and, thus, the concentration of aminosilane has less of an effect on their R_f values. However, the data in Figures 2.5, 2.7, and 2.10 show that Co^{2+} is more affected by the change in aminosilane concentration on the surface than Pb^{2+}. This difference was used to separate Co^{2+} and Pb^{2+} by increasing the infusion time to 30 min, yielding a retention order of $Fe^{3+} > Cu^{2+} > Co^{2+} > Pb^{2+}$. Similar results have been found in studies of metal ion uptake on silica gels supports modified with an amine or hydroxy groups.[33, 45-48] The results of this and other studies indicate that Cu^{2+} and Fe^{3+} are ideal for separation studies since they bind strongly to chelating ligands, while Co^{2+} and Pb^{2+} are more difficult to separate. However, with careful manipulation of the ligand concentration on the surface, separation of all four metal ions can be achieved.

2.6 Conclusion

This work utilizes the concepts of chemical gradients and chelation ion chromatography to affect the separation of a mixture of four transition and heavy metal ions (Co^{2+}, Pb^{2+}, Cu^{2+}, and Fe^{3+}). The metal ion separation was studied on unmodified TLC plates and on uniformly modified and gradient plates prepared from three different aminosilanes, three different concentrations of triamine and diamine, and three different infusion times. Separation was achieved by creating a competition between the surface immobilized chelating agents (aminosilanes) and a stronger chelating agent (EDTA) in the mobile phase. Variation in the surface density of amine groups on the stationary phase via changes in the aminosilane concentration or the infusion time produced small albeit useful changes in the R_f values of the metal ions. The addition of aminosilane with two amine groups was found to be sufficient for separating Cu^{2+} and Fe^{3+} from the mixture, however, a higher concentration of triamine (0.50) and a longer infusion time (30 min) was required for complete separation of all four metals. While separation can be achieved on uniformly modified TLC plates, gradient plates spotted on the low amine end provide the advantage that all of the metal ions move off of the baseline. Future work will focus on separating a greater number of metal ions using two-dimensional gradient TLC.

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Chapter 3: Separation of Transition and Heavy Metals Using Two-Dimensional Triamine-Thiol Chelation Gradients on Thin Layer Chromatography Plates

3.1 Abstract

Two-dimensional multi-component stationary phase gradients were prepared for chelation thin layer chromatography (TLC). Controlled rate infusion (CRI) was used to modify the plates using N-[3-(trimethoxysilyl)propyl]diethylenetriamine and 3-mercaptopropyltrimethoxysilane. Chelation ion chromatography (CIC) was employed, using a stronger chelating agent, ethylenediamintetraacetic acid (EDTA), in the mobile phase. The separation of six metal ions (Co^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, and Hg^{2+}) was compared on uniform plates and on aligned, opposed, and orthogonal 2D gradients. The results show that the retention, and thus separation, of the metal ions is dependent on the spotting end and the direction of the gradient and that the order of retention can be manipulated by reversing the direction of the gradients. Fe^{3+} and Hg^{2+} were heavily retained on all plates, indicating a high affinity for the triamine-thiol stationary phase, while Co^{2+} and Pb^{2+} were the least retained. Nearly complete separation was obtained on the orthogonal triamine-thiol gradient.

3.2 Introduction

Thin layer chromatography (TLC) is a widely employed technique to separate both simple and complex mixtures. As in other forms of chromatography, separation is achieved through careful selection of the stationary phase, such as silica gel, alumina, cellulose, or polyamide, and the mobile phase, which is chosen based on the polarity of analytes that need to be separated. TLC is typically done by developing the plate in one direction (termed "one-dimensional"); however, for more complex mixtures, two-dimensional (2D) TLC may be used.[1, 2] In 2D TLC, the plate is developed in one direction, then rotated 90º and developed a second time.[1, 2] Two-dimensional TLC has been used previously to separate plant extracts, pesticides, and vitamins.[1-8] Horvat et al.used 2D TLC to separate and qualitatively identify metal ions in honey.[9] Most studies involving 2D TLC rely on changing the mobile phase in each dimension or by coupling or grafting differing materials so that analytes not separated in the first dimension can be separated in the second dimension.[1, 3, 6, 8] However, such methods are not always practical or efficient and, when coupling or grafting materials, care must be taken to ensure that all analytes of interest are transferred to the second dimension.

Another method for separating complex mixtures involves the use of gradients. While gradient mobile phases may be used, they are difficult to utilize in TLC. An alternate paradigm to the mobile phase gradient is to use a stationary phase gradient.[10] Gradient surfaces exhibit a gradual change in physical or chemical properties along the length of the surface.[10-16] Such gradients have been used extensively for the study of directed transport, protein adsorption, polymerization kinetics, and cell growth.[13, 16] Genzer et al. also used 2D orthogonal polymer gradients to study the formation of nanoparticle assemblies, protein adsoption, cell adhesion, and polymer chain conformations.[17] More recently, gradient surfaces have also been applied to stationary phases in chromatography as a means of separating complex mixtures.[10, 11, 18-20] Gradient stationary phases in chromatography can be classified as discontinuous or continuous. Discontinuous gradients are prepared by serially connecting TLC plates or chromatography columns.[12, 18, 19, 21, 22] For example, Cimpoiu et al. used discontinuous gradients composed of silica gel and cellulose to separate a mixture of vitamins.[18] Continuous gradients are prepared by gradually changing the functional groups along the length of the TLC plate or chromatography column.[10-12, 18, 23, 24] The advantage of a continuous gradient is that there may be synergistic effects between neighboring functional groups. Often, continuous gradients are single-component; however, more recently, multi-component gradient have been used to improve retention and control selectivity.[11]

Our group has previously used continuous single-component gradients to separate mixtures of weak acids and bases, over-the counter drugs, metals, and pyrimidine nucleobases, and metal ions;[10, 11, 23, 25] we have also developed multi-component amine-phenyl gradients on TLC plates, which were effectively used to separate water- and fat-soluble vitamins.[11] In the case of both single- and multi-component gradients, there are also silanol groups present on the surface whose concentration will vary depending on the extent of modification.[11] To make these gradients, we rely on controlled rate infusion (CRI).[10, 11, 14, 23, 25-27]

In CRI, a continuous stationary phase gradient is prepared by exposing a silica substrate to a functionalized organoalkoxysilane in a time-dependent fashion.[10] The organoalkoxysilane reacts with silanol groups on the silica surface to form a modified surface with a predictable variation in the degree of functionality.[10, 28] CRI has been used to prepare the single-component and multi-component gradients as discussed above[10, 11, 14, 23, 25-27, 29] and to prepare orthogonal gradients by rotating the substrate 90º and preparing a second gradient, as decribed by Kannan, et al.[27]

We have also used CRI to prepare single-component one-dimensional gradients with N-[3-(trimethoxysilyl)propyl] ethylenediamine or N-[3-(trimethoxysilyl)propyl] diethylenetriamine to study the coordination and separation of transition and heavy metals.[25, 27] Our prior work utilizes CRI and chelation ion chromatography, which relies on the competition between an immobilized chelating ligand in the stationary phase and a free chelating ligand in the mobile phase.[30-58] By varying the concentration of the immobilized ligand and the rate of infusion, we were able to use small changes in retention to separate four metal ions.[25]

In this work, we use CRI to prepare 2D multi-component chelation gradients on TLC plates to separate a greater number of transition and heavy metals. Our prior work utilized single-component gradients in one dimension to separate four metal ions. In this work, we use two-dimensional multi-component chelation gradients prepared using N-[3-(trimethoxysilyl)propyl] diethylenetriamine (triamine) and 3-mercaptopropyltrimethoxysilane (thiol) to separate six metal ions (Co^{2+}, Pb^{2-}, Ni^{2+}, Cu^{2+}, Fe^{3+}, and Hg^{2+}). Triamine and thiol were chosen as Co^{2+}, Pb^{2-}, Ni^{2+}, and Cu^{2+} are considered borderline acids and bind to borderline bases such as amines, and Pb^{2-} and Hg^{2+} (a soft acid) are known to bind preferrentially to thiols.[59, 60] The triamine and thiol gradients were prepared so that they were either aligned, opposed, or orthogonal to each other. In some cases, the metal ions are separated using a stationary phase with uniform modification in one dimension and one or more gradients in the other dimension; in other cases, the metal ions are separated using gradients in both dimensions. We demonstrate how retention, and thus separation, can be influenced depending on whether or not a gradient is used in each dimension and on the direction of the gradient in each dimension.

3.3 Experimental

3.3.1 Reagents

N-[3-(trimethoxysilyl)propyl] diethylenetriamine (97%, referred to as triamine) was purchased from Acros Organics, and 3-mercaptopropyltrimethoxysilane (98%, referred to as thiol) was purchased from Alfa Aesar. Trimethoxysilylpropyl modified(polyethylenimine) (referred to as polyamine), N-(trimethoxysilylpropyl)ethylenediamine triacetic acid, trisodium salt (referred to as EDTA silane), and 1-[3-(Trimethoxysilyl)propyl]urea (referred to as urea) were purchased from Gelest. Cobalt (II), lead (II), and copper (II) acetates, as well as mercury (II) nitrate, were obtained from Fisher Scientific. Nickel (II) nitrate was obtained from J. T.

Baker Chemical Co., and iron (II) perchlorate was obtained from Sigma Aldrich. Nickel (II) chloride and mercury (II) acetate, which were used for the characterization studies, were obtained from Sigma Aldrich and Alfa Aesar, respectively. Ethylenediaminetetraacetic acid (EDTA) and dimethylgloxime (DMG) were purchased from Fisher Scientific. Dibasic potassium phosphate was obtained from Sigma Aldrich. Ethanol (200 proof USP/ACS grade) was obtained from Pharmaco-Aaper. The TLC plates were silica gel F_{254} from EMD Millipore; the plates were 20 x 20 cm with a 250 μm layer thickness.

3.3.2 Preparation of stationary phase (triamine-thiol)

The TLC plates were cut into 4 x 4 cm squares using a glass cutter and cleaned by soaking in ethanol. The plates were dried and activated by heating in an oven at 160º C for 30 min and then cooled to room temperature before use. Unmodified plates were used as received. Uniformly modified and gradient plates were soaked in ethanol for ~10 min before use. Both uniformly modified and gradient plates were exposed to a triamine solution for 30 min, rinsed with ethanol, dried, and then exposed to a thiol solution for 30 min, rinsed with ethanol, and dried. The triamine solution was prepared by mixing ethanol : triamine : DI H_2O in a 20 : 0.50 : 0.004 volumetric ratio. The thiol solution was prepared by mixing ethanol : thiol : 0.1 M HCl in a 20 : 0.20 : 0.20 volumetric ratio and stirring for 5 min to promote hydrolysis. Then, 0.20 ml of 0.3 M NH_4OH was added, and the solution was stirred for 25 min to neutralize the acid and promote condensation. The thiol solution was allowed to sit undisturbed for 90 min before use.

Uniformly modified plates were soaked in the triamine and thiol solutions, respectively, for a set period of time. To prepare a gradient using CRI, the plates was placed vertically in a sample vial, and the silane solution was infused into the sample vial using a syringe pump (Harvard Apparatus PHD 2000 Infusion) at an infusion rate of 0.41 mL/min. Three types of gradients were prepared: aligned, opposed, and orthogonal. A schematic illustrating the gradient preparation is shown is Figure 3.1. The aligned gradients were prepared by placing the plate in the same direction in the sample vial to be infused with the triamine and thiol solutions, respectively. The opposed gradient was prepared by infusing the plate with the triamine solution, inverting the plate, and then infusing the plate with the thiol solution. The orthogonal plate was prepared by infusing the plate with the thiol solution, rotating the plate 90º, and then infusing the plate with the thiol solution. All of the plates were rinsed thoroughly with ethanol after being removed from both the triamine and thiol solutions. After modification, the plates were air dried and then placed in the oven at 160 ºC for 1 hr.

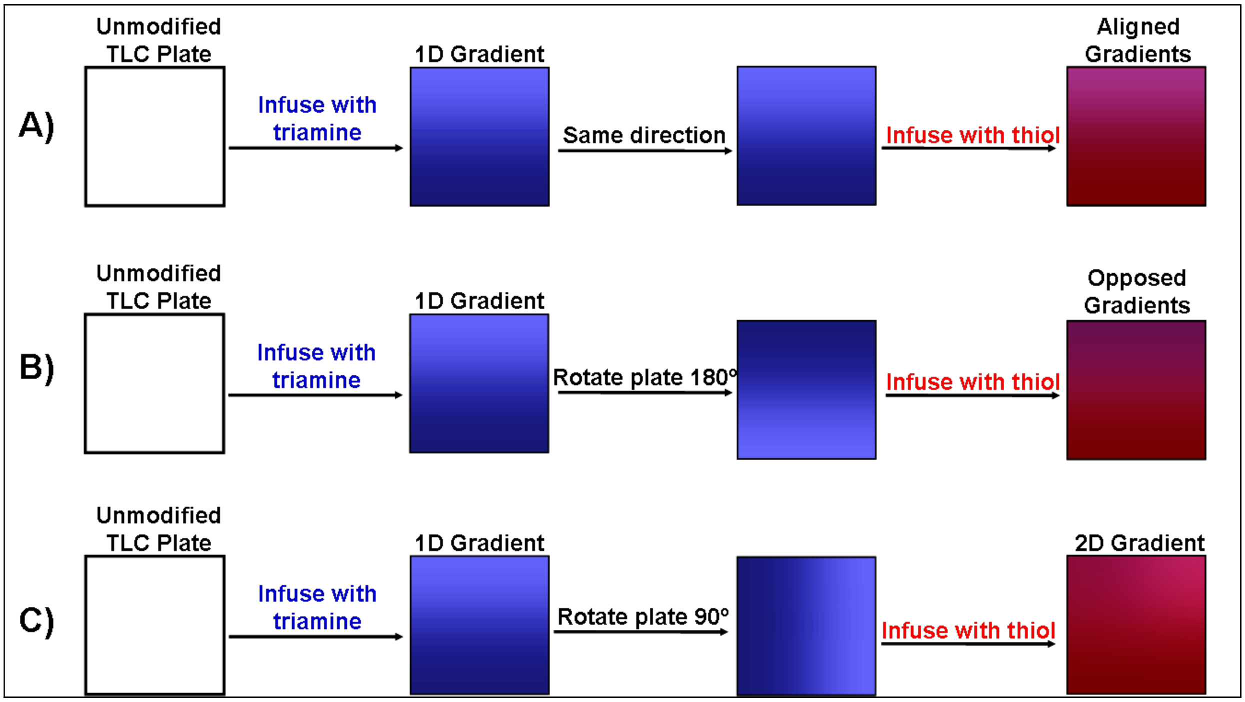

Figure 3.1 Preparation of 2D triamine + thiol gradients: A) gradients aligned in the same direction, B) gradients in opposing directions, and C) gradients orthogonal to each other.

3.3.3 Preparation of other stationary phases

The TLC plates were cut, cleaned, and activated as described in section 3.3.2. Gradient plates were prepared by infusing the plate with a silane in the x-direction, rotating the plate 90º, and then infusing the plate with another silane in the y-direction. The gradients used in the x- and y-direction are listed in Table 3.1 below

Table 3.1 Silanes Used in the X- and Y-Directions

Silane used in the x-direction	**Silane used in the y-direction**
Diamine	Diamine
Triamine	Triamine
Diamine	Triamine
Diamine	Polyamine
Triamine	Polyamine
Triamine	Urea
EDTA silane	Triamine

The silane solutions listed in Table 3.1 were prepared as follows:

- Diamine, triamine, and polyamine (20 : 0.50 : 0.004 ethanol : amine : DI H_2O v/v/v)
- Urea (20: 1.00: 0.004 ethanol: urea: DI H_2O)
- EDTA silane (20: 0.20 : 0.20 : 0.20 methanol: EDTA silane :conc HCl : DI H_2O)

3.3.4 Separation of metal ions

The metal salts ($Co(C_2H_3O_2)_2$, $Pb(C_2H_3O_2)_2$, $Ni(NO_3)_2$, $Cu(C_2H_3O_2)_2$, $Fe(ClO_{4)3}$, and $Hg(NO_3)_2$ were dissolved at a concentration of 5 mg/mL in 0.1 M HCl. A mixture was prepared by dissolving 5 mg of each of the six metal salts in 0.1 M HCl. The mixture was spotted on unmodified, uniformly modified, and gradient plates ~0.5 cm from the bottom and on the left side of the plate. For the aligned gradients, the plates were spotted on the low triamine - low thiol end (termed LALT) or on the high triamine - high thiol end (termed HAHT). For the opposed gradients, the plates were spotted on the low triamine - high thiol end (termed LAHT) or on the high triamine - low thiol end (termed HALT). The orthogonal plates were spotted on the low end of each gradient (termed LALT diagonal).

After spotting, the plates were allowed to dry for ~5 min. A mobile phase was prepared using 0.1 M EDTA/0.1 M K_2HPO_4 (pH ≈6.5) : acetone 50 : 50 v/v, and the mobile phase chamber was presaturated before developing the plates. The plates were developed in the x-direction, dried overnight in a desiccator, and then developed in the y-direction. The solvent front was developed to 0.5 cm from the top in both directions. For the unmodified plates, the metal ions faced a bare silica surface in both directions; on the uniformly modified plates, the metal ions faced a uniform concentration of triamine and thiol in both directions. For the aligned (LALT and HAHT) and opposed (LAHT and HALT) gradients, the metal ions faced a uniform concentration of triamine and thiol in the x-direction and a gradient in the y-direction; metal ions on the orthogonal gradient (LALT diagonal) faced a gradient in both directions. An illustration of the direction the metal ions travel on each gradient is shown in Figure 3.2.

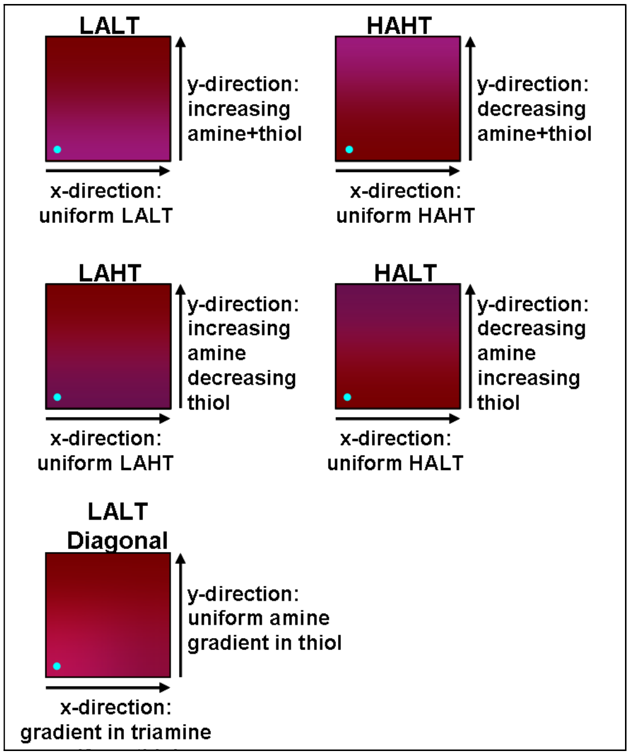

Figure 3.2 Direction the metal ions travel on 2D aligned (LALT and HAHT) plates [top], 2D opposed (LAHT and HALT) plates [middle], and 2D orthogonal (LALT Diagonal) plates.

Once the plates were dried after being developed in both directions, they were visualized under UV light at 254 nm. Co^{2+}, Pb^{2-}, Cu^{2+}, Fe^{3+}, and Hg^{2+} were circled in pencil under the UV. To detect Ni, the plates were dried overnight, then dipped in 1% DMG (in ethanol) and left overnight again. The plates were photographed using a digital camera, and the distance traveled by each metal ion in the x- and y-directions was measured. The retention factors for each metal ion in the x-direction (R_{fx}) were calculated using eq. 1,

$$R_{fx} = \frac{\text{distance traveled by metal ion in the x-direction}}{\text{distance traveled by the solvent front in the x-direction}} \qquad (1)$$

The retention factors for each metal ion in the y-direction (R_{fy}) were calculated similarly, using the distance traveled by the metal ion in the y-direction and the distance traveled by the solvent front in the y-direction. Standard deviations were calculated using R_{fx} and R_{fy} from three plates.

To verify the identity of the metal ions, six plates of each type were prepared, and one metal ion (Co^{2+}, Pb^{2-}, Ni^{2+}, Cu^{2+}, Fe^{3+}, and Hg^{2+}) was spotted on each plate. The plates were developed in the x- and y-directions as described above, and the R_{fx} and R_{fy} values were compared to the spots on the plates with the mixtures.

3.4 Results and Discussion

3.4.1 Separation of Co^{2+} and Pb^{2} on other stationary phases

Initial experiments were performed on diamine + diamine, triamine + triamine, diamine + triamine, diamine + polyamine, triamine + polyamine, triamine + urea, EDTA silane + triamine, and triamine + thiol 2D orthogonal gradients using Co^{2+} and Pb^{2+} as a test mixture. The structures of the silanes are shown in Figure 3.3 below. Photographs of the plates are shown in Figure 3.3, and the retention factors are given in Table 3.2.

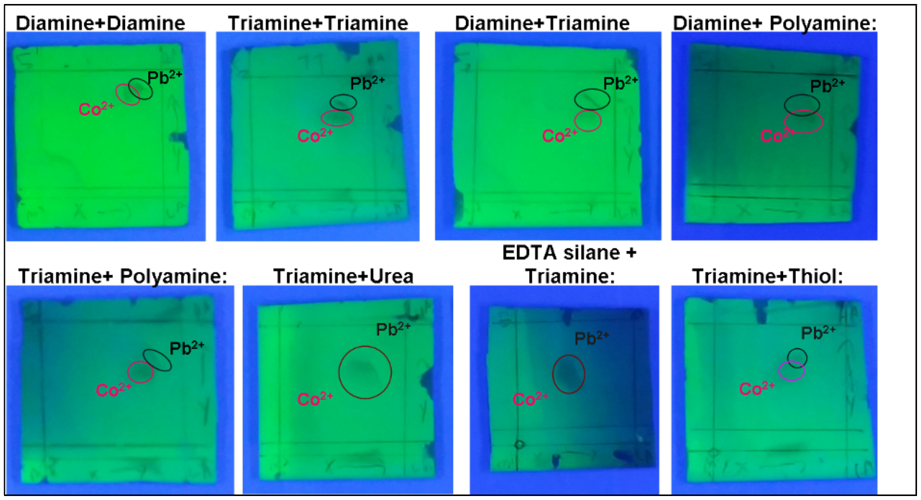

Figure 3.3 Photographs of 2D TLC plates under UV light (254 nm) showing separation of Co^{2+}(pink) and Pb^{2+}(white) on 2D gradients.

Table 3.2 Retention Factors for Co^{2+} and Pb^{2+} on 2D Gradients.

		R_{fx}		R_{fy}	
		Avg	Std. Dev.	Avg	Std. Dev.
Diamine + Diamine	Co^{2+}	0.76	0.03	0.70	0.07
	Pb^{2+}	0.76	0.03	0.77	0.06
Triamine + Triamine	Co^{2+}	0.74	0.02	0.63	0.02
	Pb^{2+}	0.76	0.02	0.76	0.02
Diamine + Triamine	Co^{2+}	0.81	0.03	0.66	0.03
	Pb^{2+}	0.83	0.05	0.77	0.03
Diamine + Polyamine	Co^{2+}	0.82	0.02	0.66	0.03
	Pb^{2+}	0.86	0.02	0.78	0.02
Triamine + Polyamine	Co^{2+}	0.81	0.02	0.61	0.04
	Pb^{2+}	0.83	0.02	0.75	0.00
Triamine + Urea	Co^{2+}	0.71	0.03	0.65	0.03
	Pb^{2+}	0.71	0.03	0.71	0.02
EDTA silane + Triamine	Co^{2+}	0.47	0.01	0.57	0.05
	Pb^{2+}				
Triamine + Thiol	Co^{2+}	0.51	0.04	0.51	0.01
	Pb^{2+}	0.55	0.03	0.58	0.03

As expected based on prior work, the greatest separation between Co^{2+} and Pb^{2+} is obtained on the plates modified with higher order amines (triamine + triamine, diamine + triamine, and triamine + polyamine). Diamine + diamine produces little separation due to having fewer nitrogens available for chelation. Diamine + polyamine also produces incomplete separation, most likely due to lower surface coverage produced by polyamine due to steric factors as described in previous work. Of the three plates modified with chelators other than amine (triamine + urea, EDTA silane + triamine, and triamine + thiol), triamine + thiol produced the greatest separation. Due to the affinity of thiol for heavy metals such as Pb^{2+} and Hg^{2+}, triamine + thiol was chosen for further study.

3.4.2 Fabrication of 2D triamine-thiol gradient.

In this work, two-dimensional (2D) triamine-thiol gradients were prepared on silica gel TLC plates. The gradients were prepared by infusing a triamine solution at a set rate using CRI so that bottom of the square plate was exposed to the triamine solution for a longer period of time than the top of the plate; this forms a gradient in triamine functionality that decreases from the bottom to the top of the plate. A multi-component gradient was formed by subsequently modifying the plates with a thiol functionality using CRI. In multi-component gradients, the individual components can be aligned or opposed; the 2D arrangement also allows for an orthogonal gradient. For aligned gradients, the thiol functionality is applied in the same direction as the triamine functionality, so that both the triamine and thiol decrease from bottom to top. For opposed gradients, the thiol functionality is applied in the opposite direction; therefore, the thiol gradient increases as the triamine gradient decreases. For the orthogonal gradients, the plate is rotated 90º between infusions, so the triamine would decrease from left to right while the thiol decreases from bottom to top. Prior research with amine and thiol functionalities suggests that the thiol groups condense with silanol groups at or near the amine groups, which puts the two groups in close proximity to each other.[29] The plate is modified with amine first because the amine can act as a catalyst, enhancing the condensation of thiol.[11, 14, 29, 61] The close proximity of the triamine and thiol groups should theoretically create a surface where analytes such as transition and heavy metals can coordinate to both amine and thiol groups.

3.4.3 Separation of transition and heavy metals

The separation of six transition and heavy metals (Co^{2+}, Pb^{2-}, Ni^{2+}, Cu^{2+}, Fe^{3+}, and Hg^{2+}) was evaluated on aligned, opposed, and orthogonal 2D triamine-thiol gradients For comparison, the separation was also evaluated on unmodified, uniformly modified, and one-dimensional plates. The metal ions chosen represent a range from those that are highly toxic, such as Pb and Hg, to those that are necessary for human health, such as Fe.[62] The separation will depend on the direction of the gradient (increasing or decreasing) and the alignment of the gradient (aligned, opposed, or othagonal). If the metal ions are spotted on the low end of a gradient, the metal ions will face an increasing concentration of functional groups as they move up the plate; however, if the metal ions are spotted on the high end of the gradient, the metal ions will face a decreasing concentration of functional groups.

On an unmodified 2D TLC plate, all of the metal ions except iron were not retained. The metal ions were at or near the solvent front and tended to spread out. Only Fe^{3+} was retained approximately halfway in each dimension, indicating an affinity for the silica surface, which in consistent with earlier results.[25] The one-dimensional (1D) triamine-thiol plates did retain the metal ions, yielding R_f values of 0.55 or lower; however Co^{2+} and Pb^{2+} were inseparable on both aligned and opposed gradients. Also, when the metal ions are spotted on the high amine end (regardless of thiol concentration), Fe^{3+} and Hg^{2+} do not move, and Cu^{2+} barely moves (R_f $\approx$0.10), as shown in Figures 3.4 and 3.5 and noted in Table 3.3.

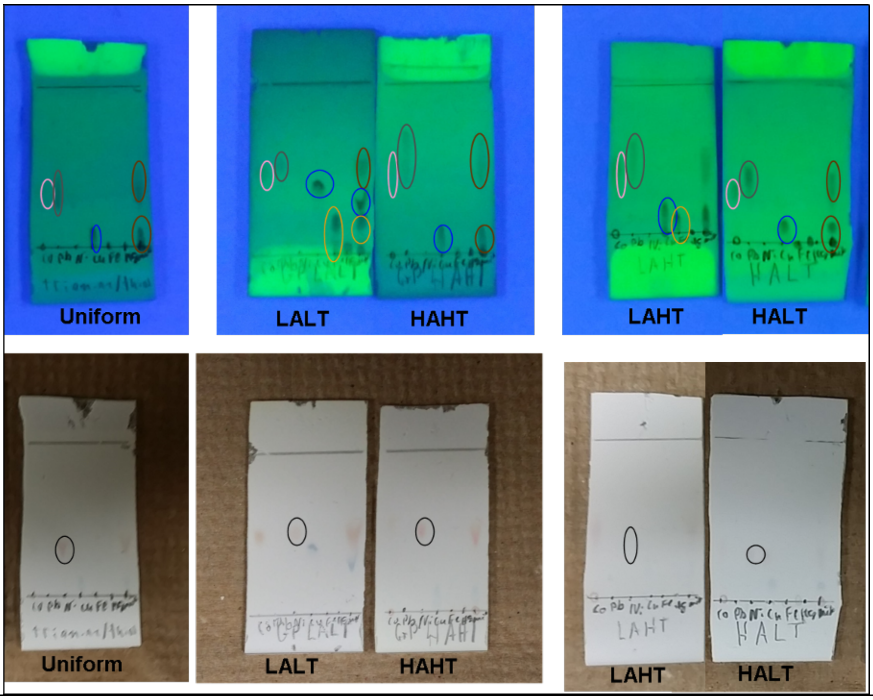

Figure 3.4 Top: Photographs of 1D TLC plates under UV light (254 nm) showing separation of Co^{2+} (pink), Pb^{2+} (gray), Cu^{2+} (blue), Fe^{3+} (orange), and Hg^{2+} (at the baseline). Bottom:

Photographs of 1D TLC plates under visible light after being dipped in dimethylgloxime (DMG). Ni^{2+} is visible as a faint pink spot (circled in black).

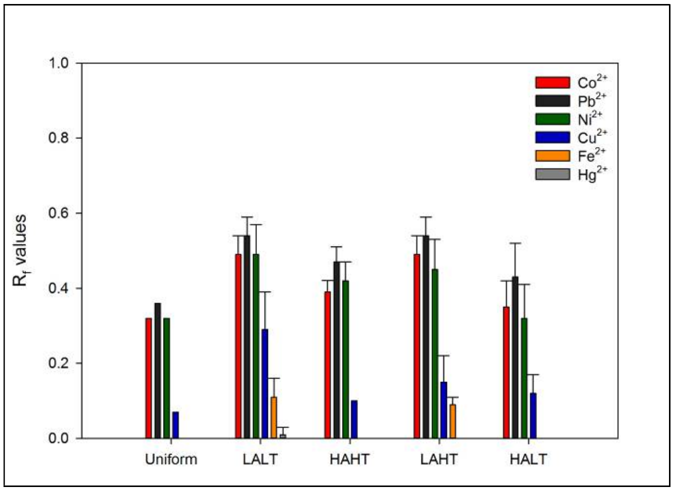

Figure 3.5 R_f values of Co^{2+} (red), Pb^{2-} (gray), Ni^{2+} (green), Cu^{2+} (blue), Fe^{3+} (orange), and Hg^{2+} (light gray) in on uniform, low triamine - low thiol (LALT), high triamine - high thiol (HAHT), low triamine - high thiol (LAHT), and high triamine - low thiol (HALT) 1D plates. (Bars are not visible for Fe^{3+} and Hg^{2+} when the R_f value is 0.00.)

Table 3.3 Retention Factors for Metal Ions on 1D Gradients.

Metal Ions	Uniform	LALT		HAHT		LAHT		HALT	
		Avg	Std. Dev.	Avg	Std. Dev.	Avg	Std. Dev.	Avg	Std. Dev.
Co^{2+}	0.32	0.49	0.05	0.39	0.03	0.49	0.05	0.35	0.07
Pb^{2+}	0.36	0.54	0.05	0.47	0.04	0.54	0.05	0.43	0.09
Ni^{2+}	0.32	0.49	0.08	0.42	0.05	0.45	0.08	0.32	0.09
Cu^{2+}	0.07	0.29	0.10	0.10	0.00	0.15	0.07	0.12	0.05
Fe^{3+}	0.00	0.11	0.05	0.00	0.00	0.09	0.02	0.00	0.00
Hg^{2+}	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00

Photographs of the 2D uniformly modified and gradient plates are shown in Figure 3.6. On the uniformly modified plate, Co^{2+} and Pb^{2+} are separated, although Ni^{2+} overlaps slightly with Co^{2+}. However, with the introduction of triamine and thiol groups, both Fe^{3+} and Hg^{2+} are strongly retained and do not move from the baseline in the x- or y-directions. This result is not surprising, as Fe^{3+} is considered a hard acid, so it binds strongly to oxygen from surface silanol groups and nitrogen from the amine groups. Hg^{2+} is considered a soft acid and binds strongly to the sulfur from thiol groups. Cu^{2+} is also strongly retained as it barely moves in either direction, indicating a high affinity for the modified surface.

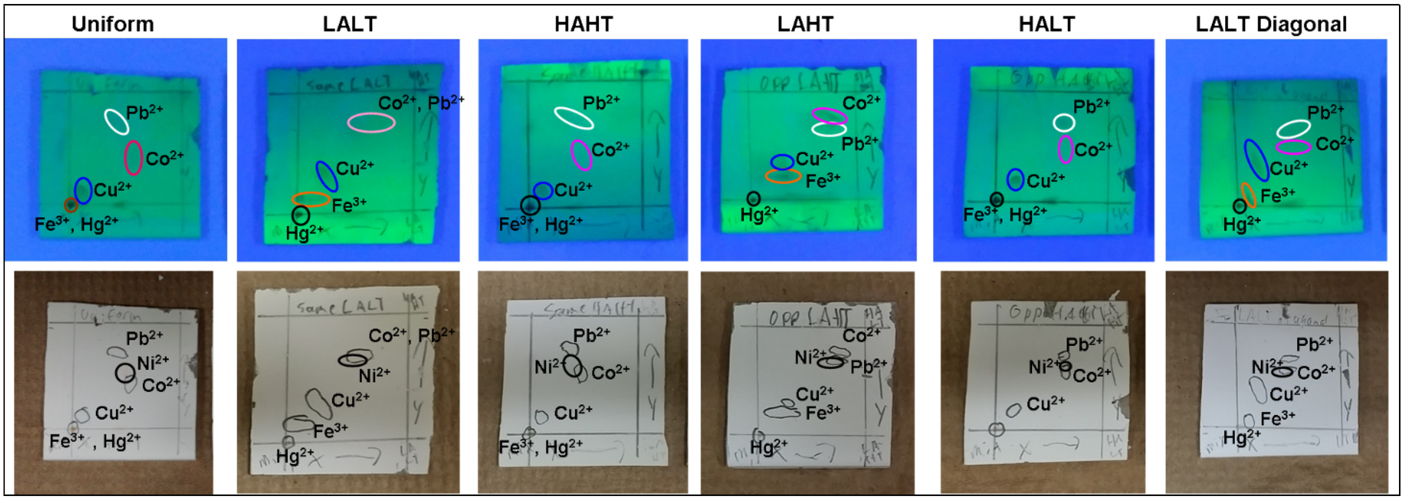

Figure 3.6 Top: Photographs of 2D TLC plates under UV light (254 nm) showing separation of Co^{2+}(pink), Pb^{2+}(white), Cu^{2+}(blue), Fe^{3+}(orange), and Hg^{2+}(black). Bottom: Photographs of 2D TLC plates under visible light after being dipped in dimethylgloxime (DMG). Co^{2+}, Pb^{2-}, Cu^{2+}, Fe^{3+}, and Hg^{2+} (which were detected under UV light) are circled in pencil; Ni^{2+} is visible as a faint pink spot (circled in black).

As expected, the retention of the metal ions on the gradient plates is influenced by whether the metal ions are spotted on the high or low end of the gradient and whether there gradients are aligned or opposed. On the aligned and opposed gradients, the metal ions face a uniform high or low concentration of triamine and thiol in the x-direction and a gradient in the y-direction, as shown previously in Figure 2. This leads to little separation in the x-direction between metal ions that have a similar affinity for the modified surface; most of the separation between groups of metal ions tends to occur in the y-direction. For example, Co^{2+} and Pb^{2+} are inseparable in the x-direction on the aligned and opposed plates but generally separate in the y-direction.

On the low amine-low thiol (LALT) aligned plates, Co^{2+} and Pb^{2+} do not separate, and Ni^{2+} overlaps both of them. While Co^{2+} tends to be slightly more sensitive to the triamine concentration, Pb^{2+} has a higher affinity for the thiol, leading to overlap. On the HAHT plate, Co^{2+} and Pb^{2+} separate, with Ni^{2+} only slightly overlapping Co^{2+}. However, Fe^{3+} and Hg^{2+} do not separate, which is consistent with the results on the uniformly modified plates. Cu^{2+} is easily separated from the other metal ions on both LALT and HAHT due to its affinity for amine groups.

On the opposed gradient plates, Fe^{3+} and Hg^{2+} again do not separate when spotted on the high amine end. Even with a low concentration of thiol on the spotting end, Hg^{2+} does not move, indicating a high affinity for the thiol. Co^{2+} and Pb^{2+} separate on both LAHT and HALT. Interestingly, their order can be reversed by spotting on the LAHT end. When Co^{2+} and Pb^{2+} are spotted on the LAHT end, Pb^{2+} is retained more strongly due to interaction with the thiol groups, while Co^{2+} moves with the mobile phase until the surface concentration of amine is high enough to retain Co^{2+}. Ni^{2+} also interacts with both amine and thiol groups, causing it to overlap with Pb^{2+} on the LAHT plate and with Co^{2+} on the HALT plate.

On the orthogonal plates (LALT diagonal) the metal ions face a gradient in both dimensions. The orthogonal gradients allow separation in the x- and y-directions. On LALT diagonal, five of the six metal ions (Co^{2+}, Pb^{2-}, Cu^{2+}, Fe^{3+}, and Hg^{2+}) are completely separated; only Ni^{2+} slightly overlaps Co^{2+}. The retention factors are shown below in Figure 3.7 and Table 3.4. While separation is also achieved on LAHT, the orthogonal gradients allow for greater separation between Cu^{2+} and Fe^{2+} and between Co^{2+} and Pb^{2+}. There is also less overlap between Co^{2+} and Ni^{2+}, providing nearly complete separation between the six metal ions.

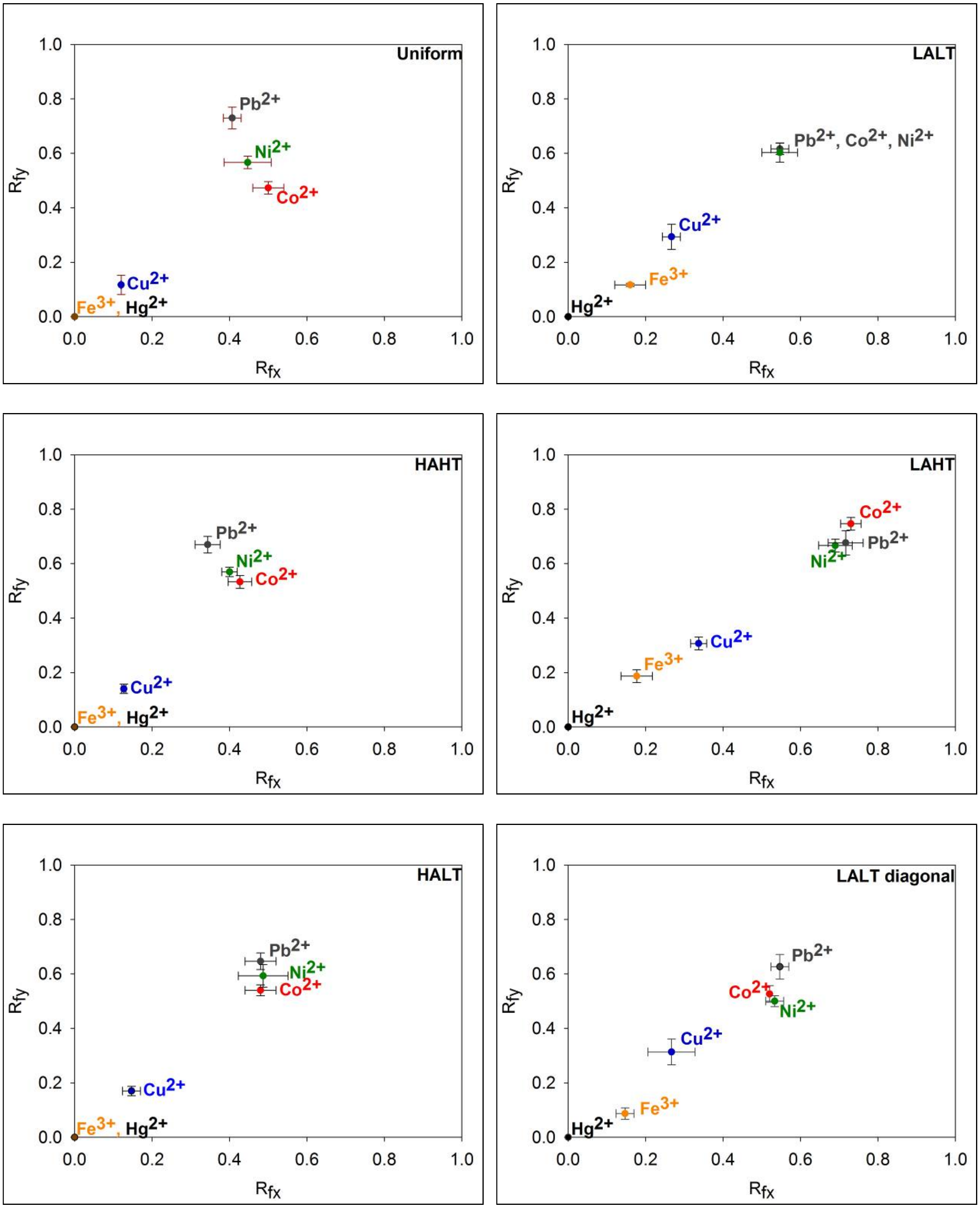

Figure 3.7 R_f values of Co^{2+} (red), Pb^{2-} (gray), Ni^{2+} (green), Cu^{2+} (blue), Fe^{3+} (orange), and Hg^{2+} (black) in the x- and y-directions on uniform, low triamine - low thiol (LALT), high triamine - high thiol (HAHT), low triamine - high thiol (LAHT), high triamine - low thiol (HALT), and orthogonal plates (LALT diagonal).

Table 3.4 Retention Factors for Metal Ions on 2D Triamine-Thiol Gradients.

	Metal Ions	R_{fx}		R_{fy}	
		Avg	Std. Dev.	Avg	Std. Dev.
Uniform	Co^{2+}	0.50	0.04	0.47	0.02
	Pb^{2+}	0.41	0.02	0.73	0.04
	Ni^{2+}	0.45	0.06	0.57	0.02
	Cu^{2+}	0.12	0.00	0.12	0.04
	Fe^{3+}	0.00	0.00	0.00	0.00
	Hg^{2+}	0.00	0.00	0.00	0.00
LALT	Co^{2+}	0.55	0.02	0.62	0.02
	Pb^{2+}	0.55	0.02	0.62	0.02
	Ni^{2+}	0.55	0.05	0.60	0.04
	Cu^{2+}	0.27	0.02	0.29	0.05
	Fe^{3+}	0.16	0.04	0.12	0.01
	Hg^{2+}	0.00	0.00	0.00	0.00
HAHT	Co^{2+}	0.43	0.03	0.53	0.02
	Pb^{2+}	0.34	0.03	0.67	0.03
	Ni^{2+}	0.40	0.02	0.57	0.02
	Cu^{2+}	0.13	0.01	0.14	0.02
	Fe^{3+}	0.00	0.00	0.00	0.00
	Hg^{2+}	0.00	0.00	0.00	0.00
LAHT	Co^{2+}	0.73	0.03	0.75	0.02
	Pb^{2+}	0.69	0.04	0.67	0.02
	Ni^{2+}	0.72	0.05	0.68	0.05
	Cu^{2+}	0.34	0.02	0.31	0.02
	Fe^{3+}	0.18	0.04	0.19	0.02
	Hg^{2+}	0.00	0.00	0.00	0.00
HALT	Co^{2+}	0.48	0.04	0.54	0.02
	Pb^{2+}	0.48	0.04	0.65	0.03
	Ni^{2+}	0.49	0.06	0.59	0.04
	Cu^{2+}	0.15	0.02	0.17	0.02
	Fe^{3+}	0.00	0.00	0.00	0.00
	Hg^{2+}	0.00	0.00	0.00	0.00

3.5 Conclusion

Two-dimensional multi-component chelation gradients were prepared on thin layer chromatography plates and applied to the separation of transition and heavy metals. Initial experiments with 2D gradients showed that the greatest separation occurred on 2D plates modified with higher order amines and on triamine-thiol plates. The separation of six transition and heavy metals was studied on uniformly modified and on aligned, opposed, and orthogonal 2D gradients. The retention, and thus separation, of the metal ions was influenced by the end of the plate on which the metal ions were spotted, the presence or absence of a gradient in each dimension, and the direction of the gradients. Nearly complete separation was obtained on the low amine-high thiol (LAHT) gradient; the separation was improved slightly by employing a gradient in each dimension. Future work will focus on applying chelation gradients to liquid chromatography in order to separate complex mixtures of transition and heavy metals.

3.6 References

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Chapter 4: Conclusions and Future Work (Part 1)

4.1 Conclusions

Gradient surfaces have been used for a wide variety of applications, including directing liquid transport and screening properties such as adsorption, chemical reactions, polymerization, and cell growth. Many different methods have been developed to prepare gradient surfaces; however, they are sometimes tedious and do not allow for control over the gradient profile. Controlled-rate infusion (CRI), developed by Kannan et al., allows for control over the gradient profile by manipulating the silane concentration or infusion time.[1-4] The ability to prepare surface gradients with amine, phenyl, and thiol functionalities using CRI has been demonstrated in prior work.[1-8] Aminosilanes were chosen specifically due to the self-catalyzing ability of the amine group. Both single-component and multi-component gradients have been prepared, and their usefulness has been demonstrated in the separation of complex mixtures such as weak acids and bases, over-the-counter drugs, and water- and fat-soluble vitamins.[1, 4, 6, 7] Kannan et al.also demonstrated the use of aminosilane gradients to study the coordination complexes of metal ions.[3]

In this work, gradients prepared using CRI were applied to the separation of transition and heavy metals. Chelating gradients were prepared on TLC plates using mono-, bi-, and tri-dentate ligands. The gradient profiles were evaluated using XPS to confirm the presence and extent of the gradient. As expected based on previous results, the degree of modification could be manipulated by changing the aminosilane precursor, the aminosilane concentration, or the infusion rate. The stationary phase was endcapped using isobutyl to prevent streaking due to interaction with residual silanol groups. CIC was employed by creating a competition between the chelating ligands (amine functionalities) in the stationary phase and a stronger chelating agent (EDTA) in the mobile phase. The retention of the four metal ions, and thus the separation, was manipulated using the presence or absence of a gradient, the concentration of the aminosilane, the rate of infusion, and the number of amine groups. Complete separation of the four metal ions was obtained using a high concentration of triamine and a longer infusion time.

After successful separation of four transition and heavy metal ions, the method was expanded to two-dimensional chelation gradients. One-component and two-component 2D gradients were prepared on TLC plates. One-component gradients were prepared using the same aminosilane (diamine or triamine) in the x- and y-directions. Two-component gradients were prepared using a different aminosilane (diamine, triamine, or polyamine) or a different functional group (triamine + urea, EDTA silane, or thiol) in each direction. Preliminary results with Co^{2+} and Pb^{2+} showed that separation was greatest on one-component and two-component aminosilane gradients and triamine + thiol gradients. Further study was completed on the triamine + thiol gradients in order to separate six transition and heavy metals (Co^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, and Hg^{2+}). Aligned and opposed gradients were prepared so that the metal ions were separated using a uniform triamine + thiol concentration in the x-direction and an aligned or opposed gradient in the y-direction. Orthogonal gradients were also prepared so that the metal ions were separated using gradients in both the x- and y-directions. It was demonstrated that the retention of the metal ions could be influenced by whether the metal ions were spotted on the low or high end of a triamine or thiol gradient and whether the gradients were aligned, opposed, or orthogonal. Nearly complete separation was obtained on the orthogonal gradient.

Overall, chelation gradients allow for greater control over retention, and thus separation, of transition and heavy metals. The initial work showed that small changes in retention produced by variation in the surface density of amine groups could be used to separate metal ions that have similar affinities for the stationary phase. Adding additional chelating ligands and additional dimensions provides another means of influencing retention to separate complex mixtures of metal ions.

4.2 Future Work

4.2.1 Metal-ion binding on multi-component gradients

Multi-component amine-phenyl and amine-thiol gradients have been prepared in prior work.[5, 7] In this work, triamine-thiol multi-component gradients were utilized for the separation of transition and heavy metals. As discussed in Chapter 1, previous work by Kannan et al.involved the use of diamine and triamine gradients to study the coordination complexes of Cu^{2+} and Zn^{2+} using XPS.[3] This work could be extended to study the coordination complexes of transition and heavy metals on multi-component gradients, such as the triamine-thiol gradients used in this work, in order to further optimize stationary phases for metal ion separation. XPS could be used to determine the ratio of the nitrogen to metal and sulfur to metal peak areas.

Alternatively, metal uptake studies, such as those described in sections 1.5.2 and 1.6, could be used to assess the strength of metal ion binding. The modified silica could be scraped from the TLC plates and soaked in metal ion solutions of known concentration. The solution would then be centrifuged, and the concentration of the metal ion in the supernatant would be determined using ultraviolet–visible (UV-Vis) spectroscopy, atomic absorption spectroscopy, or ICP. The difference between the known starting concentration of the solution and the final concentration of the solution is the concentration of the metal ion absorbed by the substrate. A higher metal ion uptake would indicate a higher affinity for the stationary phase, whereas a lower metal ion uptake would indicate less affinity for the stationary phase.

4.2.2 Application of chelation gradients to liquid chromatography

Aminosilane gradients were prepared on monolithic columns by Dewoolkar et. al.[7] Similar gradients could be prepared using silanes with chelating ligands such as diamine, triamine, or thiol. Previous research demonstrated that the order of elution was the same on uniformly modified and single-component gradient columns; however, there were slight differences in the degree of retention. [7] These slight differences in selectivity could be useful for the separation of transition and heavy metals, particularly those that have similar affinities for chelating ligands, as demonstrated in the first part of this work. Multi-component gradients could be used to further improve the selectivity in order to separate complex mixtures of transition and heavy metals. Aligned and opposed triamine-thiol gradients could be prepared to investigate the separation of transition and heavy metals and possible synergistic effects from multi-component gradients. Using EDTA as a mobile phase, the metal ions would be detected using UV-Vis spectroscopy or amperometry.[9]

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Part 2: Evaluation of the Effectiveness of POGIL-PCL Workshops

Chapter 5: Introduction (Part 2)

5.1 Abstract

The focus of Part 2 of this work is on how faculty change their teaching methods and how a network begins. The work begins with an evaluation of the effectiveness of workshops on Process-Oriented Guided Inquiry Learning in the Physical Chemistry Laboratory (POGIL-PCL) and continues with a focus on the growth and characteristics of the POGIL-PCL network. Prior research indicates that the process of change involves several stages that occur over time. Personal communication and support from experienced colleagues are considered important factors throughout the process of change. For instructors who wish to change their teaching methods, faculty workshops are one means of learning about new teaching methods, obtaining new materials, and, in some cases, gaining access to a support network as they go through the process of change. In this chapter, several types of faculty workshops and their effectiveness will be discussed. Later, three models of the process of change and theories of network development are presented. Finally, several elements of survey design will be examined.

5.2 Effectiveness of faculty workshops

Faculty workshops are often used as a means of disseminating teaching materials and promoting the implementation of new teaching methodologies. Many recent workshops have focused on promoting the implementation of active learning methods. There have been numerous studies on the effectiveness of such workshops.[1-18] Most studies have focused on the rate of implementation[1-3, 10] and on building a community of instructors.[4-6, 11, 13-15, 17, 18] These studies will be discussed below.

5.2.1 Rate of implementation

Some studies have focused mainly on the rates of implementation and the factors that affect an instructor's decision to implement a new teaching method.[1-3, 10, 16] Lewis and Lewis studied the effectiveness of workshops on ChemConnections, which are collaborative, inquiry-based modules based on questions that are designed to be interesting and socially relevant.[10] Lewis and Lewis found that the length of the workshops and the length of time since attending the workshop influenced the rate of implementation.[10] Participants who attended workshops lasting two days or longer had higher rates of implementation (59%) than those who attended workshops lasting less than two days (29%). Lewis and Lewis also found that a higher percentage of participants who attended the most recent workshops reported planned usage (23%) compared to those who attended earlier workshops (9%).[10]

Stains et al. also found that the length of time since attending the workshops influenced the rate of implementation; however, the authors also raised concerns over whether implementation is sustained over time.[16] Stains et al. used the Approaches to Teaching Inventory,[19] which is designed to characterize instructors' attitudes and beliefs about teaching, to survey instructors who attended two-day workshops on teaching pedagogies before, immediately after, and one year after attending the workshops; their study also included a control group of instructors who did not attend the workshops.[16] For instructors who attended the workshops, there was a statistically significant difference in their survey scores before and immediately after the workshops; however, there was no significant difference one year later.[16] Other studies have focused only on implementation following the workshops. For example, Baker et. al found that 63% of instructors who attended a training workshop implemented the teaching methods,[2] and Burke and Greenbowe found that 92% of instructors who attended a workshop on active learning methodologies found the workshops "useful" or "very useful."[3] However, the concerns raised by Stains et al. have been raised in other studies as well.[3, 7, 10, 12]

Several studies have addressed the factors that affect whether instructors implement new teaching methodoigies.[3, 4, 7-10, 12, 14, 16, 20-24] Barriers to implementation include situational constraints such as not teaching the relevant courses or teaching a multi-section course; other factors included the time needed to implement the new teaching method and resistance from students.[3, 4, 7-10, 12, 14, 16, 20-24] Stains et al.also cited concerns over support for faculty who plan to implement after attending the workshops.[16]

5.2.2 Building a community of instructors

To sustain implementation, some researchers have focused on building a community of instructors to support and encourage faculty who are interested in changing their teaching methods.[4-6, 11, 13-15, 17, 18] Some communities have focused mainly on introducing new teaching methodologies and providing feedback and support to help interested faculty members overcome barriers to implantation. Lynd-Balta et al.and Sirium et al.have described learning communities in which small groups of instructors meet regularly to discuss new teaching methods and receive feedback and support from colleagues.[11, 14, 15] The faculty who participated in these learning communities reported that they had either already implemented or were planning to implement the teaching methods discussed in the learning communities.[11, 14, 15] Sirium and Madigan created five similar learning communities that met biweekly for one year each. Over a three-year period, 41 out of 53 instructors who participated in the learning communities reported implementing the teaching methods discussed in the learning communities.[15]

Some researches have attempted to improve implementation rates by requiring support from the instructors' home institution. In a study by Wood and Handelsman, potential participants in the National Academies Summer Institute on Undergraduate Education in Biology were required to submit an application that included a commitment from the instructors' home institution to support instructors who intended to implement new teaching methods.[18] Henderson also surveyed department chairs and asked them to rate whether instructors who had attended a workshop for new faculty had a less traditional teaching style than other faculty members.[9] According to the survey responses, 70.7% of the participants believed they had a less traditional teaching style, whereas 58.6% of department chairs believed the participants had a less traditional teaching style.[9]

Several studies have noted the importance of engaging workshop participants in the community. The POGIL Biochem project, described by Murray et al., addressed this issue by creating development style workshops in which instructors participate in generating materials for classroom use.[12] When the 18 instructors who participated in the workshops were surveyed eight months after the final workshop, 100% of the respondents reported implementing three or more POGIL activities, and 94% reported implementing seven or more activities. However, Murray et al.acknowledge that it remains to be seen whether this implementation will be sustained long term.[12]

5.3 Process-Oriented Guided Inquiry Learning in the Physical Chemistry Laboratory (POGIL-PCL)

5.3.1 POGIL and POGIL-PCL

Process-Oriented Guided Inquiry Learning (POGIL) is a student-centered teaching method that incorporates guided inquiry and cooperative learning.[25-37] POGIL utilizes the learning cycle, which consists of three phases: exploration, concept invention, and application (shown in Figure 5.1 below).[25, 38] In the exploration phase, students investigate scientific concepts or phenomena through demonstrations or experiments. In the concept invention phase, students discuss what they have learned, identify patterns, and learn the relevant terminology. In the application phase, students apply their learning to new situations.[25, 38] POGIL is based on the concept of constructivism, which is the idea that students must be actively engaged in constructing their own knowledge based on prior learning and experience.[28]

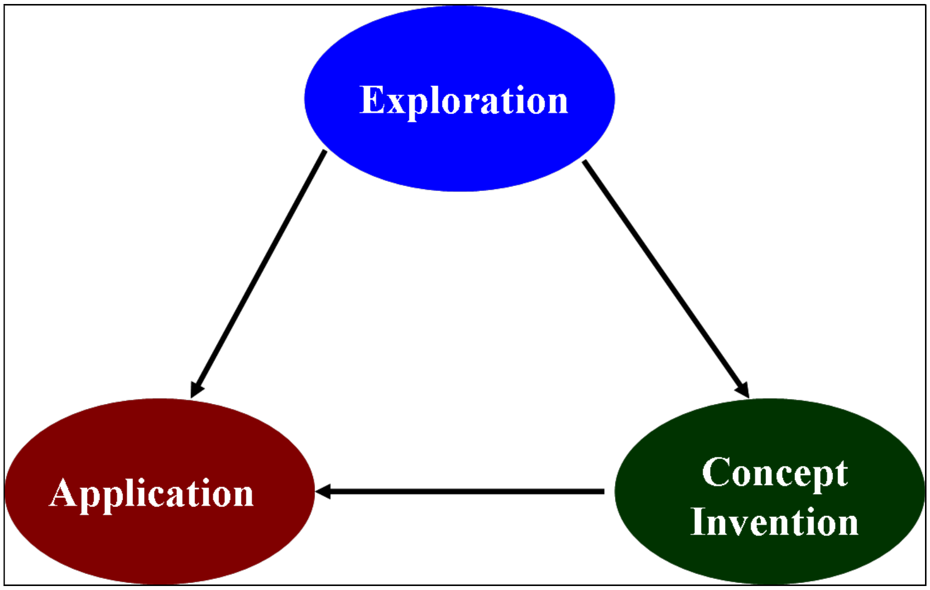

Figure 5.1 The three phases of the learning cycle: exploration, concept invention, and application.

POGIL-PCL refers specifically to POGIL being implemented in the physical chemistry laboratory. In traditional physical chemistry laboratories, students are given lengthy deriviations followed by instructions on how to complete the experiment. Students often focus their attention on ensuring that their results agree with published results rather than on the meaning of the results.[39] In contrast, POGIL-PCL experiments begin with a question that can only be answered completing the experiment. Students are expected to approach the problem like scientists. Rather than being given a lengthy background containing the theory and equations, students answer a few pre-experiment questions and propose an outcome based on prior knowledge. Students are given limited instructions for the protocol and are expected to analyze and explain the data themselves.[27, 32, 39] The instructor's role is to facilitate the discussion, asking guiding questions as necessary. Students are expected to use equations to model the data and answer a series of "thinking about the data" questions, which require them to explain their results.[39]

5.3.2 Outcomes of POGIL

Numerous studies have examined the outcomes of using active learning methods such as POGIL. Several studies have noted a decrease percentage of students who earn grades of D, W, or F in courses that implement POGIL.[30] In addition, several studies have found that students report that they retain more of the course material.[30, 40] From a broader perspective, Freeman et.al. conducted a metaanalysis of 225 studies on active learning and concluded that, "If the experiments analyzed here had been conducted as randomized drug trials of medical interventions, they may have been stopped for benefit – meaning that enrolling patients in the control condition might be discontinued because the treatment being tested was clearly more beneficial."[41] Many studies focus on student achievement or content learning; however, another benefit of POGIL is that students learn skills such as teamwork, cooperation, communication, critical thinking, problem-solving, and metacognition.[25]

5.4 Process of change

Instructors who wish to change their teaching methods go through multiple stages of change. There are several models that describe the process of change.[4, 14, 20-25, 42-51] Three of these models will be discussed in this work: Lewin's model of change, Rogers' diffusion of innovation theory, and situational learning. Kurt Lewin's model of change and situational learning will be discussed below; Roger's diffusion of innovations theory will be discussed in detail in Chapter 6.

5.4.1 Lewin's model of change

Lewin's model of change involves three stages:[4, 14, 52]

- Unfreezing: This stage involves challenging one's beliefs or current assumptions. In this stage, instructors may question the effectiveness of certain teaching methods.
- Cognitive restructuring: The instructor explores new teaching methods with the goal of finding a method that they believe is more effective.
- Refreezing: In this stage, the instructor adopts a new teaching method.

Often, unfreezing occurs before an instructor attends a workshop, and instructors come to the workshops in the cognitive restructuring stage.[14] Generally, refreezing occurs after the workshops. Refreezing can be the most challenging stage as instructors deal with the challenges of implementing a new teaching method and, in some cases, receive negative feedback regarding the teaching method.[4] Refreezing typically refers to an instructor adopting a new teaching method; however, in some cases, refreezing may occur when an instructor reverts back to their original teaching methods.[4, 14, 52] Providing support for instructors as they deal with challenges in the refreezing stages can increase the likelihood of adopting a new teaching method and help to prevent instructors from reverting back to previously used teaching methods.[14]

5.4.2 Situational learning

Situational learning can be described as learning by doing.[47-51] In situational learning, participants engage in a "community of practice."[49] Participants begin on the periphery of the community as beginners or novices.[47-51] By collaborating and interacting with others in the community and engaging in the practice being taught, the participant moves from the periphery to the core of the "community of practice," becoming an expert or master.[47-51]

5.5 Network development

5.5.1 Growth of networks

Individuals in a network may be referred to as nodes or actors. [53-55] There are three types of actors in a network: central, peripheral, and isolated.[54] Central actors are those that have the greatest number of connections to others in the network; due to their position, central actors have a large influence on the network. Peripheral actors have fewer connections than central actors; their effect on the network is limited due to their lack of connections. Isolated actors have no connection to others in the network and, therefore, have no influence on the network; however, isolated actors may later become connected to the network with support from those in the network.[54] Actors or nodes become connected to the network or become more central to the network through interaction and collaboration. More frequent interaction with others in the network leads to stronger ties to the network.[54, 56]

5.5.2 Effectiveness of networks

Networks can provide an avenue for change. A network provides its members with both the opportunity to learn about new teaching methods and a support system as they implement new teaching methods.[56, 57] Instructors may learn about the new teaching method from others in the network, or they may learn about the new teaching method from another source and then join the network to learn more.[44, 45, 56] Instructors who are new to the network or who are learning about the new teaching method for the first time may feel that it is too risky to implement the new teaching method.[44, 45] However, being part of a network provides the instructors with contacts they can reach out to for support and guidance.[56] This support system is particularly important for those who may be the only instructors using the teaching method at their institution and for those who may be the only instructors in their discipline at their institution. The studies discussed in section 5.2.2 indicate that networks, or learning communities, which are more formal networks created for the purpose of adopting new teaching methods and supporting instructors in the process of implementation,[56] can be effective in promoting implementation.[4-6, 11-15, 17, 18, 56, 58]

5.5.3 Types of networks

Networks can be categorized as organic or artificially created. Organic networks arise from existing relationships, whereas artificially created networks promote new relationships for the purpose of change.[56] Organic networks typically have a greater influence and are more likely to be successful in promoting change. In artificially created networks, the time and effort required to create new relationships can delay the change process and decrease the likelihood of sustaining change.[56] Earlier research by Rogers and Beal confirms that personal influence, which is greater in organic networks, is a major factor in the process of change.[45]

Networks can also be categorized as relational or structural, formal or informal, and hierarchical or non-hierarchical, and expressive or instrumental.[56] These types of networks will be discussed in Chapter 7 in relation to the POGIL-PCL network.

5.6 Survey design

The effectiveness of faculty workshops is often evaluated using surveys. Surveys must be designed carefully to capture the desired data and to avoid potential bias. Two issues related to survey design will be discussed here: response shift bias and Likert scale design.

5.6.1 Response shift bias

Surveys on participants' experiences may be conducted before or after the workshop. When the survey is conducted after the workshop, the participants' responses to retrospective questions may be affected by their experiences at the workshop due to response shift bias.[59-61]

Response shift bias occurs when an individual's evaluation of their own knowledge or beliefs is changed due to an intervention.[59, 60] Howard documented response shift bias in his 1980 article in which he explained that, when using self-reporting, researchers assume that the respondent's understanding of concepts being assessed does not change due to the intervention.[60] Numerous other researchers, including Drennan and Hyde, Klatt and Taylor-Powell, D'Eon et al., and Nasmith and Steinert, have noted that retrospective accounts may differ from pre-intervention responses to survey questions.[59-63] Some researchers have found that retrospective accounts are more accurate because survey respondents do not have the knowledge to accurately access themselves before the intervention.[59, 60] D'Eon et al.also found that response shift bias was negligible when the workshop was focused on skill development rather than on knowledge acquisition.[62]

5.6.2 Likert scale design

Likert scales are often used in surveys to assess the attitudes or beliefs of respondents. Likert scales may be unipolar or bipolar, can vary in length, and may or may not include a midpoint.[64] To generate meaningful data, each of these aspects should be considered when designing Likert-scale questions.

Unipolar Likert scales have one construct, such as importance, with varying levels; for example, the scale may range from "extremely important" to "not important". Bipolar Likert scales have two opposite constructs, such as agreement and disagreement; as an example, one commonly used Likert scale ranges from strongly disagree to strongly agree.[64] Unipolar scales do not have a conceptual midpoint; for bipolar constructs, the midpoint is a neutral response.[64]

The length of Likerts scales can range from two points to as many as 20 or more points.[64] Using too few points may make it difficult to distinguish between the attitudes or beliefs of different respondents. However, when too many points are used, the meaning of each point becomes less clear.[64, 65] Several researchers have indicated that the optimal length for Likert scales in between four and seven points.[64, 65] Masters found that the reliability of Likert scales increased as the number of points increased from two to four points.[65] Masters, as well as Matell and Jacoby, found no increase in reliability when the number of points was increased beyond seven.[65, 66]

Likert scales may or may not include a midpoint.[64] The disadvantage of using a midpoint, particularly when the midpoint is a neutral response, is that the respondents may select the midpoint to avoid taking sides or choosing a more extreme position.[64, 67-69] Bishop, Kalton et. al. and Krosnik all found that respondents were more likely to select the midpoint when it was explicitly offered than when it was not shown on the scale.[67-69]

5.7 Overview of dissertation

Understanding the factors that interest instructors in changing their teaching methods and the factors that affect whether instructors adopt new teaching methods is essential to support faculty throughout the process of change and to promote faculty involvement in a network. Some studies have found that implementation rates are typically high following the workshops but that implementation is not sustained over time. One often cited concern is support for faculty who are attempting to implement new teaching methods. Literature focused on the process of change and on network development has often emphasized the importance of communication with peers; this communication and support is necessary as instructors work to implement new teaching methods and overcome challenges related to implementation.

In Chapter 6, the factors that initially interested instructors in changing their teaching methods and the factors that affect whether instructors adopt new teaching methods are analyzed.

In Chapter 7, the growth of the POGIL-PCL network is examined. One of the major factors in the initially high rate of implementation and in sustaining the implementation is the support provided by the workshops. Personal contact and collaboration are important both in the early stages of change, in the later stage of implementation, and in the growth of the POGIL-PCL network.

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Chapter 6: Evaluating the Effectiveness of POGIL-PCL Workshops

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6.1 Abstract

The POGIL-PCL (Process-Oriented Guided Inquiry Learning in the Physical Chemistry Laboratory) project has developed a series of workshops to introduce faculty to POGIL-PCL and to facilitate the development of new experiments. More than 60 faculty members from various institutions have attended these workshops. Workshop participants were surveyed in order to evaluate the effectiveness of the workshop and better understand why faculty choose to adopt POGIL-PCL. Of the participants who completed the survey, 77% had used POGIL-PCL experiments. The results of the survey show that personal influence is a major factor in all stages of the adoption process.

6.2 Introduction

Workshops are often used as a means of disseminating new teaching methodologies to interested faculty. Some studies on the effectiveness of workshops have focused mainly on the rate of adoption of a particular teaching method,[1-4] while others have focused on the development of a community of instructors dedicated to reform.[5-13] Prior studies have addressed the usefulness of workshops designed to promote implementation of various active learning techniques, such as Just-in-Time Teaching, Problem-Based Learning, Peer-Led Guided Inquiry, and POGIL.[3, 4, 7, 14, 15] Studies by Baker et al. and Stains et al. have investigated the impact of workshops designed to introduce faculty to multiple active learning techniques at three-day workshops.[3, 15] These studies have found that intensive workshops can have a significant impact on instructors' use of active learning techniques and that instructors often had a more student-centered approach to teaching after attending workshops.[3, 4, 14-17] However, the extent of change is often variable, and some researchers have raised concerns about whether these changes are sustained long-term.[1, 14, 15, 18] An understanding of the process of reform and the factors that lead to change is crucial in order to promote the implementation of innovative teaching methods. We begin with a discussion of the POGIL-PCL project and then explore the factors that influence instructors' decisions to adopt POGIL-PCL.

6.2.1 POGIL-PCL workshops

The POGIL-PCL project has developed guided-inquiry experiments for the physical chemistry laboratory at POGIL-PCL workshops. The project objectives are to design, write, revise, and test guided-inquiry experiments, to encourage faculty to adopt POGIL-PCL, and to foster the community of physical chemistry faculty. POGIL-PCL workshops were designed to accomplish these goals. In addition, much of the work of the project continues after participants attend the workshops, including additional writing, reviewing, and testing. The workshops are described in detail in this section, and the structure of POGIL-PCL experiments is described more fully in the next section.

A sample agenda for the two-day workshops is shown in Appendix 1. The workshops open with participants doing a POGIL-PCL experiment. Immersion in a POGIL-PCL experiment allows faculty to get a sense of how the experiments work from students' perspectives and to observe how the experiments are facilitated. After this experience, participants then discuss the key elements of a POGIL-PCL experiment, the differences between traditional and POGIL experiments, and the facilitation of a POGIL-PCL experiment. Next, workshop participants review previously written experiments using a screening rubric (Appendix 2). The rubric emphasizes the key elements of POGIL-PCL experiments. By using the rubric, faculty better understand the general experiment structure and simultaneously learn about additional experiments.

A key part of the workshops is the opportunity to write a POGIL-PCL experiment. The writing portion of the workshops has been instrumental in expanding the number of POGIL-PCL experiments available, which is one of the goals of the project. Workshop participants work in groups of two to four people on the experiment they have chosen. Participants have revised existing POGIL-PCL experiments, converted standard physical chemistry experiments into POGIL experiments, or used their own ideas for new POGIL-PCL experiments. Up to eight hours over the course of the workshop are dedicated to writing and editing experiments. Instructors continue to work on the experiments after they leave the workshop in a variety of ways, including:

- writing and/or revising their own experiments and instructor's handbook
- testing the experimental procedure for newly developed experiments at their institution (alpha-testing)
- writing reviews of new experiments written by others
- implementing a fully-developed experiment (exactly as written by others) at their institution, and writing a review (beta-testing)

One criticism of some education research and dissemination methods is that instructors are simply given the materials and told what to do; the instructors have little or no involvement in developing materials. The lack of interaction between researchers and instructors often leads to problems with implementation.[19] The writing portion of POGIL-PCL workshops addresses this concern by allowing instructors to focus on developing materials suitable for use in their own laboratories and by fostering collaboration among participants and researchers (facilitators).

Development-style workshops have been developed for the POGIL Biochem project [14]. The collaboration occurs not only between participants and facilitators but also between new participants and experienced participants (those who have previously attended workshops). The planned time for social interaction and networking among participants and facilitators further reinforces the collaboration and network among the new and experienced participants.

At the end of the workshop, participants provide feedback for the workshop facilitators. Participants are asked to fill out a Workshop Assessment form listing strengths of the workshops, the improvements the workshop needs, and any insights they gained from the workshop. The feedback provided by workshop participants is used to improve future workshops.

The workshops described in the previous paragraphs and illustrated in Appendix 1 are two-day workshops. The POGIL-PCL Project also holds half-day workshops at the Biennial Conference on Chemical Education (BCCE). Because the workshops at the BCCE are only a few hours long, the agenda emphasizes experiencing and then discussing a POGIL-PCL experiment. The workshops at BCCE provide instructors with an introduction to POGIL-PCL, but, because the BCCE workshops are so short, participants do not have as much time for the socializing and networking with other physical chemistry faculty that occurs at the two-day workshops. The BCCE workshops also do not include time for writing and development of experiments. Approximately half of the faculty who have attended the BCCE workshops have later attended the two-day workshops.

The workshops were advertised via email, announcements at pogil.org, conference presentations at regional and national American Chemical Society meetings, and at the 2012 Biennial Conference on Chemical Education.

6.2.2 The POGIL-PCL experiment structure

POGIL-PCL is a student-centered approach that utilizes guided inquiry and collaborative learning [20-31]. The model of the POGIL-PCL learning cycle shown in Figure 1 was developed through the discussion and testing of experiments at the workshops.[32] Students work through multiple "data-think cycles" (see Figure 6.1) in which they answer guiding questions, formulate a hypothesis, run an experiment, and analyze the resulting data. Specific experimental parameters such as concentrations or masses of reagents, volumes of reagents, and the number of trials necessary to obtain enough data, are determined by the students in small groups or as a whole class. The experiments end with in-depth questions that require students to apply the concepts they have learned. POGIL-PCL experiments rely on data-pooling by the students, so one experiment is often carried out simultaneously by the whole class. A few instructors who attended workshops have reported using POGIL-PCL experiments in a round-robin setting, in which different teams of two to four students carry out different experiments in the same class period.

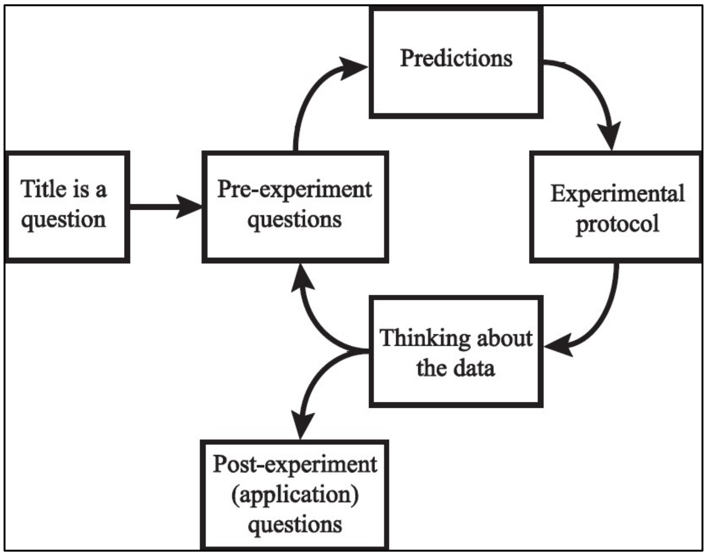

Figure 6.1 Diagram of the POGIL-PCL cycle. The experiment begins with the title as a question, includes multiple "data-think" cycles, and concludes with a set of post-experiment questions focusing on application. (Reproduced by permission from Ref. 32. Copyright 2014 American Chemical Society.)

6.2.3 Process of change

Some of the faculty who attend POGIL-PCL workshops have previously attended workshops and currently use POGIL in their laboratory or lecture courses, while others are new to POGIL. The faculty who attend workshops include:

- those who have heard about POGIL and are interested in learning more,
- those who have begun to use POGIL at their institutions, and
- those who primarily use POGIL at their institutions.

This process of change from traditional laboratory teaching methods to using POGIL goes through several stages. The diffusion of innovations theory developed by Rogers describes the process of implementing change in five stages: knowledge, persuasion, decision, implementation, and confirmation.[33, 34] The first stage, knowledge, involves becoming aware of the innovation and learning how it is used. In the persuasion stage, an instructor begins to form an opinion based on the perceived advantages, disadvantages, and complexities of the innovation, the compatibility with their current environment, and the opinions of their peers. After learning of the innovation and forming an opinion about it, the instructor makes a decision to adopt or reject the innovation. An instructor may initially decide to adopt then later reject the innovation or discontinue use, or initially reject the innovation and later adopt it. Following the decision to adopt, the instructor enters the implementation stage. During the implementation stage, an instructor may seek support from more experienced users of the innovation. The final stage in this process of change is the confirmation stage, in which instructors seek support for their decision to adopt.[33, 34]

Instructors who attend POGIL-PCL workshops may be at any of the five stages in the diffusion of innovations. Instructors who are in the knowledge stage may be dissatisfied with the experiments they currently use and come to the workshops to learn about another way to teach a lab course, while those who are in the persuasion stage have heard about POGIL and want to learn more about it in order to decide whether they want to try POGIL experiments in their laboratory course. Some are in the implementation stage and are looking for support to deal with the challenges they have encountered or for more experiments for their course. More experienced participants may be in the confirmation stage and come to the workshop for the support from like-minded instructors.

After the workshop, instructors continue to move through these stages. Those who choose to implement may try previously developed experiments, or they participate in beta-testing. Beta-testing is the process of testing and reviewing experiments that are under development; once an experiment has been successfully tested, it may be considered ready for distribution to the community. After beta-testing the experiments with their students, instructors provide feedback to the authors of the experiment. This interaction plays an important part in developing experiments for the POGIL-PCL project and in supporting instructors in both the implementation and confirmation stages. Developers provide the experiments to instructors to implement with different groups of students, and instructors provide the developers with feedback on what did and did not work with the experiment.

As instructors move through the change process, many factors affect their willingness to adopt a new teaching method. These factors include interest in new methods, support from colleagues and administrators, time involved in implementing the new method, research showing the effectiveness of the new method, availability of resources, and the ease or difficulty of implementation.[33-41] Dissatisfaction with current teaching methods is often considered a prerequisite for change. [37, 38, 40, 41] Personal influence is also considered to be a major factor in the adoption process, particularly for those who adopt later.[42] Those who adopt early, when an innovation is still new, may not have as many sources of personal influences because few people have adopted the innovation. Those who adopt later on are likely to seek information and support from early adopters who have more experience with the innovation.[42]

6.2.4 Research questions

POGIL-PCL workshops are designed to support instructors at various stages of implementation and to involve faculty in developing materials for POGIL-PCL experiments. In this study, we seek to understand what factors influence instructors at different stages of adopting POGIL-PCL. Specifically, the research questions are:

- What factors initially interest instructors in changing their teaching method?
- What factors affect whether instructors adopt new teaching methods?
- To what extent are the workshops effective? Do participants adopt POGIL-PCL experiments after the workshop?

6.3 Methods

6.3.1 Workshop assessment

At the end of each workshop, participants were asked for their feedback on the strengths of the workshop, the improvements needed for future workshops, and any insights they gained from the workshop. The SII (strength, improvements, and insights) forms were collected at five workshops from January 2012 through January 2014. The responses were analyzed for common themes such as networking, hands-on experience with POGIL, and insights into teaching.

6.3.2 Survey

The POGIL-PCL Survey was administered via REDCap.[43] Participants who attended two-day POGIL-PCL workshops or half-day POGIL-PCL workshops at BCCE between January

2012 and January 2014 were contacted via email and asked to complete the survey. No identifying information was collected in the survey. Approval for the survey was obtained from the Institutional Review Board at Virginia Commonwealth University on July 29, 2014. The survey was open to workshop participants on September 5, 2014 and closed on October 13, 2014, giving participants approximately five weeks to respond. The response rate was 69% (62 email invitations were sent out; 43 completed responses were obtained). The survey included questions focusing on participants' experiences and attitudes both before and after the workshop.

6.3.3 Data analysis

For most of the survey questions, respondents were asked to check all answers that applied. Percentages for each answer choice were calculated from the total number of responses for each question. For several of the questions, there was an "other" response respondents could select if they did not agree with any of the available responses or if they had another response to add. After the survey was closed, the "other" responses were categorized with the provided responses or new categories were created based on common themes in the written answers. For example, for the question "How did you find out about the POGIL-PCL workshop," several of the respondents who selected "other" stated that they heard about it at a POGIL national meeting or ACS meeting; these responses were placed in the category, "I attended a seminar or meeting in which POGIL-PCL was discussed." Similarly, several of the respondents who selected "other" stated that they were invited by one of the organizers. These responses were categorized with the response "It was recommended by a colleague," and the category was expanded to "It was recommended by a colleague, or I was invited by one of the organizers." For the question, "What made you decide not to use POGIL-PCL," a common theme among the "other" responses was that the instructor had not taught a lab course since the workshop; a new category was created to include those responses.

6.4 Results and Discussion

The questions in the POGIL-PCL Survey were divided into two categories: those that address the factors that initially interest instructors in changing their teaching methods and those that address whether instructors adopt new teaching methods. Responses were analyzed for common themes in order to understand what motivates faculty in the earlier stages (knowledge and persuasion) and later stages (implementation and confirmation) of the change process. The SII responses were also analyzed for common themes related to the survey questions.

6.4.1 SII responses

Several common themes were seen in the SII responses, such as the value of networking, hands-on experience with POGIL-PCL labs, time to develop experiments, and insights into teaching physical chemistry laboratories. Since participants completed the SII forms before leaving the workshops, the SII forms yield insight into participants' initial impressions of the POGIL-PCL workshops. Most of the improvements suggested were related to scheduling or organization. Over time, there is a noticeable decrease in the percentage of workshop participants who suggested improvements. For two out of the first three workshops (January 2012 and February 2013), all of the respondents suggested improvements; in June 2012, 50% of the respondents suggested improvements. The percentage decreased to 37% for the July 2013 workshop and 40% for the January 2014 workshop, which suggests that the workshop effectiveness has improved over time. For every workshop, all participants listed multiple strengths, including collaboration or networking with other physical chemistry faculty and the opportunity to experience a POGIL-PCL experiment.

6.4.2 Survey: Initial factors that engage instructors

One of the goals of the survey was to determine what factors initially interest instructors in changing their teaching methods. This goal addresses the knowledge and persuasion stages in the diffusion of innovations theory. While some instructors who attend the workshops may be in the later stages (implementation and confirmation), the goal was to understand instructors' initial thought processes when they first learned about POGIL-PCL. Three questions on the POGIL-PCL Survey addressed the factors that initially interest instructors to possibly change their teaching methods:

1. How did you find out about the POGIL-PCL workshop?
2. Which of the following describes your reason(s) for coming to a POGIL-PCL workshop?
3. Which of the following would encourage (or has encouraged) you to use POGIL in your lab(s)?

The possible responses and percentages for each response for question 1 (How did you find out about the POGIL-PCL workshop?) are shown in Figure 6.2. The two most common responses were "I attended a seminar or meeting in which POGIL-PCL was discussed" (45%) and "It was recommended by a colleague, or I was invited by one of the organizers" (40%). In contrast, a much smaller percentage of respondents selected the response "I read about it on the POGIL website" (6%). The data here indicate that actively speaking about the workshop with a person, such as a colleague or a seminar speaker, has a greater influence on an instructor's decision to come to a workshop and learn more about the POGIL-PCL than passive, impersonal communication such as reading about the workshop on the website. Rogers and Beal, as well as Jacobsen, also found that personal influence was a major factor in an individual's decision to adopt change.[36, 42] Rogers and Beal argue that impersonal communication (like mail) is easy to ignore and that individuals who are unsure about a new idea are more likely to be reached by person-to-person communication.[42]

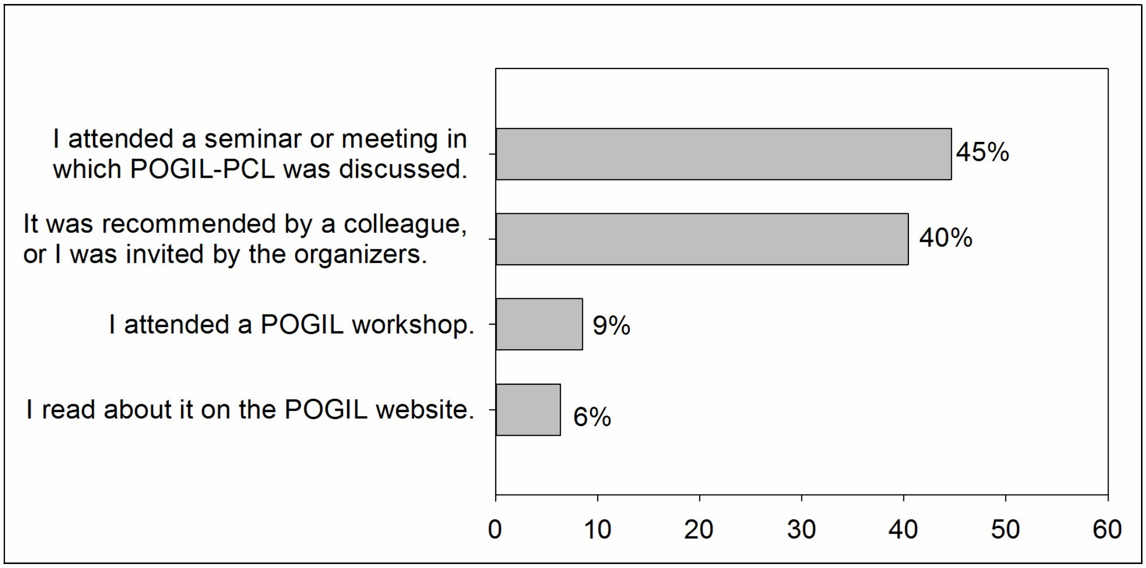

Figure 6.2 Percent of total responses for the question, "How did you find out about the POGIL-PCL workshop?" Respondents were asked to select all answers that applied.

Another question addressed instructors' reasons for coming to a workshop. The top three responses in Figure 6.3 were given in the survey; the bottom three responses were common themes among respondents who selected "other." The belief that students do not get much from traditional labs or experiments, the desire for students to be active learners, and feeling that students are more concerned with getting the correct answer than the process of learning accounted for over 90% of the responses. A desire to get students more engaged in lab and involved in the process of learning appears to play an important role in instructors' decision to come to a workshop, although the workshop itself may have influenced respondents' answers to this question. The survey responses are consistent with the discussion at the workshops and with the ultimate design of the POGIL-PCL experiments, as illustrated in Figure 6.1, that arose out of these workshop discussions. Comments from instructors also supported this conclusion. One instructor commented, “I wanted access to labs that are more appropriate for upper level labs- that get students to think about what they are doing, why they are doing it, and what the results mean.” Another instructor commented, “I want my students to learn to think. Thinking rarely seems to occur in traditional labs.”

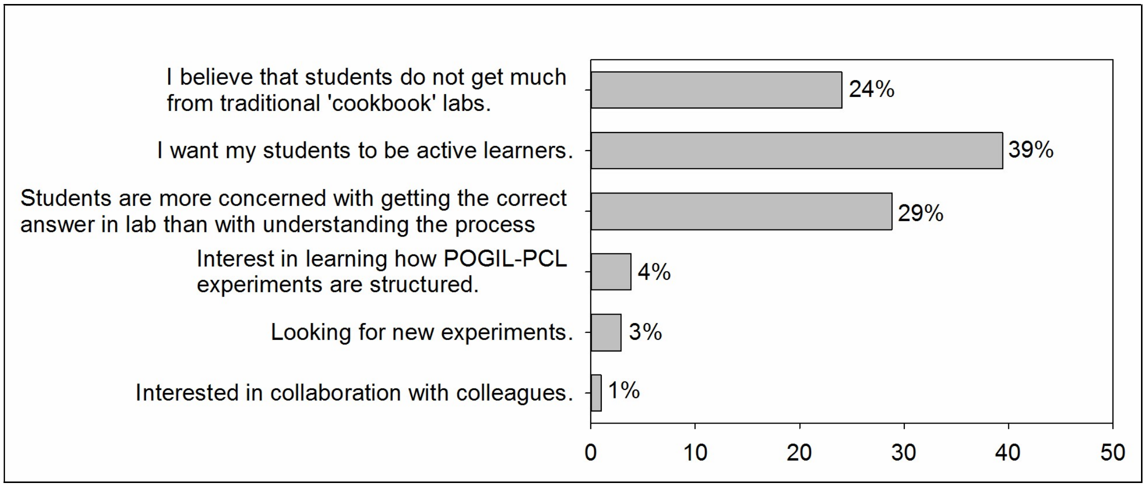

Figure 6.3 Percent of total responses for the question, “Which of the following describes your reason(s) for coming to a POGIL-PCL workshop?” Respondents were asked to select all answers that applied.

The third question addresses the factors that encourage instructors to implement POGIL-PCL in their laboratory. Instructors’ responses are shown in Figure 6.4. Research and statistics showing the effectiveness and long-term benefits of POGIL had a large impact on instructors’ decisions to implement POGIL; however, hands-on experience with POGIL labs or experiments received the highest response rate (22%). Hands-on experience was also a common theme among the strengths participants cited on the SII forms. The hands-on experience provided at the workshops allow instructors to see how the experiments work from the student’s perspective and to observe how those who currently use POGIL in their lab courses facilitate the experiments. This experience is a key component of the third, or decision, stage of Roger’s theory of the diffusion of change.[33] Another study also emphasized the importance of hands-on experience at workshops.[4] Again, direct personal influence was also a factor in encouraging instructors to implement POGIL. Personal influence in this case occurred during and after the workshop in the form of support from the POGIL community, learning about POGIL from colleagues, and interacting with other physical chemistry faculty.

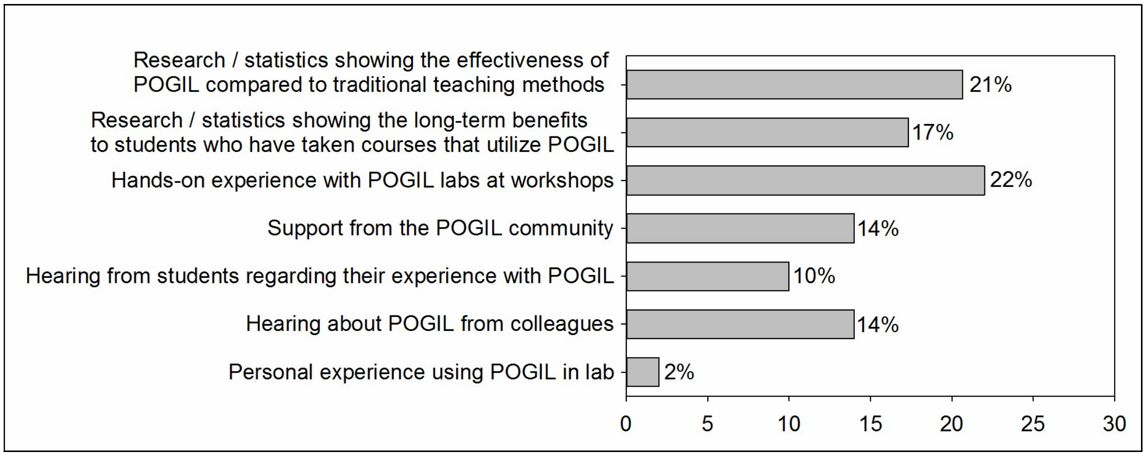

Figure 6.4 Percent of total responses for the question, "Which of the following would encourage (or has encouraged) you to use POGIL in your lab(s)?" Respondents were asked to select all answers that applied. (The last answer, "personal experience using POGIL in lab," was a common theme among those who selected "other.")

6.4.3 Survey: Factors that affect whether instructors adopt new teaching methods

To understand the factors that affected whether instructors implemented POGIL, survey respondents were asked, "After the POGIL-PCL workshop, how have you used POGIL in your lab(s)?" The goal here was to determine if instructors moved into the implementation stage after attending the workshop. If a respondent indicated they had used POGIL at all, they were asked what types of follow-up would be helpful to them. If they indicated they had not used POGIL since the workshop, respondents were asked what made them decide not to use POGIL.

Table 6.1 shows the percentages, sorted by frequency, of instructors who had used POGIL in their lab. Of the instructors who responded, 77% had used POGIL to some extent in their lab. ("To some extent" refers to the sum of the categories "mostly used POGIL labs," "used POGIL labs regularly," and "tried a few POGIL labs.") As shown in Figure 6.5, email/Skype with POGIL facilitators and follow-up workshops were the most commonly selected forms of support. Personal influence was a key factor in motivating instructors to change their teaching methods; the responses here indicate personal influence is also an important factor when instructors are making the decision to implement POGIL. Burke et al. also found that many workshop participants value the interaction provided at workshops, as it allows them to network with colleagues in their field and discuss challenges associated with implementation with more experienced practitioners.[4]

Table 6.1 Percentage of Respondents Who Use POGIL at Each Frequency

Mostly used POGIL labs	19%
Used POGIL labs regularly	23%
Tried a few POGIL labs	35%
Do not use POGIL labs	23%

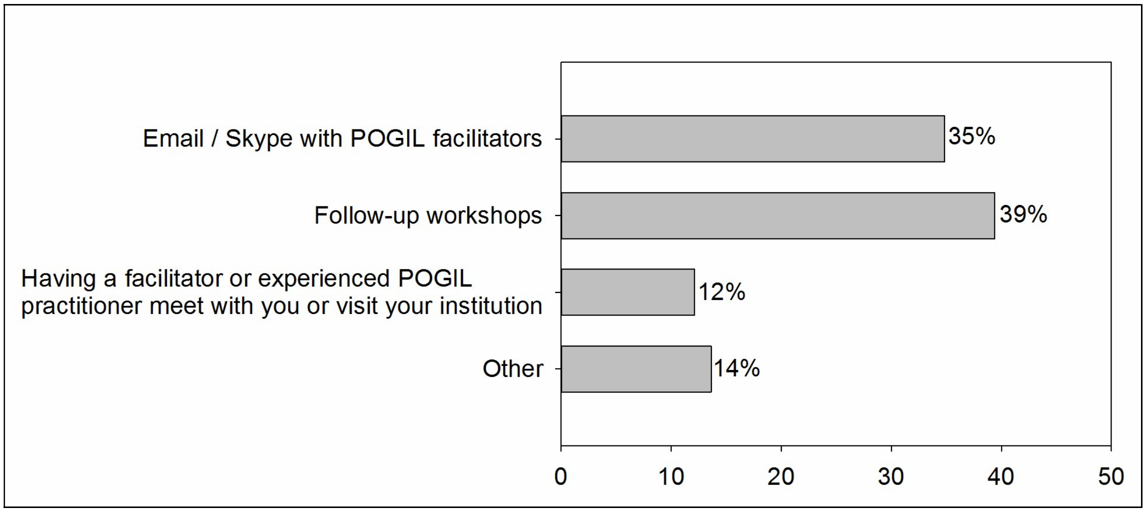

Figure 6.5. Percent of total responses for the forms of support (email/Skype, follow-up workshops, or visiting with a facilitator or experienced POGIL practitioner) that would be helpful for instructors as they begin to implement POGIL. Respondents were asked to select all answers that applied.

Of the respondents who said they had not used POGIL since the workshop, the most commonly cited reason was that the instructor had not taught a lab course since the workshop (57%), followed by the course being taught round-robin style (29%). Using POGIL-PCL in a round-robin format could be an area for future study, given that a round-robin setting does provide some logistical challenges because POGIL-PCL experiments rely heavily on collaboration both within and between groups of students.

Survey respondents were also asked about their past experience with POGIL. Instructors were asked to recall whether their experiences had been mostly positive, somewhat positive due to either issues with the activities or resistance from students and/or other faculty, or if they had a lot of difficulty with the activities or resistance from student and/or other faculty. Over fifty percent of the survey respondents reported that their experience had been mostly positive. Given that instructors were more encouraged to implement POGIL in their laboratory when they had hands-on experience with the experiments, it seems that prior experience with POGIL would have an effect on an instructor's decision to use POGIL-PCL experiments. It was hypothesized that instructors whose prior experience was more positive would be more likely to use POGIL-PCL experiments. Figure 6.6B shows that, when instructors reported having a mostly positive experience in the past, 83% had used POGIL-PCL experiments to some extent, with 32% mostly using POGIL-PCL experiments. (Again, "to some extent" refers to the sum of the categories "mostly used POGIL labs," "used POGIL labs regularly," and "tried a few POGIL labs.") However, for instructors whose experience was not mostly positive (i.e., somewhat positive or a lot of difficulty), 67% had used POGIL-PCL experiments to some extent, and only 5% were mostly using POGIL-PCL experiments. As expected, those who had a more positive experience with POGIL before coming to the workshop were more likely to try POGIL-PCL after the workshop.

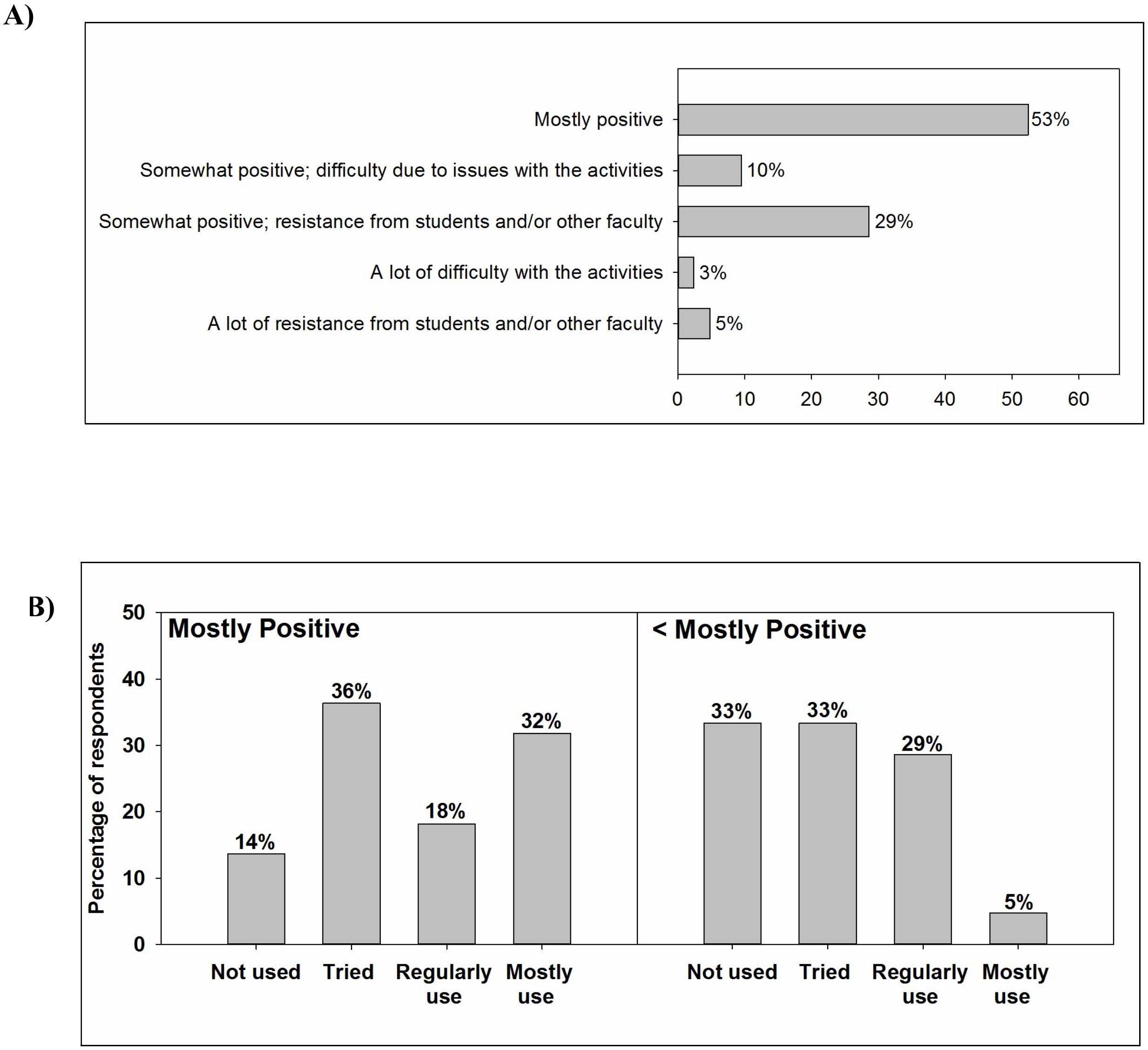

Figure 6.6 A) Percentage of instructors who reported having a mostly positive experience, somewhat positive experience, or a lot of difficulty with POGIL in the past. B) Left: percentage of instructors who reported using POGIL-PCL when their prior experience was mostly positive, Right: percentage of instructors who reported using POGIL-PCL when they reported having a somewhat positive experience or a lot of difficulty.

It should be noted, however, that, even when instructor's experience was not mostly positive, some still chose to try POGIL-PCL after attending the workshop. Despite reporting difficulty with the activities and/or resistance from students and/or faculty in the past, 67% of instructors (Figure 6B) had chosen to use POGIL-PCL experiments, with sizable percentages having tried a few experiments or regularly using the experiments in their labs. This result speaks to the effectiveness of the workshops. Although some instructors recalled less than positive experiences with POGIL in the past, they chose to attend a workshop and decided to try some of the experiments.

6.4.4 Open questions

There are several remaining questions regarding the workshops and the adoption of POGIL-PCL. Several instructors reported that they had not used POGIL-PCL experiments because they have not taught a laboratory course since the workshop. This study was conducted 7 months after the last workshop. Lewis and Lewis conducted a study on workshop effectiveness more than a year after the last workshop in a series of workshops and still found that a larger percentage of participants from the last workshop reported planned use of the activities rather than actual use (compared to participants from earlier workshops).[1] This brings up the question of how long to wait after workshops are conducted to administer an implementer's survey. Conducting a survey too early means that some participants will not have had a chance to implement the new teaching method; however, waiting too long may make it more difficult to capture instructors' initial impressions and influences. In our case, more than 75% of survey respondents had used the experiments in their laboratories. Another follow-up survey would need to be done to determine whether that percentage would be significantly different if the survey were conducted at times long after the workshops attended.

There is also the question of whether instructors will continue to use POGIL years after they have attended the workshops. Five or ten years after their initial decision to implement

POGIL, will instructors still be using POGIL-PCL? One study by Stains et al. found that, while instructors who attended workshops changed their teaching methods immediately after attending a workshop, these changes were not sustained a year later.[15] In this study, the responses from instructors, particularly those regarding their reason for coming to a POGIL-PCL workshop, indicate that workshop participants believe in the goals of the POGIL-PCL project. Future studies will be necessary to determine how many instructors continue to use POGIL-PCL.

One question that is perhaps more difficult to answer is how instructors who have attended the workshops implement POGIL-PCL experiments. Do they implement the experiments as written, or do they modify them? How do different instructors facilitate the experiments? These questions can be answered to a certain extent by asking instructors about their implementation and has been addressed in a follow-up survey. When viewed collectively rather than individually, self-assessments can provide some indication of workshop success.[44] Faculty could also be interviewed individually or in focus groups. However, it is difficult to fully answer these questions without observing individual instructors because faculty are self-reporting their activities. Alternatively, faculty could be observed teaching their courses using an observation rubric developed for laboratory courses.[45-47]

6.5 Conclusion

The POGIL-PCL survey was designed to uncover factors that initially interested instructors in changing their teaching methods and factors that affected whether instructors adopted new teaching methods. The data collected from the survey show that personal influence (contact with colleagues, seminar speakers, facilitators, and other members of the POGIL community) is an important factor in the early stages of adoption when instructors are becoming aware of POGIL-PCL and deciding to learn more about it (knowledge and persuasion) and in the later stages of adoption when instructors begin to implement POGIL-PCL. While instructors who attend the workshops are in different stages of the process of change, 77% of instructors who responded to the survey moved into the implementation stage to some extent. Instructors' initial experience with POGIL also heavily influenced their decision to use POGIL-PCL; of those who had a mostly positive experience 32% were mostly using POGIL-PCL, compared with only 5% of those whose experience was not mostly positive.

Several open questions have been discussed, including how long to wait after the workshop to conduct a survey and how different instructors implement POGIL in their laboratory courses. A follow-up survey has been conducted to address these questions. Future papers will discuss results of this follow-up survey and focus on the development of a POGIL-PCL network over time.

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Chapter 7: Building the POGIL-PCL Network

7.1 Abstract

A series of POGIL-PCL (Process-Oriented Guided Inquiry Learning in the Physical Chemistry Laboratory) workshops has been conducted over a three year period (2012-2015) to introduce interested faculty to POGIL-PCL, develop new experiments for the physical chemistry laboratory, and to support faculty as they move through the process of implementation. The 70 instructors who have attended the workshops were surveyed annually from 2014 to 2016 to determine implementation rates, analyze the growth of the POGIL-PCL network, and ascertain how instructors have implemented the experiments. Approximately 77% of survey respondents reported that they had used POGIL-PCL experiments. The survey results and data collected from the workshops show that 43% of participants have attended more than one workshop and 82% have participated in the network in at least one way outside of the workshop.

7.2 Introduction

Through a series of workshops, the POGIL-PCL (Process-Oriented Guided Inquiry Learning in the Physical Chemistry Laboratory) project has worked to develop guided-inquiry experiments for physical chemistry laboratories and to support faculty in the process of implementation. The goal of POGIL-PCL is to teach both content knowledge and process skills such as critical thinking, problem-solving skills, and teamwork.[1, 2] POGIL-PCL has been described in detail, along with an example of a POGIL-PCL experiment.[2] In a previous paper, we described the structure of POGIL-PCL workshops and the results of a survey on the effectiveness of the workshops.[3] In this paper, we will describe the results of two follow-up surveys and explore how the POGIL-PCL network has developed over time.

7.2.1 POGIL-PCL workshops

Eight two-day POGIL-PCL workshops were conducted over the past three years. In addition, two half-day workshops have been conducted at the Biennial Conference on Chemical Education (BCCE). The two-day workshops include time for participants to experience at least one POGIL-PCL experiment and to participate in writing a POGIL-PCL experiment, as well as time for networking and socializing. The half-day workshops at BCCE allow participants to experience and discuss a POGIL-PCL experiment. Particularly at the two-day workshops, there is a mix of new and experienced participants. Because participants have varying levels of experience, there are two "tracks": participants may choose to try out more than one experience, or they may work on developing experiments. A partial agenda showing the two tracks is shown in Box 7.1. More recently, a two-day dissemination-only workshop was conducted. Over the past three years, the number of attendees at each workshop has increased. This growth and the development of the POGIL-PCL network will be major focus of this paper. (For a detailed description of the workshops and a full agenda, see Chapter 6.[3])

Box 7.1

Day 1		
POGIL-PCL experiment writing: pre-selected experiment	Elements of and facilitation of a POGIL physical chemistry experiment.	
	Experiencing a POGIL experiment: Select one	
	a. Mg-HCl b. Phase diagram c. B-naphthol	d. Apple enzyme e. Chick pea f. Iodine clock
Day 2		
POGIL-PCL experiment writing: continue from day 1	Experiencing a POGIL experiment: Select one	
	a. Mg-HCl b. Phase diagram c. B-naphthol	d. Apple enzyme e. Chick pea f. Iodine clock

7.2.2 Network development

Workshops can have a significant impact on instructors' teaching methods. Much research has focused on the impact of workshops on the implementation of new teaching methods.[4-23] One common theme in several articles on the subject is the value of support for instructors as they implement new teaching methods.[4, 6-9, 12-14, 16-24] The support provided by a learning community or network can be an invaluable resource as instructors move through the process of change.[4, 6-9, 12-14, 16-26]

A network typically begins with a small number of people and increases in size over time.[25, 27] Many factors influence the growth of a network, including contact with others in the network, exposure to information about innovation, years of professional experience, and personal beliefs regarding the innovation.[24-28] Communication with peers is a theme of network development.[24, 26-28] Some researchers posit that there is a certain threshold, or critical mass, that must be reached before an individual will consider adopting an innovation.[24, 28] This threshold refers to the number of peers or colleagues an individual is in contact with over a period of time. Rogers refers to this as the "diffusion effect" and states that "until an individual has a certain minimum level of information and peer influence from his or her system's environment, he or she is unlikely to adopt" (p. 235).[29] In some cases, this diffusion occurs through a relational network, in which influence occurs through contact with peers or colleagues. In other cases, diffusion occurs through a structural network, meaning that the influence an individual has is related to their position in the network.[27] Often, there is some overlap between the two, and diffusion occurs through both relational and structural means.

7.2.3 Network characteristics

Networks can be characterized in several ways based on the strength of ties between members, the formality of the communication and interaction, the degree of hierarchy, and the types of relationships.[25, 26] Ties between members can be characterized as strong or weak. Strong ties include frequent interaction between members who have known each other for a long period of time. Weak ties include less frequent interaction between members who are distant from each other.[26] Strong ties are often more likely to promote change due to the nature of the relationship; however, weak ties can aid in the diffusion of ideas across a network.[26]

Communication and interaction can also be formal or informal, hierarchical or non-hierarchical, and expressive or instrumental.[25, 26] Formal networks have more structure and organization than informal networks.[26] Hierarchical networks have a top-down approach, leading to one-way communication; non-hierarchical networks allow for two-way communication, leading to greater sharing of knowledge and ideas.[26] Expressive relationships are more social and based on friendship, whereas instrumental relationships are strictly professional and used to disseminate information and ideas.[25, 26]

7.2.4 Research questions

Our current work focuses on the development of a network of POGIL-PCL instructors and how this network has developed. The research questions guiding this work are:

- How has the POGIL-PCL network developed over time?
- What are the characteristics of the POGIL-PCL network?
- What motivates instructors to become part of the POGIL-PCL network?
- How do instructors implement POGIL-PCL?

7.3 Methods

SII Forms. Before participants left the workshops, they were asked to complete an SII (Strengths, Improvements, and Insights) form. A total of 159 SII forms were collected from eight workshops. The responses were compiled and analyzed for common themes such as networking.

Workshop surveys. Participants who attended the two-day POGIL-PCL workshop or the half-day POGIL-PCL workshop at BCCE were asked to complete two surveys, one in 2015 and one in 2016. The 2015 survey was a follow-up to an earlier survey conducted in 2014. Some questions from the 2014 survey were revised and expanded, and additional questions were added regarding instructors' experience with POGIL before and after the workshops, their motivation to use POGIL-PCL, their plans to implement POGIL-PCL, and demographic information. The 2016 survey focused on instructors' participation in the network and on their implementation of POGIL-PCL. Both surveys were administered anonymously via REDCap.[30] Approval for the 2015 survey was obtained on May 29, 2015 from the Institutional Review Board at Virginia Commonwealth University; an amendment for the 2016 survey was approved on May 16, 2016. In 2015, the survey was sent to 56 participants from the nine workshops conducted between January 2012 and February 2015; 48 responses were received, yielding a response rate of 86%. In 2016, they survey was sent to 65 participants from all ten workshops conducted between January 2012 and June 2015; 44 responses were received, yielding a response rate of 68%.

Data Analysis. Percentages for each answer choice were calculated from the total number of responses so that the percentages for each question added up to 100. Some of the questions only required respondents to select one response, but other questions asked respondents to check all that applied. At the end of the survey, instructors were asked if they had any additional comments about their experiences with POGIL-PCL. The responses were assessed for common themes including networking and student learning.

7.4 Results and Discussion

The second survey in 2015 (which was a follow-up to the 2014 survey) was designed to explore how the POGIL-PCL network has developed and to better understand the characteristics of the network. The second survey in 2016 was designed to further explore how instructors participate in the POGIL-PCL network and to learn how workshop participants implement POGIL-PCL at their institutions. The survey responses were analyzed for common themes related to networking, implementation, and motivation. Data from the 2015 survey was used to assess the growth and characteristics of the network; data from the 2016 survey was used to probe the characteristics of the growth and characteristics of the network in more detail, to assess whether instructors continue to implement over time, and to assess how instructors implement POGIL-PCL. The SII responses were also assessed specifically for comments related to networking.

7.4.1 Development of the POGIL-PCL network

The POGIL-PCL network has grown steadily since the first workshop in January 2012. The network began with 9 instructors who attended the first workshop; since then, a total of 70 instructors have attended workshops over the past three years. This is a 680% increase in the size of the network. Of the 70 instructors who attended workshops, 43% attended more than one. Given that more frequent interaction leads to stronger ties, the POGL-PCL network is comprised of both strong and weak ties. Figure 7.1 shows the number of instructors who have attended each workshop, with the grey arrows, white diagonals, and black dotted areas representing those who have attended workshops previously, those who have attended BCCE workshops, and those who are new to the workshops, respectively.

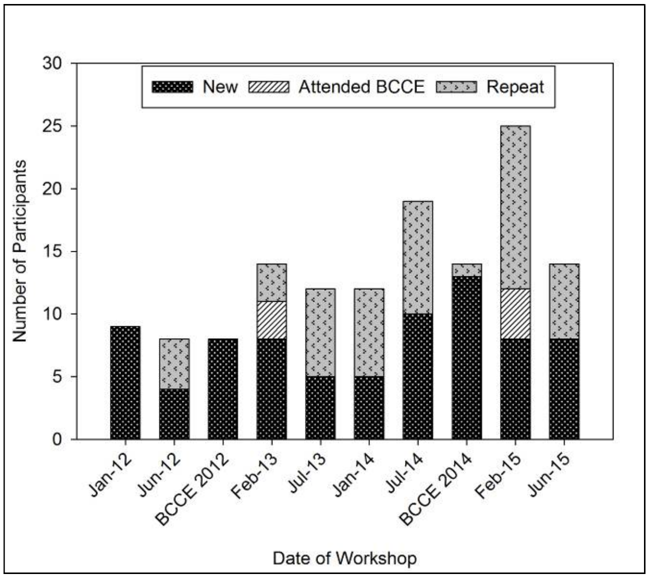

Figure 7.1 Number of workshop attendees at the ten workshops between January 2012 and February 2015. (Black dotted areas represent new participants, white diagonal represents past BCCE attendees, and grey arrows represents repeat attendees.)

Not only has the number of workshop attendees increased, but the number of instructors using POGIL-PCL has also increased. In the 2015 survey, instructors were asked about their use of POGIL-PCL before and after the workshops. In the 2016 survey, instructors were asked more specifically whether they used POGIL-PCL about 10%, 25%, 50%, 75%, or all of the time. Figure 7.2 shows a comparison of the number of instructors who reported using POGIL-PCL experiments before and after the workshops.

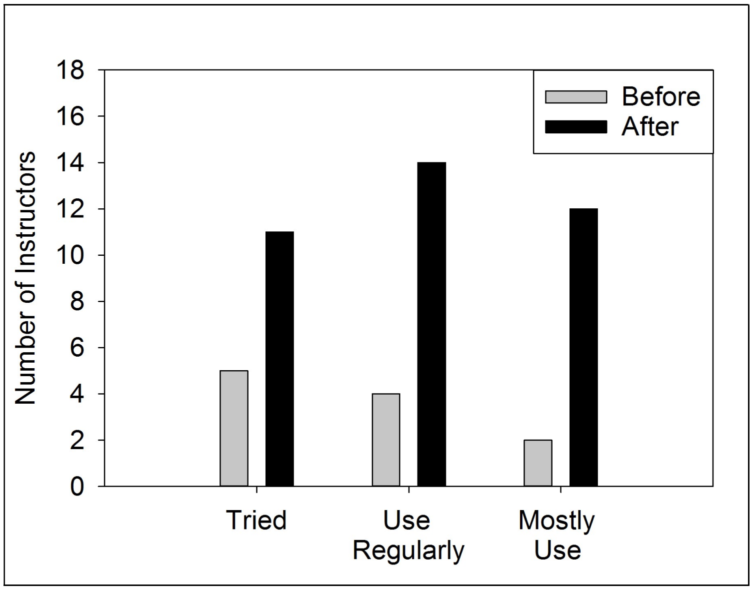

Figure 7.2 Comparison of the number of instructors who tried a few POGIL-PCL experiments, who used POGIL-PCL experiments regularly, and who mostly used POGIL-PCL experiments before and after the workshops (Data from 2015 survey).

There is a noticeable increase in the number of instructors who tried POGIL-PCL experiments, who used POGIL-PCL experiments regularly along with a few traditional experiments, and who mostly use POGIL-PCL experiments. Overall, there is a 230% increase in the number of instructors who used POGIL-PCL. After the workshop, 77% of survey respondents have used POGIL-PCL experiments to some extent, with over 50% using them regularly or most of the time.

Once instructors choose to implement POGIL-PCL, most instructors plan to continue using it. Of the instructors who chose to adopt POGIL-PCL, only one instructor reported that they did not plan to use POGIL-PCL in the future. The instructor cited the length of time needed for POGIL experiments and student resistance to POGIL as reasons for discontinuing use. The majority of instructors said that they planned to use POGIL experiments most of the time (51%) or that they planned to use POGIL experiments along with a few traditional experiments (46%).

Additionally, once instructors begin using POGIL-PCL, they tend to implement more frequently over time. In the 2016 survey, instructors were asked when they began using POGIL-PCL and how often they used the experiments. Instructors who began using POGIL-PCL less than one year ago used POGIL-PCL experiments 10 to 50% of the time. Instructors who began using POGIL-PCL more than 1 year but less than three years ago included a wide range, implementing as little as 10% of the time to as much as 100% of the time. Those who began using POGIL-PCL more than three years ago generally used POGIL-PCL at least 75% of the time, although there was a small percentage that only used the experiments 25 to 50% of the time. The histogram in Figure 7.3 shows the distribution of instructors who implement at each frequency.

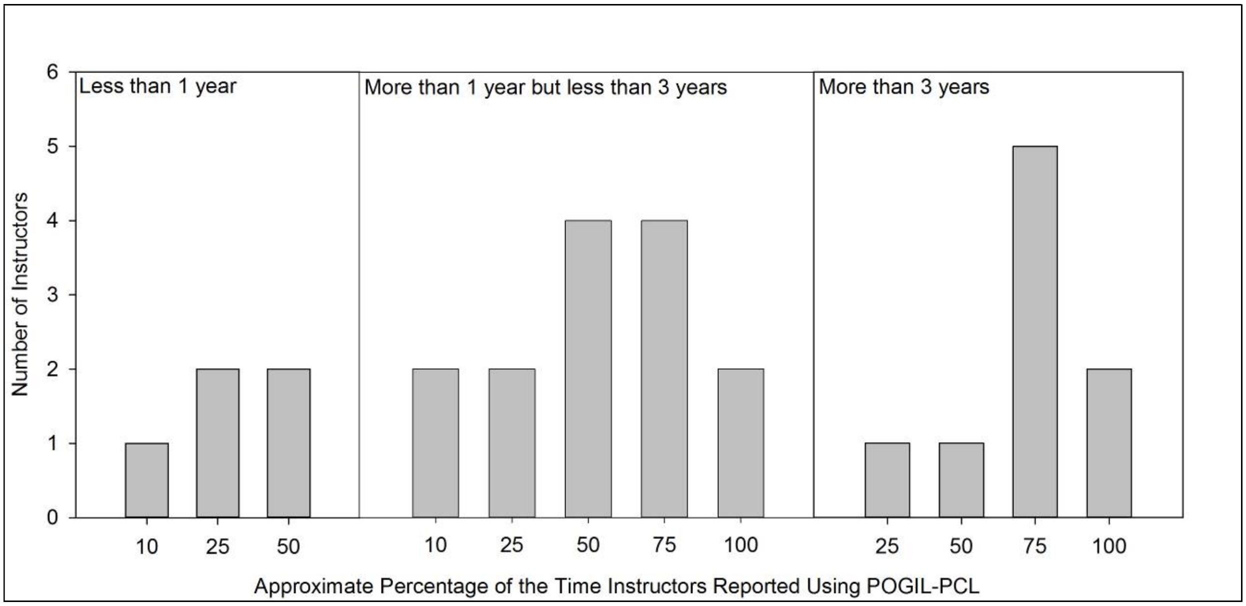

Figure 7.3 Number of instructors who report using POGIL-PCL 10, 25, 50, 75, or 100% of the time for instructors who have been using POGIL-PCL less than 1 year (left), more than 1 year but less than 3 years (middle), and more than 3 years (right). (Data from 2016 survey)

In addition to implementing POGIL in the laboratory after attending the workshop, some instructors choose to implement POGIL in the classroom as well. Instructors who reported implementing POGIL-PCL were asked, “Has using POGIL in the lab influenced your teaching methods in the classroom?” The responses are shown in Figure 7.4.

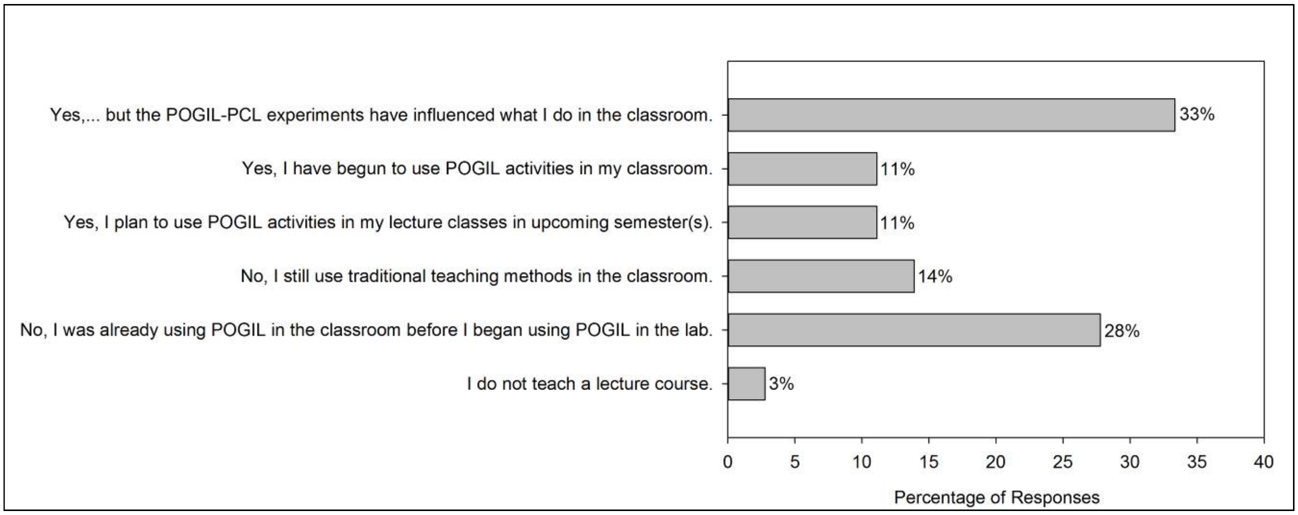

Figure 7.4 Percentage of responses for the survey question, “Has using POGIL in the lab influenced your teaching methods in the classroom?” (In the survey, the first response reads, “Yes, I was using POGIL in the classroom before I used it in the lab, but the POGIL-PCL experiments have influenced what I do in the classroom.”) (Data from 2015 survey)

A third of respondents stated that they were using POGIL in the classroom before using it in the lab but POGIL-PCL had influenced what they do in the classroom. Another 22% reported that they had begun to use POGIL activities in their classroom or planned to use POGIL in the upcoming semester(s). The responses to this question show that the growth of the network is not limited to the laboratory. Once instructors see the benefit of POGIL-PCL, some are encouraged to use it in their other courses as well.

Participants also contribute to the growth of the network by recommending the workshops to others. As shown in Figure 7.5, 84% of survey respondents had recommended the workshops to at least one person. Many instructors (68%) recommend the workshops to multiple people. Not only do instructors return to the workshops themselves and implement POGIL in their own laboratories and classrooms, they also encourage others to join the network as well.

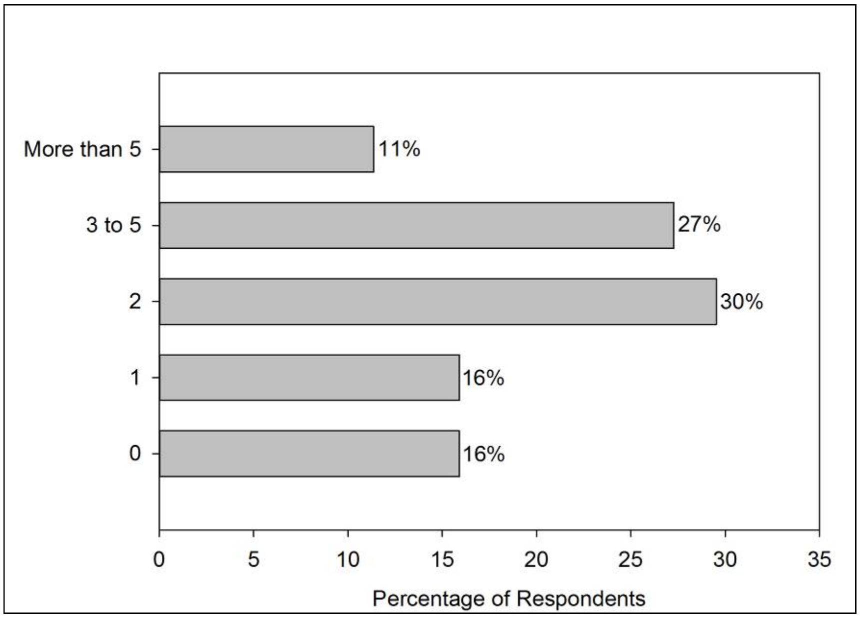

Figure 7.5 Percentage of respondents who recommended the workshops to 0, 1, 2, 3 to 5, or more than 5 people. (Data from 2016 survey)

7.4.2 The value of networking

When asked how they found out about the POGIL-PCL workshop, 90% of respondents say that they heard about the workshop from someone else, including attending a seminar or workshop in which POGIL was discussed or talking to a colleague or workshop organizer about POGIL-PCL. Thus, networking often begins before participants attend the workshop. Nearly half of the SII responses mention networking as one of the strengths of the workshop. Many of the workshop participants value opportunities for collaboration provided at the workshops. Box 7.2 shows some of the SII comments that highlight the value of networking.

Box 7.2

"It was nice to have a group of physical chemists together to talk about POGIL issues specific to p-chem."

"Excellent mix of participants; not all have the same strengths."

"The teamwork/ workshop structure for conceptualizing new labs was a strength."

"Getting together with other (usually) like-minded physical chemists"

"A good, diverse, friendly, group of physical chemists"

"Community of physical chemists, especially for those of use who are the only pchemist at our institutions...; Really liked how all of this was 'energizing' for my work with pchem students"

"Eating all meals together was very valuable because of the conversations we had during those times."

"The open discussions were helpful because people shared a lot of different perspectives and ideas. "

"Collaboration provides energy, ideas, motivation, feedback, community"

The networking and collaboration continues after the workshop has ended. Survey respondents who indicated that they had adopted POGIL-PCL were asked what forms of follow-up would be helpful to them. The responses are shown in Figure 7.6.

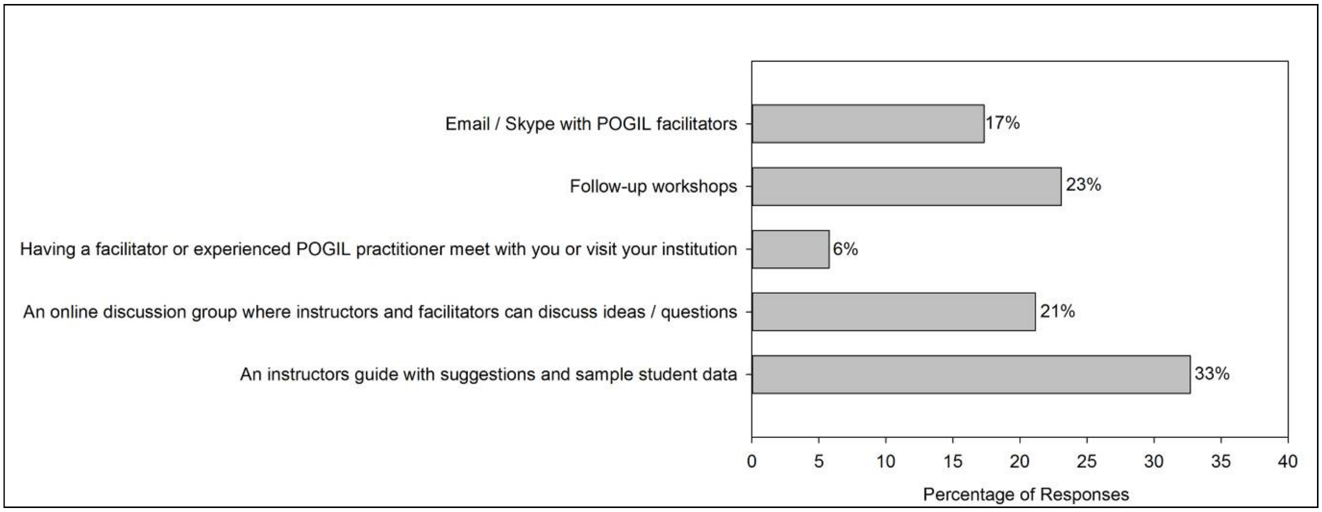

Figure 7.6 Percentage of responses for the survey question, "What type(s) of follow-up would be (or have been) helpful to you as you implement POGIL-PCL?"

Nearly 70% of the responses include forms of networking (email/Skype with facilitators, follow-up workshops, and discussion with other instructors and facilitators). While 33% of the responses selected is the instructor's guide, the majority of respondents (90%) also selected a form of networking as the type of follow-up that would be helpful to them.

Instructors were also asked who they would consider to be their contacts in the POGIL-PCL network (i.e., people they would contact for support, advice, or information about experiments). Ninety-five percent of instructors selected the workshop facilitators, followed by 73% who selected "others who have attended the workshop." A smaller percentage (32%) selected "others who have utilized guided inquire in their courses." This data indicates that the POGIL-PCL network in non-hierachical; communication is two-way between participants and between participants and facilitators.

7.4.3 Participation in the network

Participants also continue to network by working together between workshops to write, revise, and test experiments. At the workshop, participants are asked to commit to testing experiments in their laboratory courses and provide feedback to the developers. Participants often volunteer to help develop instructors' guides for experiments, which is one of the forms of follow-up that instructors request. This work outside of the workshops is vital to the ongoing development of POGIL-PCL experiments. Survey respondents were asked how they had participated in the network outside of the workshops. The responses are shown in Figure 7.7.

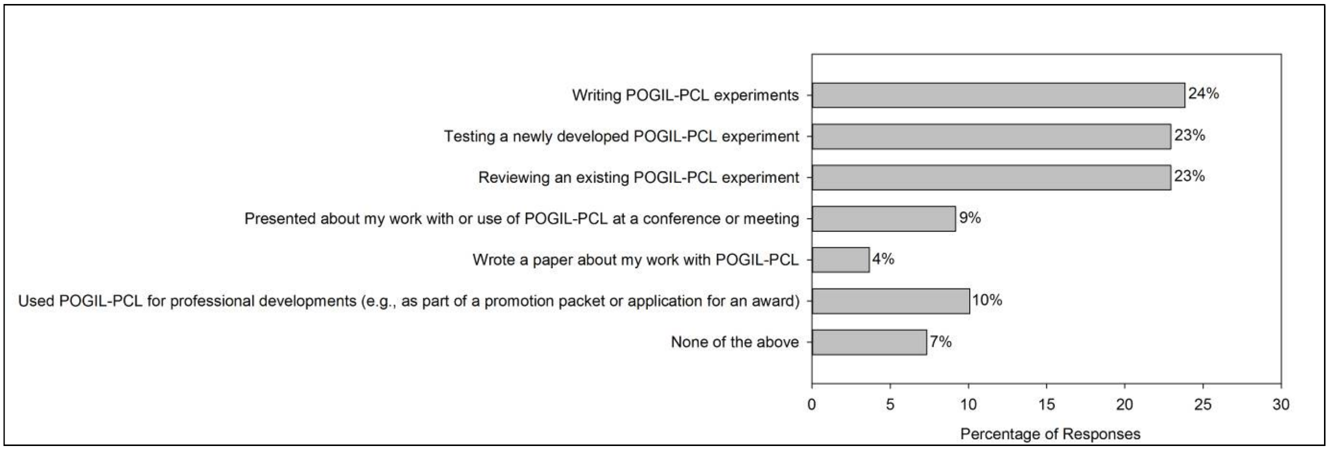

Figure 7.7. Percentage of responses for the question, "Have you participated in any of the following?" (Data from 2016 survey)

Overall, 82% of survey respondents participated in the network in at least one way outside of the workshops; 59% of survey respondents participated in the network in two or more ways outside of the workshops. Most commonly, instructors participated by writing, testing, or reviewing POGIL-PCL experiments. Instructors also participated by presenting about their work or use of POGIL-PCL at a conference or meeting. Considering that 90% of instructors who attend the workshops heard about the workshops from someone else, presentations by those who have attended the workshops are valuable to the growth of the network.

The responses were further analyzed to see if there was a difference in participation between those who are currently using POGIL-PCL in their courses and those who are not currently using POGIL-PCL. Of those who are currently using POGIL-PCL in their courses, 89% had participated in the network in at least one way outside of the workshops, and 79% had participated in two or more ways. In comparison, 69% of those who not currently using POGIL-PCL in their courses had participated in at least one way outside of the workshops, and 25% had participated in two or more ways. Thus, those who are currently using POGIL-PCL appear to be more involved in the network than those who are not currently using POGIL-PCL. However, even instructors who are not currently using POGIL-PCL continue to be involved in the network. Several instructors commented that they were not using POGIL-PCL because they are not currently teaching a physical chemistry laboratory but they planned to use POGIL-PCL in the future.

7.4.4 Motivation to implement POGIL

It is clear that the POGIL-PCL network has grown significantly in the past three years and that participants value the networking and collaboration that occurs before, during, and after the workshops. If we are to sustain this growth and continue to support members of the POGIL-PCL network, it is crucial that we understand what motivates instructors to come to workshops and to implement POGIL-PCL. This topic was discussed in detail in our previous paper but will be discussed here briefly. The survey questions mentioned in this section were asked in our first survey (in 2014) but were revised to include more detail in the 2015 survey.

Survey respondents were asked what motivated them to come to a POGIL-PCL workshop. The responses, shown in Figure 7.8, show that instructors who come to POGIL-PCL workshops have a strong desire for students to be active learners, to develop thinking skills, and to understand what they are doing in lab.

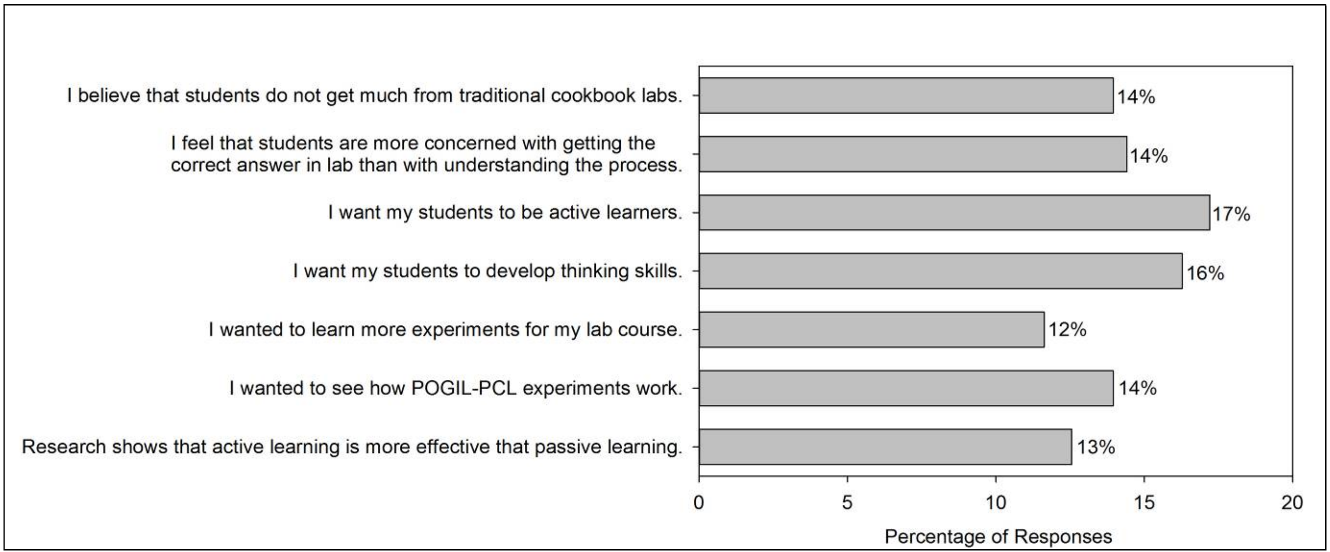

Figure 7.8 Percentage of responses for the survey question, "Which of the following describes your motivation for coming to a POGIL-PCL workshop?" (Data from 2015 survey)

Approximately 8% of survey respondents said that they came only to learn more experiments for their course and/or to see how POGIL-PCL experiments work. While other instructors chose those responses as well, most also selected responses related to student learning. Much of instructors' motivation to come to POGIL-PCL comes from a constructivist position, which says that students must be actively engaged in constructing new ideas based on their knowledge and experience. This idea of having students construct their own understanding is a key part of the POGIL philosophy. Clearly, many instructors who come to POGIL-PCL workshops already share this philosophy. One instructor commented, "As faculty, we know that engaging, process driven learning improves students' deeper understanding, and certainly it complements their broader understanding." Another instructor said, "Having students learn to start thinking like scientists is more fun for me and more useful for the students. It is a joy to watch students develops enough confidence to explore the parameters of a problem without being afraid to be wrong."

Instructors were also asked what would encourage them to use POGIL in their lab courses and in the classroom. The responses were similar to our previous results. For both the laboratory and classroom, hands-on experience with POGIL at workshops and support from the POGIL community were the most highly selected responses, along with research and statistics showing the effectiveness of POGIL and personal experience with POGIL (Figure 7.9). The responses to this question reinforce instructors' desire for more workshops (mentioned earlier) and the value of the POGIL-PCL network (providing support).

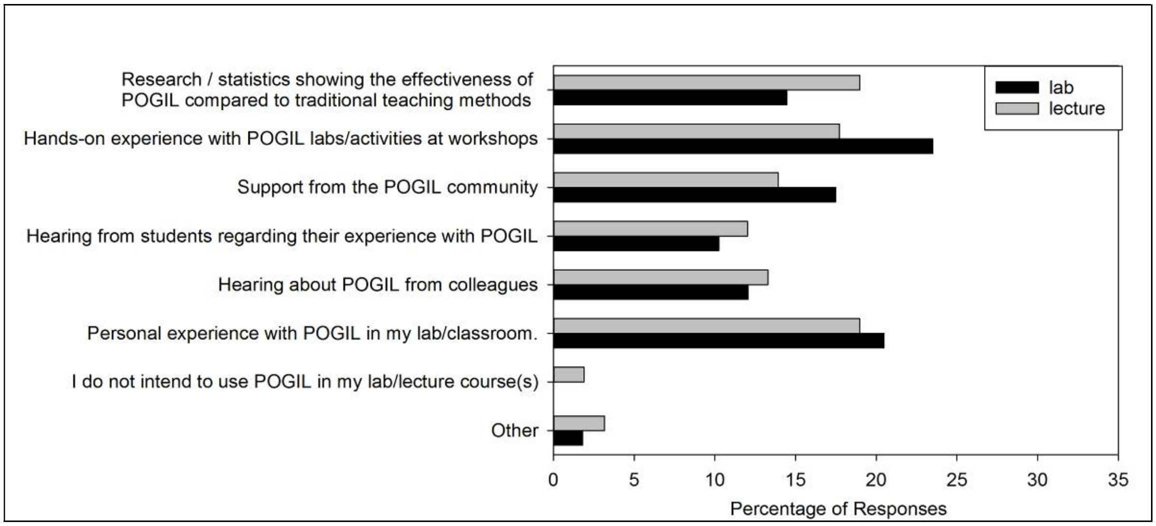

Figure 7.9 Percentage of responses for the survey question, "Which of the following would encourage (or has encouraged) you to use POGIL in your lab/lecture courses?" (Data from 2015 survey)

In the 2016 survey, instructors were asked to rank key components of POGIL-PCL experiments and common learning goals in physical chemistry laboratory courses as very important, moderately important, slightly important, or not important. The seven items instructors were asked to rank were:

- Making a prediction, regardless of whether the prediction is right or wrong
- Answering the pre-experiment, thinking about the data, and post-experiment questions correctly
- Learning/mastery of the physical chemistry concept
- Making decisions about how to carry out the experiment
- Interacting with other students/working together as a group
- Learning from mistakes in the lab or from making an incorrect prediction
- Modeling data

As shown in Figure 7.10, the majority of instructors ranked “making a prediction, regardless of whether it is right or wrong”; “interacting with other students/working together as a group”; and “modeling data" as very important, with about 30% ranking these items as moderately important. Making predictions and having students work as a group are key parts of the POGIL-PCL model. From the data, it appears that instructors value these goals as well. Modeling data is a key component in all physical chemistry laboratories, so it is expected that most instructors would rank modeling data as very important or moderately important.

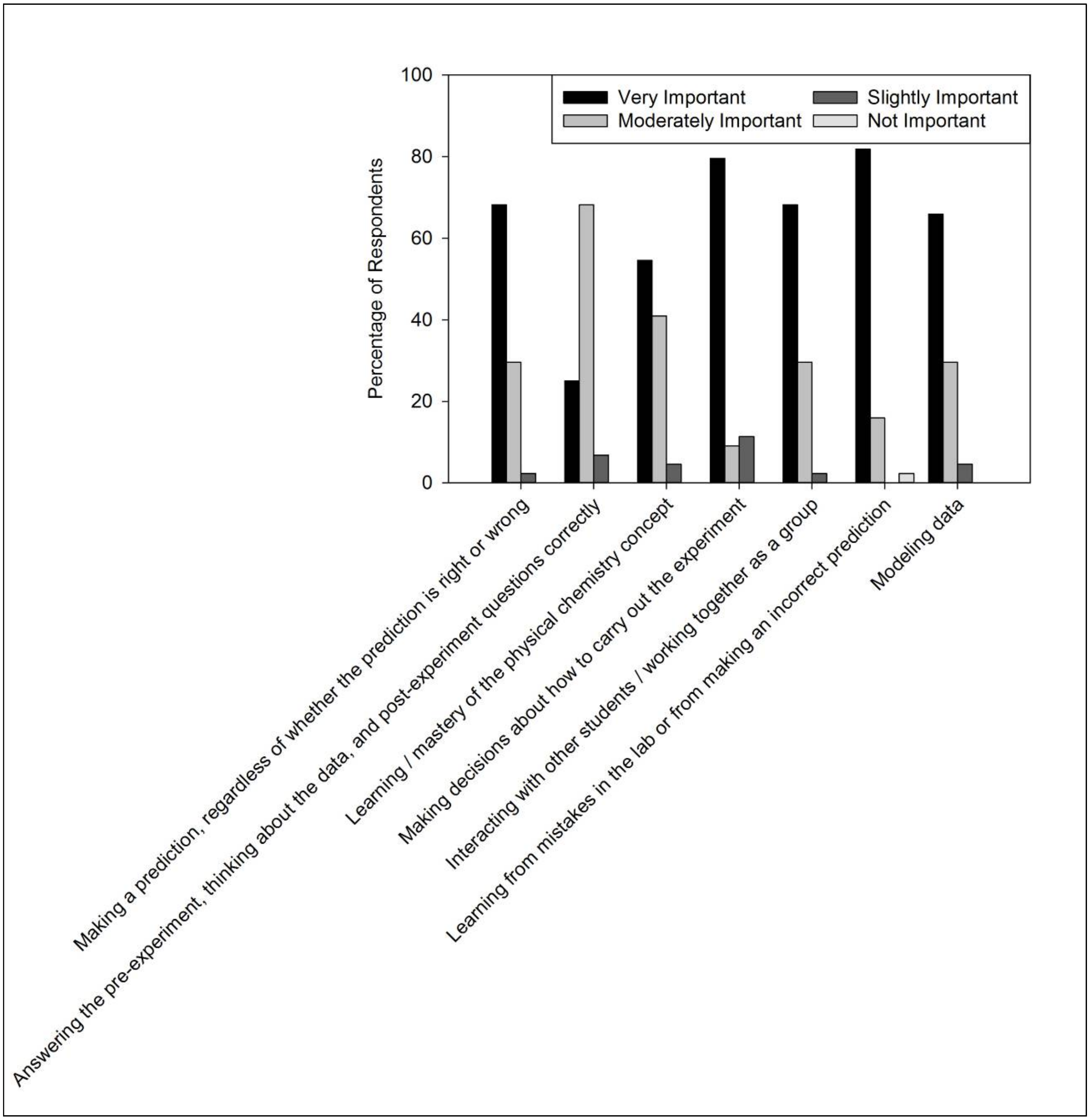

Figure 7.10 Percentage of respondents who ranked each item as very important, moderately important, slightly important, or not important. (Data from 2016 survey)

Over 80% of instructors ranked “making decisions about how to carry out the experiment” and “learning from mistakes in the lab or from making an incorrect prediction” as very important. These two points are also key parts of the POGIL-PCL model. Having students make decisions about how to carry out the experiment rather than being given the experiment parameters is one of the key features that distinguishes POGIL-PCL experiments from traditional physical chemistry experiments. Learning from mistakes and confronting misconceptions are also built into the POGIL-PCL model. Many instructors who attend the POGIL-PCL workshops value these goals as well.

For “learning/mastery of the physical chemistry concept”, the ranking was split between very important and moderately important. POGIL-PCL experiments focus on both conceptual learning and process skills; the rankings here are consistent with this focus. For the last item, “answering the pre-experiment, thinking about the data, and post-experiment questions correctly”, the majority of instructors selected moderately important, with 25% selecting very important. The pre-experiment, thinking about the data, and post-experiment questions are a part of all POGIL-PCL experiments. However, many of the questions (particularly thinking about the data and post-experiment questions) are designed to have students draw conclusions based on data and apply what they have learned; therefore, there is not usually one “correct” answer.

7.4.5 Instructors’ implementation of POGIL-PCL

After attending the workshops, many instructors chose to implement POGIL-PCL in their laboratories. In the 2015 survey, survey respondents were asked whether they implemented the experiments as written or modified them in some way. If instructors indicated they had modified the experiments, they were asked how they modified the experiments. Based on the responses to the questions in the 2015 survey, the questions were revised, and instructors’ responses were probed in more detail in the 2016 survey. In the 2016 survey, 46% of respondents said they modified the experiments in some way. Figure 7.11A shows how instructors modified the experiments.

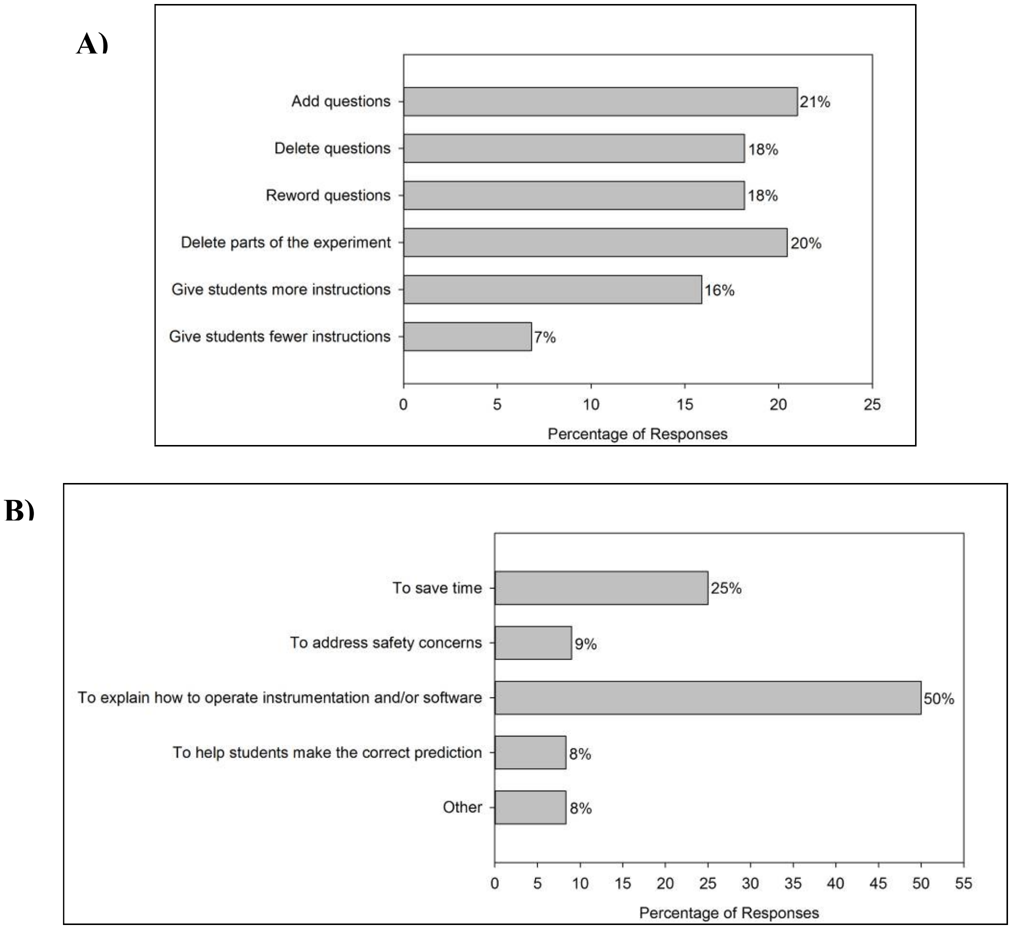

Figure 7.11 A) Percentage of responses to the question, “How do you change the experiments?” B) Percentage of responses to the question, “Why do you give students more instructions?” (Data from 2016 survey)

In order to better understand how these changes impact learning outcomes, instructors who said that they deleted questions or parts of the experiment or gave students more instructions were asked why they made these changes. All of respondents who deleted questions or parts of the experiment did so due to time constraints; 36% also felt some questions or parts of the experiment were not necessary. POGIL-PCL experiments are intended to take two full lab periods; some instructors may choose to spend less time per experiment in order to complete additional experiments or address other learning goals.

Adding questions may be done to address additional learning goals. Adding instructions was the most concerning change. More instructions limits the extent to which students are making their own predictions and coming to their own understanding of their observations However, as shown in Figure 7.11 B, 50% of respondents said that they added instructions to explain how to operate instrumentation and/or software. Given that there are multiple manufacturers of common instruments and many versions of the software that accompanies these instruments, it is not surprising that some instructors would add additional instructions on the operation of instruments and/or software. The second most common response was adding instruction to save time (25%). It is unclear whether adding instructions to save time affects learning outcomes. If students are given fewer opportunities to explore and investigate, the development of critical thinking, problem solving, and teamwork may be subverted.

Another aspect of implementation is ensuring that students are actively involved in the learning cycle and constructing their own knowledge. In the 2016 survey, instructors were asked whether they required students to complete pre-experiment questions before coming to lab, whether students make decisions about how to carry out the experiment, and whether students are required to make a prediction or hypothesis before beginning the experiment. The responses are shown in Table 7.1.

Table 7.1. Percentage of Respondents Who Require Students to Complete Pre-Experiment Questions, Make Decisions, and Make Predictions. (Data from 2016 survey)

Do you require students to complete pre-experiment questions before coming to lab?	
Yes, I require students to complete pre-experiment questions before coming to lab.	85.7
No, students complete pre-experiment questions in class.	14.3
Do students in your course make decisions about how to carry out the experiment?	
Yes	96.4
No	3.6
Do you require students to make a prediction or hypothesis before beginning the experiment?	
Yes	100
No	0

Most instructors required students to complete pre-experiment questions before coming to lab, although a small percentage (14%) had students do the questions in class. “No, students do not do pre-experiment questions” was also given as an answer choice; however, no one selected that answer. Most instructors also require students to make decisions in lab, and all instructors required students to make a prediction or hypothesis before beginning the experiment.

Instructors were also asked whether they had the whole class do the same experiment simultaneously or whether they did the experiments round-robin. Only 13.5% of respondents indicated that they did the experiments in a round-robin setting. While POGIL-PCL experiments can be difficult to implement round-robin given that POGIL relies heavily on collaboration and teamwork, these responses show that doing experiments in a round-robin format is possible.

The final question regarding implementation asked instructors how their students show what they have learned. As expected, all of the survey respondents required students to write a lab report (29% required formal lab reports in the style of a journal article, 46% required less formal lab reports, and 25% required some combination of formal and less formal lab reports).

In addition, 7% of instructors also had students take a quiz on concepts they should have learned from the experiment.

7.4.6 POGIL-PCL network demographics

Approximately 83% of survey respondents teach at primarily undergraduate institutions, with the remaining 17% teaching at research universities. Instructors were asked to estimate how many students at their institution had completed at least one POGIL-PCL experiment. The results are shown in Figure 7.12 A.

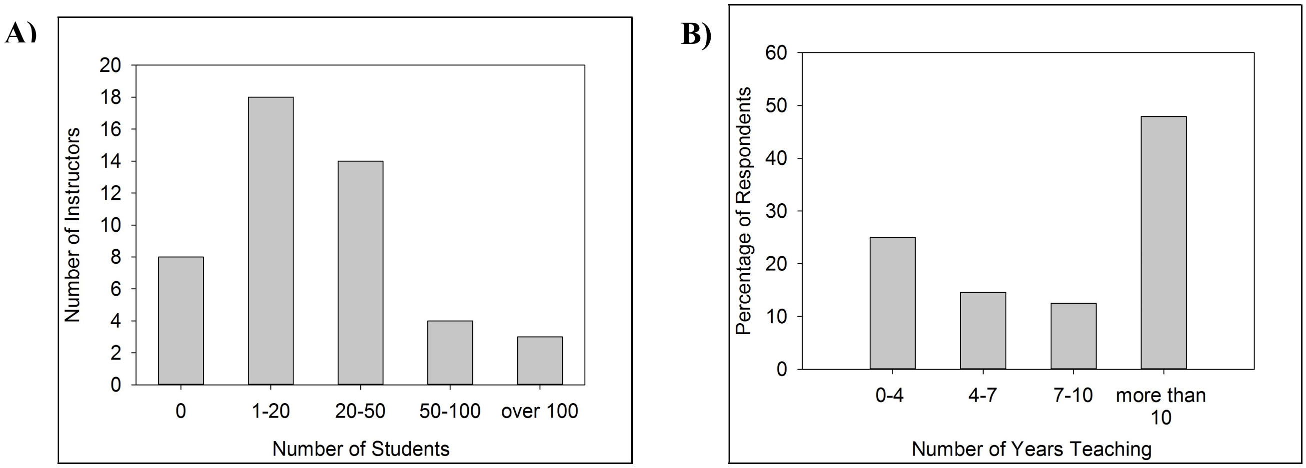

Figure 7.12 A) Number of students who have completed at least one POGIL-PCL experiment at their institution as reported by instructors. B) Percentage of survey respondents who have been teaching at their institution for each of the above ranges. (Data from 2015 survey)

At a minimum (using the lower ends of these ranges), approximately 800 students at various institutions have completed POGIL-PCL experiments.

Instructors were also asked how many years they have been teaching at their institution. It was hypothesized that the majority of instructors who attended POGIL-PCL workshops would be newer instructors who were looking for experiments that aligned with their teaching philosophy. The results in Figure 7.12 B show that the majority of instructors who attend POGIL-PCL workshops are actually established instructors. Almost half of the instructors have been teaching more than 10 years. Only 25% have been teaching less than 4 years. Several instructors commented on how POGIL-PCL has changed their perspective. One instructor stated, "This is the most fun I have had teaching experimental chemistry in a long run." Another commented, "Hard for me to overcome my traditional teaching method, but seeing student's responses and interactions (as well as better reports) have made me convert." It seems that many instructors who have come to POGIL-PCL workshops are dissatisfied with the results of their current teaching method and are looking for a method that is more in line with their philosophy.

Many instructors who come to the workshops have some knowledge of and/or experience with POGIL. Instructors were asked how familiar they were with POGIL before attending a workshop. As shown in Figure 7.13, 57% of instructors had used POGIL in some of their courses but not in the physical chemistry lab. Another 27% had heard of POGIL but had varying levels of familiarity with it. There were smaller percentages on either end of the spectrum: 7% of respondents had never heard of POGIL, while 9% of respondents had used POGIL in the physical chemistry lab. Based on the survey responses, many instructors have already begun to use POGIL or are interested in using POGIL in their courses even before they came to the workshops.

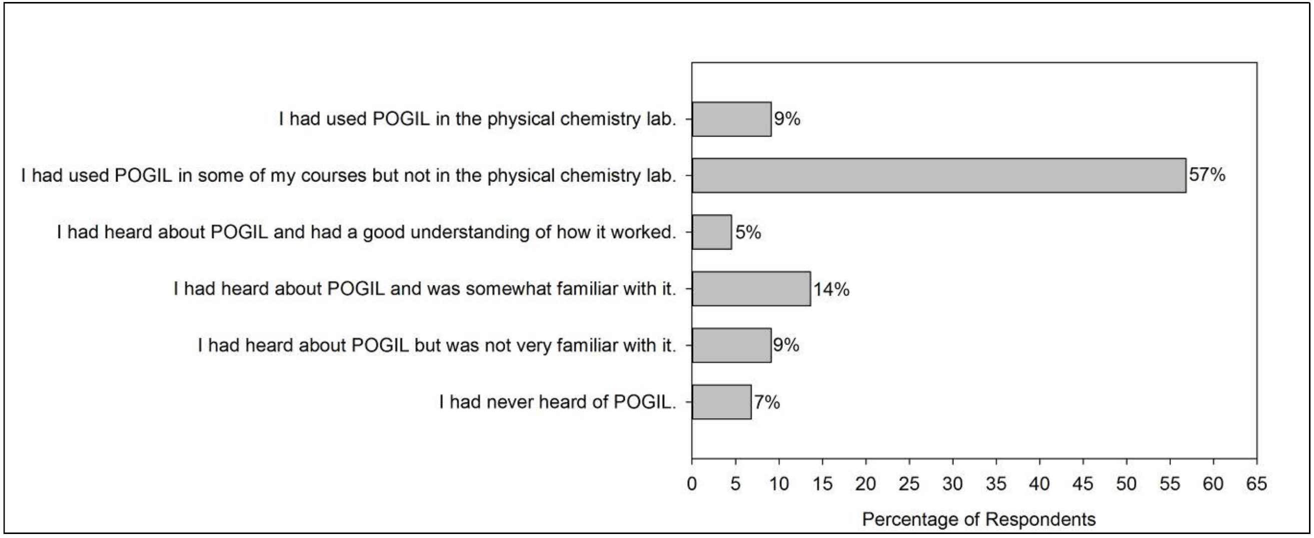

Figure 7.13 Percentage of responses for the question, “How familiar were you with POGIL before you attended your first workshop?” (Data from 2015 survey)

7.4.7 Additional comments

At the end of the survey, instructors were asked, “Is there anything else you would like to tell us about your experience with POGIL-PCL?” Some of the comments are highlighted in Box 7.3. Several instructors commented on how much they value the opportunity to network with other physical chemistry instructors and the support from the POGIL-PCL community. The workshops provide more than just new experiments, they provide a growing network to support instructors who are interested in POGIL-PCL.

Box 7.3

“Having access to a community to pchem laboratory teachers has greatly improved my understanding and my teaching of physical chemistry topics. I look forward to engaging with the group.”

“The workshop was a great chance to discuss ideas with colleagues....”

“I have found the POGIL-PCL community to be very helpful.”

“...since I've started doing some POGIL-PCL labs, a few of my more POGIL-resistant colleagues have become more open to it. One even asked me for an example lab so that she can look at possibly revising some of her traditional labs to facilitate a more active learning approach."

"I also valued the opportunity to network and talk with other physical chemists. I am the sole physical chemist at my institution and being integrated into a community of physical chemists who are committed to being good educators has been beneficial for me and for my students."

"The POGIL-PCL community is a great community and I'm glad that I'm part of it."

7.5 Conclusion

The POGIL-PCL network has grown considerably since the first workshop in January 2012. The number of workshop attendees has increased 680% over the last three years. In addition, 77% of survey respondents report having used POGIL-PCL experiments to some extent after attending the workshops. Not only do instructors implement POGIL in their physical chemistry laboratories, but many also choose to use it in other courses. The responses from the SII forms and survey questions, as well as the additional comments, show that workshop participants value the networking, collaboration, and support provided by the POGIL-PCL network. The support from the POGIL community and hands-on experience with POGIL experiments are major factors in encouraging instructors to implement POGIL in their courses; their own motivation to engage students in active learning is an important factor as well. The non-hierarchical nature of the POGIL-PCL network encourages two-way communication among participants and facilitators, so that those with strong and weak ties can participate in the network and undergo change.

This article focused on the growth of the POGIL-PCL network and the characteristics of instructors who choose to become part of the POGIL-PCL network. Much of this growth has occurred as a result of continued workshops and support. One question that remains is whether the POGIL-PCL network will continue to develop in the absence of the workshops. Will those who have adopted continue to use POGIL-PCL in the future? Will instructors continue to adopt with the support of colleagues, or are the workshops necessary to continue the growth of the network? How would an online community contribute to the growth of the network? Future papers will explore these questions.

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Chapter 8: Conclusion and Future Work (Part 2)

8.1 Conclusions

Faculty workshops have been used to disseminate teaching materials to interested faculty, to promote the implementation of new teaching methodologies, and, in some cases, to build a community of instructors. There are several models that describe the process of change that instructors go through as they change their teaching methods, including Lewin's model of change (unfreezing, cognitive restructuring, and refreezing), Roger's diffusion of innovations (knowledge, persuasion, decision, implementation, and confirmation), and situational theory.[1-5] Some studies such as Stains et al., have raised concerns over whether changes are sustained long-term.[6] Many studies have focused on building a community to support instructors as they move through the process of change. Research on network development reinforces the idea that providing a support system can be effective in promoting implementation. Organic networks, which are created from existing relationships, strong ties, which involve frequent interaction, and expressive relationships, which are more social and friend-based, tend to have more influence and are more likely to promote change.

This work focuses on the factors that influence instructors at various stages in the process of change and on the growth of the POGIL-PCL network. The first survey focused on the factors that initially interest instructors in changing their teaching method, the factors that affect whether instructors adopt new teaching methods, and the rate of adoption that occurs after participants attend the POGIL-PCL workshop. The survey showed that 77% of instructors who responded to the survey implemented POGIL-PCL to some extent. Personal contact and collaboration were found to be important in the early stages of the process of change (knowledge and persuasion) and in the later stages. Hearing about the workshops from a colleague or seminar speaker were the most common way instructors found out about the workshops. Similarly, email/Skype with POGIL facilitators and follow-up workshops were the most common forms of support that instructors selected as helpful as they began to implement POGIL-PCL.

The second and third surveys focused on the growth of the POGIL-PCL network. Nine instructors attend the first workshop in January 2012; the network now includes 70 instructors who have attended POGIL-PCL workshops over a three year period. The data collected from the third survey in 2016 shows that instructors who choose to implement POGIL-PCL experiments tend to implement more frequently over time. When asked about additional ways in which they participated in the network after coming to the workshops, 82% of survey respondents participated in the network in at least one way such as writing, revising, or testing a POGIL-PCL experiments; and 59% participated in two or more ways. Additionally, the majority of survey respondents (84%) recommended the workshop to at least one person. Responses from survey respondents indicate that participants value the networking, collaboration and support provided by the workshop and often choose to participate beyond attending the workshops and implementing the experiments.

8.2 Future work

8.2.1 Growth of the network in the absence of the workshops

The last POGIL-PCL workshop was held in June 2015. It remains to be seen whether instructors will continue to implement POGIL-PCL and whether new instructors will join the network in the absence of the workshop. Previous research on learning communities and network development has shown that having a support system is instrumental in promoting change.[1, 3, 5-15] Many of the learning communities meet regularly for a period of time (i.e., a year). It is often unclear whether the changes made are sustained after the learning communities end their regular meetings. Murray et al. found that changes were sustained 8 months later[11]; however it would be useful to determine if these changes are sustained over a larger period of time. The surveys utilized in this work could be repeated yearly to see if instructors continue to implement POGIL-PCL and participate in the network. Instructors who access the experiments from POGIL.org could also be included in the survey.

8.2.2 Contribution of an online community to the growth of network

Several online meetings have been conducted to share and discuss ideas, provide feedback, and answer questions regarding the POGIL-PCL experiments. One open question is how the online community will contribute to the support and growth of the network. While the online meetings would allow participants to share ideas, discuss experiments in development, and seek support and advice, it would not allow new participants to experience a POGIL-PCL experiment as previous participants have at the two-day and BCCE workshops. To assess the effectiveness of the online meetings, short surveys similar to the SII forms used at the workshops, could be conducted after the meetings. Also, instructors who attend the online meetings could be included in the surveys discussed in 8.2.1.

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Appendix 1 (Sample Workshop Agenda)

Arrival	7:15 pm	Dinner for participants who arrive by 7:15 pm; walk to restaurant.	
Day 1	7:35 am	Meet in hotel lobby to walk/drive to VCU campus.	
	8:00 - 9:00 am	Breakfast & coffee. Overview of agenda. Workshop goals.	
	9:00 - 11:00 am	Experiencing a POGIL experiment: *Does myoglobin unfold in the body?*	
	11:00 – 11:15 am	Break (snacks, coffee/tea, water available).	
	11:15 am – 12:00 pm	Experiencing a POGIL experiment: *Does myoglobin unfold in the body?* continued	
	12:00 - 1:00 pm	Lunch – catered	
	1:00 – 5:30 pm	POGIL-PCL experiment writing: pre-selected experiment	Elements & facilitation of a POGIL phys chem expt. Experiencing a POGIL experiment: Select one a. Mg-HCl b. Phase diagram c. B-naphthol d. Apple enzyme e. Chick pea f. Iodine clock
	Take a break!	Snacks, coffee, tea, and water available.	
	5:30 – 5:45 pm	Report progress from writing or doing experiments: prepare giant sticky with title/topic & challenges	
	5:45 – 6:15 pm	Report progress from writing or doing experiments: groups give a 30-second elevator talk; museum walk following where participants can add comments or questions	
	6:15 - ?	Dinner.	
Day 2	8:00am	Breakfast & coffee/tea served.	
	8:30 – 8:40 am	Overview and goals for day two.	
	8:40 – 9:40 am	Teams review experiments using the initial screening rubric with discussion; each team reviews one (or two) experiments.	
	9:40 – 11:40 am	POGIL-PCL experiment writing: continue from day 1	Experiencing a POGIL experiment: Select one a. Mg-HCl b. Phase diagram c. B-naphthol d. Apple enzyme e. Chick pea f. Iodine clock
	11:40 am – 12:00 pm	Next steps: lead authors, beta testing, reviewing.	
	12:00 – 1:30 pm	Lunch – walk to restaurant.	
	1:30 – 2:00 pm	Working groups update posted summaries	
	2:00 – 3:00 pm	Report out & museum walk & questions	
	3:00 – 3:15 pm	Group photo.	
	3:15 – 4:15 pm	Workshop assessment & commitment forms. Closure. Travel reimbursement.	
	4:30 pm	Travel home safely!	

Appendix 2 (screening rubric)

Laboratory Experiment Initial Screening Rubric, POGIL-PCL[1]

This rubric guides initial review of a laboratory experiment to determine how well the activity supports process-oriented and guided-inquiry learning in the physical chemistry laboratory. The review pertains only to the written description of the experiment, protocol, and pre/post lab questions included and not to how an instructor might facilitate its use. A "yes" response should indicate that evidence for that characteristic can be found in the activity itself. The evidence must be explicit, i.e. reviewers should not assume that an instructor using the activity will provide anything that seems to be missing. If evidence is found, then a "yes" response is appropriate, irrespective of the perceived quality of that characteristic. If no explicit evidence can be found, then a "no" response is appropriate.

	ESSENTIAL CHARACTERISTICS	Yes	No	Comments --
1	The experiment begins with a conceptual question, typically as the title of the experiment.			
2	The expected outcome of the experiment and concepts developed are known to the instructor but not to the students.			
3	The learning objectives incorporate the knowledge and skills needed for students to answer the conceptual question.			
4	The experiment follows the POGIL-PCL template: pre-experiment questions, experimental protocol, thinking about the data questions, and post-experiment questions. More than one cycle, based on one experimental protocol, of pre-experiment, TATD, and post-experiment questions is preferable.			
5	Students develop a hypothesis, model and/or conclusion that integrates available information and/or prior knowledge and can be convincingly justified.			
6	Students are expected to engage in problem solving, decision-making, and/or experimental design tasks.			
7	Students are expected to observe, collect and process information (describe, tabulate, summarize, calculate, and/or transform data to another representation).			
8	Students are led to apply mathematical models to data; when appropriate, students are guided to model data graphically in order to obtain results.			
9	Students demonstrate their understanding of the developed concepts through application and/or by developing questions for further research.			
10	Students are cued to share or interact with each other, including coming to consensus on key experimental design or data analysis decisions.			

Reference

1. Cole , R., University of Iowa; Bauer, C., University of New Hampshire, Personal Communication. 2012.

Appendix 3 (2014 survey)

Workshop Survey

Please complete the following survey. The results from this survey will be used as part of a research study to evaluate the effectiveness of POGIL-PCL workshops. The survey should take no more than 15 minutes. Please answer all of the questions. If you need to stop during the survey, you may save and return later. You will be given a validation code, which you will need to save and enter when you resume the survey.

Participation in this survey is voluntary. The results of this survey may be used in future publications. At the end ofthe survey, you may choose to have your responses not be included in future publications if you wish. Your answers will be used to help improve the quality of future POGIL-PCL workshops.

Please print or save this page for your records.

Background

Please indicate which workshop you attended. (Check all that apply.)
- ☐ One 2-day POGIL-PCL workshop
- ☐ More than one 2-day POGIL-PCL workshop
- ☐ A POGIL-PCL workshop at BCCE

How did you find out about the POGIL-PCL workshop?
- ☐ I attended a seminar in which POGIL-PCL was discussed.
- ☐ I read about it on the POGIL website.
- ☐ I attended a POGIL workshop.
- ☐ It was recommended by a colleague.
- ☐ Other (please explain) ____

Past Experience with POGIL

Which of the following describes your use of POGIL before coming to the POGIL-PCL workshop?
- ○ I did not use POGIL.
- ○ I tried POGIL activities a few times but did not use them regularly.
- ○ I use POGIL regularly, along with some lecture / traditional methods.
- ○ I mostly use POGIL in my course(s).

In which laboratory course(s) have youused POGIL? (Please check all that apply.)
- ☐ General chemistry
- ☐ Physical chemistry
- ☐ Other

Please list the laboratory courses in which you have used POGIL.

____

Which of the following describes your experience using POGIL? (Please check all that apply.)

- ☐ My experience has been mostly positive.
- ☐ My experience has been somewhat positive, but I have encountered some difficulty due to issues with the activities.
- ☐ My experience has been somewhat positive, but I have encountered some resistance from students and/or other faculty.
- ☐ I have had a lot of difficulty with the activities.
- ☐ I have encountered a lot of resistance from students and/or other faculty.
- ☐ Other

Please describe your experience with POGIL.

____

Using POGIL

Which of following would encourage (or has encouraged) you to use POGIL in your lab(s)? (Please check all that apply.)

- ☐ Research / statistics showing the effectiveness of POGIL compared to traditional teaching methods
- ☐ Research / statistics showing the long-term benefits to students who have taken courses that utilize POGIL
- ☐ Hands-on experience with POGIL labs at workshops
- ☐ Support from the POGIL community
- ☐ Hearing from students regarding their experience with POGIL
- ☐ Hearing about POGIL from colleagues
- ☐ Other (Please explain) ____

Which of the following describes your reason(s) for coming to a POGIL-PCL workshop? (Please check all that apply.)

- ☐ I believe that students do not get much from traditional "cookbook" labs.
- ☐ Students are more concerned with getting the correct answer in lab than with understanding the process.
- ☐ I want my students to be active learners.
- ☐ Other (Please explain) ____

After the POGIL-PCL workshop

After the POGIL-PCL workshop, how have you used POGIL in your lab(s)?

- ○ I have not used POGIL.
- ○ I have tried a few POGIL labs.
- ○ I use POGIL labs on a regular basis in my course(s) but still use a few traditional labs.
- ○ I use POGIL labs most of the time in my course(s).

Please list the POGIL-PCL experiments you have used (or plan to use). (Please specify whether you have already used the experiment or are planning to use the experiment in the future.)

____

What type(s) of follow-up would be helpful to you as you begin to use POGIL-PCL? (Please check all that apply.)

- ☐ Email / Skype with POGIL facilitators
- ☐ Follow-up workshops
- ☐ Having a facilitator or experienced POGIL practitioner meet with you or visit your institution
- ☐ Other (Please explain) __________________________________

What made you decide not to use POGIL-PCL? (Please check all that apply.)

- ☐ My course is taught round-robin style.
- ☐ I think POGIL labs would take too much time per experiment.
- ☐ My students are required to use certain instruments, and there are no POGIL experiments using those instruments.
- ☐ I think that students would be too resistant to doing POGIL labs.
- ☐ I do not think my colleagues would be very supportive if I tried to implement POGIL.
- ☐ I believe that it would be difficult to train my TA's to use POGIL.
- ☐ Other (Please explain) __________________________________

What instrument(s) are your students required to use?

____

Using POGIL in the lecture

Has using POGIL in the lab influenced your teaching methods in the classroom?

- ○ No, I was already using POGIL in the classroom before I began using POGIL in the lab.
- ○ No, I still use traditional teaching methods in the classroom.
- ○ Yes, I am planning to use some POGIL activities in my classes in upcoming semester(s).
- ○ Yes, I have begun to use some POGIL activities in my classroom.
- ○ Yes, I mostly use POGIL in my classroom now.
- ○ Other (Please explain) __________________________________

Do you use POGIL in your lecture course(s)?

- ☐ No, I do not use POGIL in my lecture course(s).
- ☐ No, but I plan to use POGIL in the future.
- ☐ Yes, I use a combination of lecture and POGIL.
- ☐ Yes, I mostly use POGIL in my lecture.

Additional Questions

Is there anything else you would like to tell us about your experience with POGIL-PCL?

____

Thank you for taking the time to complete our survey. We are currently conducting research to determine the effectiveness of POGIL-PCL workshops.

May we use your survey responses as part of a research study to assess the effectiveness of POGIL-PCL workshops?

- ○ Yes
- ○ No

Appendix 4 (2015 survey)

Workshop Survey

Please complete the following survey. The results from this survey will be used as part of a research study to evaluate the effectiveness of POGIL-PCL workshops. The survey should take no more than 15 minutes. Please answer all of the questions. If you need to stop during the survey, you may save and return later. You will be given a validation code, which you will need to save and enter when you resume the survey.

Participation in this survey is voluntary. The results of this survey may be used in future publications. At the end of the survey, you may choose to have your responses not be included in future publications if you wish. Your answers will be used to help improve the quality of future POGIL-PCL workshops.

Please print or save this page for your records.

Background

Please indicate which workshop(s) you attended. (Check all that apply.)

- ☐ One 2-day POGIL-PCL workshop
- ☐ More than one 2-day POGIL-PCL workshop
- ☐ A POGIL-PCL workshop at BCCE

How did you find out about the POGIL-PCL workshop?

- ☐ I attended a seminar or meeting in which POGIL-PCL was discussed.
- ☐ I read about POGIL-PCL on the POGIL website.
- ☐ I attended a POGIL workshop.
- ☐ POGIL-PCL was recommended by a colleague.
- ☐ I was invited by one of the organizers.
- ☐ I read about the POGIL-PCL workshops in a Journal of Chemical Education article.

Which of the following describes your motivation for coming to a POGIL-PCL workshop? (Please check all that apply.)

- ☐ I believe that students do not get much from from traditional "cookbook" labs.
- ☐ I feel that students are more concerned with getting the correct answer in lab than with understanding the process.
- ☐ I want my students to be active learners.
- ☐ I want my students to develop thinking skills.
- ☐ I wanted to learn more experiments for my lab course.
- ☐ I wanted to see how POGIL-PCL experiments work.
- ☐ Research shows that active learning is more effective that passive learning.

Past Experience with POGIL

Which of the following describes your use of POGIL before coming to the POGIL-PCL workshop?

- ○ I did not use POGIL.
- ○ I tried POGIL activities a few times but did not use them regularly.
- ○ I use POGIL regularly, along with some lecture / traditional methods.
- ○ I mostly use POGIL in my course(s).

Select the courses for which you used POGIL before attending a POGIL-PCL workshop. (Please check all that apply.)

- ☐ General chemistry lecture
- ☐ General chemistry lab
- ☐ Physical chemistry lecture
- ☐ Physical chemistry lab
- ☐ Other (Please list)

Please list other courses in which you have used POGIL. (Please specify whether it is a lecture or lab course.) ____

Please select the number on the scale that best describes your prior experience with POGIL.

Mostly negative Mostly positive

☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

(Place a mark on the scale above)

Based on your prior experience, please select the number on the scale that best describes your students' response to POGIL.

Very resistant and/or negative Very accepting and/or positive

☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

(Place a mark on the scale above)

Based on your prior experience, please select the number on the scale that best describes the responses you have received from colleagues and/or administrators.

Very resistant and/or negative Very accepting and/or positive

☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

(Place a mark on the scale above)

Based on your prior experience, please select the number on the scale that best describes how well the POGIL activities worked in your classroom or lab.

Had difficulty Worked well

☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

(Place a mark on the scale above)

Which of the following would encourage (or has encouraged) you to use POGIL in your ...?
Lab course(s)? (Please check all that apply.)

- ☐ Research / statistics showing the effectiveness of POGIL compared to traditional teaching methods
- ☐ Hands-on experience with POGIL labs at workshops
- ☐ Support from the POGIL community
- ☐ Hearing from students regarding their experience with POGIL
- ☐ Hearing about POGIL from colleagues
- ☐ Personal experience with POGIL in my lab.
- ☐ I do not intend to use POGIL in my lab course(s)
- ☐ Other (Please explain) _______________________________

Lecture course(s)? (Please check all that apply.)

- ☐ Research / statistics showing the effectiveness of POGIL compared to traditional teaching methods
- ☐ Hands-on experience with POGIL activities at workshops
- ☐ Support from the POGIL community
- ☐ Hearing from students regarding their experience with POGIL
- ☐ Hearing about POGIL from colleagues
- ☐ Personal experience with POGIL in my classroom.
- ☐ I do not intend to use POGIL in my lecture course(s)
- ☐ Other (Please explain) _____________________________

After the POGIL-PCL workshop
After the POGIL-PCL workshop, how have you used POGIL in your lab course(s)?

- ○ I have not used POGIL.
- ○ I have tried a few POGIL experiments.
- ○ I use POGIL experiments on a regular basis in my course(s) but still use a few traditional experiments.
- ○ I use POGIL experiments most of the time in my course(s).

Please list the POGIL-PCL experiments you have used (or plan to use). (Please specify whether you have already used the experiment or are planning to use the experiment in the future.)

____

Do you use the experiments as written, or do you modify them in some way (add/delete questions, change citation style or grammar, delete parts of the experiment, etc.)?

- ○ Use the experiments as written
- ○ Modify the experiments as needed

How do you modify the experiments? (Please select all that apply.)

- ☐ Add some questions
- ☐ Delete some questions
- ☐ Change citation style or grammar
- ☐ Delete parts of the experiment
- ☐ Give students more instructions
- ☐ Give students fewer instructions

Does the whole class do the same experiment simultaneously, or are you doing the experiments round robin?

- ○ Simultaneous
- ○ Round robin

Based on your experience thus far, do you plan to continue using POGIL experiments in the future?

- ○ Yes, I plan to use POGIL experiments most of the time in future courses.
- ○ Yes, I plan to use POGIL experiments along with a few traditional labs.
- ○ No, I will not use POGIL in the future.

What made you decide not to use POGIL-PCL in the future?

- ☐ POGIL experiments take too much time.
- ☐ There are not enough POGIL-PCL materials available.
- ☐ My students are too resistant to POGIL.
- ☐ My colleagues/administrators are not supportive.
- ☐ Other (Please explain) ________________________________

What type(s) of follow-up would be (or have been) helpful to you as you implement POGIL-PCL? (Please check all that apply.)

- ☐ Email / Skype with POGIL facilitators
- ☐ Follow-up workshops
- ☐ Having a facilitator or experienced POGIL practitioner meet with you or visit your institution
- ☐ An online discussion group where instructors and facilitators can discuss ideas / questions.
- ☐ An instructors' guide with suggestions and sample student data

What made you decide not to use POGIL-PCL? (Please check all that apply.)

- ☐ My course is taught round-robin style.
- ☐ I think POGIL labs would take too much time per experiment.
- ☐ My students are required to use certain instruments, and there are no POGIL experiments using those instruments.
- ☐ I think that students would be too resistant to doing POGIL labs.
- ☐ I do not think my colleagues would be very supportive if I tried to implement POGIL.
- ☐ I believe that it would be difficult to train my TA's to use POGIL.
- ☐ I have not taught a lab course since the workshop.
- ☐ I am satisfied with my course as it is.
- ☐ My course is established, and changing it would require too much time / effort.

Using POGIL in the lecture

Has using POGIL in the lab influenced your teaching I do not teach a lecture course methods in the classroom?

- ○ No, I was already using POGIL in the classroom before I began using POGIL in the lab.
- ○ No, I still use traditional teaching methods in the classroom.
- ○ Yes, I plan to use POGIL activities in my lecture classes in upcoming semester(s).
- ○ Yes, I have begun to use POGIL activities in my classroom.
- ○ Yes, I mostly use POGIL in my classroom now.
- ○ Yes, I was using POGIL in the classroom before I used it in the lab, but the POGIL-PCL experiments have influenced what I do in the classroom.

What made you decide not to use POGIL in your lecture course? (Please check all that apply.)

- ☐ I do not teach a lecture course,
- ☐ I think POGIL activities would take too much time in the classroom.
- ☐ There are too many required topics to cover.
- ☐ I teach at a university with multiple sections that uses a common syllabus.
- ☐ I think that students would be too resistant to POGIL.
- ☐ I think it would be difficult to learn to use POGIL in the classroom.
- ☐ I am satisfied with my course as it is.
- ☐ My course is established, and changing would require too much time / effort.

Do you use POGIL in your lecture course(s)?

- ☐ No, I do not use POGIL in my lecture course(s).
- ☐ No, but I plan to use POGIL in the future.
- ☐ Yes, I use a combination of lecture and POGIL.
- ☐ Yes, I mostly use POGIL in my lecture.

Census Data

At what type of institution do you teach? (Please check all that apply.)

- ☐ Primarily undergraduate
- ☐ Research - MS
- ☐ Research - Doctoral
- ☐ Minority-serving
- ☐ Public
- ☐ Private

Please estimate the number of students who have completed at least one POGIL-PCL experiment at your institution.

- ○ 0
- ○ 1-20
- ○ 20-50
- ○ 50-100
- ○ over 100

How many years have you been teaching lab at your institution?

- ○ 0-4 years
- ○ 4-7 years
- ○ 7-10 years
- ○ more than 10 years

Additional Questions

Is there anything else you would like to tell us about your experience with POGIL-PCL?

____

Thank you for taking the time to complete our survey. We are currently conducting research to determine the effectiveness of POGIL-PCL workshops.

May we use your survey responses as part of a research study to assess the effectiveness of POGIL-PCL workshops?

- ○ Yes
- ○ No

Appendix 5 (2016 survey)

Workshop Survey
Please complete the following survey. The results from this survey will be used as part of an ongoing research study to evaluate the effectiveness of POGIL-PCL workshops. The survey should take no more than 15 minutes. Please answer all of the questions. If you need to stop during the survey, you may save and return later. You will be given a validation code, which you will need to save and enter when you resume the survey.

Participation in this survey is voluntary. The results of this survey may be used in future publications. At the end of the survey, you may choose to have your responses not be included in future publications if you wish. Your answers will be used to help improve the quality of future POGIL-PCL workshops.

For the purposes of this survey, please note that POGIL refers to the knowledge of or use of POGIL in any context (not necessarily related to the physical chemistry laboratory), while POGIL-PCL refers specifically to the use of POGIL in the physical chemistry laboratory.

Please print or save this page for your records.

How have you been involved in the POGIL-PCL community? (Please check all that apply.)

- ☐ Attended one or more 2.5 day workshops
- ☐ Attended a 1.5 day workshop (summer 2015) or a workshop at BCCE
- ☐ Obtained experiments from POGIL.org

Approximately how long ago did you attend your first POGIL-PCL workshop?

- ○ Less than 1 year
- ○ More than 1 year but less than 3 years
- ○ More than 3 years

When did you most recently attend a POGIL-PCL workshop?

- ○ Less than 1 year
- ○ More than 1 year but less than 3 years
- ○ More than 3 years

How familiar were you with POGIL before you attended your first POGIL-PCL workshop?

- ○ I had never heard of POGIL.
- ○ I had heard about POGIL but was not very familiar with it.
- ○ I had heard about POGIL and was somewhat familiar with it.
- ○ I had heard about POGIL and had a good understanding of how it worked.
- ○ I had used POGIL in some of my courses but not in the physical chemistry lab.
- ○ I had used POGIL in the physical chemistry lab.

How familiar were you with POGIL before you visited POGIL.org to obtain experiments?

- ○ I had not heard of POGIL; I was looking for new physical chemistry experiments and was referred to the site by a colleague.
- ○ I had heard about POGIL but was not very familiar with it.
- ○ I had heard about POGIL and was somewhat familiar with it.
- ○ I had heard about POGIL and had a good understanding of how it worked.
- ○ I had used POGIL in some of my courses but not in the physical chemistry lab.
- ○ I had used POGIL in the physical chemistry lab.

Are you currently using POGIL-PCL in your courses?

- ○ Yes
- ○ No

When did you begin using POGIL-PCL in your courses?

- ○ Less than 1 year
- ○ More than 1 year but less than 3 years
- ○ More than 3 years

How often do you use POGIL-PCL experiments in your course?

- ○ All of the time
- ○ About 75% of the time
- ○ About 50% of the time
- ○ About 25% of the time
- ○ About 10% of the time

Have you participated in any of the following? (Please check all that apply.)

- ☐ Writing POGIL-PCL experiments
- ☐ Testing a newly developed POGIL-PCL experiment
- ☐ Reviewing an existing POGIL-PCL experiment
- ☐ Presented about my work with or use of POGIL-PCL at a conference or meeting
- ☐ Wrote a paper about my work with POGIL-PCL
- ☐ Used POGIL-PCL for professional developments (e.g., as part of a promotion packet or application for an award)
- ☐ None of the above

Do you implement the experiments as written, or do you change them in some way (change or reword questions, delete parts of the experiments, or give students more or fewer instructions)?

- ○ Implement the experiments as written
- ○ Change the experiment in some way

How do you change the experiments? (Please check all that apply.)

- ☐ Add questions
- ☐ Delete questions
- ☐ Reword questions
- ☐ Delete parts of the experiment
- ☐ Give students more instructions
- ☐ Give students fewer instructions

Why do you delete questions or parts of the experiment? (Please check all that apply.)

- ☐ I delete them due to time constraints.
- ☐ I feel some questions or parts of the experiment are not necessary.

Why do you give students more instructions? (Please check all that apply.)

- ☐ To save time
- ☐ To address safety concerns
- ☐ To explain how to operate instrumentation and/or software
- ☐ To help students make the correct prediction
- ☐ To help students get the correct answer
- ☐ Other

Please explain why you give students more instructions.

____

Do you require students to complete pre-experiment questions before coming to lab?

- ○ Yes, I require students to complete pre-experiment questions before coming to lab.
- ○ No, students complete pre-experiment questions in class.
- ○ No, students do not do pre-experiment questions.

Do students in your course make decisions about how to carry out the experiment?

- ○ Yes
- ○ No

Do you require students to make a prediction or hypothesis before beginning the experiment?

- ○ Yes
- ○ No

How do your students show what they have learned? (Please check all that apply.)

- ☐ Students are required to write a formal lab report in the style of a journal article.
- ☐ Students are required to write a lab report (less formal, but must contain processed data, explanations, and/or answers to post-experiment questions).
- ☐ Students turn in processed data and answers to post-experiment questions.
- ☐ Students take a quiz on concepts they should have learned from the experiment.

Is there anything else you would like to share with us about your implementation of POGIL-PCL?

Please rank each of the following as very important, moderately important, slightly important, or not important.

Making a prediction, regardless of whether the prediction is right or wrong

- ○ Very important
- ○ Slightly important
- ○ Moderately Important
- ○ Not important

Answering the pre-experiment, thinking about the data, and post-experiment questions correctly

- ○ Very important
- ○ Slightly important
- ○ Moderately Important
- ○ Not important

Learning / mastery of the physical chemistry concept

- ○ Very important
- ○ Slightly important
- ○ Moderately Important
- ○ Not important

Making decisions about how to carry out the experiment

- ○ Very important
- ○ Slightly important
- ○ Moderately Important
- ○ Not important

Interacting with other students / working together as a group

- ○ Very important
- ○ Slightly important
- ○ Moderately Important
- ○ Not important

Learning from mistakes in the lab or from making an incorrect prediction

- ○ Very important
- ○ Slightly important
- ○ Moderately Important
- ○ Not important

Modeling data

- ○ Very important
- ○ Slightly important
- ○ Moderately Important
- ○ Not important

Who would you consider to be your contacts in the POGIL-PCL network (i.e., people you would contact for support, advice, or information about experiments)? (Please check all that apply.)

- ☐ The workshop facilitators
- ☐ Others who have attended the workshops
- ☐ Other instructors who have utilized guided inquiry in their courses

How many people have you recommended the POGIL-PCL workshops to?

- ○ 0
- ○ 1
- ○ 2
- ○ 3 to 5
- ○ More than 5

May we use your survey responses as part of a research study to assess the effectiveness of POGIL-PCL workshops?

- ○ Yes
- ○ No

Appendix 6 (Example POGIL-PCL experiment)

What Are the Kinetic Parameters of a Heterogeneous Reaction?[1]

Heterogeneous reactions are examples of the economically important corrosion process. The reaction studied in this experiment is the oxidation of magnesium ribbon by dilute hydrochloric acid. Studying the rate of this or any reaction provides valuable insight into how the reaction takes place.

Pre-experiment questions Part One

1. What is the other product of this reaction? Write the balanced chemical equation (both molecular and net ionic) for this reaction, including the states of reactants and products.
2. The "quantity", or measurable property, of a reactant or product is important when determining kinetics parameters. Such quantities might include but are not limited to concentration or something analogous to concentration, such as mass, pressure, volume, surface area, length, width, density or something else. What is the appropriate quantity to use for each reactant and product in this reaction? Explain your choice.
3. Suggest at least one experimental method that could be used to follow the progress of this reaction, and justify your suggestion.
4. In your lab notebook before lab, calculate the pressure in both atm and mmHg exerted if 20.0 mL of 0.10 M HCl reacts with excess magnesium in a 125-mL flask at 298 K. What mass of magnesium reacts? What would be the pressure if 1.0 M HCl is used?
5. Sketch a picture of the apparatus in your notebook.
6. Why is it especially important to wear safety goggles for this experiment?

General protocol (Read entire protocol before starting the experiment.)

The following protocol will be used for all kinetics measurements in this lab. The pressure of hydrogen gas will be used to monitor the reaction progress. Use this protocol with a sample of magnesium and a volume of HCl(aq) that you think is sufficient to completely react with magnesium sample.[2] Be sure to wear safety goggles while doing the experiment.

1. Obtain a sample of magnesium, and record any appropriate measurements for the sample.
2. Obtain a sample of hydrochloric acid, make any necessary dilutions, and record the concentration of hydrogen ion.
3. Choose a flask or test tube that can accommodate the stopper for the gas pressure sensor and place the magnesium in the flask such that it can be completely covered by the HCl solution. For example, magnesium ribbon must be weighted by a loop of copper wire.
4. Place the flask or test tube with the Mg and a separate flask containing the volume of HCl solution for the trial into the water bath to equilibrate. Record the temperature of the water bath.

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[1] Adapted from Halpern, A. M.; McBane, G. C. *Experimental Physical Chemistry: A Laboratory Textbook*. (W. H. Freeman: 2006) and Birks, J. P.; Walters, D. L. *J. Chem. Ed.* **1993**, *70*, 587-598.

[2] While we don't always follow a reaction to completion, having that amount of reactants is usually good to ensure a sufficiently fast reaction.

5. Begin monitoring pressure as a function of time and do so for at least one minute before starting the reaction.
6. Quickly add the HCl solution to the flask or test tube containing the magnesium and immediately stopper the flask. You must hold the stopper in place while continuously swirling the flask as the reaction proceeds so no gas escapes.
7. When the reaction is complete or has slowed significantly, stop the data collection, remove the flask from the bath, and use the stopcock to carefully release the pressure in the flask. The reaction products must be disposed of appropriately.
8. Multiple runs should be made for each set of reaction conditions to ensure reproducibility. (At least two runs must be reproducible to within 10%.)

Experiment Part One

You will be provided with at least two types of solid magnesium and 1.0M HCl(aq). Verify that the water bath is set at 25°C.[3]

Qualitatively, how does the magnesium affect the magnesium-hydrochloric acid reaction rate? The class should gather data such that:

- at least two forms of magnesium are tested, using the same mass of each form; and
- at least two different masses for each form of magnesium are tested.

(It is not possible to change the mass of magnesium rod.) When selecting the amounts of magnesium to use, consider your answer to #4 in the pre-experiment questions.

Thinking About the Data (TATD) Part One

1. After each trial, you have a graph of pressure versus time. What parameter is determined from the slope of this graph at short times? (What time frame is appropriate for "short time"?)
2. Why is this method called the *initial rates method* for the determination of kinetics parameters?
3. Qualitatively, how can this slope be used to determine the effect of the magnesium on the reaction rate?
4. Determine the slope of the pressure versus time curve for each trial, and report your results in a shared spreadsheet. As a class, review the tabulated data. Write a statement to express the effect of magnesium on the reaction rate. Write this statement in your lab notebook and on the board. Each person in class should be able to verbalize this statement without reading it.
5. Which measurable property of magnesium determines the reaction rate? Explain your reasoning. (The class should come to a consensus.)
6. Which form of magnesium is most appropriate for measuring the property identified in TATD 5?

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[3] If the lab is particularly warm, the water bath should be set at 30°C.

Pre-Experiment Questions Part Two

Physical chemistry is a quantitative science in which data is modeled. The model is often (but not always) a known equation based on a definition or concept. Modeling is accomplished by graphing the data and fitting the equation using least squares analysis. The slope and intercept of the fitted line are related to modeling parameters.

The rate law equation for the magnesium-hydrochloric acid reaction is

$$\text{rate} = \left(\frac{dP_{\text{H}_2}}{dt} \right) = kS_{\text{Mg}}^{a} \left[\text{H}^{+} \right]^{b}$$

7. In your groups define all the parameters in this equation.
8. What is varied to determine the order of the reaction with respect to the magnesium? What is varied to determine the order of the reaction with respect to hydrogen ion? What is not varied in each determination? What parameters in this equation are constants?
9. Take the logarithm of both sides of the rate law equation. Show how *a* and *b* can be determined by a linear least squares fit of rate versus the quantities identified in TATD 7. The class must reach consensus on the identity of the independent and dependent variables, the slope, and the intercept.
10. How many data points are needed to confirm a linear relationship for the experimental results?

Experiment Part Two

With your classmates design a set of experiments that will allow determination of the parameters in the rate law keeping in mind the answers to TATD 7-10. After consulting with your instructor about your experimental design and making any appropriate revisions, perform these experiments using the same protocol as for the initial trials. Obtain the initial rate for each set of experimental conditions from your pressure versus time data. Using your answers to TATD 7-10 and class data, obtain values for *a*, *b*, and *k*.

Thinking About the Data Part Two

11. Write the rate law for this reaction.
12. Write a general statement summarizing the effect of the magnesium and hydrogen ion quantities on the reaction rate.
13. Would you expect the rate to change if HNO_3 were used in place of HCl? What do you expect the rate to change if $HC_2H_3O_2$ were used in place of HCl? Justify your answers.

Pre-Experiment Questions Part Three

Thus far all experiments have been conducted at constant temperature. The next experiment explores the effect of temperature on the reaction rate.

14. Based on previous experience, predict the effect of increasing temperature on the reaction rate.
15. Which parameter(s) is/are most likely to be affected by temperature? Justify your answer.

16. Recall (or look up) the Arrhenius equation. Is your answer to TATD 14 consistent with the Arrhenius equation? Explain.
17. Linearize the Arrhenius equation. The class must reach consensus on the identity of the independent and dependent variables, the slope, and the intercept.
18. What data must be collected to determine the activation energy?

Experiment Part Three

Design a set of experiments that will allow determination the temperature dependence of the rate constant and thus the activation energy, keeping in mind the answers to TATD 14-18. After consulting with your instructor about your experimental design and making any appropriate revisions, perform these experiments using the general protocol. Obtain the activation energy for this reaction using shared data, and compare this result to the reported value.

Thinking About the Data Part Three

19. Write a general statement summarizing the effect of the activation energy on the rate constant.
20. Consider a reaction with the same rate law but twice the activation energy. Write a general statement comparing the temperature dependence of the reaction rates for the two reactions; you may want to do calculations at 25ºC and 50ºC.

Post-lab Questions

1. Why is it important to linearize equations?
2. Why are reaction rates measured at “short times”?
3. What considerations are important when choosing experimental parameters?
4. Read the following paper, Hibashi, F. *J. Chem. Educ.*, **1965**, *42*, 318-322, paying close attention to the section describing corrosion reactions of metals in acidic solution that evolve hydrogen. Are your results consistent with the mechanism proposed in this paper? Discuss the mechanism.
5. What are the kinetic parameters of a heterogeneous reaction?