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I am submitting herewith a thesis written by John Walter Clavier entitled "Investigation of Imprinted Sol-Gel Sorbents Containing Phosphonate Ligands." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirement for the degree of Master of Science, with a major in Chemistry.



Craig Barnes, Major Professor

We have read this thesis
and recommend its acceptance.



Accepted for the Council



Associate Vice Chancellor and
Dean of the Graduate School

**Investigation of Imprinted Sol-gel Sorbents Containing
Phosphonate Ligands**

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

John Walter Clavier

December 2000

Dedication

**This thesis is dedicated to my wife,
parents, and family,
from whom I draw support,
love and encouragement.**

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Abstract

This thesis describes the development of sol-gel materials containing bifunctional phosphonate ligands for the extraction of Sr^{+2} and UO_2^{+2} ions from solution. Previous techniques developed for removing Sr^{+2} and UO_2^{+2} ions from aqueous solutions have focused on solvent extraction methods. The extraction technique proposed here utilizes mesoporous sol-gel containing functionalized areas of phosphonate bifunctional compounds of the form $\equiv\text{SiCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$, $(\equiv\text{SiCH}_2\text{CH}_2\text{CH}_2)_2\text{C}[\text{P}(\text{O})(\text{OEt})_2]_2$, and $((\equiv\text{SiCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OEt})_2)_2(\text{OCH}_2\text{CH}_2\text{O}))$. By using a solid phase extraction sorbent, organic waste is minimized during the extraction process. The efficiency of Sr^{+2} and UO_2^{+2} ions extraction by these developed materials was investigated. Studies found that Sr^{+2} and UO_2^{+2} did not absorb onto the phosphonate ester based ligand sorbents. Imprinted phosphonic acid based sorbents did exhibit high affinities for both Sr^{+2} over nonimprinted phosphonic acid based sorbents. These studies also showed no selectivity between Sr^{+2} and Ca^{+2} . As for UO_2^{+2} , there was no increase in affinity for UO_2^{+2} between the imprinted and nonimprinted phosphonic acid based sorbents. However both sorbents showed selectivity between Ca^{+2} and UO_2^{+2} . Finally, the imprinted phosphonic acid sorbents had fast kinetics and could be regenerated in 2.0 M HCl.

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Chapter One

Introduction an Background

1.1 The Cold War and Its Legacy of Environmental Problems

With Japan on the brink of defeat, the United States needed a way to end World War II without sending thousands of American soldiers to their death with an invasion of mainland Japan. Starting in 1942, the U.S. Army Corps of Engineers began to develop technology capable of producing nuclear weapons under the Manhattan Project. In July of 1945, the first atomic explosion was seen in the Alamogordo desert.¹ Later that year, on August 6, the first atomic bomb was dropped on Hiroshima, Japan. Three days later, the second atomic bomb was dropped on Nagasaki, Japan. Japan surrendered after having two Japanese cities and thousands of human lives destroyed on August 14, 1945, ending World War II.

About this time, the western world was beginning to fear the communist power of the Soviet Union and vice versa. This fear would lead up to the now infamous Cold War. During this time, the United States and the Soviet Union began stockpiling nuclear weapons which required massive manufacturing efforts. These efforts continued until the 1980s when public concerns about safety and environmental problems caused various aspects of production to shut down. Finally in 1991, the Soviet Union dissolved, shutting down nuclear weapon production in the former Soviet Union countries and greatly reducing nuclear production in the United States. Although today the United States

maintains a reduced arsenal of nuclear weapons and a limited production capability, nuclear weapon manufacturing has been suspended ¹

During this time of stockpiling nuclear materials and weapons, the required manufacturing efforts generated large volumes of waste, resulting in considerable environmental contamination. For example, from 1944 until 1957, untreated liquid low-level radioactive waste from the Oak Ridge National Laboratory was discharged into White Oak Creek, which then flowed directly into the Clinch River. Today, the waters of White Oak Creek carry sediments contaminated with strontium-90, tritium, cesium-137, cobalt-60, and PCBs. These contaminants come from past laboratory discharges and waste storage area seepages.¹

Today, one of the Department of Energy's (DOE) Office of Environmental Management's primary missions with respect to many former nuclear weapons production sites is environmental restoration, waste management, nuclear material and facility stabilization, and technology development.¹ The DOE is responsible for maintaining all accumulated waste from DOE sites across the country. 89% (900 million curies) of this radioactive waste is associated with waste directly from weapons production, and the other 11% (110 million curies) has been generated from energy production.¹ 94% of this radioactive waste is classified as high-level waste (highly radioactive) which is stored in either highly acidic or a highly caustic solution. Most of the liquids contain toxic heavy metals, and some of the high-level waste also contains organic solvents and

cyanide compounds. This waste is stored mostly in underground single-shell tanks that are leaking (100 million gallons are estimated to have leaked to date) and considered unsafe by current standards.¹

The radioactivity in high-level waste comes from fission fragments and their daughter products resulting chiefly from the splitting of uranium-235 in production reactor fuel. Although radiation levels and health risks caused by short-lived fission products decrease dramatically in a few hundred years, risk attributable to long-lived isotopes in high-level waste will not change over thousands of years.¹ Most of the initial decay period and associated radioactivity is produced by cesium-137, strontium-90, and their short-lived daughter products. Radioactivity from long-lived isotopes (plutonium, americium, and uranium) form elements such as technetium-99 and carbon-14 which become the dominant component and pose the largest long-term potential risk.¹

Strontium-90 and cesium-137 are also found in transuranic waste and acidic low-level waste. Low-level waste is generated from many of the support facilities and activities (wastewater treatment, equipment maintenance) associated with both weapons production and nonweapons activities. Low-level waste is also generated from treated high-level waste and environmental restoration. Today there are massive volumes of low-level waste. Some low-level waste contains uranium-235, strontium-90, and cesium-137 which must be removed and routed to high-level waste sites before the low-level waste can be

disposed. The high-level waste may eventually be vitrified in borosilicate glass and buried in a geologic repository.¹

1.2 Toxicity of Strontium-90 and Uranium-235

Radionuclides with very long half-lives may be quite persistent in the environment but of such low activity that little environmental damage is caused. Radionuclides with intermediate half-lives are the most dangerous. They persist long enough to enter living systems while still retaining a high activity. Because they may be incorporated within living tissue, radionuclides of "life elements" are particularly dangerous.² Much concern has been expressed over strontium-90, a common waste product of nuclear weapons production and testing. This element is interchangeable with calcium in bone. Strontium-90 enters the environment either through surface water or by aquifers. Cattle could ingest the contaminated water which could eventually enter the bodies of offspring and humans by way of the cow's milk.^{2,3} Once in the liver, strontium-90 destroys or causes mutations which lead to cancer, liver failure, and eventually death for acute doses in dogs and mice.³

The metal uranium is chemically very active and can react with most elements except rare gases. It forms oxides with air, producing either UO_2 or U_3O_8 . Although uranium is the source of most fissionable isotopes, its fate in ecosystems has been poorly investigated.^{4,5} As with strontium, uranium is transported into organisms by air (from dust in the mining process), digestion

(milk, water, or food), or wounds. Blood is the principal carrier of uranium to such target organs as the liver.^{4,5} Once in the system, some forms of uranium pass through the system such as UO_2 or U_3O_8 , but other forms like uranium hexafluoride are very harmful to the liver, kidneys, and bone system.⁴ Once in the liver and kidneys, uranium destroys or causes mutation of cells which leads to cancer, liver failure, and eventually death for acute doses in mice, dogs, and rabbits.^{4,5}

1.3 Methods of Separation

Two techniques developed for the separation of metal ions from aqueous solution involve phase transfer and ion exchange. Phase transfer systems consist of the transfer of a solute in a mixture from one phase to another. One major type of phase transfer system is solvent extraction, a process in which a substance (metal ion) is transferred from solution in one solvent (water) to another solvent (organic) without any chemical change taking place.²

Separation of the organic phase from the aqueous phase results in a lower concentration of the metal ion in the aqueous phase. The major advantage of solvent extraction is that the process has fast kinetics and high metal ion selectivity. The disadvantages of solvent extraction include high cost, toxicity to the aqueous phase, and the large amounts of organic solvents needed for the process.⁶

Ion exchange is a means of removing cations or anions from solutions by binding them onto a solid resin, which can be regenerated by treatment with acids, bases, or salts.² In general, such solid supports have taken the form of functionalized organic polymers due to ease of preparation. There are special ion exchange resin configurations that have been designed for the removal of heavy metals such as copper, lead, nickel, and zinc from otherwise innocuous sludge constituents.⁷ Advantages of ion exchange over solvent extraction include the retention of extractant, ease of separation due to the heterogeneous nature of the system, and its sensitivity with dilute concentrations.⁸ The disadvantages of ion exchange are its slow kinetics due to the hydrophobicity of the organic support and lower selectivity for target metal ions than solvent extraction.

1.4 Mesoporous Sol-gel Process

In 1992, scientists at Mobil Oil research successfully synthesized ordered mesoporous metal oxide materials using surfactant micellar structures as templates.⁹ These mesoporous sieves can, for example, possess a hexagonal array of uniform mesopores. They can be synthesized with uniform channels varying from approximately 15 Å to greater than 100 Å in size. The relatively large pore sizes in these materials make them very attractive for applications such as catalysts, catalytic supports, and sorbents, especially when the molecules involved are too large to fit in the microporous channels of

conventional zeolites. The large pore materials typically have surface areas above 700 m²/g and hydrocarbon sorption capacities of 0.7 cc/g and greater.⁹

Mesostructure synthesis relies on surfactant micelles or liquid-crystal arrays of micelles as structure directing agents (templates) for the assembly and polymerization of inorganic precursors at the surfactant-solution interface.

Mesoporous silica molecular sieves have been prepared by the hydrolysis of tetraethylorthosilicate in the presence of low-cost, nontoxic, and biodegradable polyethyleneoxide surfactants, which act as the template. This nonionic, surfactant-neutral, inorganic-precursor templating pathway to mesostructures uses hydrogen bonding interactions between the hydrophilic surfaces of flexible micelles and Si(OC₂H₅)_{4-x}(OH)_x hydrolysis products to assemble an inorganic oxide framework.¹⁰ Removal of the organic template via calcination or extraction results in the mesoporous metal oxide.

A proposed mechanism for the formation of mesoporous silicon oxides is shown in **Figure 1.4**.⁹ Rodlike organic micelles (biodegradable polyethyleneoxide surfactants) are formed in aqueous solution and interact with the silicate precursors (tetraethylorthosilicate) to yield a stable structure with a few monolayers of silica around the outside walls. Spontaneous agglomeration of these composite species into a hexagonally packed arrangement is followed by further condensation of the silicate species to form the mesoporous material. Removal of the surfactant molecules by calcination or extraction results in the formation of silica with hexagonal arrays of tubular pores.⁹

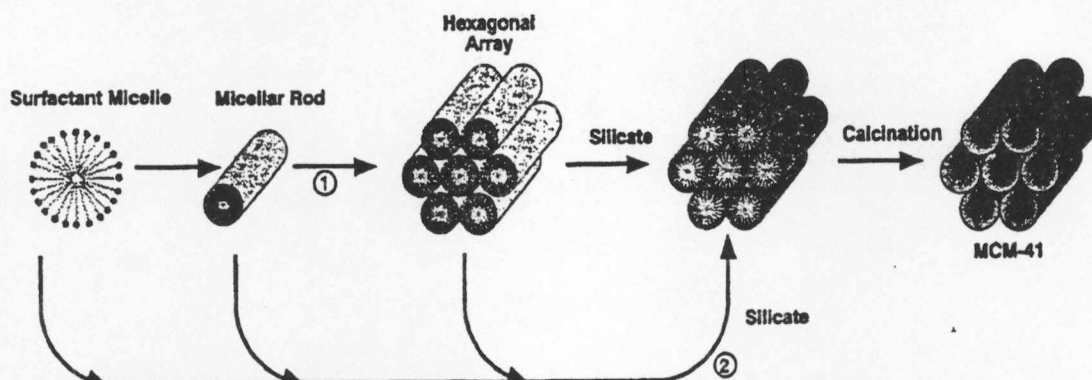
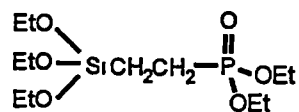


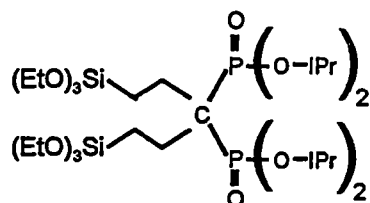
Figure 1.4 Mechanism for the formation of mesoporous material.⁹

1.5 Functionalized Monolayers on Mesoporous Support

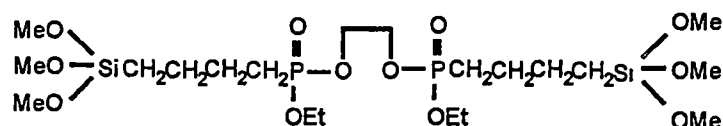
Recently, a new class of mesoporous material was developed based on organized monolayers of functional molecules bound to a mesoporous support (FMMS).¹¹ The functional molecules are attached to the mesoporous support similar to the preparation of self assembled monolayers (SAMs). FMMS can be engineered for surface area and pore size easier than SAMs. This is important because pore size is important for applications involving heavy metal uptake. Another disadvantage of SAMs is that the packing and order of ligands onto silica surfaces are defined by intermolecular forces.¹² In the case of FMMS, bifunctional molecules containing a hydrophilic head used for grafting to the gel and a hydrophobic functional tail provide the van der Waals interaction which is the driving force for the self-assembly of the molecule into the mesoporous material.¹² Within the context of FMMS based sorbents, three ligands (**Figure 1.5.1**): diethylphosphatoethyltriethoxysilane (mono phosphonate ligand), diethyltriethoxysilyl tetraisopropyl methanediphosphonate (bis phosphonate



Mono phosphonate



Bis phosphonate



Linked phosphonate

Figure 1.5.1 Phosphonate ligands chosen for the functionalized monolayer for the mesoporous supports.

ligand), and diethoxy dipropyltrimethoxysilyl glycol diphosphonate (linked phosphonate ligand) were chosen for the functionalized monolayer for the mesoporous supports.

These ligands are composed of two important parts. The first part is that the ligand must contain a group which may be covalently tethered to the surface of a porous silicate based sol-gel. This is accomplished by hydrolysis and covalent attachment of a triethoxysilane group. In the presence of water, the triethoxysilane group will hydrolyze and condense onto Si-OH groups on the pore surface of the mesoporous sol-gel. The second important part the ligand

must have is functional group, such as a phosphonic acids, that will bind hard oxophilic cations such as Sr^{+2} and UO_2^{+2} . Phosphonic acid groups are well known for their affinity for divalent and trivalent metal cations.^{13,14,15}

Instead of simply grafting ligands to the surface of mesoporous silica, the technique known as molecular imprinting to enhance the metal ion selectivity as illustrated in **Figure 1.5.2**. The technique of molecular imprinting involves the incorporation of a template (the metal ion) and a bifunctional ligand. The two are mixed together so that the metal binds to a set of ligands (step one). The complex assembly is then grafted to the surface of mesoporous silica (step two). Finally, the metal ion template is removed via acid (step three). This leaves what may be referred to as an imprinted cavity composed of the ligands and possibly surface binding sites which reflect the size and electronic signature of the initial template.

1.6 Arbuzov Rearrangement

The Michaelis-Arbuzov rearrangement, also known as the Arbuzov rearrangement, is one of the most versatile pathways for the formation of carbon-phosphorus bonds and involves the reaction of an ester of trivalent phosphorus with alkyl halides.^{16,17} **Figure 1.6a** shows the Arbuzov arrangement is the reaction of an alkyl halide with a trialkyl phosphite, yielding a dialkylphosphonate.

A possible reaction mechanism for the Arbuzov reaction is shown in **Figure 1.6.2**. The lone pair of electrons of the phosphite attacks the alkyl group

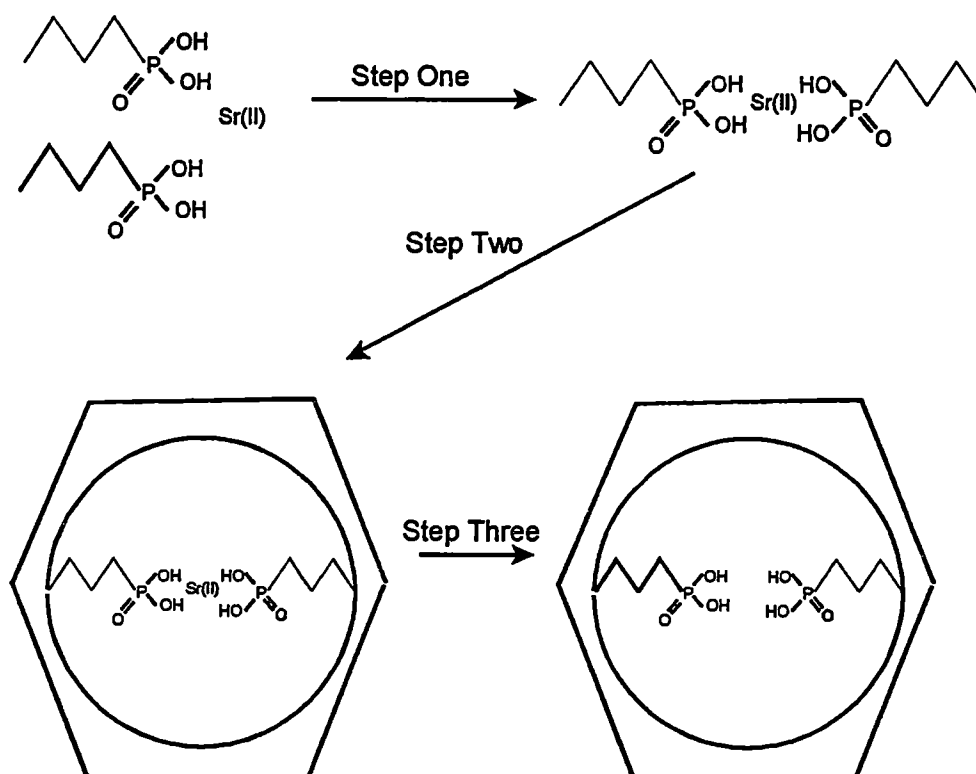
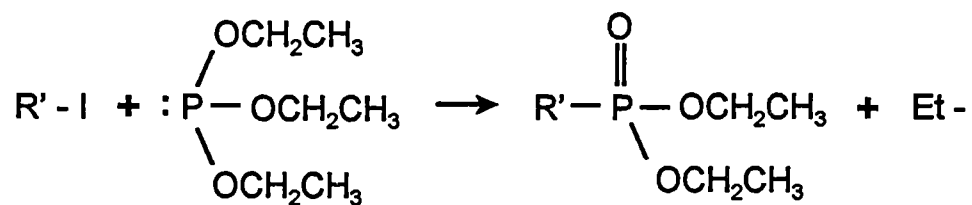


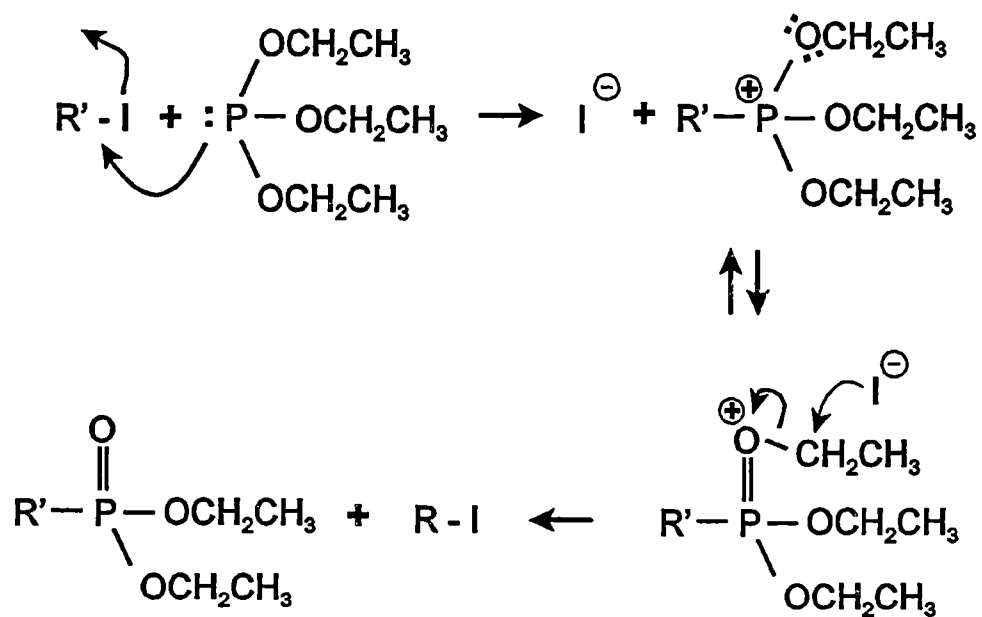
Figure 1.5.2 Molecular Imprinting

of the alkyl halide to form the addition compound **2** in which the alkyl group of the alkyl halide is attached to the phosphorus. In the next step, iodide attacks the methylene group which causes the positive charge to dissociate to the oxygen forming the double bond with the phosphorous forming a dialkylphosphonate and an iodidealkyl compound. During the transformation, a trivalent phosphorus P(III) is converted into a pentavalent phosphorus P(V).^{16,18}



R' = Alkyl group

Figure 1.6.1 Arbuzov rearrangement



R' = Alkyl group

Figure 1.6.2 Mechanism of the Arbuzov rearrangement

1.7 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) is one of the most powerful tools available to chemists and biochemists for determining and analyzing the structures of organic and inorganic compounds. NMR spectroscopy is based upon the measurement of absorption of electromagnetic radiation in the radio-frequency region of roughly 4 to 600 MHz. In contrast to ultraviolet, visible, and infrared absorption, spin active nuclei of atoms are involved in the absorption process.¹⁹ In the nuclear magnetic resonance experiment, transitions are induced between different energy levels by irradiating the nuclei with a magnetic field of the correct quantum energy, with electromagnetic waves of the appropriate frequency.²⁰ This condition enables the magnetic component of the radiation to interact with the nuclear dipole. Transitions from the lower to the upper energy level correspond to an absorption of energy, and those in the reverse direction to an emission of energy. Both transitions are possible. Each transition is associated with a reversal of the spin orientation. Due to the population excess in the lower level the absorption of energy from the irradiating field is the dominant process. This is the observed signal.²⁰ The intensity of an NMR absorption is proportional to the concentration.

1.7.1 Solution State NMR

Currently, state of the art NMR instruments use superconducting magnets

that have a much higher magnetic field strength than their predecessors. This gives these instruments much increased resolution and greater sensitivity. Instead of sweeping the magnetic field while irradiating the sample with electromagnetic energy in the radio frequency (rf) region, modern instruments irradiate the sample with a short pulse ($\sim 10^{-5}$ s) of rf radiation.^{19,21} This rf pulse excites all the nuclei at once. With the pulse method, a spectrum can be produced in as little as 5 seconds. The data are collected as a function of time. After the pulse, a signal is produced in the probe, and this signal contains information about the peaks simultaneously. The time domain signal must be transformed into a function of frequency before frequency domain absorption signals can be identified.^{19,21}

To transform the signal from the time domain to the frequency domain, a computer must carry out what is called a Fourier transformation (FT). After excitation by a radio frequency pulse, the signal is detected as a voltage in the NMR probe. Then, after amplification, the signal is digitized and stored in memory of the computer. Once enough data points are acquired to give the required digital resolution, the acquired data can be transformed by the Fourier method to a frequency spectrum.^{19,21} **Figure 1.7.1** shows a schematic diagram of a NMR.

A variety of solution state NMR instruments have been used in this study. They include the Bruker AC-250 MHz and AMX-400 MHz and the Varian Inova

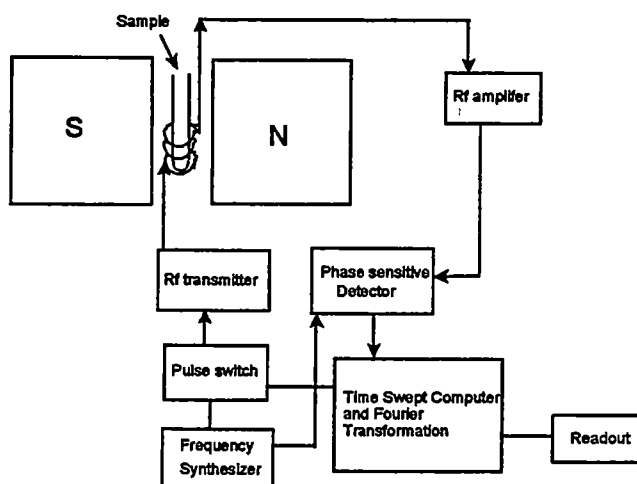


Figure 1.7.1 Schematic diagram of a nuclear magnetic resonance spectrometer ^[19].

600 MHz Fourier transform spectrometers. The nuclei studied on these instruments include ^1H , ^{13}C , ^{29}Si , and ^{31}P .

1.7.2 Solid State NMR

Sharp, high-resolution lines are a common feature of solution NMR spectra. In contrast, in solids fast molecular tumbling no longer occurs, and so this factor causes broad lines in the NMR spectra of powder samples. Fortunately, there is a simple way of resharpenering NMR signals for solid samples called magic angle spinning (MAS).²² In MAS, the sample is simply spun at a high rate of speed about an axis inclined at a magic angle ($55^\circ 74'$) with respect to the applied field (Figure 1.7.2).

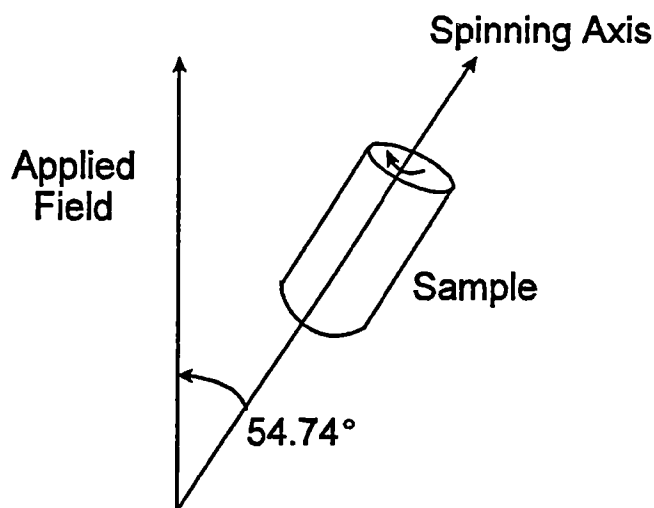


Figure 1.7.2 Magic angle spinning

A Varian 400 MHz solid state NMR instrument was used to study the following nuclei: ^{13}C , ^{29}Si , and ^{31}P . Two pulse programs were used. The first one, cross polarization with magic angle spinning (CP-MAS), gives spectra of solids that are not easily quantifiable but have a quality approaching that obtained routinely with solution NMR. Cross polarization refers to the transfer of magnetization from an abundant spin such as ^1H to a dilute spin such as ^{13}C .²² Cross polarization results in transverse magnetization for a dilute spin which is considerably larger than that which could be obtained by simply applying a 90° pulse to the dilute spin. It is not a high-resolution technique but improves signal to noise and accordingly is used extensively when observing ^{13}C and other dilute spins in solid samples.²² CP-MAS also helps to reduce the effective relaxation time of nuclei such as ^{13}C and ^{29}Si . It is often combined with ^1H decoupling

during acquisition. The other pulse program is referred to as Bloch decay. Bloch decay conditions use a normal one pulse excitation while decoupling other nuclei.

1.8 Brunaur-Emmett-Teller Gas Adsorption Analysis (BET)

The surface of a powder is an important factor which determines many of its properties. The Brunaur-Emmett-Teller (BET) method is the most widely used procedure for the determination of surface area of a powder. A BET gas adsorption analyzer consists of a gas storage system, a gas dosing system, a pressure measuring device, and a sample unit to which the gas is to be delivered.²³ A known amount of adsorbate gas is expanded into the sample system, and the amount which is unabsorbed is determined by applying the gas laws. The amount of gas adsorbed onto the surface of the solid sample is the quantity of gas unaccounted for.^{23,24}

Pores can be characterized according to their size. The pore size is a real observation, which indicates if the material contains macropores (>500 Å in diameter), mesopores (20 Å to 500 Å), or micropores (<20 Å).^{23,25} Porosity of powders and other porous solids can be conveniently characterized by gas adsorption. Two common parameters used to describe porosity are total pore volume and pore size distribution. The total pore volume can be described as the amount of vapor adsorbed at a relative pressure P/P_0 , close to unity. An assumption is made that at this relative pressure, the pores are filled with liquid

adsorbate. The volume of N₂ gas adsorbed, V_{ads} , can then be converted to the volume of the liquid N₂, V_{liq} , contained in the pores by the following equation:²³

$$V_{liq} = \frac{P_a V_{abs} V_m}{RT} \quad (\text{Eq. 1.8.1})$$

In this equation, P_a and T are ambient pressure and temperature, and V_m is the molar volume of the liquid adsorbate (34.7 cm³ / mole for nitrogen). The average pore size can then be estimated by the pore volume. Assuming cylindrical pore geometry, the average pore radius r_p can be written as:

$$r_p = \frac{2 V_{liq}}{S} \quad (\text{Eq. 1.8.2})$$

where V_{liq} is obtained from equation 1.8.1 and S is the BET surface area.

The distribution of pore volume with respect to pore size is called the pore size distribution. The pore size distribution indicates which sizes of pores make up the majority of the pore volume.²³ A narrow pore size distribution is represented by a sharp peak on a plot of pore volume versus average pore diameter (**Figure 1.8**), and indicates that a solid is made up of fairly uniform pore size throughout the bulk of the material.

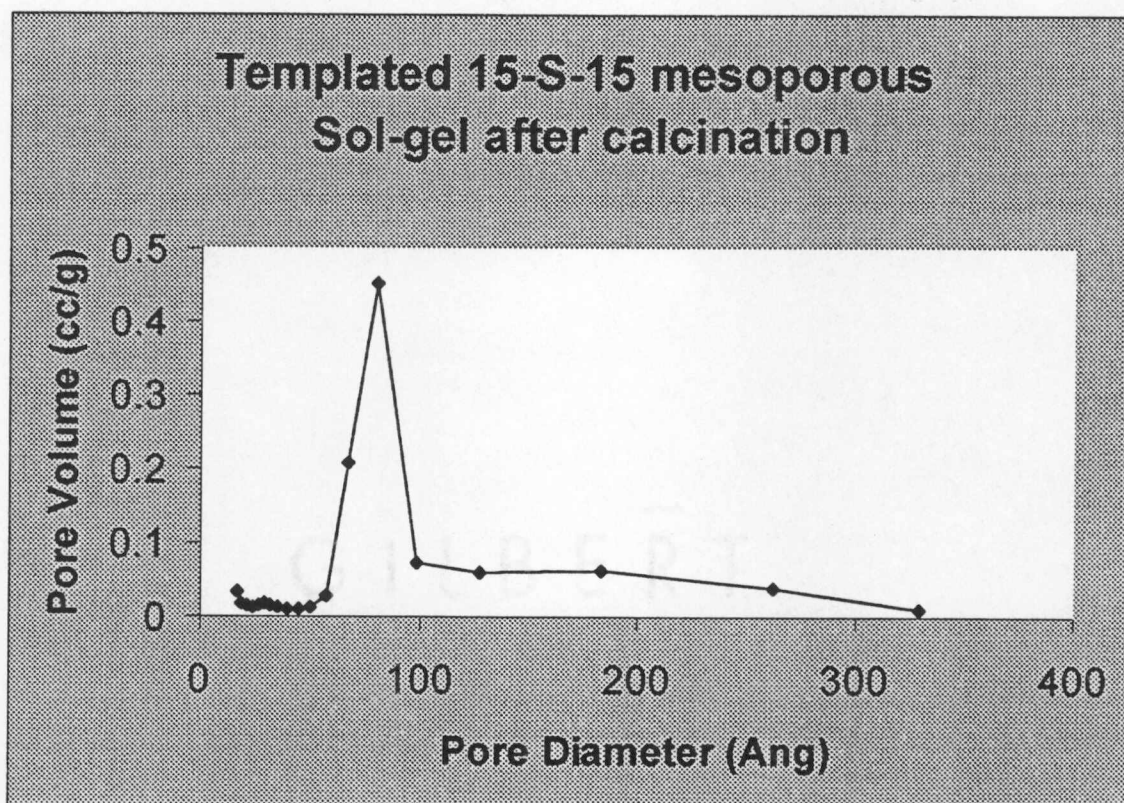


Figure 1.8 Plot of pore size distribution

1.9 Atomic Emission Spectroscopy (AE)

Atomic emission spectroscopy is a method of spectrochemical analysis that is based on the transformation of the sample into the vapor state and its subsequent excitation in a chemical flame. The spectrum of radiation emitted by the vapor state is characteristic of the elements contained in the sample (qualitative analysis). The intensity of a unique spectral line is a measure of the concentration of the metal emitting that line (quantitative analysis).²⁶

Some advantages of atomic emission compared to chemical methods of analysis are its sensitivity (10^{-5} to 10^2 ppm), its precision (1% or better), and

rapidity. Generally, atomic emission is more convenient, faster to use, and relatively free from interferences when compared with atomic absorption for difficult to determine elements.¹⁹ The limit of detection for strontium is as low as 0.02 mg/L with flame emission using a C_2H_2/N_2O flame.²⁷ Another advantage is the rather simple construction and operation of the flame photometer compared with other physical methods of analysis. The possibility of simultaneously analyzing two or more elements in the same sample, or to analyze minute quantities of sample materials are also advantages of the technique. A possible disadvantage is that the sample must be converted into a liquid solution. Another disadvantage is the interference effect in the analysis of samples with a complex and varying composition, which arises when the emission signal for a given concentration of analyte also depends on the presence and concentration of contaminants in the solution, such as HCl or other metals.²⁶ This problem can be avoided if the composition of the standard samples closely resembles that of the sample to be analyzed.

The methodology for atomic emission is similar to atomic absorption and is shown in the schematic diagram, in **Figure 1.9**. Typical atomic absorption instrumental components are: a spectral light source, a chopper system, a flame, a nebulizer, a monochromator, a detector with its power supply, and lock-in amplifier system connected to a suitable readout recorder or a digital integrator. In the case of atomic emission, the instrument is operated without the light source and the chopper system is located between the flame and the monochromator.²⁶

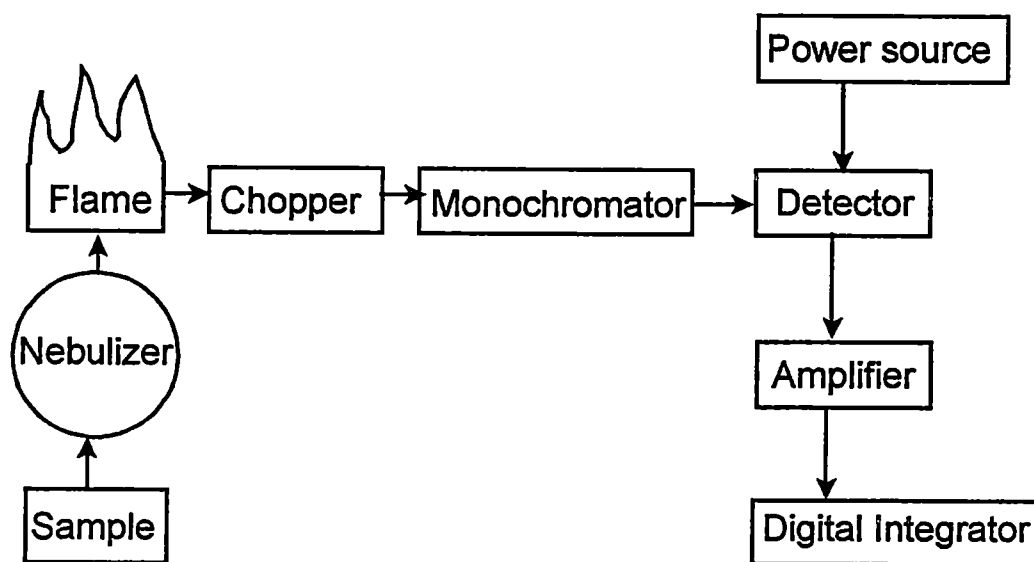
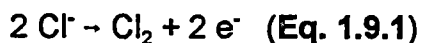


Figure 1.9 Schematic diagram of atomic emission

In atomic emission analysis the sample to be analyzed is first converted to liquid form. This solution is aspirated into a pneumatic nebulizer and dispersed as a fine spray of droplets. This spray is carried into the flame by the gas that operates the nebulizer. The flame is produced on a burner by combustion of a fuel gas (C_2H_2) with an oxidant gas (N_2O). Under the influence of the high temperature of the flame the solvent evaporates and the remaining dry aerosol particles volatilize from the solid or molten state into the gaseous state.²⁶

The flame temperature plays an important role in the excitation and usually in the atomization of the sample. High temperatures are required with strontium because chemical interferences can occur when strontium comes in contact with carbonate ions and phosphate ions. A C_2H_2 / N_2O flame achieves temperatures high enough to enhance the rate of decomposition of strontium compounds, thus

reducing the effects of chemical interferences. The loss of neutral atoms due to ionization of strontium is considerable at this high temperatures. To reduce this effect, an ionization suppressor is used.²⁷ Ionization suppressors such as KCl act by supplying electrons to the flame to reduce Sr^{2+} ions formed in the flame. For example, chloride ions are oxidized supplying electrons for the reduction of strontium.



Flame emission analysis is similar to atomic absorption except the sample itself is the source of light. Rather than photons of light being absorbed by the metal atoms in the flame, photons of light are emitted as metal atoms that are excited and then relax back to their ground state. A suitable line or band of the element is selected from the flame spectrum by a spectral filter or monochromator and it is detected by means of a photcell (barrier-layer cell or photomultiplier tube). The photocurrent of the cell is often amplified by electronic means before it is measured by a read-out meter.²⁶

After deciding upon the conditions for the analysis, it was necessary to prepare a calibration curve from a series of standard solutions. These standards have the approximate concentration and chemical make up of the actual samples. Typically a five (blank, 0.19, 0.38, 0.75, 1.5 ppm) point calibration curve for the different pH buffered strontium standards is prepared. An average calibration curve had a R^2 of 0.999 based on simple least square fitting of the data to a line.

1.10 Ultraviolet / Visible Spectroscopy (UV/vis)

When electromagnetic radiation passes through a compound, a portion of the radiation is usually absorbed by the compound. Ultraviolet / visible spectroscopy is used to measure the amount of light absorbed at each wavelength of the visible and UV regions by a compound. The amount of radiation that is absorbed depends on the wavelength of the radiation and the composition of the compound. The absorption of UV/vis radiation causes excitation of electrons in orbitals of lower energy to orbitals of higher energy.²¹

Instruments for measuring the absorption of ultraviolet and visible radiation are made up of a source, wavelength selector, sample container, radiation detector, signal processor, and readout device.¹⁹ All measurements performed in this study were performed using a Hewlett-Packard 8452A Diode Array spectrophotometer with a deuterium lamp. Deuterium lamps give a continuous output in the ultraviolet region of 160 nm to 820 nm.

Absorbance is directly proportional to the pathlength (b) through the solution and the concentration (c) of the absorbing species as seen in **Equation 1.10**. When the concentration is expressed in moles per liter and the cell length is in centimeters, the absorptivity is called molar absorptivity (ϵ)^[19].

$$A = \epsilon bc \quad (\text{Eq 1.10})$$

After deciding upon the conditions for the analysis, it was necessary to prepare a calibration curve from a series of standard solutions. These standards should have the approximate concentration and composition of the actual samples.

1.11 Spectrophotometric Measurement of Uranyl Adsorption Capacity

The adsorption capacity of sol-gel sorbents toward uranyl can be measured by Arsenazo III (2,2'-(dihydroxy-3,6-disulphonaphthalene-2,7-bisazo)bisbenzenearsonic acid, H_8A), (Figure 1.11.1). This is one of the most often used azo-dyes in spectrophotometry, especially for the determination of lanthanide and actinide ions. Arsenazo III is an octabasic weak acid.²⁸ Arsenazo III exhibits a high sensitivity to lanthanides (III) over the range of pH 3-4. Arsenazo III forms a 1:1 complex with uranyl ion.²⁹ A considerable shift of the absorption spectrum of the uranyl complex (665 nm) is observed when compared to the absorption spectrum of the reagent (530 nm) (Figure 1.11.2). This makes it possible to obtain maximum sensitivity during the determination of uranyl when working at the optimum wavelengths of 660 to 665 nm.³⁰ Under moderately acidic conditions the spectrum of the arsenazo III-lanthanide complex consists of two sharp peaks at approximately 605 and 650 nm.³¹ Previous work found that the absorbance of the 650 nm peak has its maximum intensity at pH 3-4.³¹ The detection limit obtained using the color forming reactions is extremely low (0.05 to 0.1 $\mu\text{g/mL}$ of the element).

The photometric determination of uranyl ion was carried out at pH=5.0. First, a baseline was taken using ultra pure water in the range of 400-800 nm. Second, the absorbance of the uranyl standard solution was measured and then the absorbance of the solutions which have been treated with nonimprinted and imprinted functionalized molecules bound to a mesoporous support (FMMS)

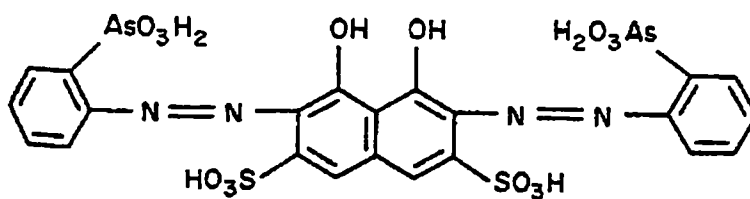


Figure 1.11.1 Structure of Arsenazo III

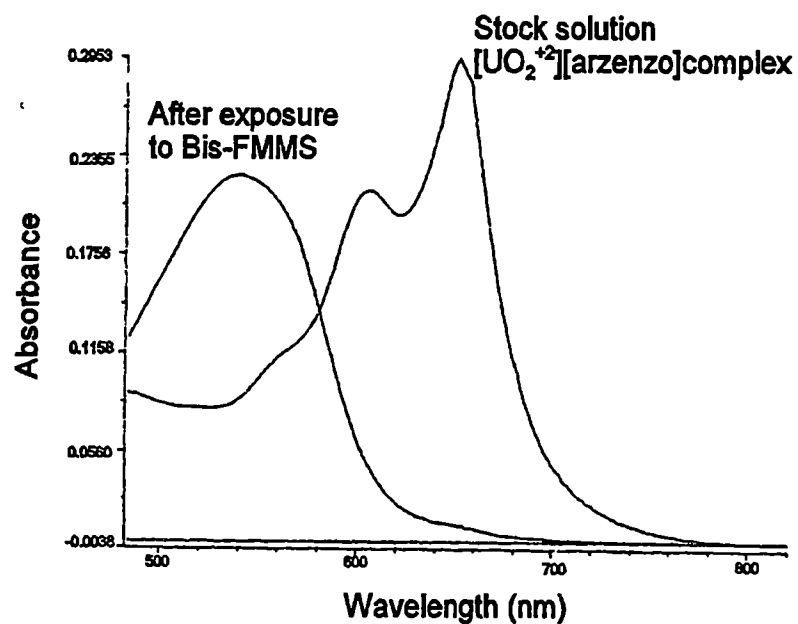


Figure 1.11.2 UV/vis spectra of Arsenazo III and Uranyl-Arsenzo III complex

sorbents were measured. The mixture of 3.0 mL of 1×10^{-5} M Arsenazo III solution, 5 μ L of 4N aqueous HCl, and 20 μ L of uranyl buffer solution (0.05 M sodium acetate/ acetic acid pH=5.0) was used for quantitatively determining the concentration of uranyl ion.³⁰ Using seven different uranyl standard solutions (blank, 3.13, 6.25, 12.5, 25, 50, 100 ppm), the molar absorptivity (ϵ) was calculated to be 2930 L / mol*cm at 652 nm for the uranyl- Arsenzo III complex.

1.12 Parameters Characterizing Adsorption of Metal Ions

Hazardous waste dissolved in groundwater can be attenuated by soil and rock by means of various sorption mechanisms. Mathematically, the distribution of a solute between groundwater and soil is expressed by a distribution coefficient (K_d). The distribution coefficient is represented by **Equation 1.12a**. C_s is the equilibrium concentration of the species in the solid phase and C_w is its concentration in water.²

$$K_d \left(\frac{\text{mL}}{\text{g}} \right) = \left(\frac{C_s}{C_w} \right) = \frac{\frac{\mu\text{g of Sr(II) absorbed}}{\text{g of gel}}}{(\mu\text{g / mL) of Sr(II) remaining}} \quad (\text{Eq. 1.12a})$$

1.13 Overview to Chapter 2, 3, and 4

In Chapter 2, the synthesis of the three ligands:
diethylphosphatoethyltriethoxysilane (mono phosphonate ligand),

diethyltriethoxysilyl tetraisopropyl methanediphosphonate (bis phosphonate ligand), and diethoxy dipropyltrimethoxysilyl glycol diphosphonate (linked phosphonate ligand) will be discussed. These ligands are composed of a group which may be covalently tethered to the surface of a porous silicate and a functional group, such as a phosphonic acid, that will bind hard oxophilic cations such as Sr^{+2} and UO_2^{+2} . Phosphonic acid groups are well known for their affinity for divalent and trivalent metal cations.^{13,14,15} These ligands are characterized using NMR and IR techniques.

In Chapter 3, mesoporous silica coated with functionalized monolayers (FMMS) will be discussed. FMMS have demonstrated a remarkable ability to absorb heavy metals from contaminated water, making it a promising tool for environmental cleanup. In this chapter, the synthesis of templated mesoporous sol-gels will be discussed. The mesoporous sieves possess a hexagonal array of uniform mesopores. They can be synthesized with uniform channels varying from approximately 15 Å to greater than 100 Å in size. Large pore size is needed for fast uptake of metal ions. This silica material will serve as a mesoporous support for functionalized monolayers of the three ligands discussed in Chapter 2.

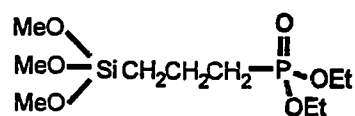
Finally in Chapter 4, the different FMMS materials described in Chapter 3 will be introduced to different metal cations to determine if these materials are selective, have fast kinetics, and have high affinity to be effective at removing low concentration of metal ions in solution. The two divalent metal cations studied are strontium and uranyl in the presence of calcium, sodium, and potassium.

Chapter Two

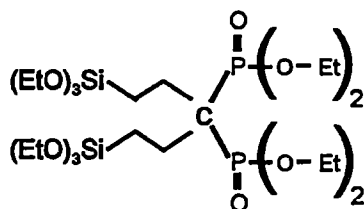
Synthesis of Phosphonate Ligands

2.1 Introduction to chapter 2

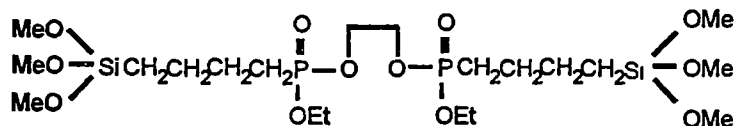
In this Chapter, the synthesis of the three ligands, diethylphosphatopropyl-3-triethoxysilane (mono phosphonate ligand), 1,7-di(triethoxysilane) 4,4 bis(diethylphosphoato) heptane (bis phosphonate ligand), and di(3-trimethoxy silyl propyl) glycol diphosphonate (linked phosphonate ligand) will be discussed (Figure 2.1.1). These ligands are composed of two important parts. The first part is a group which may be covalently tethered to the surface of a porous silicate based sol-gel. This is accomplished by hydrolysis



Mono phosphonate



Bis phosphonate



Linked phosphonate

Figure 2.1.1 Phosphonate ligands

and covalent attachment of a triethoxysilane group (**Figure 2.1.2**). In the presence of water, the triethoxysilane group will hydrolyze and condense onto the mesoporous sol-gel. The second important part the ligand must have is a functional group, such as a phosphonic acid, that will bind hard oxophilic cations such as Sr^{+2} and UO_2^{+2} . Phosphonic acid groups are well known for their affinity for divalent and trivalent metal cations.^{13,14,15}

2.2.1 Introduction to First Generation Ligand

The simplest, first generation ligand that was prepared in this study contains a single alkyl phosphonate group linked to a triethoxysilane group which can be grafted to the surface of mesoporous sol-gel.

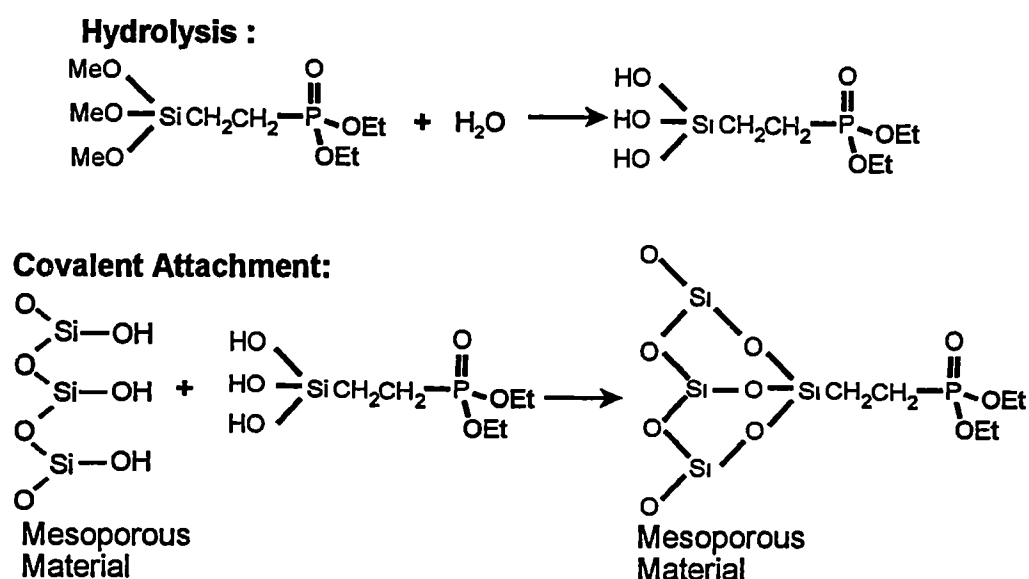


Figure 2.1.2 Hydrolysis and covalent attachment of phosphonate ligands onto mesoporous sol-gel. Note: condensation may not be complete and some Si-OH groups may remain in the final product.

Diethylphosphatoethyltriethoxysilane was at one time commercially available from Gelest but is no longer carried, so diethylphosphatoethyltriethoxysilane had to be synthesized.^{50,51} In order to synthesize the mono phosphonate ligand, a procedure had to be developed to connect a phosphonate group to a triethoxysilane group so the ligand could be grafted to mesoporous sol-gel. Initially, the desired ligand was prepared via the radical coupling between vinyltrimethoxysilane and diethylphosphite (**Figure 2.2.1.1**). A reaction was discovered that used azoisobutyric dinitrile (AIBN).³² AIBN acts as a free radical initiator in the coupling of vinyltrimethoxysilane and diethylphosphite. Subsequently, it was discovered that an Arbuzov reaction could be used to synthesize the same mono phosphonate ligand. In this case, triethylphosphite and 3-iodopropyltrimethoxysilane were reacted together (**Figure 2.2.1.2**). This synthesis proved to be the better of the two methods because it produce a cleaner product, was easier to synthesis, and took less time to produce.

2.2.2 Experimental Section

All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. NMR solvents were dried and stored over 5 Å

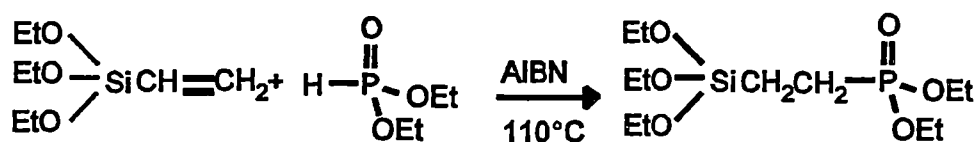


Figure 2.2.1.1 Reaction using AIBN

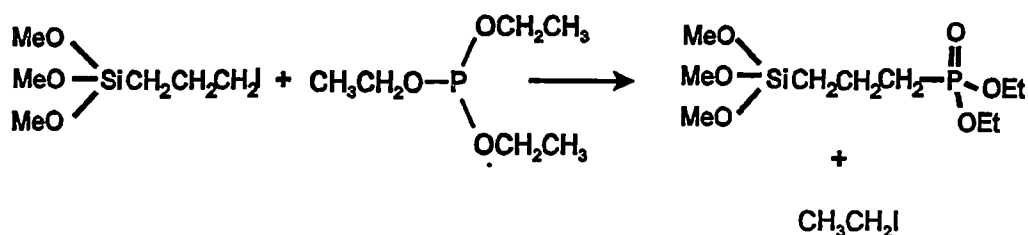


Figure 2.2.1.2 Arbuzov reaction

molecular sieves. Triethylphosphite (Strem), azoisobutyric dinitrile (K and K Laboratories), vinyltrimethoxysilane (Aldrich), 3-iodopropyltrimethoxysilane (Gelest), diethylphosphite (Aldrich), diiodomethane (Aldrich), tetraisopropyl methylenediphosphonate (Aldrich), sodium hydride (Aldrich), allyl bromide (Acros), chloroplatinic acid hexahydrate (Strem), calcium carbonate (Fisher), celite (Johns-Manville), phosphorus trichloride (Acros), anhydrous ethyl ether (Fisher), magnesium sulfate (Fisher), iodoethane (Aldrich), and triethoxysilane (Gelest) were used as received. Ethylene glycol (Mallinckrodt) and triethylamine (Fisher) were dried with NaOH and distilled. Hexane (Fisher), toluene (Fisher) and THF (Fisher) were dried with sodium alloy and distilled. NMR spectra were recorded on Bruker AC-250 and AMX-400 Fourier transform spectrometers. Chemical shifts were referenced to d-chloroform (residual ^1H -NMR δ 7.26 ppm, ^{13}C -NMR δ 77.0 ppm). ^{31}P chemical shifts were referenced to phosphoric acid (δ 0.00 ppm). ^{29}Si chemical shifts were referenced to cubic octamer silic acid trimethylsilyl ester (δ 12.4 ppm and δ -108.6 ppm).

2.2.3 Synthesis of Diethylphosphoatoethyl-3-triethoxysilane Using AIBN

Diethylphosphoatoethyl-3-triethoxysilane was synthesized using vinyltriethoxysilane, AIBN, and diethylphosphite. Under a nitrogen atmosphere Schlenk vessel, vinyltriethoxysilane (14.46 g, 0.076 mol), AIBN (33 mg), and diethylphosphite (28.99 g, 0.23 mol) were combined and heated to 110 °C and stirred vigorously for one hour. After one hour, an additional 33 mg of AIBN was added and stirred for another hour. After the second hour, a final portion of 33 mg of AIBN was added, and the solution was stirred for five more hours. The solution was allowed to cool followed by vacuum distillation (0.05 mm Hg). There were two major fractions. The first fraction, which boiled between 20-25 °C, was composed of diethylphosphite. The second fraction, which boiled between 90-110 °C, was composed of diethylphosphoatoethyl-3-triethoxysilane. This reaction gave a 40% yield.

2.2.4 Synthesis of Diethylphosphoatopropyl-3-trimethoxysilane via the Arbuzov Reaction

Diethylphosphoatopropyl-3-trimethoxysilane was synthesized using 3-iodopropyltrimethoxysilane and triethoxyphosphite. In a 50 mL three neck round bottom flask fitted with a condenser, dropping funnel, and a nitrogen line, 3-iodopropyltrimethoxysilane (7.35 g, 0.025 mol) was heated to 110 °C. Triethylphosphite (2.08 g, 0.0125 mol) was placed in the dropping funnel and added dropwise into the heated 3-iodopropyltrimethoxysilane. Nitrogen was

gently blown through the round bottom to remove iodoethane generated a byproduct in the initial Arbuzov reaction. The solution was stirred for two hours and then allowed to cool to room temperature. The mixture was then vacuum distilled (0.5 mm Hg). Three fractions were collected. The first fraction was composed of 3-iodopropyltrimethoxysilane, b.p 40-45 °C. The second fraction, which boiled between 50-55 °C, was composed of diethylethanephosphonate. The third fraction, b.p. 90-110 °C, was composed of diethylphosphoatopropyl-3-trimethoxysilane. This reaction gave a higher yield of 70% compared to the 40% yield of the AIBN reaction.

2.2.5 Characterization of Diethylphosphoatopropyl-3-trimethoxysilane (mono phosphonate ligand)

^1H , ^{13}C , ^{31}P -NMR data were all used to characterize diethylphosphoateopropyl-3-trimethoxysilane. **Figure 2.2.5.1** shows the proton spectrum of diethylphosphoatpropyl-3-trimethoxysilane. The large singlet at δ 3.5 ppm (H_a) arises from the methoxy groups attached to the silane. There are two unique multiplets assigned to protons H_b (δ 0.84 ppm) and H_c (δ 1.75 ppm). These two multiplets arise from the protons on the propyl bridge between the trimethoxysilane group and the alkyl phosphonate group. The splitting observed in these multiplets is derived from proton coupling to adjacent protons and short (^2J) and long (^3J) range phosphorus coupling. One triplet is also observed at δ 1.30 ppm (H_f). This triplet is assigned to the terminal protons of the ethoxy

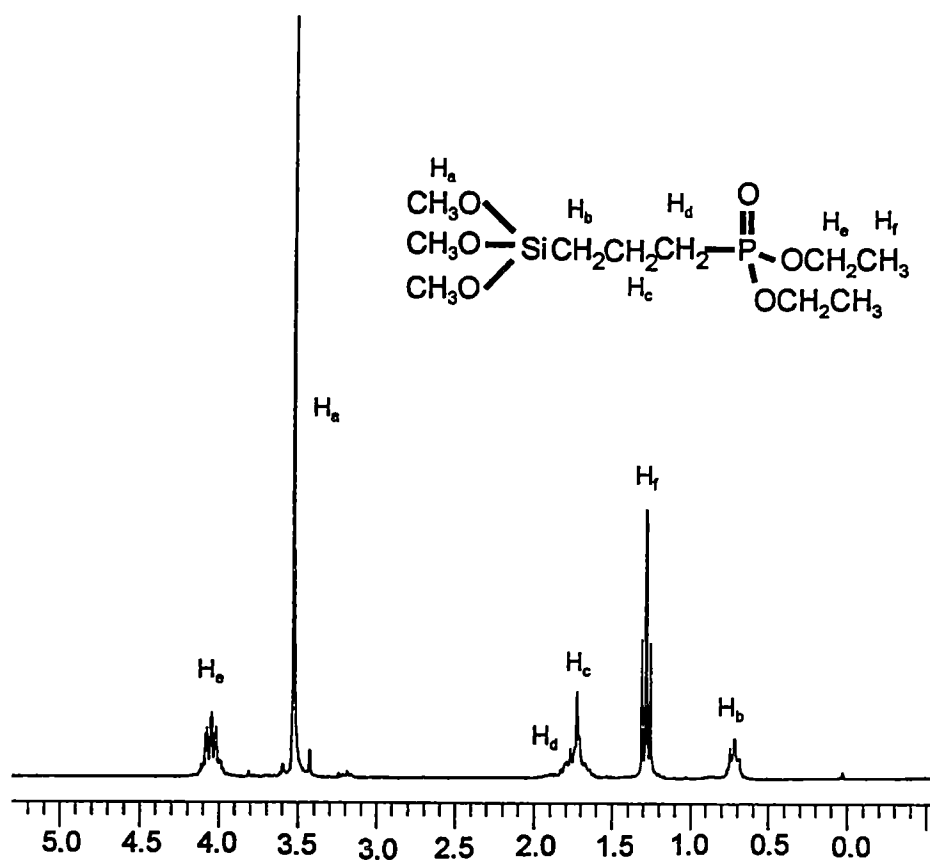


Figure 2.2.5.1 ¹H-NMR spectra of diethylphosphatopropyl-3-trimethoxysilane

groups (H_F) attached phosphorus. Downfield at $\delta 4.25$ ppm (H_e) is a multiplet which is assigned to the methylene of the ethoxy group attached to the phosphorus. The multiplet at $\delta 1.80$ ppm (H_d) is observed as a unique doublet of quartets due to the coupling of the adjacent phosphorus ($^2J_{H-P}$).

Figure 2.2.5.2 shows the carbon spectrum of diethylphosphoatopropyl-3-triethoxysilane. The triplet at $\delta 77.0$ ppm is from the solvent d-chloroform. The signal at $\delta 15.5$ ppm is due to the terminal carbons of the ethoxy group (C_f). The signal at $\delta 60.0$ ppm is the methyne carbon of the ethoxy group (C_e) and the signal is shifted downfield due to the desheilding effects of the adjacent oxygen. Carbon (C_d) gives a unique doublet at $\delta 28.0$ ppm. This doublet is due to the phosphorus coupling ($^1J_{C-P} = 139$ Hz). This coupling constant is similar to a known literature coupling constant value of $^1J_{C-P}$ 142 Hz.³³ The singlet at $\delta 49.2$ ppm is assigned to the methoxy group (C_a). The two signals furthest upfield at $\delta 9.7$ ppm and $\delta 9.9$ ppm are assign to carbons C_b and C_c . A signal ($\delta 32.4$ ppm) was observed in the ^{31}P -NMR spectrum of diethylphosphoatopropyl-3-trimethoxysilane. One signal ($\delta -50.3$ ppm) was observed in the ^{29}Si -NMR spectrum. **Figure 2.2.5.3** and **Table 2.2.5** gives the IR spectrum and signals seen for diethylphosphoatopropyl-3-trimethoxysilane.

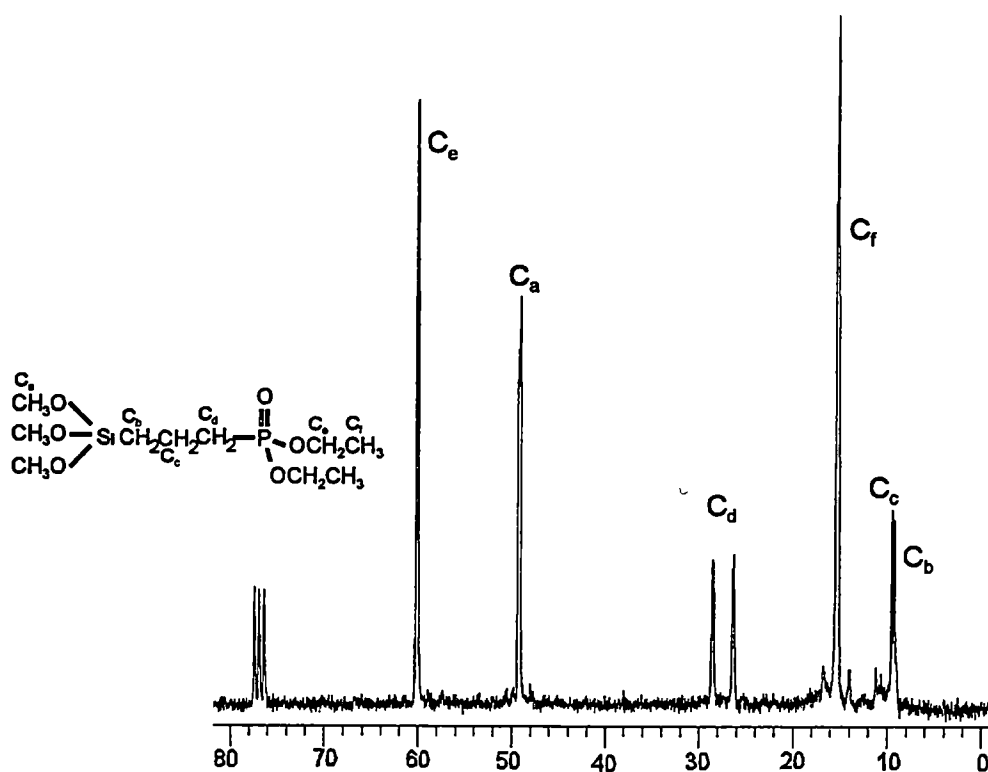


Figure 2.2.5.2 ¹³C-NMR spectra of diethylphosphatopropyl-3-trimethoxysilane

Table 2.2.5 IR assignment for diethylphosphatopropyl-3-trimethoxysilane

Assignment	Range	Comments
CH_3CH_2	2942 cm^{-1}	broad and strong
$\text{CH}_2\text{-O}$	2841 cm^{-1}	sharp and strong
$\text{P-O-CH}_2\text{CH}_3$	1231 cm^{-1}	broad and strong
P=O	1183 cm^{-1}	sharp and strong
Si-O-C	1085 cm^{-1}	broad and strong

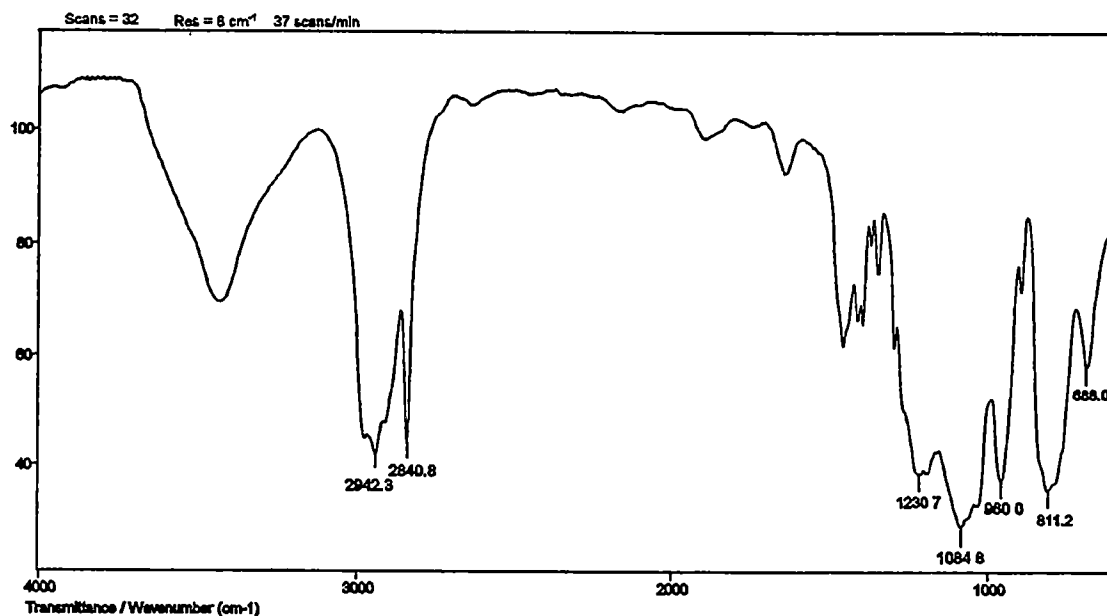


Figure 2.2.5.3 IR spectrum of diethylphosphatopropyl-3-trimethoxysilane

2.3.1 Introduction to the Second Generation Ligand

The second generation ligand contains an alkyl diphosphonate group linked to a triethoxysilane group required for binding to the surface of mesoporous sol-gel. This ligand was designed to chelate to a cationic metal ion. In general, since a chelating agent may coordinate to a metal ion in more than one place simultaneously, chelates are more stable than complexes involving unidentate ligands, such as the monophosphonate ligand described above. The stability of a metal-ligand complex tends to increase with the number of chelating sites available on the ligand.²

It is known that diphosphonate ligands have very high stability constants with trivalent metals ions such as Fe^{3+} , In^{3+} , Ga^{3+} , Gd^{3+} , and Nd^{3+} .¹⁴ For example, methylenediphosphonic acid forms a complex with Eu(III) which is 1000 times more stable than europium complex involving comparable dicarboxylate ligands.¹⁵ Diphosphonic acids are soluble in water which makes their application to the recovery of metal ions from aqueous solutions very favorable. Two diphosphonate groups, tetraisopropylmethylenediphosphonate (TIMDP) and tetraethylmethylenediphosphonate (TEMDP), were incorporated into second generation ligands. The synthesis of the diphosphonate ligand consists of the following steps (**Figure 2.3.1**). In step one, excess sodium hydride is used to deprotonate one of the methylene protons. Next, at least 2 equivalents of allylbromide are added for the alkylation of mono anion **1** to form 4,4-

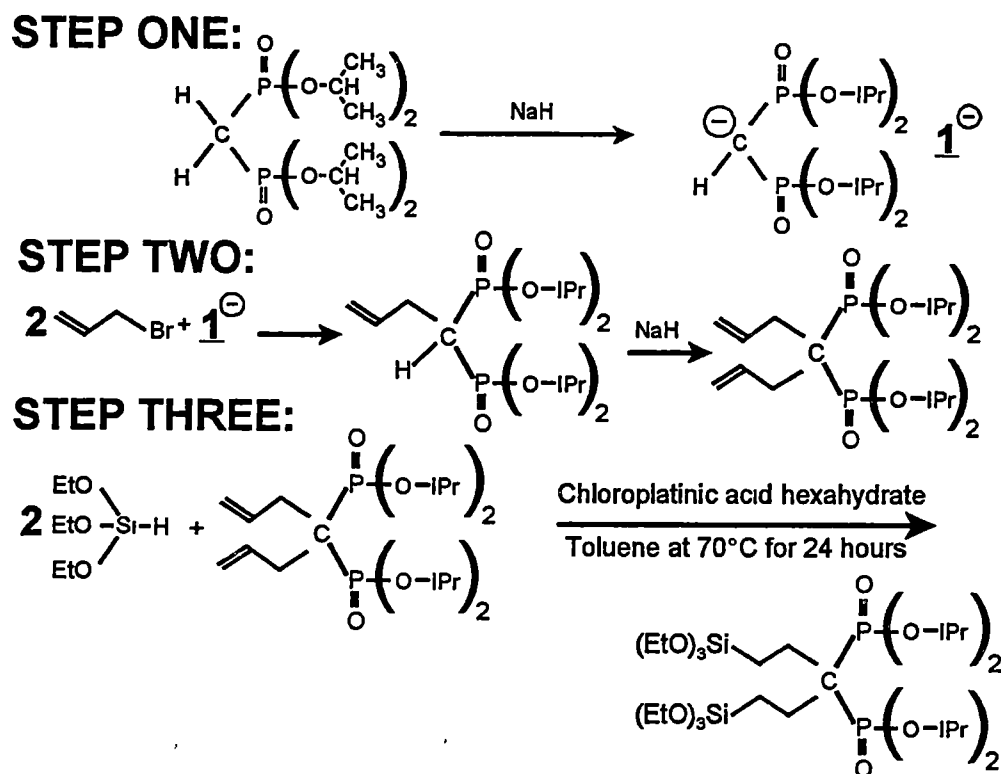


Figure 2.3.1 Synthesis of the diphosphonate ligand

diethylphosphonate 1-butene. These steps are repeated with the excess NaH and second equivalent of allylbromide to finally produce the 4,4-diethylphosphonate hepta-1,6-diene. Finally in step three, diethyltriethoxysilyl tetraisopropylmethanediphosphonate was synthesized using hydrosilylation with triethoxysilane using a platinum catalyst.

2.3.2 Synthesis of Tetraethyl Methylenedisphosphonate (TEM DP)

The synthesis of TEM DP has been reported by Kosolapoff.³⁴ The synthesis consists of a double Arbuzov reaction between diiodomethane and 2

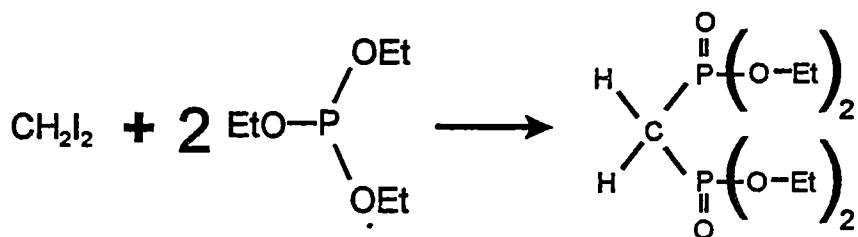


Figure 2.3.2 Synthesis of Tetraethyl
Methylenedisphosphate (TEM DP)

moles of triethylphosphite (**Figure 2.3.2**). Triethylphosphite (19.25 mL, 0.11 mol) and diiodomethane (25 mL, 0.44 mol) in a 4:1 molar ratio were mixed in 100 mL two neck round bottom flask which was attached to a N₂ line, condenser, and a distillation fraction collector. The mixture was heated rapidly in a preheated oil bath at 140 °C for 30 minutes. The signal of the start of the reaction was the rapid evolution of ethyl iodide, which was collected in the cooled fraction collector. After gas evolution had ceased, the reaction mixture was distilled under reduced pressure, 0.01 mmHg, through a 30 cm long vacuum jacketed column. Three fractions were collected. The first fraction was composed of diethyl ethanephosphonate and ethyl iodide, b.p. 20 - 55 °C (mostly at 45 -55 °C). The second fraction, which boiled between 70-75 °C, was composed of diethyl iodomethanephosphonate. The third fraction (80% yield) consisted of the desired product, tetraethyl methanediphosphonate, and boiled at 85 - 90 °C.

NOTE:

In the future, we feel that the synthesis of TEM DP could be made more efficiently by using a dropping funnel to slowly add triethylphosphite at a lower

temperature. In the above method, when diiodomethane and triethylphosphite are reacted at 140 °C, iodoethane is produced. Iodoethane is a competitor to diiodomethane in the Arbuzov reaction. Iodoethane reacts with triethylphosphite to form diethyl ethanephosphonate and another equivalent of iodoethane, both of which are unwanted. In the above reaction, iodoethane is collected in a cooled receiver. The problem with this procedure is that not all of the iodoethane is removed from the reaction mixture so that a significant quantity of diethyl ethanephosphonate is formed. During the synthesis of the linked phosphonate, discussed later, a better method was used to remove unwanted iodoethane. The use of a slow nitrogen purge and the slow addition of the phosphite into the reaction mixture minimized the competing side reaction of iodoethane with the phosphite starting material.

2.3.3 Spectroscopic Characteristics of Tetraethyl Methanediphosphonate (TEM DP)

^1H , ^{13}C , ^{31}P -NMR data were collected to characterize TEM DP. **Figure 2.3.3.1** shows the proton spectrum of TEM DP. Three signals are observed. The most upfield signal (δ 1.1 ppm) is a triplet which is assigned to the methyl group protons labeled H_C . The signal for methylene protons H_B (δ 3.85 ppm) is observed as a multiplet due to coupling of the protons from H_C and long range coupling from phosphorus (^3J). Protons H_A (δ 2.1 ppm) exhibit a large coupling to both attached phosphorus ($^2\text{J}_{\text{H-P}}$ 20 Hz) and give rise to a unique triplet.



Figure 2.3.3.2 shows the carbon spectrum of TEMP. The triplet at δ 77.0 ppm is from the solvent d-chloroform. The signal assigned to the methyl carbon C_C (δ 15.5 ppm) is a large singlet which is the terminal carbon of the ethoxy group. Carbon C_B (δ 62.0 ppm) is a doublet due to coupling to phosphorus ($^2J_{C-P}$ 6 Hz). It is the furthest downfield signal due to the deshielding effects of oxygen located next to it. Carbon C_A (δ 24.5 ppm) is split by both adjacent phosphorus ($^1J_{C-P}$ 134 Hz). The ^{31}P -NMR spectrum showed one signal at δ 20.8 ppm.

2.3.4 Synthesis of 4,4-Diethylphosphonate Hepta-1,6-diene

The alkylation of the diphosphonate was first described by Kosolapoff³⁴ and later by Cotton.³⁵ The bis phosphonate TEMDP was alkylated using NaH followed by the addition of allylbromide. An excess of NaH (1.25 g, 0.030 mol) was first added to freshly distilled THF in a dry nitrogen atmosphere filled Schlenk vessel. The deprotonation of TEMDP (1.080 g, 0.003 mol) by NaH (**Figure 2.3.4.1**) gives off hydrogen gas so a mineral oil bubbler was used to relieve pressure inside the Schlenk vessel. The mixture was stirred for one hour,

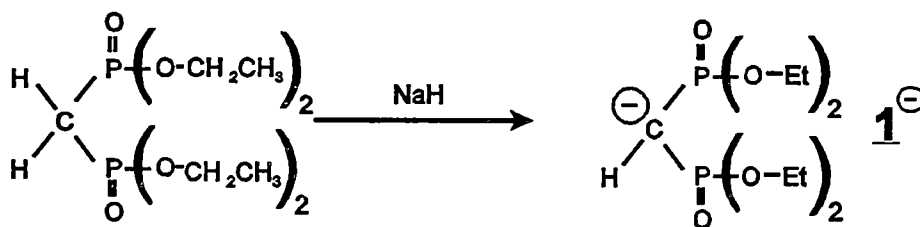


Figure 2.3.4.1 Synthesis of 4,4-diethylphosphonate hepta-1,6-diene

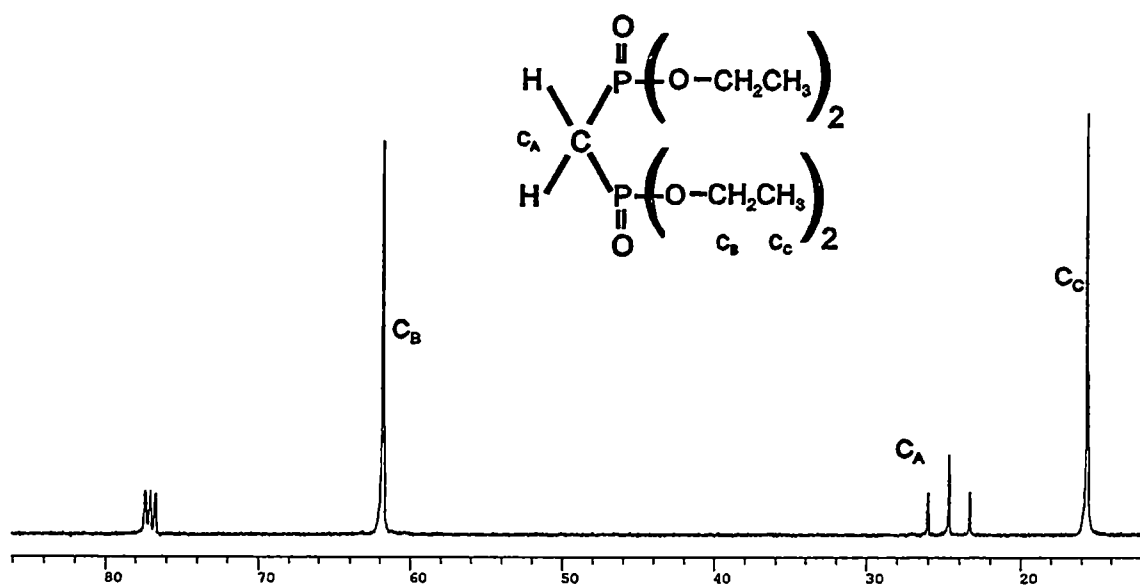


Figure 2.3.3.2 ^{13}C -NMR spectra of tetraethyl methanediphosphonate

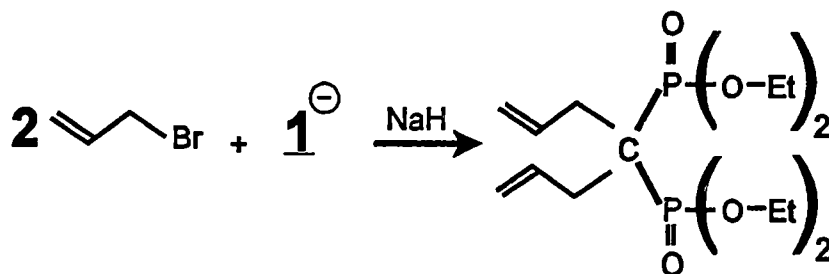


Figure 2.3.4.2 Addition of allylbromide to deprotonated 4,4-diethylphosphonate hepta-1,6-diene

after which allylbromide (0.76g, 0.0063 mol) (**Figure 2.3.4.2**) was added and the mixture was stirred for an additional 15 hours. The solvent mixture was then removed from the excess NaH by filtration through dry cotton. THF was removed via rotatory evaporation followed by a hexane wash to remove any leftover salts. Hexane was removed to leave 4,4-diethylphosphonate hepta-1,6-diene.

2.3.5 Characterization of 4,4-diisopropylphosphonate 1,6-heptene

¹H, ¹³C, and ³¹P-NMR data were used to characterize 4,4-diisopropylphosphonate hepta-1,6-diene. **Figure 2.3.5.1** show the proton spectrum of 4,4 diisopropylphosphonate 1,6-heptene. Signals observed at δ 0.8 ppm and δ 1.18 ppm are due to mineral oil which NaH was packed in. Starting with the signal furthest downfield, the splitting observes for the multiplet assigned to proton H_B (δ 5.93 ppm) is due to long range coupling to the alkyl group as well as cis and trans coupling to protons H_A.³⁶ Protons H_A give two different signals around δ 5.0 ppm. The larger doublet (J_{H-H} 2.1 Hz) δ 5.00 ppm is due to trans

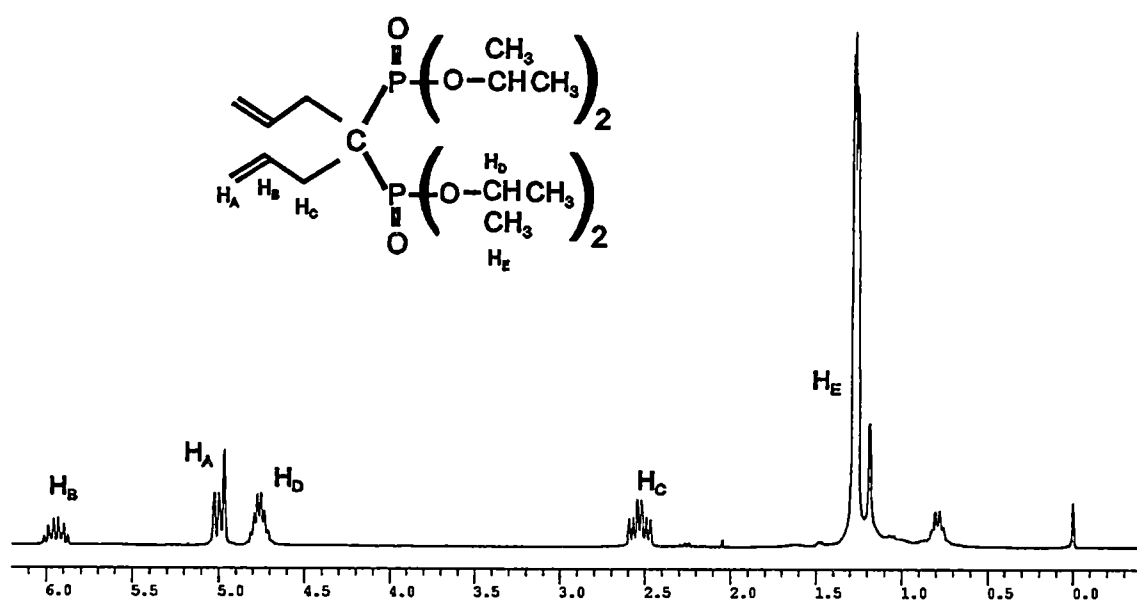


Figure 2.3.5.1 ^1H -NMR spectra of 4,4-diethylphosphonatehepta-1,6-diene

coupling to the alkyl group and the smaller doublet (J_{HH} 16.8 Hz) δ 4.97 ppm is due to cis coupling to the alkyl group. Protons H_C (δ 2.52 ppm) is observed as a doublet of triplets. The doublet of triplets is due to coupling between proton H_B which causes the doublet splitting. The triplet is derived from long range phosphorus coupling. It is important that there is not a triplet of triplets for H_C because a triplet of triplets would mean that there was mono substitution instead of disubstitution of the allyl group. Proton H_D (δ 4.75 ppm) is observed as a multiplet due to protons H_E and long range phosphorus coupling. The signal for the terminal methyl of the isopropyl protons H_E (δ 1.28 ppm) is observed as two doublets.

Figure 2.3.5.2 shows the carbon spectrum of 4,4-diisopropylphosphonate hepta-1,6-diene. The triplet at δ 77.0 is from the solvent d-chloroform. Signals at δ 1.0, 14.0, 22.0, 29.5, 32.0 ppm are due to mineral oil as mentioned above. The signal observed at δ 24.0 ppm is due to the terminal carbons of the isopropyl group (C_F). The signal observed at δ 71.0 ppm is the methyne carbon of the isopropyl group (C_E) and the signal is shifted downfield due to the deshielding effects of adjacent oxygen. The signal observed at C_D (δ 45.0 ppm) is a triplet due to coupling with both adjacent phosphorus. Carbon C_C (δ 35.5 ppm) is third carbon of the butene chain. There are two carbons located downfield at δ 117.0 and δ 134.0 ppm, and these are the alkene carbons of the butene group. The signal at δ 117.0 ppm is the terminal carbon of the alkene group. ^{31}P -NMR spectrum showed one signal at δ 26.2 ppm.

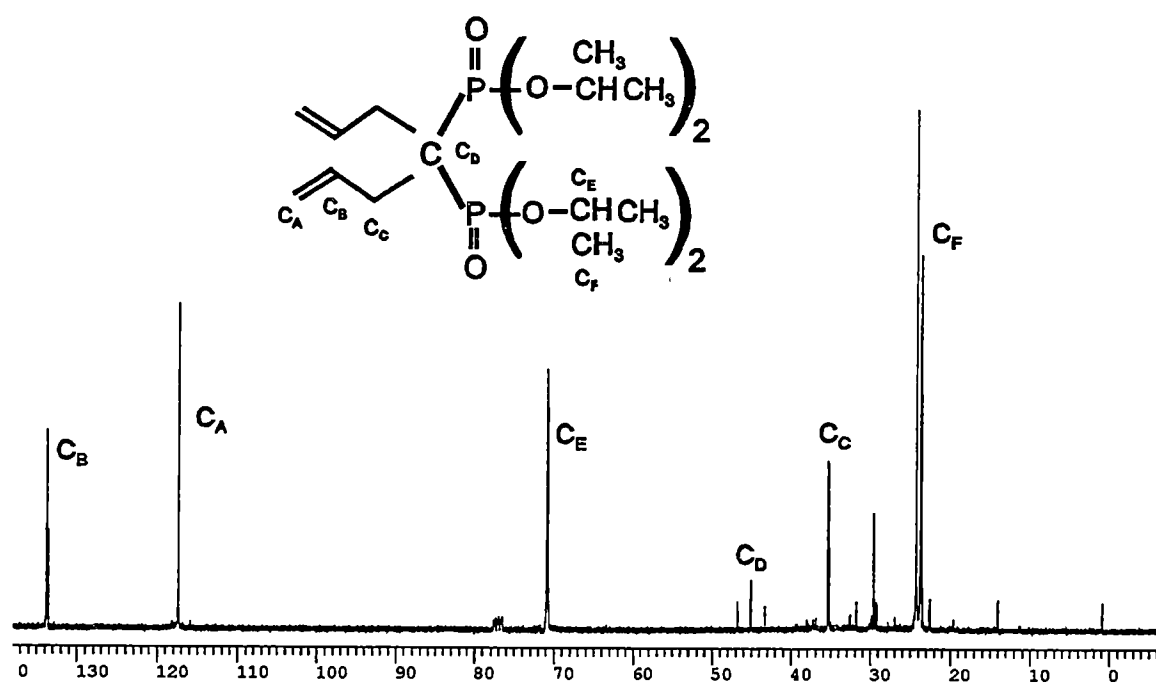


Figure 2.3.5.2 ¹³C-NMR spectra of 4,4-diethylphosphonate hepta-1,6-diene

2.3.6 Synthesis of 1,7-Di(triethoxysilane) 4,4 Bis(diethylphosphoato) heptane

heptane

Once 4,4-diethylphosphonate hepta-1,6-diene had been synthesized an ethoxysilane group used for binding to the surface of mesoporous sol-gel had to be added. This was accomplished via hydrosilylation with triethoxysilane using a platinum catalyst (**Figure 2.3.6**).^{37,38} Chloroplatinic acid hexahydrate was chosen for the platinum catalyst. In a Schlenk vessel under air containing a drying funnel filled with calcium carbonate, 50 mL of dry toluene, an excess of triethoxysilane (1.28 g, 0.0078 mol), and 4,4-diethylphosphonate 1,6-heptene (0.54 g, 0.0013 mol) were mixed together and heated to 100 °C. The solution was stirred for 10 minutes at 100 °C and then a catalytic amount of chloroplatinic acid (10 mg) was added and stirred for 15 hours. The solution slowly turned a translucent black color. The solution was then cooled to room temperature where celite was added to remove the platinum catalyst. Excess triethoxysilane and toluene were removed to leave 1,7-di(triethoxysilane) 4,4 bis(diethylphosphoato) heptane.

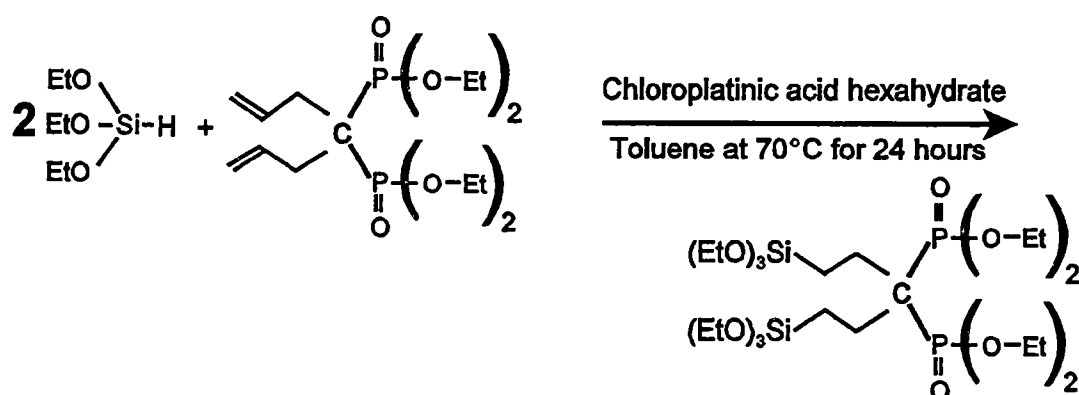


Figure 2.3.6 Synthesis of 1,7-di(triethoxysilane) 4,4 bis(diethylphosphoato)

heptane

2.3.7 Characteristics of 1,7-Di(triethoxysilane) 4,4 Bis(diethylphosphoato) Heptane (bis-phosphonate ligand)

^1H , ^{13}C , and ^{31}P -NMR data were used to characterize 1,7-di(triethoxysilane) 4,4 bis(diethylphosphoato) heptane. **Figure 2.3.7.1** shows the proton spectrum of 1,7-di(triethoxysilane) 4,4 bis(diethylphosphoato) heptane. Signals observed at δ 0.8 ppm is due to mineral oil from the second step of the synthesis of the bis-phosphonate ligand. Starting with the signal furthest downfield, there is multiplet at δ 4.09 ppm (H_f). This multiplet is assigned to the methylene of the ethoxy group attached to the phosphorus. The signal at δ 3.75 (H_b) is also a multiplet which is the methylene of an ethoxy group attached to the silicon. There are three multiplet at δ 0.5 ppm (H_c), δ 1.55 ppm (H_d), and δ 1.82 ppm (H_e); all three of these signals are assigned to the linking bridge between the silane group and the phosphonate group. One triplet is observed at δ 1.25 ppm (H_g). This triplet is assigned to the terminal protons of the ethoxy groups attached to the phosphorus. There is another triplet observed at δ 1.15 ppm (H_a). This triplet is assigned to the terminal protons of the ethoxy group attached to the silicon.

Figure 2.3.7.2 shows the carbon spectrum of the bis-phosphonate ligand. The triplet at δ 77.0 is from the solvent d-chloroform. Signals at δ 14.0, 21.0, 29.5, 32.0 ppm are due to mineral oil as mention above. The signal observed at δ 24.0 ppm and δ 23.8 ppm are the terminal carbons of the ethoxy group (C_h).

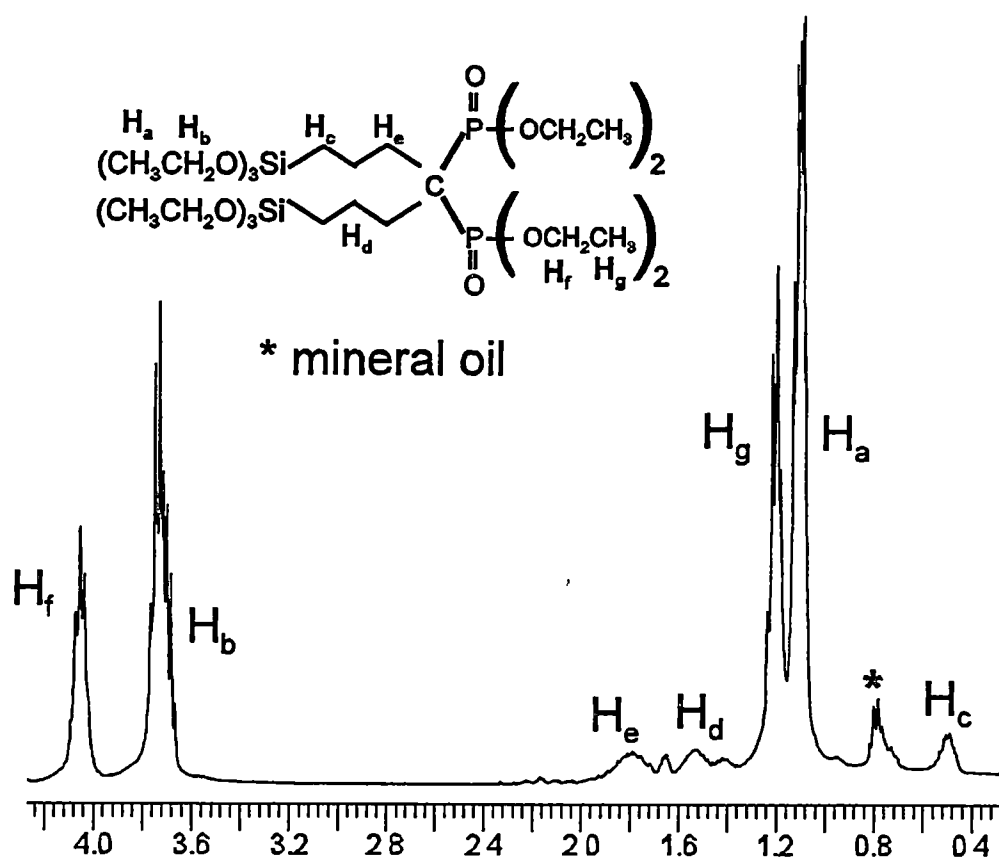


Figure 2.3.7.1 ¹H-NMR spectra of 1,7-di(triethoxysilane) 4,4 bis(diethylphosphoato) heptane

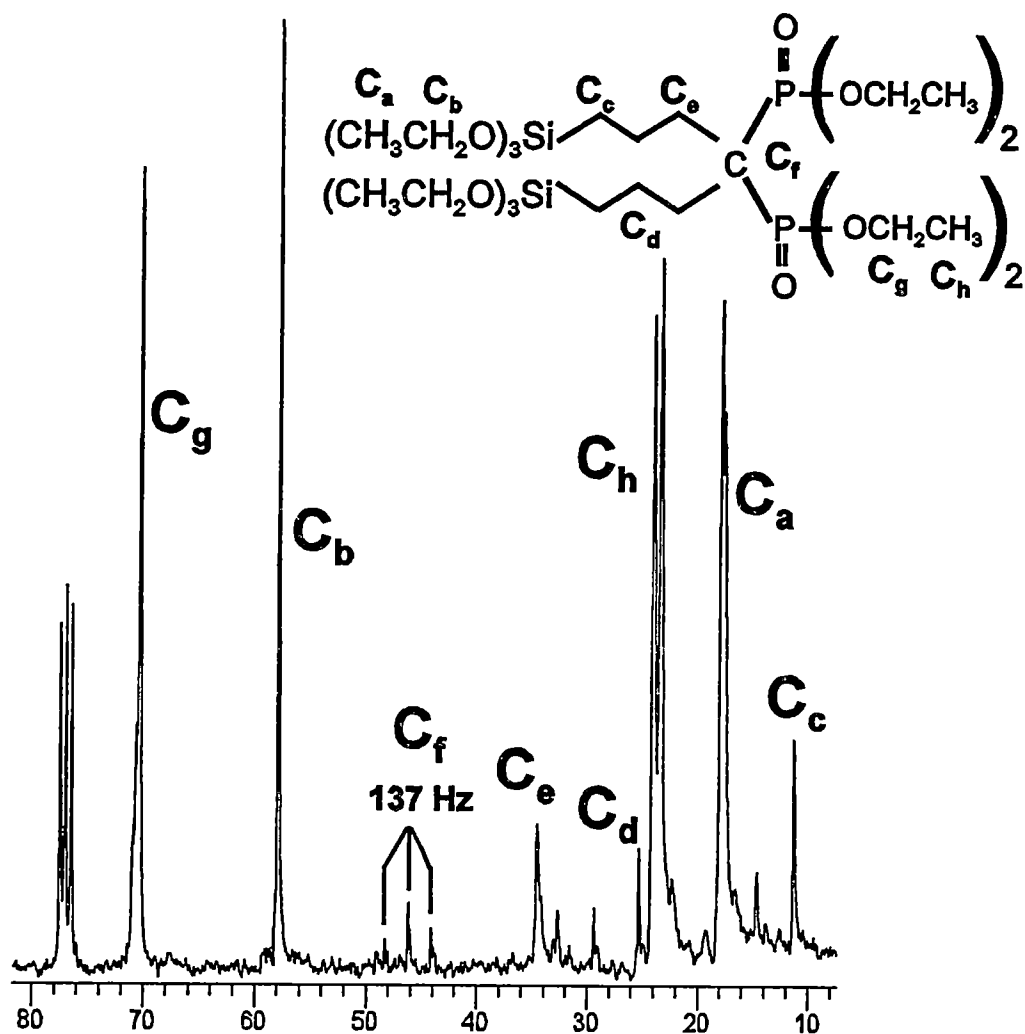


Figure 2.3.7.2 ^{13}C -NMR spectra of 1,7-di(triethoxysilane) 4,4-bis(diethylphosphato) heptane

The splitting observed is from long range phosphorus coupling. The signal observed at δ 71.0 ppm is the methylene carbon of the ethoxy group (C_g) and the signal is shifted downfield due to the deshielding effects of adjacent oxygen. Carbon (C_f) gives a unique triplet at δ 45.5 ppm. This triplet is due to the phosphorus coupling ($^1J_{C-P}$ 137 Hz). This coupling constant is similar to a known literature coupling constant value of $^1J_{C-P}$ 142 Hz.³³ The signal at (δ 35.5 ppm) is assigned to the third carbon of the linking propane chain (C_e). Two signals at δ 25.5 ppm (C_d) and δ 34.5 ppm (C_a) are also assigned to the linking propane chain. The singlet at δ 57.5 ppm (C_b) is assigned to methylene carbon of the ethoxy group attached to the silicon. Finally the singlet at δ 17.5 ppm (C_a) is assigned to the terminal carbons of the ethoxy group attached to the silicon. One signal (δ 24.7 ppm) was observed in the ^{31}P -NMR spectrum of bis-phosphonate ligand. A signal (δ -51.8 ppm) was observed in the ^{29}Si -NMR spectrum. **Figure 2.3.7.3** and **Table 2.3.7** gives the IR spectrum and signals seen for bis-phosphonate.

Attempts where made to purify bis-phosphonate ligand. Distilling the ligand was attempted under vacuum distillation (0.05 mm Hg) but high temperature caused decomposition of the ligand. Chromatography was also tried but the siloxy groups attached to the silica gel. No other methods where tried. The bis-phosphonate ligand was used as synthesized.

Table 2.3.7 IR assignment for 1,7-di(triethoxysilane) 4,4 bis(diethylphosphato) heptane

Assignment	Range	Comments
CH ₃ CH ₂	2929 cm ⁻¹	broad and strong
CH ₂ -O	2976 cm ⁻¹	sharp and strong
P-O-CH ₂ CH ₃	1246 cm ⁻¹	broad and strong
P=O	1166 cm ⁻¹	sharp and strong
Si-O-C	1078 cm ⁻¹	broad and strong

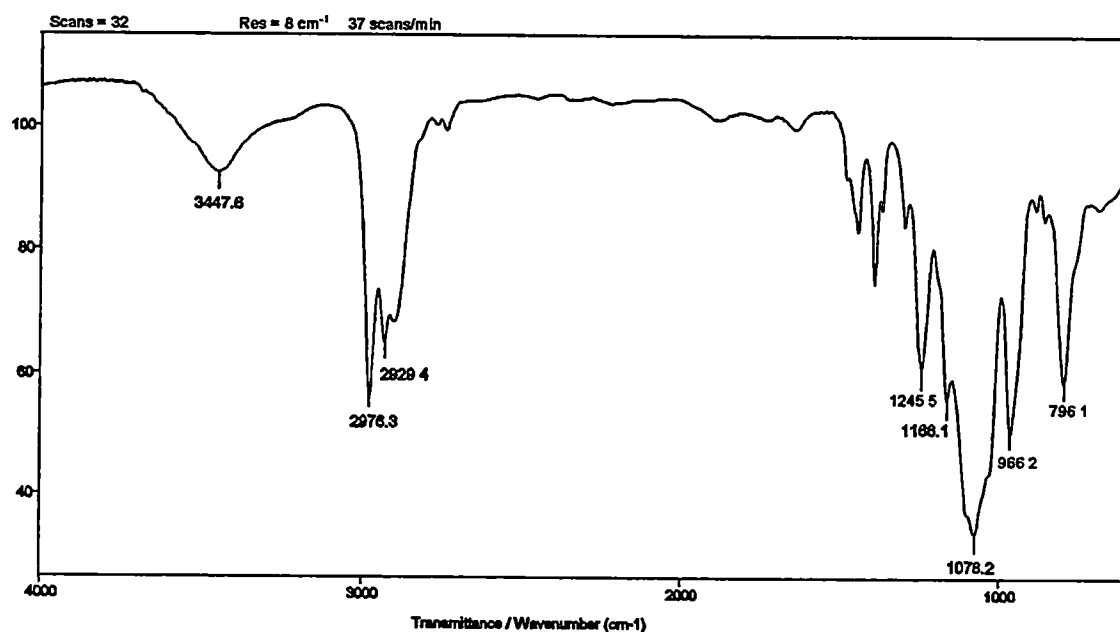


Figure 2.3.7.3 IR spectrum of 1,7-di(triethoxysilane) 4,4 bis(diethylphosphato) heptane

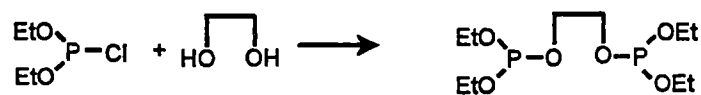
2.4.1 Introduction of Third Generation Ligand

The third generation ligand brings two mono phosphonate ligands together through a glycol bridge so that divalent metal cations can be caged in between the two linked phosphonate ligands. It was hoped that this caging effect would increase the affinity for divalent metal cations. Later (Chapter 3), it would be discovered that the glycol bridge is broken in the presence of bromotrimethylsilane. After the loss of the glycol bridge, it was discovered that there was a type of imprinting effect observed (Chapters 3 and 4). The synthesis of the linked phosphonate consists of the following steps (**Figure 2.4.1**). In the first step, chlorodiethyl phosphite is reacted with ethylene glycol to form tetraethylester of glycoldiphosphonate. In step two, a Michaelis-Arbuzov rearrangement occurs with 3-iodopropyltrimethoxysilane and the tetraethylester of glycoldiphosphonate to form di(3-trimethoxy silyl propyl) glycol diphosphonate (linked-phosphonate).

2.4.2 Synthesis of Chlorodiethylphosphite

The first step in the synthesis of the linked phosphonate is a reaction involving chlorodiethylphosphite and ethylene glycol (**Figure 2.4.2**). Commercially available chlorodiethylphosphite (Aldrich) has a side product which contains an unwanted diethyl phosphite. This diethylphosphite can not be removed from chlorodiethylphosphite easily. A procedure was found for the synthesis of chlorodiethylphosphite.³⁹ Chlorodiethylphosphite was synthesised

STEP ONE:



STEP TWO:

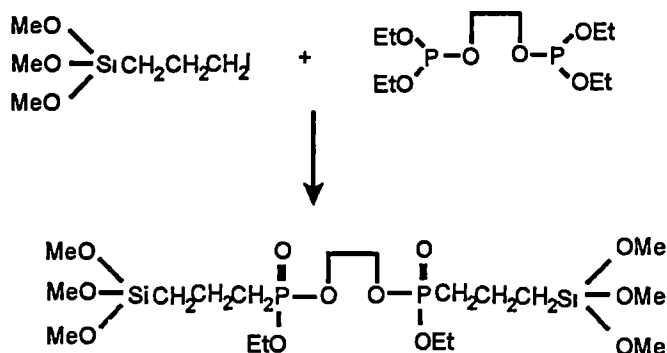


Figure 2.4.1 Synthesis of di(3-trimethoxy silyl propyl) glycol diphosphonate ligand.

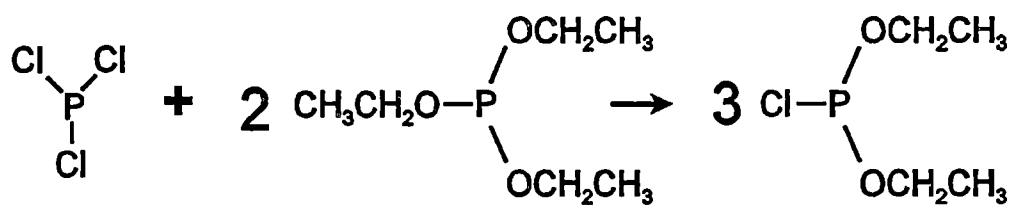


Figure 2.4.2 Synthesis of chlorodiethylphosphite

by reacting triethylphosphite (20 mL, 0.12 mol) and phosphorus trichloride (5.25 mL, 0.06 mol) in a 2:1 molar ratio. The two were refluxed at 80 °C for 30 minutes. The solution gradually turned a yellowish-green color. The liquid was vacuum distilled at 18 mm Hg and collected up to 70 °C. A small quantity of higher boiling liquid and a orange solid remained in the flask. The chlorodiethylphosphite was redistilled at 18 mm Hg. Three fractions were collected: < 50 °C, dichloroethylphosphite (25% yield) ; 50-55 °C, chloroethylphosphite (45% yield); and >55 °C, triethylphosphite and diethylphosphite (30% yield). All three fractions were colorless clear liquids.

2.4.3 Characteristics of Chlorodiethylphosphite

The second fraction boiling between 50-55 °C of was determined by ^{31}P -NMR and ^1H -NMR to be >95% pure chlorodiethylphosphite which was determined through the integration of the phosphorus signals. A ^{31}P -NMR spectrum showed that starting material phosphorus trichloride signal to be downfield at δ 220.30 ppm disappeared while a new signal for chlorodiethylphosphite phosphorus was observed at δ 167.46 ppm. As for ^1H -NMR, chlorodiethylphosphite proton signals occurs at a triplet at δ 1.25 ppm for the terminal methyl and an apparent quintet at δ 4.15 ppm for the methylene. The observed splitting is due to $^3J_{\text{H-P}}$ phosphorus coupling.

2.4.4 Synthesis of tetraethylester of glycoldiphosphonate

The following is an improved synthesis over that reported by Geffer and Rogacheva for tetraethylester of glycoldiphosphorus (**Figure 2.4.4**).⁴⁰

Triethylamine (8.99 mL, 0.0645 mol) was dissolved in dry, freshly distilled hexane (30 mL) and anhydrous ethyl ether (20 mL), and the solution stirred for 5 minutes under nitrogen at room temperature in a 100 mL 3-necked flask fitted with a reflux condenser and a dropping funnel. Chlorodiethylphosphite (6.2 mL, 0.043 mol) was added which caused triethylammonium chloride to form. The solution was stirred another 10 minutes at room temperature and then cooled to 0 °C. Dry ethylene glycol (1.20 mL, 0.022 mol) was added slowly through drop funnel. The solution was stirred for 2 hours while the temperature slowly came back to room temperature. The precipitate was removed by filtration. The filtrate was washed with 0.01 M HCl and then neutralized with water to pH 7.0. This process was necessary to remove the triethylammonium chloride. The hexane/ether layer was dried with magnesium sulfate, and the solvent was removed under vacuum via a rotatory vapor. The process was performed twice to remove all triethylammonium chloride. ¹³C-NMR and ³¹P-NMR data determine the product to be pure and in 90% yield.

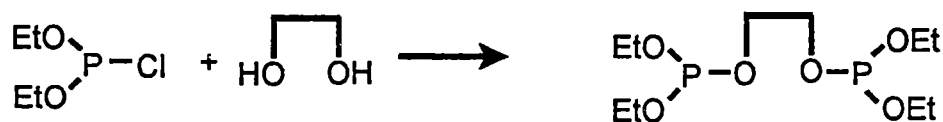


Figure 2.4.4 Synthesis of tetraester of glycoldiphosphonate

2.4.5 Characteristics of Tetraethylester of Glycoldiphosphonate

^1H , ^{13}C , ^{31}P -NMR data were all used to characterize tetraethylester of glycoldiphosphorus. **Figure 2.4.5.1** shows the proton spectra of tetraethylester of glycoldiphosphorus. Three major signals are observed. The furthest upfield triplet (δ 1.25 ppm) is assigned to the methyl group protons labeled H_A . The signal for the methylene protons H_B (δ 3.86 ppm) is observed as a quartet due to coupling to neighboring protons (H_A). The signal at δ 3.93 ppm is assigned to protons H_C . The signal at δ 3.93 ppm is a multiplet which arises from coupling to the adjacent protons of H_C and short (^2J) and long (^3J) range coupling to the two adjacent phosphorous.

Figure 2.4.5.2 shows the carbon spectrum of the tetraethylester of glycoldiphosphorus. The triplet at δ 77.0 ppm is from the solvent d-chloroform. Methyl carbons C_A (δ 17.00 ppm) is observed as a singlet, which is the terminal carbon of the ethoxy group. Carbon C_B (δ 58.00 ppm) is a doublet due to the long range coupling of phosphorus ($^2\text{J} = 9$ Hz). The signal for the glycol carbons C_C (δ 62.00 ppm) is observed as a multiplet. This multiplet is derived from long ($^3\text{J}_{\text{C-P}}$) and short ($^2\text{J}_{\text{C-P}}$) range phosphorus coupling. The chlorodiethylphosphite ^{31}P -NMR signal at δ 167.42 ppm is replaced by a new upfield signal at δ 140.12 ppm assigned to the glycoldiphosphonate. This is consistent with literature ^[41] reports for this compound. No other phosphorus signals were observed.

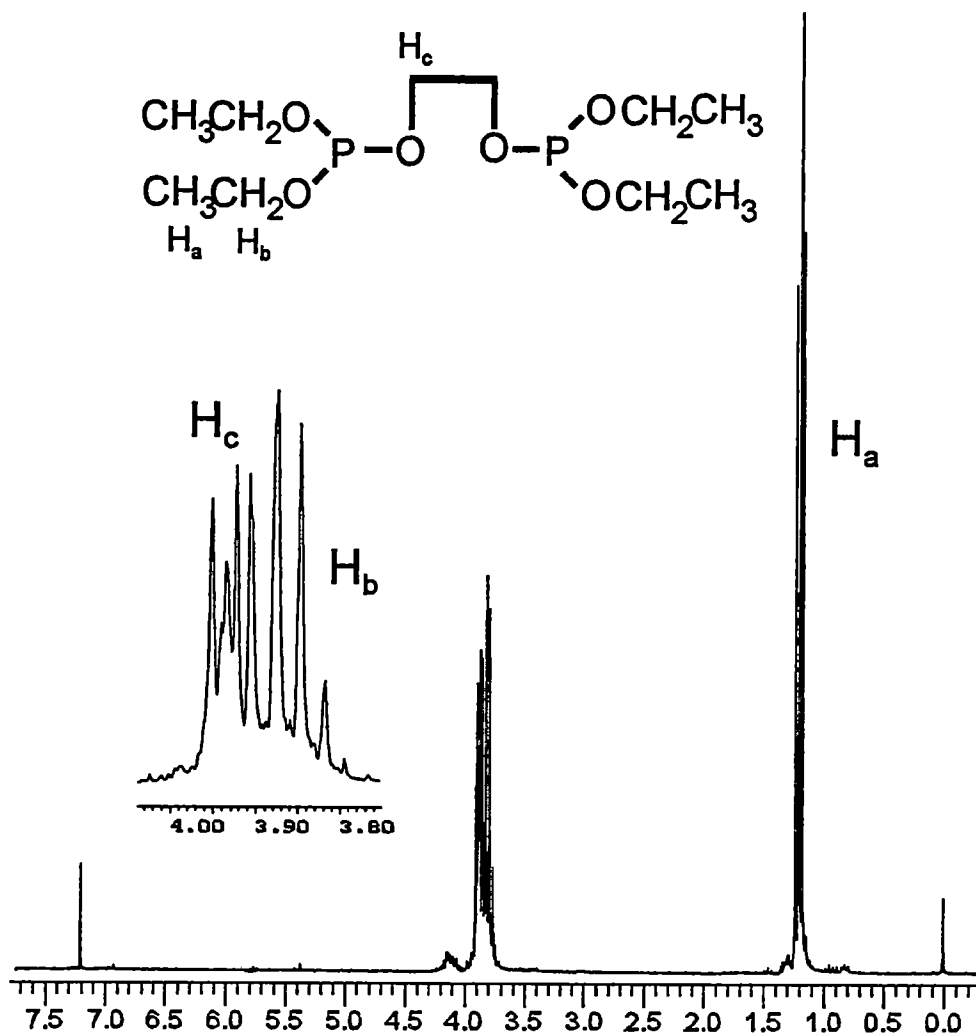


Figure 2.4.5.1 ¹H-NMR spectra of tetraethylester of glycoldiphosphonate

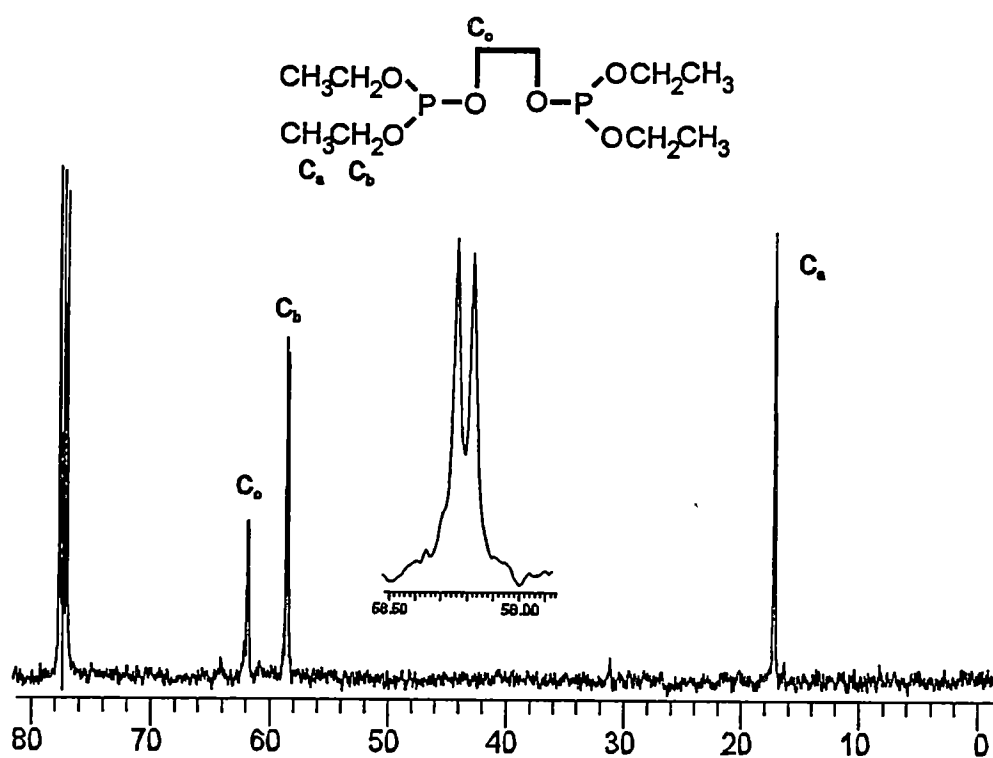


Figure 2.4.5.2 ^{13}C -NMR spectra of tetraethylester of glycoldiphosphonate

2.4.6 Synthesis of di(3-trimethoxy silyl propyl) glycol diphosphate (linked phosphonate)

Step two involves an Arbuzov reaction in which 3-iodopropyltrimethoxysilane (compound **A**) and the tetraethylester of glycoldiphosphorus (compound **B**) (**Figure 2.4.6**) are reacted together at a 1:4 molar ratio.⁴⁰ First, 3-iodopropyltrimethoxysilane (18.16 mL, 0.092 mol) under nitrogen at room temperature in a 250 mL 3-neck flask is fitted with a reflux condenser, drop funnel, and a valve for regulating dry nitrogen. It is important to have a moderate nitrogen flow into the system to remove the unwanted side product iodoethane (compound **D**). The solution was heated to 100 °C in a silicon oil bath. The tetraethylester of glycoldiphosphorus (6.5 mL, 0.023 mol) was added dropwise via the drop funnel. The solution was stirred for 6 hours. Excess 3-iodopropyltrimethoxysilane was removed by vacuum distillation 0.05 mm Hg to leave the product.

Note:

If this reaction is performed in a closed system, iodoethane which is a competitor to 3-iodopropyltrimethoxysilane during the Arbuzov reaction builds up. Iodoethane reacts with tetraethylester of glycoldiphosphorus to form the glycol linked diethanephosphonate ester and another equivalent of iodoethane, both of which are unwanted. ³¹P-NMR can be used to determine if the unwanted product (δ 34.59 ppm) is formed because the desired product gives a signal at δ 32.71 ppm.

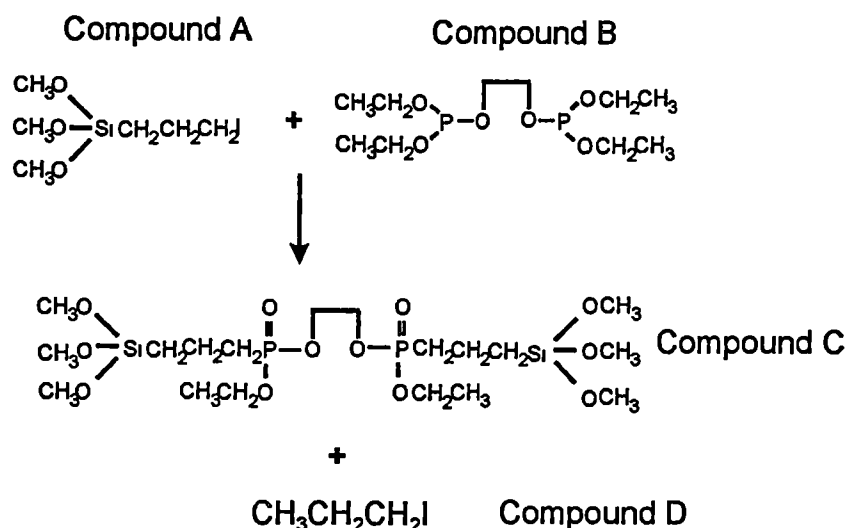


Figure 2.4.6 Arbuzov Reaction for Linked Phosphonate

2.4.7 Characteristics of the linked phosphonate

^1H , ^{13}C , and ^{31}P -NMR data were all used to characterize the linked phosphonate ligand. **Figure 2.4.7.1** shows the proton spectrum of the linked phosphonate ligand. The most upfield signal (δ 0.74 ppm) is a triplet which is assigned to the methylene protons H_b adjacent to the silicon group. ^1H -NMR data for compound **A** (3-iodopropyltrimethoxysilane) showed a triplet due to the coupling of H_d by two equivalent protons (H_c) which was centered at δ 3.2 ppm, deshielded because of the iodine bound to the terminal C_d of compound **A**. After the reaction, this triplet was no longer observed, and a new upfield multiplet was observed at δ 1.15 ppm. This new upfield signal appears as a doublet of triplets. The large coupling constant of $^1J_{\text{H-P}}$ 20.01 Hz is indicative of phosphorus-proton coupling. The doublet of triplets at δ 1.15 ppm is due to the coupling of H_b by the

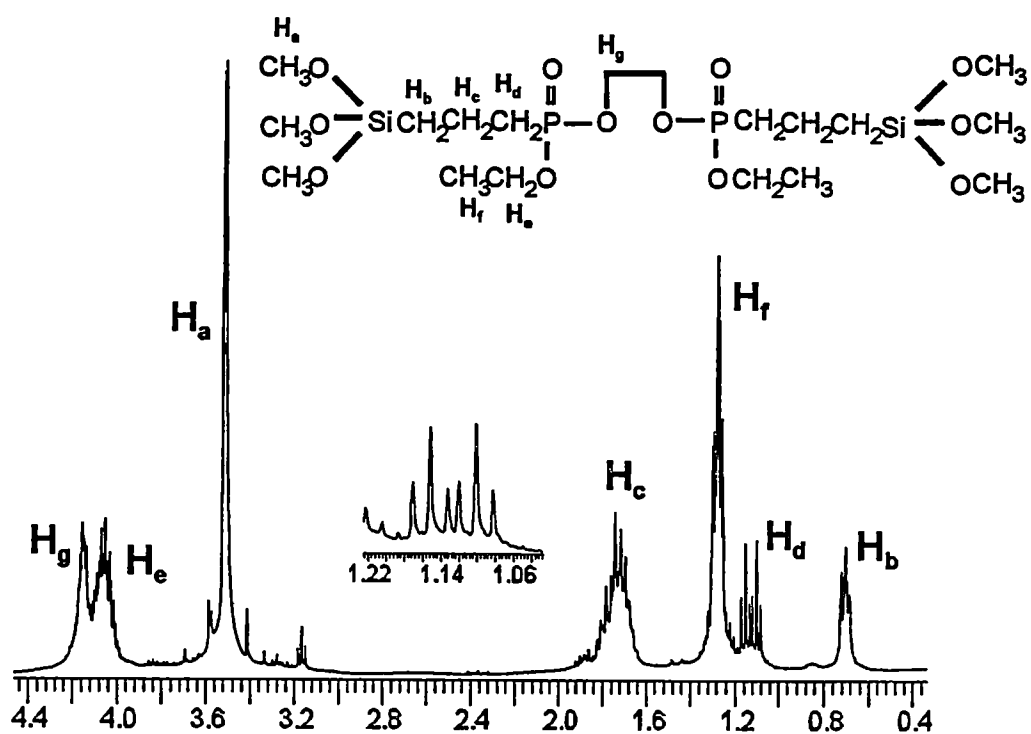


Figure 2.4.7.1 ¹H-NMR spectra of linked phosphonate

two equivalent H_C ($^3J_{HH} = 7.51$ Hz) and coupling to the phosphorus ($^2J_{HP} = 20.01$ Hz). The signal for H_C of the propylene bridge (δ 1.75 ppm) is observed as a multiplet because of proton coupling of H_B and H_D . The signal at δ 3.5 ppm arises from the protons of the methoxy group (H_A). The triplet (δ 1.28 ppm)(H_F) and multiplet (δ 4.05 ppm)(H_E) are assigned to the ethoxy groups. The most downfield signal (δ 4.18 ppm) is a multiplet which is assigned to the linking glycol bridge (H_G). The observed multiplet is due to coupling to the adjacent protons (H_G) and short and long range phosphorus coupling from the adjacent phosphorus. All signals were assigned by correlation with the spectra of compounds **A** and **B** (tetraethylester of glycoldiphosphorus).

Figure 2.4.7.2 shows the carbon spectrum of the linked phosphonate ligand. The triplet at δ 77.0 ppm is due to the solvent d-chloroform. Carbon C_D of compound **C** gave a unique doublet at δ 28.0 ppm. This doublet is due to the phosphorus coupling ($^1J_{CP} = 139$ Hz). This coupling constant is similar to the known literature coupling constant value of $^1J_{CP}$ 142 Hz.³³ The singlet at δ 49.19 ppm is assigned to the methoxy group (C_A). The two most upfield signals at δ 9.71 ppm and δ 9.87 ppm are assigned to carbons C_B and C_C . Two important signals to discuss are the glycol carbons (C_G) at δ 64.0 ppm and the ethoxy group carbons (C_E) at δ 61.0 ppm. The intermediate linked diphosphite (compound **B**) showed a 2:1 ratio for the ethoxy group carbons and the glycol carbons. After the Arbuzov reaction, the two sets of carbon signals exhibit an intensity ratio of roughly 1:1, as expected. The last two signals at δ 15.79 ppm and δ 16.21 ppm



are assigned to the terminal carbons of the ethoxy groups (C_F). ^{31}P -NMR spectra for compound **C** showed a new signal at δ 32.71 ppm relative to the previous signal at δ 140.0 ppm for the starting material linked phosphite of compound **B**. A signal (δ -50.1 ppm) was observed in the ^{29}Si -NMR spectrum. **Figure 2.4.7.3** and **Table 2.4.7** gives the IR spectrum and signals seen for the linked phosphonate.

Table 2.4.7 IR assignment for the linked phosphonate

Assignment	Range	Comments
CH ₃ CH ₂	2945 cm ⁻¹	broad and strong
CH ₂ -O	2841 cm ⁻¹	sharp and strong
P-O-CH ₂ CH ₃	1230 cm ⁻¹	broad and strong
P=O	1192 cm ⁻¹	sharp and strong
Si-O-C	1086 cm ⁻¹	broad and strong

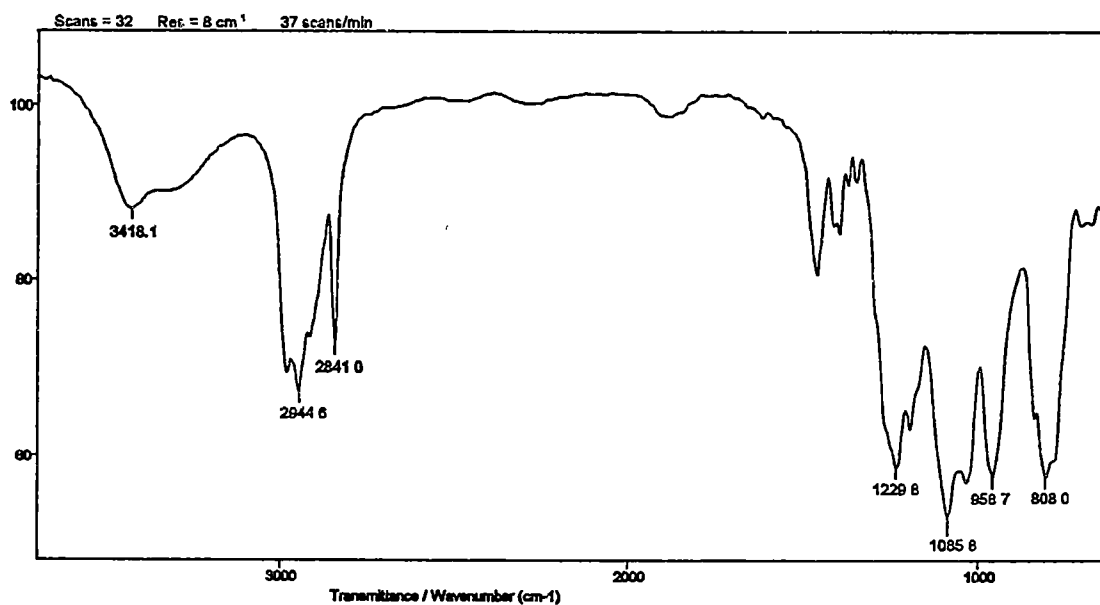


Figure 2.4.7.3 IR spectrum of the linked-phosphonate ligand

Chapter Three

Grafting Phosphonate Ligands onto Mesoporous Sol-gel

3.1 Introduction

The U.S. Department of Energy (DOE) and industry are faced with the challenge of removing a wide range of contaminated waste from the environment. Cation species such as Hg^+ , Pb^{2+} , and Cr^{3+} , and anion species such as Cl^- , NO_3^- , CrO_4^{2-} , and AsO_4^- are encountered in mixed wastes, processing wastes, groundwater, and dilute waste streams. For example, an estimated 2.5 million pounds of mercury exists in the contaminated water and soil at the DOE Oak Ridge Site.⁴²

Mesoporous silica coated with functionalized monolayers (FMMS) have demonstrated a remarkable ability to absorb heavy metals from contaminated water, making it a promising tool for environmental cleanup applications. In simulated test of the Savannah River Site radioactive wastes in holding tank L, this FMMS material reduced the mercury concentration below the U.S. Environmental Protection Agency's elemental limits for hazardous wastes and even below drinking water standards.¹¹ In this chapter, the synthesis of templated mesoporous sol-gel will be discussed first. This silica material will serve as a mesoporous support for functionalized monolayers of the three ligands discussed in the previous chapter.

3.2.1 Introduction to Templated Mesoporous Sol-gel

In 1992, scientists at Mobil Oil research successfully synthesized ordered mesoporous materials using surfactant micellar structures as templates.⁹ These new materials were then incorporated with functionalized monolayers (FMMS). FMMS have demonstrated a remarkable ability to absorb heavy metals from contaminated water, making them a promising tool for environmental cleanup. The three phosphonate ligands described in Chapter 2 will be used to form three new FMMS materials. The phosphonate ligands are first grafted to the surface of the mesoporous gel. This mesoporous gel has a high surface area ($500 \text{ m}^2/\text{g}$) and has mesopores ($75 \text{ \AA}$). Large pore size is needed for fast uptake of metal ions. Phosphonate ligands do not have a high affinity for divalent metal cations, but phosphonic acids do have a high affinity for divalent metal cations. Phosphoric acids are synthesized via saponification of corresponding phosphonate ester using TMSBr and water. These new phosphoric acid monolayers on mesoporous supports will then be studied in the presence of strontium and uranyl which will be discussed in Chapter 4.

3.2.2 Experimental Section

All synthesis and manipulations were performed in air using standard techniques. Tetraethyl orthosilicate (Aldrich), tergitol type 15-S-15 (Sigma), absolute ethyl alcohol USP (200 proof) (AAPER Alcohol and Chemical Co.), and trimethylbromosilane (Gelest) were used as received. NMR spectra were

recorded on the solid state Varian 400 MHz and the solution Bruker 400 MHz Fourier transform spectrometers. Chemical shifts were referenced to d-chloroform ($^1\text{H-NMR}$ δ 7.26 ppm solution NMR), phosphoric acid ($^{31}\text{P-NMR}$ δ 0.00 ppm solid state NMR), adamantane ($^{13}\text{C-NMR}$ δ 31.53 and δ 22.50 ppm solid state NMR), d-chloroform (δ 77.00 ppm solution NMR), and cubic octamer silicic acid trimethylsilyl ester ($^{29}\text{Si-NMR}$ δ 12.4 ppm and δ -108.6 ppm solid state NMR). Brunaur-Emmett-Teller (BET) surface area and pore size distribution measurements were conducted on a Quantachrome Corporation Nova-1000 Gas Sorption Analyzer. Nitrogen was used as the adsorbent.

3.2.3 Synthesis of Templated Mesoporous Sol-gel

The templated mesoporous sol-gel was prepared using a 10:1:560 molar ratio of tetraethyl orthosilicate (TEOS): surfactant (15-S-15) : H_2O .¹⁰ 15-S-15 was mixed rapidly in water for 30 minutes. The TEOS was then dissolved in the template solution. White solids formed within 5 minutes. The precipitated products were allowed to age under moderate stirring for 12 hours. The precipitated product was filtered, air dried at room temperature, and then calcined in air at 2 K min^{-1} to 873 K for 12 hours to remove the template.

Note:

The template can also be extracted from the as-synthesized, air-dried products by washing with ethanol.¹⁰ Calcination was the method used to remove the template from all of the materials reported in this thesis.

3.2.4 Characterization of Templated Mesoporous Sol-gel

BET and ^{29}Si -NMR data were collected to characterize the mesoporous sol-gel. Cross polarization magic angle spinning (CP-MAS) NMR gives spectra of solids that is not easily quantifiable but has a quality approaching that obtained routinely with solution NMR. **Figure 3.2.4.1** is a ^{29}Si CPMAS NMR spectrum for the mesoporous sol-gel which shows three peaks at δ -108.2, -110.6, and -117.1 ppm. These peaks represent Q^2 (δ -108.2), Q^3 (δ -110.6), and Q^4 (δ -117.1) of the sol-gel.⁴³

BET N_2 adsorption measurements were used to determine the distribution of pore sizes and the surface area of the gel. After calcination, the specific surface area for the gel was $444 \text{ m}^2/\text{g}$ with a total pore volume of 0.95 cc/g . Most solids with high surface area are to some extent porous. **Figure 3.2.4.2** is a well defined standard Z shaped hysteresis loop. The very large step located in the relative pressure range of 0.7 to 0.9 is typical for mesoporous material. The pore size distribution indicates if the material contains macropores ($>500 \text{ \AA}$), mesopores ($20 \text{ \AA}$ to $500 \text{ \AA}$), or micropores ($<20 \text{ \AA}$). **Figure 3.2.4.3** shows the distribution of pore diameters for the templated 15-S-15 sol-gel. There is a narrow distribution of pore sizes between 60 to $100 \text{ \AA}$ with a maximum pore diameter of $80 \text{ \AA}$. This narrow pore size distribution is in the desired mesopore range. There is a trace of micropores and no trace of macropores. Based on the pore size distribution both micro and meso pores contribute very little to the

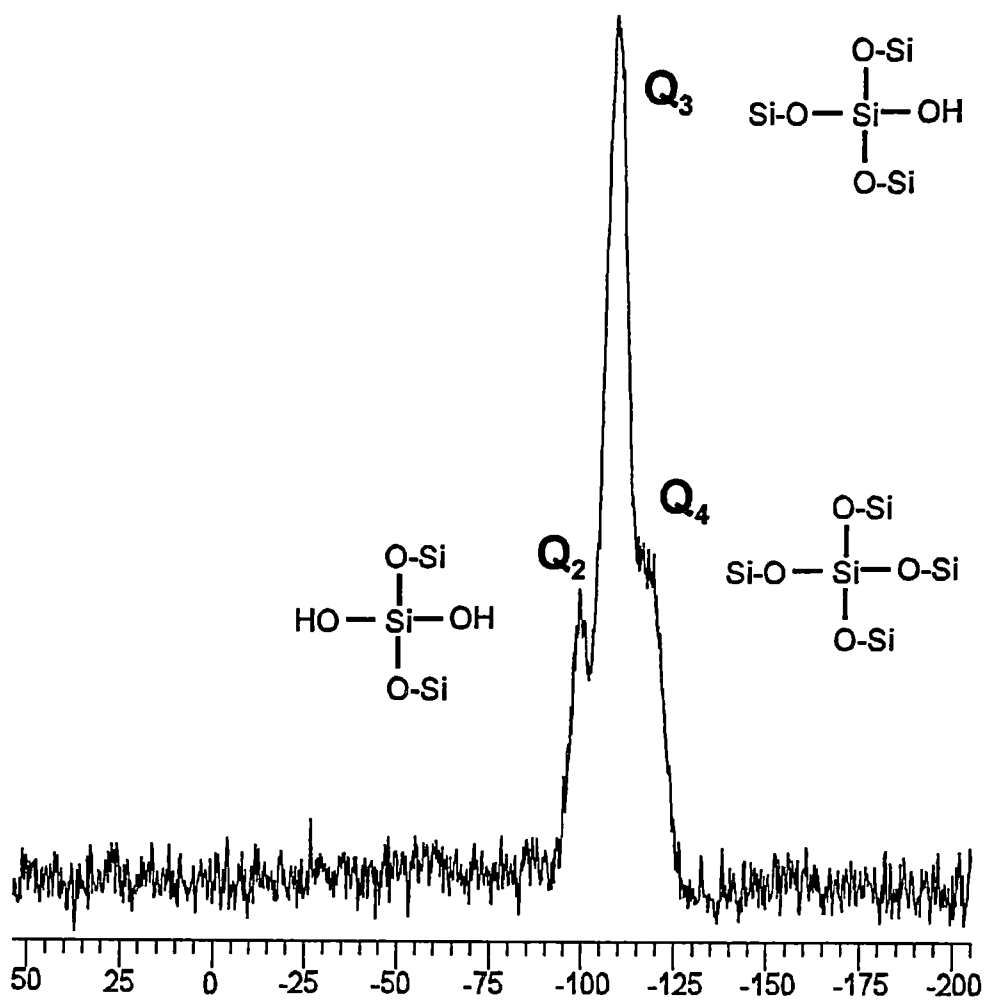


Figure 3.2.4.1 ^{29}Si -NMR spectrum of untreated mesoporous sol-gel

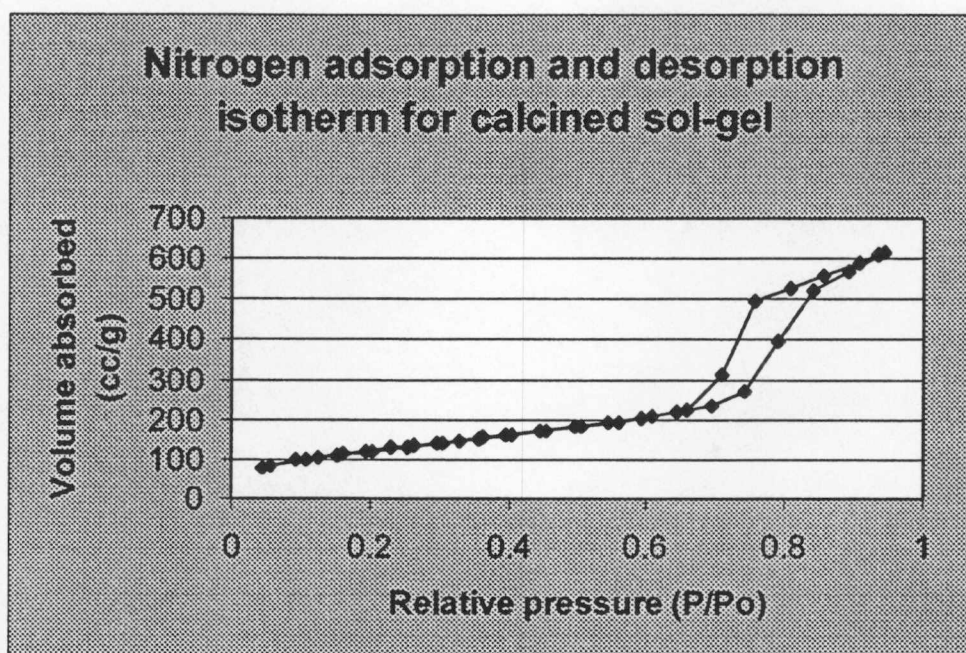


Figure 3.2.4.2 Nitrogen adsorption and desorption isotherm for calcined sol-gel.

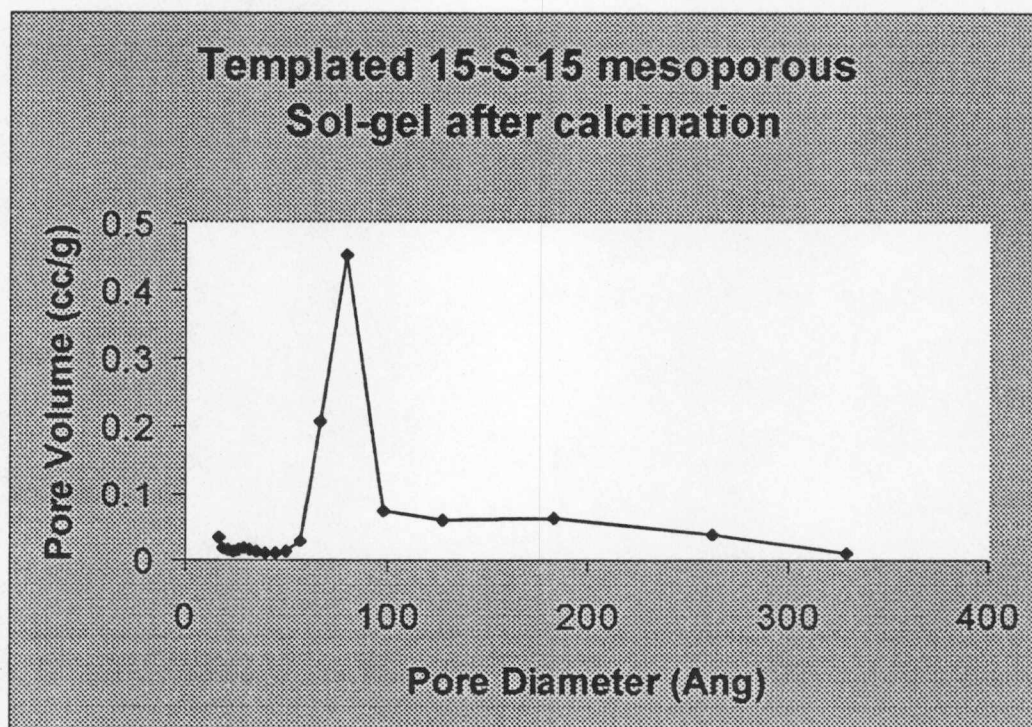


Figure 3.2.4.3 distribution of pore diameters for the templated 15-S-15 sol-gel

overall pore volume and surface area of this material. It is important to have large pore sizes now because later when the ligands are grafted to the sol-gel the pore size will decrease. The pore size has to be large enough for the ligand to fit inside and still have the space for fast metal cation absorption.

3.3.1 Introduction to grafting of functionalized ligands onto mesoporous gel

Recently, a new class of mesoporous material was developed based on organized monolayers of functional molecules bound to a mesoporous support (FMMS).¹¹ The functional molecules are attached to the mesoporous support similar to the preparation of self assembled monolayers (SAMs). FMMS can be engineered for surface area and pore size easier than SAMs. The following sections will discuss the formation of functionalized monolayers on mesoporous silica used for this project. Models for the bifunctional ligands selected are known to have an affinity for divalent metal cations as described in the previous chapter. These bifunctional ligands will be grafted onto mesoporous sol-gel and characterized using solid state NMR and BET measurements.

3.3.2 Grafting of ligands onto mesoporous sol-gel

The following procedure was based on Dr. Feng and coworkers' work at Pacific Northwest National Laboratory.¹¹ To prepare the FMMS material, calcined mesoporous silica was stirred in ethanol containing water for 30

minutes. The calcining step dehydrates the silica surface and removes most of the silanols. The calcined material is allowed to hydrate itself from the ethanol and exposure to a humid atmosphere. After the initial hydration, 15% (by weight) of the desired ligand was added to the suspension and stirred overnight at 60 °C. After cooling to room temperature, the ethanol was decanted and replaced with toluene. The toluene solution was then refluxed for another 6 hours, at which time the mixture was filtered and washed with 2-propanol, acetone, and water. The FMMS material was then dried to remove the excess water.

3.3.3 Characterization of the FMMS Material

BET and ^{31}P , ^{29}Si -NMR data were collected to characterize the FMMS material. BET data revealed that the maximum in the pore size distribution had decreased as expected. The average pore size for the calcined mesoporous silica was 84 Å; after grafting of the ligand, the average pore size decreased to 75 Å, still large enough for the metal cations to flow through for fast transport and uptake. Along with a decrease in pore size, the specific surface area and the pore volume both decreased as well. The specific surface area decreased from 444 m²/g to 409 m²/g, and the total pore volume dropped from 0.95 cc/g to 0.72 cc/g.

Solid state NMR studies was used to characterize the grafting of the ligands to the mesoporous silica. ^{13}C -NMR studies were attempted for all samples, but due to the low sensitivity of carbon and the low concentration of

ligand present, ^{13}C spectra were not obtained. ^{29}Si -NMR investigations were also attempted but again, due to the low concentration of silicon from the ligand, no signal was obtained. However, the ^{31}P isotope of natural occurring phosphorous is 100% abundant and therefore exhibits much higher sensitivity than either ^{13}C and ^{29}Si - NMR ⁴¹, ^{31}P -NMR spectra for the coated sorbents were obtained. All ^{31}P -NMR experiments were done under Block decay conditions where one pulse is used while decoupling protons. **Figure 3.3.3** shows the spectrum of the three bifunctional phosphonate ligands grafted to the silicate surface. The liquid state NMR phosphorus signal of the free mono phosphonate ligand was observed at δ 32.4 ppm. Once the mono phosphonate ligand was grafted to the sol-gel, the phosphorous signal was observed at δ 25.6 ppm using the solid state NMR. Similar results were observed for the bis and linked phosphonate ligands as summarized in **Table 3.3.3**.

Table 3.3.3 chemical shifts of ^{31}P of bifunctional ligands

sorbent	liquid state (ppm)	solid state (ppm) phosphonate	solid state (ppm) phosphoric
Mono FMMS	32.4	25.6	25.4
Bis FMMS	24.7	20.1	16.3
Linked FMMS	32.7	26.5	27.1

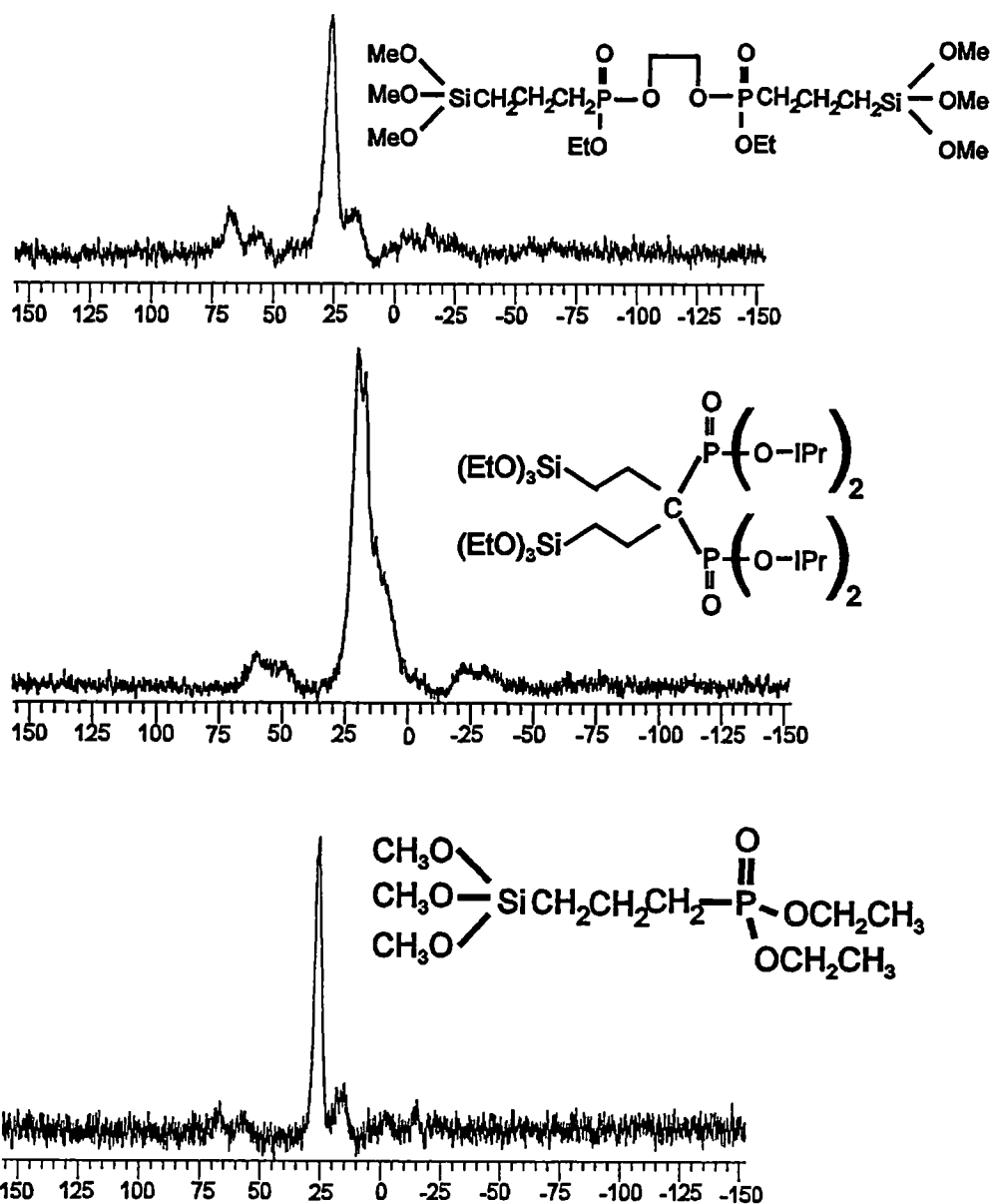


Figure 3.3.3 ^{31}P -NMR spectrum of functional ligands attached to sol-gel. See **Table 3.3.3** for a list of chemical shifts.

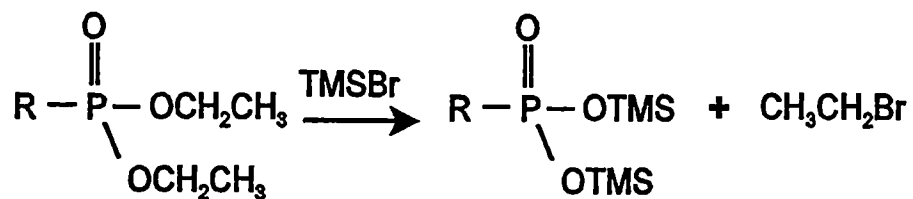
3.4.1 Introduction to the Dealkylation of the Phosphonate Ligand to Phosphonic Acid

Once the FMMS material had been prepared, they were placed into Sr^{+2} solution for uptake studies. These studies showed that the phosphonate ligands did not absorb Sr^{+2} readily. It is well known that phosphonic acids do exhibit high affinities for divalent metal cations such as Sr^{+2} and UO_2^{+2} .^{13,14,15} Since phosphonic acids do bind divalent metal cations and phosphonate ligands appear not to, a method had to be developed to convert the phosphonate ligands into phosphoric acids.

Phosphonic acids ($\text{RP}(\text{O})(\text{OH})_2$) are synthesized via saponification of corresponding phosphonate ester $\text{RP}(\text{O})(\text{OR}')_2$. Acid or base-catalyzed hydrolytic saponification with prolonged heating is effective for this purpose. Although, these methods tend to be effective, functional groups tend to be sensitive to these harsh conditions.⁴⁴ For example, strong base will break down the silica matrix while strong acid could decompose the functionalized ligand. A more recent procedure for the hydrolysis of phosphonate esters under mild conditions involves two steps (**Figure 3.4.1.1**). Step one involves the use of trimethylbromosilane (TMSBr) which transesterifies the alkyl phosphonate. Step two involves the trimethylsilane esters being desilylated by water.^{44,45}

TMSBr is also a silylating agent. The silica matrix has many silanol groups, and silylation will occur when TMSBr is present (**Figure 3.4.1.2**). The silanols on the silica matrix also have an affinity for divalent metal cations under

Step One:



Step Two:

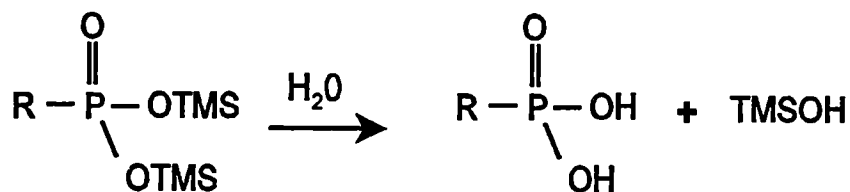


Figure 3.4.1.1 Dealkylation of phosphonate ligand

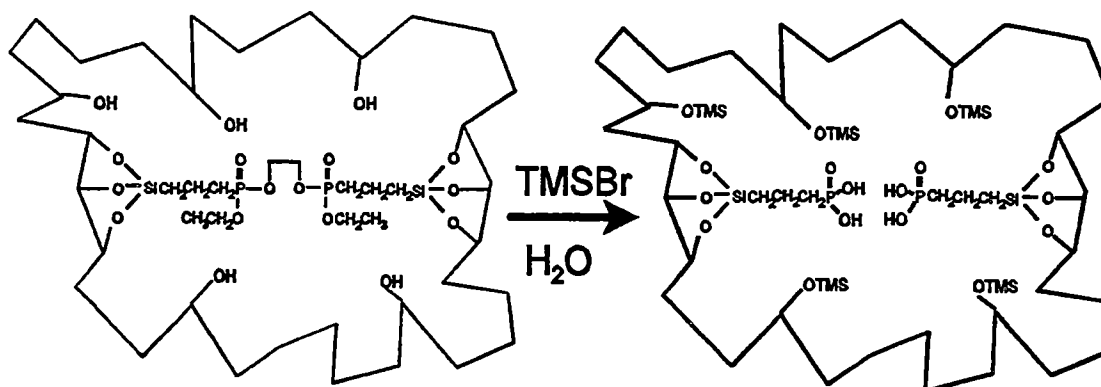


Figure 3.4.1.2 Dealkylation and silylation of phosphonate groups and silanols using TMSBR.

basic conditions. However, once the silanols have been silylated, they no longer have the ability to bind to divalent metal cations. This is an interesting function of these FMMS material. Once treated with TMSBr, only the functionalized ligands will bind metal cations because the silica surface has been neutralized with nonpolar trimethylsilane groups.

3.4.2 Dealkylation of the Phosphonate Group to Phosphonic Acid

Dealkylation of the phosphonate group was performed in THF. A 200 mg sample of dry FMMS was stirred in 10 mL THF. After one hour, an excess (0.3 mL) of TMSBr was added and stirred overnight. Excess TMSBr, bromoethane, and THF were removed under high vacuum (0.5 mm Hg). Water was then added to the FMMS and stirred for 4 hours to hydrolyze the trimethylsilane phosphonate ester.

3.4.3 Characterization of the Phosphonic Acid Monolayer on Mesoporous Support

The phosphonic acid monolayer was characterized using BET and solid state NMR. CPMAS ^{13}C -NMR was attempted for all samples, but due to the sensitivity of carbon and the low concentration of ligand present, ^{13}C spectra were not obtained. CPMAS ^{29}Si -NMR data was collected. As before there is a low concentration of silicon from the ligand, so no data were obtained for the silicon of the ligand. **Figure 3.4.3.1, 2, 3, 4, and 5** shows the spectra of the

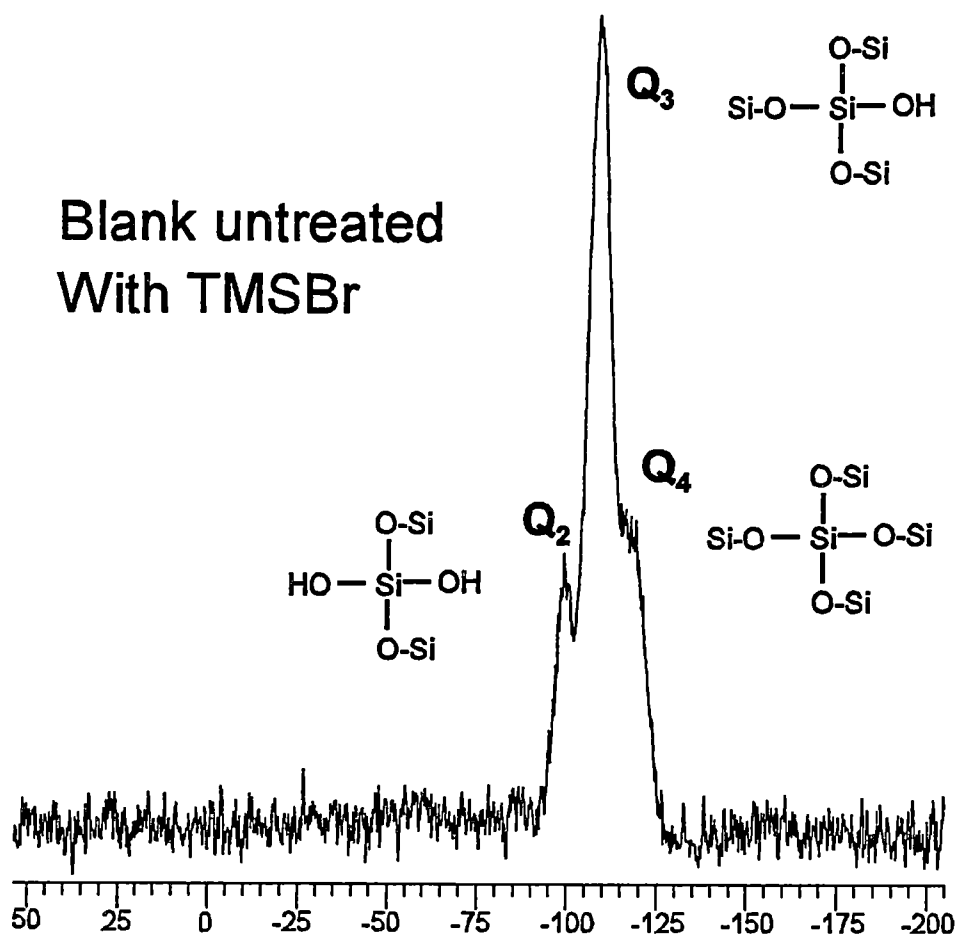


Figure 3.4.3.1 ^{29}Si -NMR spectrum of blank mesoporous sol-gel untreated with TMSBr

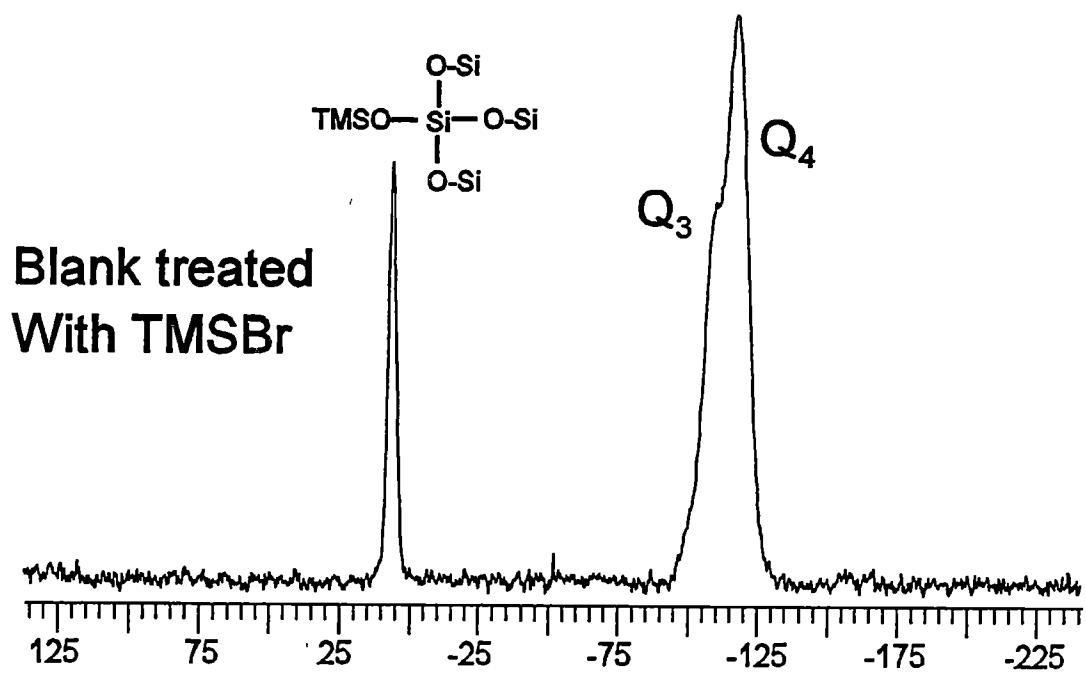


Figure 3.4.3.2 ^{29}Si -NMR spectrum of blank mesoporous sol-gel treated with TMSBr.

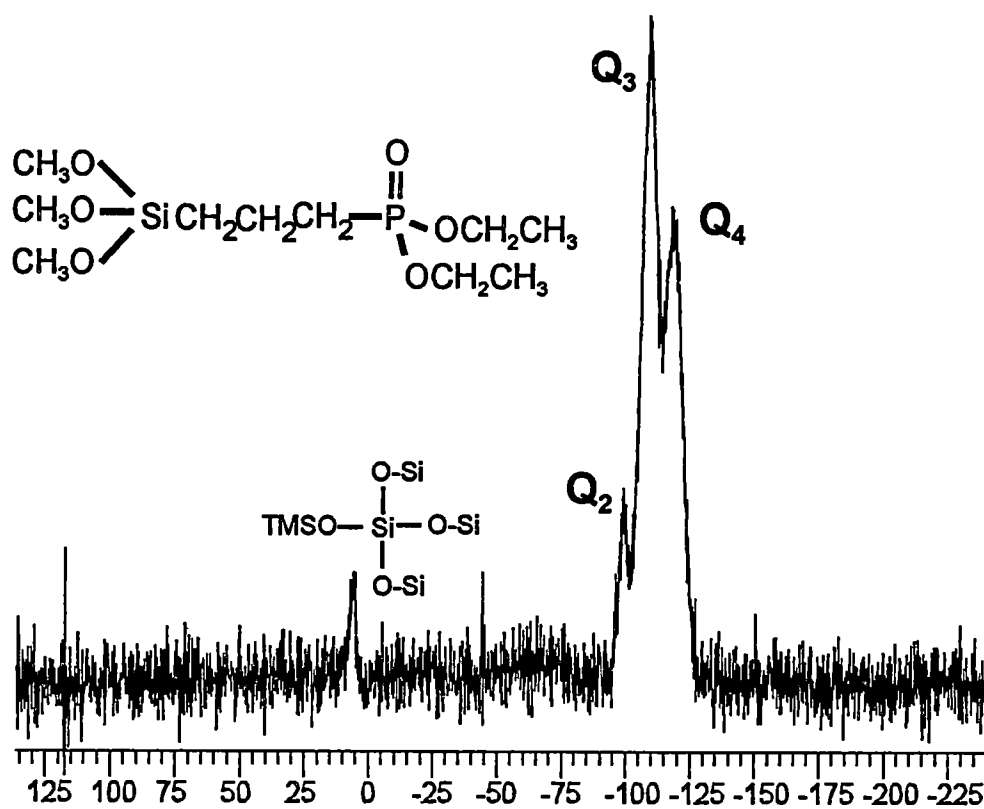


Figure 3.4.3.3 ^{29}Si -NMR spectrum of mono-FMMS material treated with TMSBr.

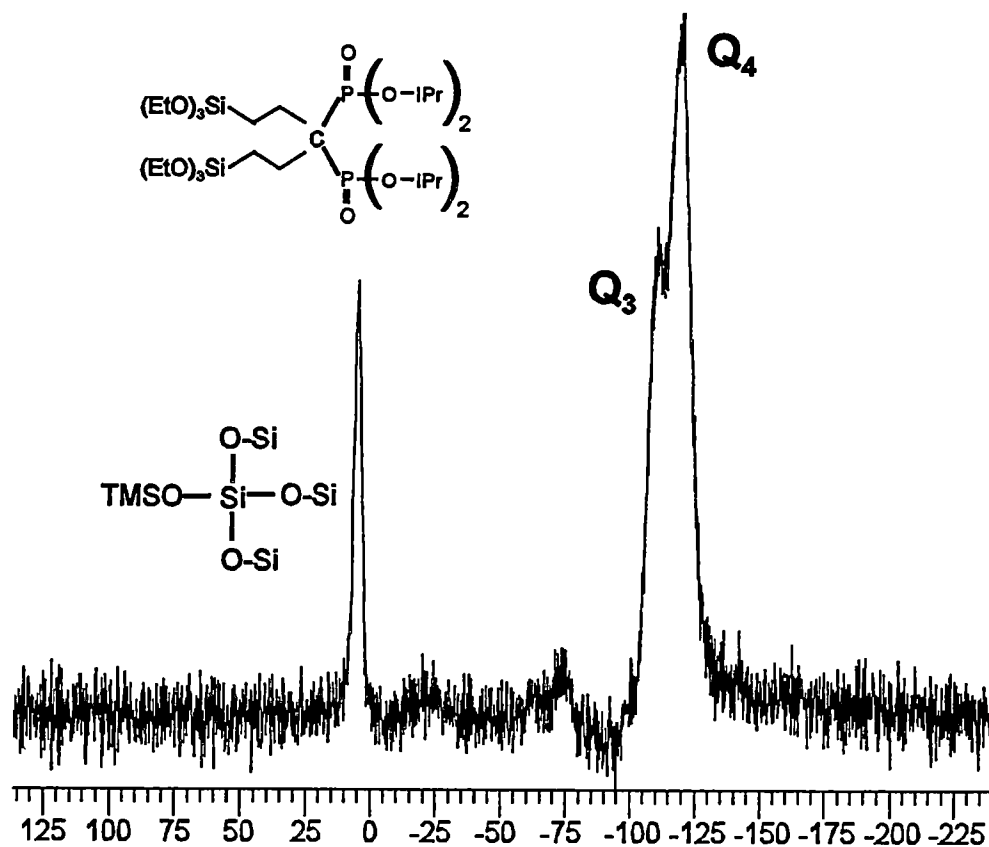


Figure 3.4.3.4 ^{29}Si -NMR spectrum of bis-FMMS material treated with TMSBr.

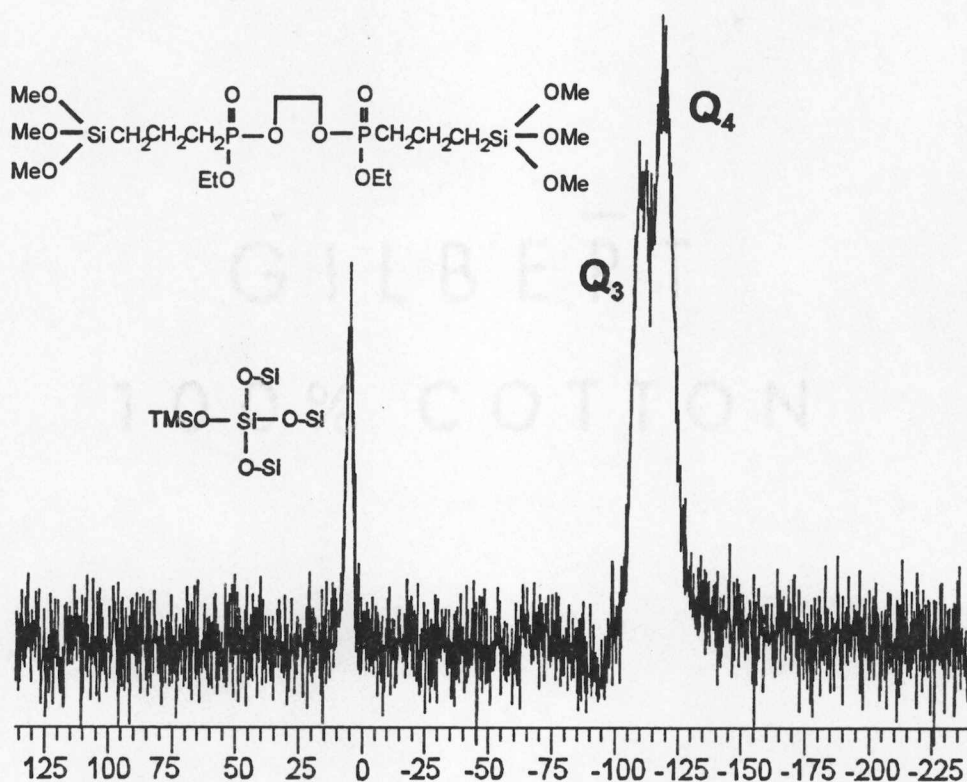


Figure 3.4.3.5 ^{29}Si -NMR spectrum of linked-FMMS material treated with TMSBr.

blank untreated, blank treated, mono, bis, and linked phosphoric acid FMMS. Previously (**Figure 3.4.3.1**), there were three peaks at δ -108.2 (Q^2 - $Si(OSi)_2(OH)_2$), -110.6 (Q^3 - $Si(OSi)_3(OH)$), and -117.1 (Q^4 - $Si(OSi)_4$) ppm. Each of these peaks is associated with the silica matrix. After silylation, the peak at δ -108.2 disappeared while a new peak at δ 5.62 ppm (Si-OTMS) appeared (**Figure 3.4.3.2**). For the mono, bis, and linked-FMMS material spectra (**Figure 3.4.3.3, 4, and 5**), peaks δ -110.6, and -117.1 ppm represent Q^3 and Q^4 silicons. After silylation, the Q^3 peak at δ -110.6 ppm decreases in intensity while the Q^4 peak at δ -117.1 ppm increases in intensity. The reason for the increase of the Q^4 signal (δ -117.1 ppm) is due to the silylation of the surface silanol group thereby creating new $Si(OSi)_4$ sites.

^{31}P -NMR data were also obtained. All ^{31}P -NMR experiments were done under block decay where one pulse excitation is used. **Figure 3.3.3** shows the spectra of mono, bis, and linked phosphonate ligands on mesoporous sol-gel. Once saponification had occurred, a shift in the chemical shift was observed for phosphorous. For the mono phosphonate ligand, the phosphorous signal is observed at δ 21.95 ppm. After saponification, the new signal is observed at δ 25.37 ppm. The same was also observed for the bis phosphonate ligand, the phosphorous signal is observed at δ 16.32 ppm. After saponification, the new signal is observed at δ 19.98 ppm. Finally for the linked ligand, the phosphorous signal is observed at δ 26.50 ppm. After saponification, the new signal is observed at δ 27.07 ppm.

BET sorption measurements were used to determine the distribution of pore sizes and the surface area of the gel. After saponification and silylation of the surface, the specific surface area for the gel was $387 \text{ m}^2/\text{g}$ with a total pore volume of 0.53 cc/g . **Figure 3.4.3.6** is a well defined standard Z shaped hysteresis loop. The very large step located in the relative pressure range of 0.4 to 0.8 is typical for mesoporous material. **Figure 3.4.3.7** shows the distribution of pore diameters for the FMMS material after dealkylation and silylation. There is a narrow distribution of pore sizes between 29 to $44 \text{ \AA}$ with the maximum pore volume occurring at $36 \text{ \AA}$. This narrow pore size distribution is in the mesopore range which is desired. It is important to have large pore sizes now because the pore size has to have the space for fast cation metal absorption.

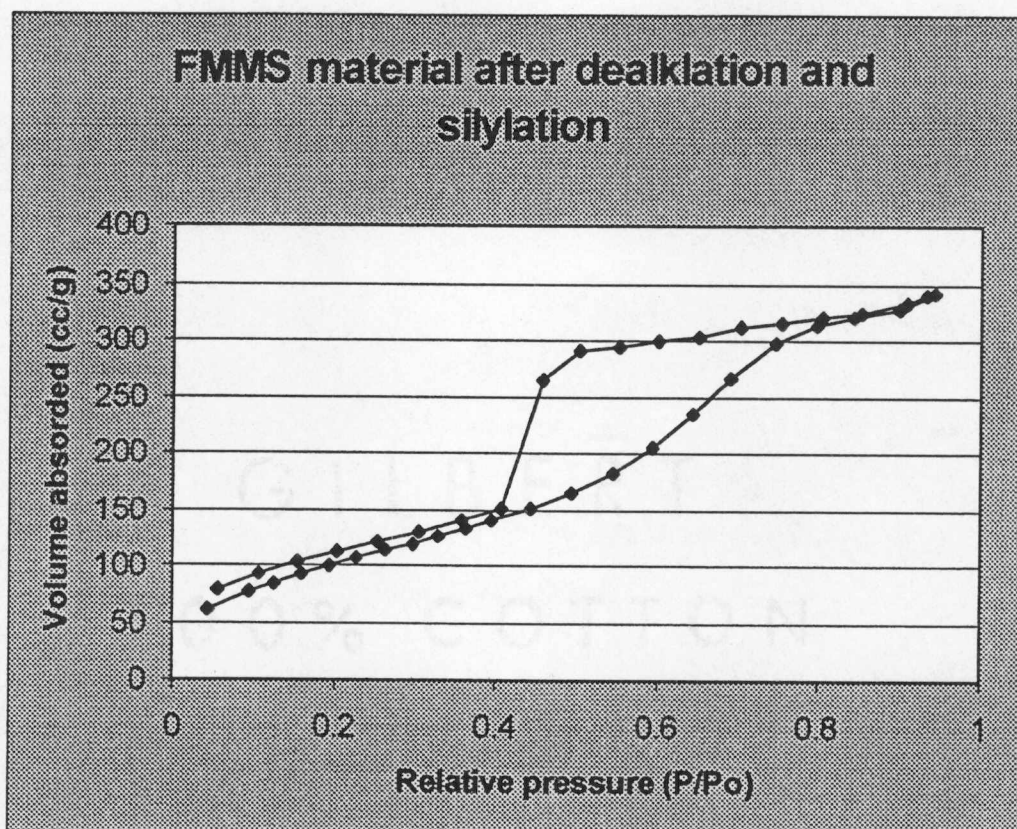


Figure 3.4.3.6 FMMS material after dealklation and silylation.

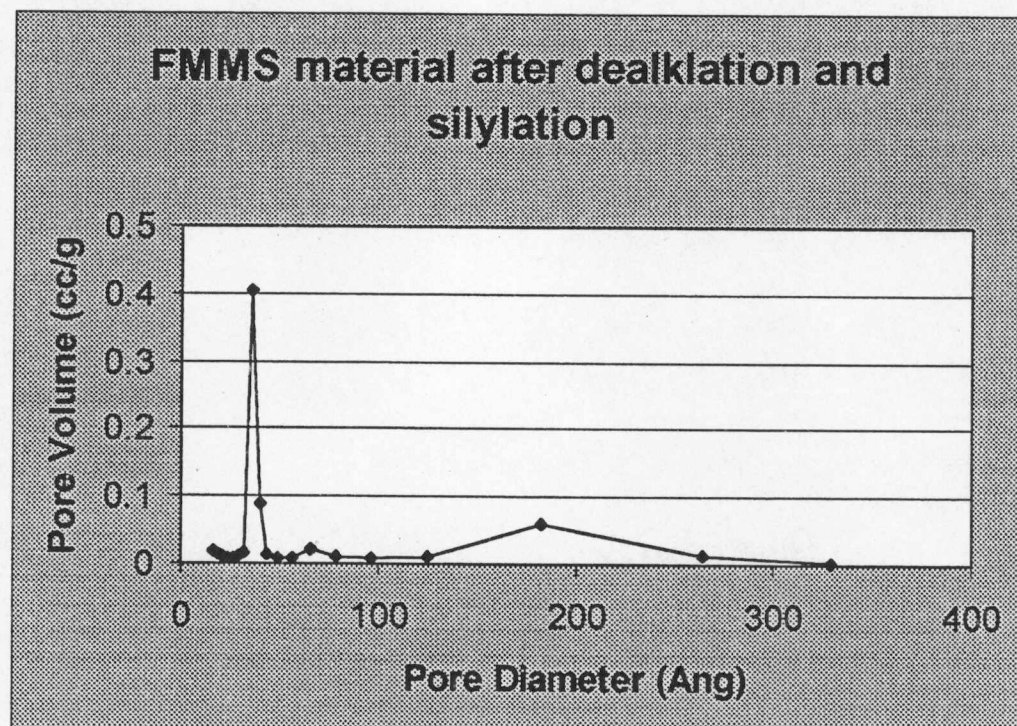


Figure 3.4.3.7 FMMS material after dealklation and silylation.

Chapter Four

Strontium and Uranyl Uptake Studies

4.1 Introduction

Two techniques developed for the separation of metal ions from aqueous solution involve phase transfer and ion exchange. Phase transfer systems consist of the transfer of a solute in a mixture from one phase to another (solvent extraction). The disadvantages of solvent extraction include high cost, toxicity to the aqueous phase, and the large amounts of organic solvents needed for the process.⁶ Ion exchange is a means of removing cations or anions from solutions onto a solid resin which can be regenerated by treatment with acids, bases, or salts.² Advantages of ion exchange over solvent extraction include the retention of extractant, ease of separation due to the heterogeneous nature of the system, and its sensitivity with dilute concentrations.⁸ The disadvantages of ion exchange are its slow kinetics due to the hydrophobicity of the organic support and lower selectivity for target metal ions than solvent extraction.

A metal ion sorbent that combines the favorable characteristics of solvent extraction (fast kinetics, selectivity) and ion exchange materials (solid support and sensitivity in dilute systems) would be ideal for environmental cleanup applications. Mesoporous silica coated with functionalized monolayers (FMMS)

have demonstrated a remarkable ability to absorb heavy metals quickly and selectively from contaminated water.¹¹ The silica matrix is also stable and resistant to chemical degradation up to pH = 12.0.

Concentrating of pollutants is another important factor in the management of waste. A contaminant that has been concentrated is generally much easier and more economical to handle than one that is dispersed in a large quantity of water or soil.² The use of FMMS materials allows large quantities of water that is contaminated with waste to be cleaned up and the waste to be placed into smaller, more, maintainable containers. In this chapter, different FMMS materials will be introduced to different metal cations to determine if these materials are selective, have fast kinetics, and have high affinity to be effective at removing low concentrations of metal ions in solution. The two divalent metal cations studied were strontium and uranyl in the presence of calcium, sodium, and potassium.

4.2.1 Experimental Section

All manipulations were performed in air. All dilutions were performed in class A volumetric glassware. Strontium chloride (Fischer), uranyl nitrate (Fischer), trizma (Aldrich), imidazole (Aldrich), HCl (Fischer), sodium acetate (Fischer), glacial acetic acid (Fischer), and arsenazo III (Aldrich) were used as received. Ultra pure water was used for all standards, dilutions, and stock solutions. All salts were dried at 100 °C before use. An upgraded Perkin Elmer

5100 atomic adsorption spectrometer was used to analyze all calcium and strontium solutions. A Hewlett Packard 8452A diode array UV / vis spectrophotometer was used in the analysis of the uranyl solutions.

4.2.2 pH Buffers

All pH buffers were made from known buffer recipes.⁴⁶ The following pH buffers were made for the metal cation uptake studies: pH=2.0 (0.05M HCl / KCl), pH=3.6 (0.05M sodium acetate / acetic acid), pH=5.0 (0.05M sodium acetate / acetic acid), pH=7.0 (0.05M Imidazole / HCl), pH=8.5 (0.05M Trizma / HCl), and pH=12 (0.05M NaOH / KCl). When choosing the buffers, two issues had to be considered. First, the buffers should not act as strong competitive binders for the target metal ion, and second the buffer could not interfere when using atomic emission or UV/ vis techniques. For example, pH buffers in the middle of the pH scale are usually made with phosphates. Phosphates, however, have appreciable affinities for divalent metal cations and phosphates are an interference for strontium when using atomic emission, so phosphate buffers cannot be used. Described below are the recipes for the individual buffers used in these studies:

pH=2.0 (0.05M HCl / KCl):

Mix 6.5 mL of 0.05M HCl with 25 mL of 0.05M KCl and dilute to 100 mL with H₂O.

pH=3.6 (0.05M sodium acetate / acetic acid):

Mix 3.7 mL of 0.05 M sodium acetate with 46.3 mL of 0.05M acetic acid and dilute to 100 mL with H₂O.

pH=5.0 (0.05M sodium acetate / acetic acid):

Mix 14.8 mL of 0.05M acetic acid with 35.2 mL of 0.05 M sodium acetate and dilute to 100 mL H₂O.

pH=7.0 (0.05M Imidazole / HCl):

Mix 12.15 mL of 0.05M HCl with 25 mL of 0.05 M Imidazole and dilute to 100 mL with H₂O.

pH=8.5 (0.05M Trizma / HCl):

Mix 14.7 mL of 0.1M HCl with 50 mL of 0.1M Trizma and dilute to 100 mL with H₂O.

pH=12 (0.05M NaOH / KCl):

Mix 6.0 mL of 0.05M NaOH with 25 mL of 0.05M KCl and dilute to 100 mL with H₂O.

4.3.1 Preliminary Binding of Sr⁺² Using Mono, Bis, and Linked FMMS

Preliminary binding studies were performed first to determine if the FMMS materials did bind divalent metal cations, such as Sr⁺² and UO₂⁺², and also to determine the pH range for optimum metal cation uptake. As mentioned above, buffer solutions were used for the pH studies. All samples for these studies were prepared in the same manner. It is necessary to have a defined amount of gel per volume of divalent metal cation solution. A ratio of 200:1 metal solution to FMMS material was chosen in order to compare results with those reported in the literature.⁴⁷ For this study, blank gel, mono phosphonic acid FMMS, bis

phosphonic acid FMMS, and linked phosphonic acid FMMS samples were all studied to determine Sr^{+2} uptake at different pH conditions. All of these samples were treated with TMSBr as discussed in the previous chapter. A 50 mg sample was weighed out and placed into a vial containing 10 mL of 25mg/L SrCl_2 in the appropriate buffered pH. The solution was allowed to stir for 24 hours. A kinetics study was performed later to determine the appropriate mixing time required for maximum binding. The solution was filtered and the filtrate was analyzed using atomic emission spectroscopy after dilution of samples so the signal would be on scale. Tables 4.3.1.1, 2, 3, 4 show the results of the preliminary binding at different pHs.

Table 4.3.1.1 Sr^{+2} extraction by treated blank sorbent

pH	Stock solution Sr(II) (ppm)	Final conc. of Sr(II) (ppm)	% Sr(II) absorbed	$K_d \text{ Sr(II)}_a$
pH = 2.0	23.0	23.0	0 ± 3.0	0
pH = 3.6	22.7	21.5	5 ± 3.0	10
pH = 5.0	26.2	26.1	0 ± 3.0	1
pH = 7.0	25.6	19.25	25 ± 3.0	70
pH = 8.5	22.3	4.75	79 ± 3.0	740
pH = 12.0	21.0	9.85	53 ± 3.0	230

$a K_d$ is in units of $[\mu\text{g } \text{Sr}^{+2} / \text{g sol-gel}]/[\text{ppm } \text{Sr}^{+2} \text{ remaining}]$

Table 4.3.1.2 Sr⁺² extraction by Mono FMMS sorbent

pH	Stock solution Sr(II) (ppm)	Final conc. of Sr(II) (ppm)	% Sr(II) absorbed	K _d Sr(II) _a
pH = 2.0	23.0	23.0	0 ± 3.0	0
pH = 3.6	22.7	21.6	5 ± 3.0	10
pH = 5.0	26.2	25.7	2 ± 3.0	5
pH = 7.0	25.6	19.0	26 ± 3.0	80
pH = 8.5	22.3	5.75	74 ± 3.0	580
pH = 12.0	21.0	9.85	53 ± 3.0	230

a K_d is in units of [μg Sr⁺² / g sol-gel]/[ppm Sr⁺² remaining]

Table 4.3.1.3 Sr⁺² extraction by Bis FMMS sorbent

pH	Stock solution Sr(II) (ppm)	Final conc. of Sr(II) (ppm)	% Sr(II) absorbed	K _d Sr(II) _a
pH = 2.0	23.0	20.3	12 ± 3.0	20
pH = 3.6	22.7	13.6	40 ± 3.0	130
pH = 5.0	26.2	12.6	52 ± 3.0	210
pH = 7.0	25.6	8.1	68 ± 3.0	450
pH = 8.5	22.3	7.6	67 ± 3.0	400
pH = 12.0	21.0	4.3	79 ± 3.0	750

a K_d is in units of [μg Sr⁺² / g sol-gel]/[ppm Sr⁺² remaining]

Table 4.3.1.4 Sr⁺² extraction by Linked FMMS sorbent

pH	Stock solution Sr(II) (ppm)	Final conc. of Sr(II) (ppm)	% Sr(II) absorbed	K _d Sr(II) _a
pH = 2.0	23.0	18.9	16 ± 3.0	40
pH = 3.6	22.7	14.9	34 ± 3.0	100
pH = 5.0	26.2	15.1	58 ± 3.0	300
pH = 7.0	25.6	8.6	66 ± 3.0	400
pH = 8.5	22.3	0.8	97 ± 3.0	5700
pH = 12.0	21.0	2.5	91 ± 3.0	1900

a K_d is in units of [μg Sr⁺² / g sol-gel]/[ppm Sr⁺² remaining]

As mentioned in the previous chapter, all of the FMMS materials were treated with TMSBr followed by water. This was performed to hydrolyze the esters to phosphoric acids and to silylate the residual silanol groups on the pore surface of the gel. The silanols on the silica matrix also have an affinity for divalent metal cations under basic conditions. However, once the silanols have been silylated, they no longer have the ability to bind to divalent metal cations. Once treated with TMSBR, only the tethered phosphoric acid ligands will bind metal cations because the silica surface has been neutralized with nonpolar trimethylsilane groups. Table 4.3.1.1 shows the Sr⁺² uptake of the blank gel which contains no tethered ligands. If all the silanol groups had been neutralized all results would read zero. In acidic solutions, these gels basically exhibit no uptake because protonation of sites and the low concentrations of silanol groups. Starting at pH 7.0, there is significant uptake of Sr⁺². There are

two possible reason for this. First, there still could be unreacted silanol groups. Second, under basic conditions, some of the TMS groups could hydrolyze thus uncovering some silanol sites again. **Table 4.3.1.5** shows the mono, bis, and linked FMMS material uptake after the blank gel has been subtracted of the % strontium absorbed by the blank gel at the same pH. The Sr(II) uptake values seen here are due solely to the different tethered ligand present in these samples. This table shows the binding of the ligands and not the gel.

The mono FMMS material exhibits very little affinity for Sr^{+2} . One reason for the low uptake of strontium is the coordination of the ligands on the surface of the mesoporous gel. The mono ligand, when grafted to the gel, is placed randomly (**Figure 4.3.1.1**) and has only one binding site. This is the reason for the low strontium uptake. For the bis and linked FMMS, there is higher uptake of

Table 4.3.1.5 % Sr^{+2} uptake after blank subtraction

pH	Mono FMMS	Bis FMMS	Linked FMMS
pH = 2.0	0 ± 3.0	12 ± 3.0	16 ± 3.0
pH = 3.6	0 ± 3.0	35 ± 3.0	29 ± 3.0
pH = 5.0	2 ± 3.0	52 ± 3.0	58 ± 3.0
pH = 7.0	1 ± 3.0	44 ± 3.0	42 ± 3.0
pH = 8.5	0 ± 3.0	18 ± 3.0	48 ± 3.0
pH = 12.0	0 ± 3.0	26 ± 3.0	38 ± 3.0

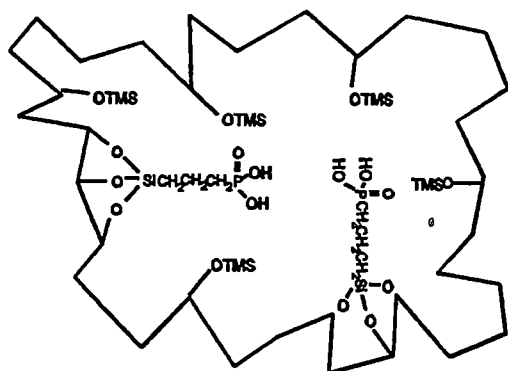


Figure 4.3.1.1 Randomly placed mono ligand.

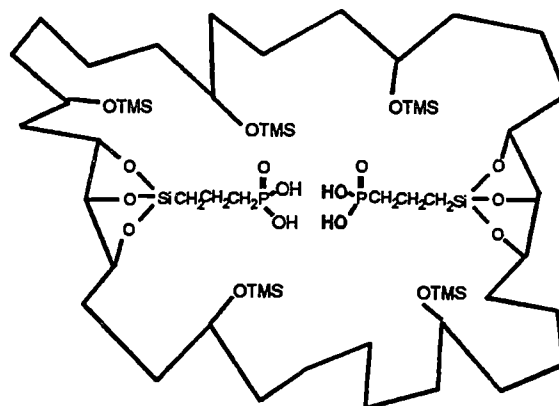


Figure 4.3.1.2 linked ligand after TMSBr.

strontium. Both of these materials contain two binding sites for strontium to coordinate with. **Figure 4.3.1.2** shows the difference between the mono FMMS and the linked FMMS after treatment with TMSBr and hydrolysis. With the mono FMMS, the ligands are randomly grafted to the gel. In the link FMMS, there are two mono ligands in close proximity with each other, providing two binding sites for the strontium.

The FMMS material at pH = 5.0 had the largest uptake of strontium of all the pHs even though uptake at all pHs above pH = 5.0 was similar. These FMMS materials appear to remove strontium better when in neutral or slightly acidic solutions. The ligand does not appear to be affected when the concentration of OH⁻ is higher.

4.3.2 Kinetics Studies of Sr⁺² Uptake Using FMMS Material

Since it was determined that the FMMS materials did bind strontium, it was necessary to determine how fast the strontium was taken up by the gels. The rate of uptake was measured by placing the gels into 25 mg/L SrCl₂ solution at pH = 5.0 in a 0.05 M acetate buffer. The gels and solutions were stirred for different time intervals. The times the gels stirred and their percent uptake are shown in Table 4.3.2.

The FMMS material appears to reach equilibrium with respect to strontium binding after one hour. Results after one hour exhibit only slight improvements in uptake. In other studies, similar studies showed faster kinetic uptake of 5 to 10 minutes.⁴⁸ One reason for slower kinetic uptake in these FMMS materials is the fact that they are more hydrophobic due to silylation of the silanols using TMSBr. These materials become nonpolar and tend to float on top of the strontium solution. After about 30 minutes of vigorous stirring the FMMS material appears to be fully wetted by the solution. Because of this slow process, all solutions were allowed to stir for 5 hours.

4.3.3 Recyclability of FMMS Material after Strontium Uptake

It was seen that in 0.05 M HCl / KCl buffer at pH = 2.0 there was low uptake of strontium. There was low strontium uptake because most of the binding sites were protonated. Since 0.05 M HCl did not allow strontium binding, 1.0 M HCl was used for the removal of strontium for FMMS materials. The 50

Table 4.3.2 Kinetic study (pH = 5.0) linked FMMS

TIME	Percent uptake of Sr^{+2}
10 minutes	22 ± 3.0
30 minutes	30 ± 3.0
1 hour	56 ± 3.0
18 hours	57 ± 3.0
24 hours	58 ± 3.0

mg of FMMS material was allowed to stir for five hours in 25 mL of 1.0 M HCl. After this time the FMMS material was filtered and washed with water and then a buffer depending on the pH studied. **Table 4.3.3** shows the recyclability of the linked FMMS material after strontium uptake. This table shows one sample that has gone through the process of strontium uptake and acid wash three times.

After each acid wash, there was a slight decrease in the amount of strontium absorbed because not all of the strontium was removed from the FMMS material after the acid wash. In the future, the use of 2.0 M HCl could be used for the acid wash.

4.3.4 Imprinting Effects Using the Mono and Bis FMMS Material

With the encouraging results of the functionalized mesoporous materials in hand, it was deemed appropriate to attempt to imprint. Instead of simply grafting ligands to the surface of mesoporous silica, the technique known as molecular imprinting to enhance the metal ion selectivity was investigated in

Table 4.3.3 Recyclability of Linked FMMS in pH = 5.0 solution

Cycle #	Initial Conc. of Sr^{+2} solution	Conc. after Sr^{+2} uptake	Sr^{+2} conc. in acid wash
1	22.3	6.4	15.9
2	22.3	6.8	15.3
3	22.3	7.2	14.9

conjunction with this family of ligands. **Figure 4.3.4.1** illustrates conceptually molecular imprinting. The technique of molecular imprinting involves the incorporation of a template (the metal ion) and a bifunctional ligand. The two are mixed together so that the metal binds to a set of ligands. The complex assembly is then grafted to the surface of the mesoporous silica. Finally, the metal ion template is removed via acid wash. This leaves what may be referred to as an imprinted cavity composed of the ligands and possibly surface binding sites which reflect the size and electronic signature of the initial template.

In this study, the template is strontium and the bifunctional ligands are the mono and bis phosphonate ligands. The reason the linked phosphonate was not chosen was the fact that during transesterification and dealkylation using TMSBr to form the phosphonic acid, the glycol bridge is broken forming two mono phosphonic acids. As for the mono and the bis phosphonate ligands, the phosphonic acid groups are easily formed using TMSBr. The phosphonic acid

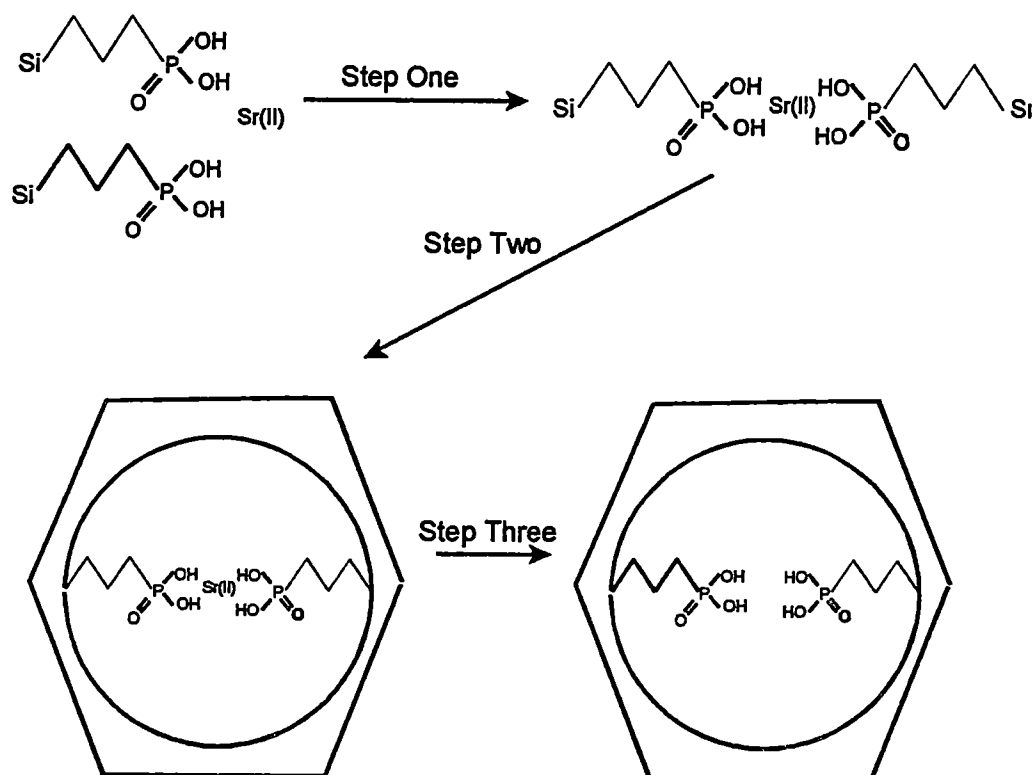


Figure 4.3.4.1 Molecular Imprinting

form is needed because this form, in contrast to the ester, exhibits high affinity for divalent metal ions.

For a 1.0 g sample of FMMS material, 210 μL of functionalized ligand is needed to achieve a coating of 15% by weight assuming all ligands become covalently bound to the silicate surface. Second, the phosphonate ligand is transesterification using TMSBr. An appropriate amount of SrCl_2 is dissolved in a small amount of ultra pure water to give a 1:2 metal to ligand ratio when mixed with the TMS-treated ligand. The phosphonate ligand and the SrCl_2 solution are

mixed together. First, the water desilylates the TMS ester forming the phosphonic acid which then binds the strontium ion. The solution is mixed for 5 minutes, and then added to a solution of 1.0 g mesoporous sol-gel in a 10% ethanol/water (by volume) solution. The solution is stirred overnight at 60 °C. After cooling to room temperature, the solution was decanted and replaced with toluene. The toluene solution was then refluxed for another 6 hours, at which time the mixture was filtered and washed with 2-propanol, acetone, and water. The imprinted FMMS material was then dried to remove the excess water. 6M HCl was then added to the templated FMMS material to remove the strontium ion. The solution was stirred for 5 hours. After two acid washes, the filtrate was tested for the presence of strontium using atomic emission. There was no strontium present in the filtrate, consistent with removal of all the strontium template. **Figure 4.3.4.2** and **4.3.4.3** show the conceptual differences between

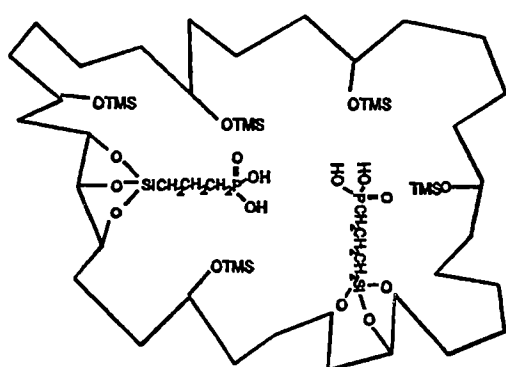


Figure 4.3.4.2 Nonimprinted FMMS material

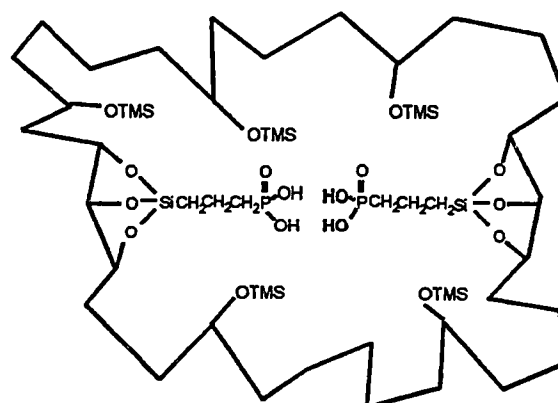


Figure 4.3.4.3 Imprinted FMMS material

the imprinted material and the nonimprinted material. The organization of the ligands on the imprinted FMMS material allows for higher binding capability than does the nonimprinted FMMS material.

All metal ion solutions were buffered to pH = 5.0 using 0.05 M sodium acetate/acetic acid buffer. 50 mg of imprinted FMMS material was weighed out and placed into a vial containing 10 mL of 25 mg/L Sr^{+2} . The solution was stirred for 5 hours. The solution was filtered and both the filtrate and the initial standard solutions were analyzed via atomic emission spectroscopy. **Table 4.3.4** shows the results comparing the imprinted FMMS material to the nonimprinted FMMS material.

The untreated TMSBr blank gel has a high affinity for strontium compared to the TMSBr treated blank gel. The high affinity for strontium in the untreated blank is from the silanol surface sites. Once treated with TMSBr, the silanol sites no longer have an affinity for strontium because they are now TMS sites. The nonimprinted (TMSBr treated) mono phosphonate FMMS material had very little affinity for Sr^{+2} . As mentioned earlier in this chapter, this is due to random tethering of the ligands on the surface of the mesoporous gel. The mono ligand when grafted to the gel is placed randomly and the mono ligand has one binding site. There was significant improvement in the uptake of strontium with the imprinted mono FMMS material samples. For the imprinted mono-FMMS and bis-FMMS material, there was two types of samples, one that was treated with TMSBr and one that was untreated. Results show very little difference in the

Table 4.3.4 Imprinting vs. Nonimprinted FMMS Material

Sorbent	Stock sol. Sr(II) (ppm)	Final conc. of Sr(II) (ppm)	% Sr(II) absorbed	K_d Sr(II) _a	K'
blank gel no TMSBr	10.0	4.1	59 ± 3.0	300	
blank gel	103.2	95.9	7 ± 3.0	15	
nonimprinted gel (mono)	103.2	92.3	11 ± 3.0	30	
imprinted gel (mono)	103.2	39.7	62 ± 3.0	320	10
imprinted gel (mono) TMSBr treat	103.2	41.2	60 ± 3.0	320	10
nonimprinted gel (bis)	103.2	55.0	47 ± 3.0	140	
imprinted gel (bis)	103.2	54.5	47 ± 3.0	140	1
imprinted gel TMS (bis) TMSBr treated	103.2	56.7	45 ± 3.0	140	1
nonimprinted gel (linked)	103.2	42.4	59 ± 3.0	310	

$a = K_d$ is in units of $[\mu\text{g Sr}^{+2} / \text{g sol-gel}] / [\text{ppm Sr}^{+2} \text{ remaining}]$

$K' = k_{\text{imprinted}} / k_{\text{nonimprinted}}$

affinity for strontium. These results suggest that the ligands alone are binding the strontium and not surface site on the mesoporous gel. Both the imprinted mono and nonimprinted linked FMMS material, showed similar results. One advantage of the imprinted mono-FMMS material over the nonimprinted linked-FMMS material is that it is cheaper to produce.

In conclusion, the imprinted mono FMMS material showed a significant increase in affinity for strontium because there are now two mono phosphonic acids for each strontium (**Figure 4.3.4.3**) compared to the nonimprinted phosphonic acid which is randomly orientated. As for the bis FMMS material, there was no improvement in Sr^{+2} uptake in the imprinted samples compared to the nonimprinted samples.

4.3.5 Competitive Loading of Sr^{+2} and Ca^{+2} Using FMMS Material

Most wastewater solutions containing strontium also contain many other metal cations such as calcium, potassium, sodium, and magnesium.^{1,42} These alkali metals are introduced into wastewater systems primarily through tap water and acid / base treatment. Usually, the concentrations of these alkali metals are much higher than strontium. **Table 4.3.5.1** shows an average alkali metal concentration of a waste holding tank located at the Transuranic Waste Storage and Disposal site at Hanford, Washington.⁴²

For the study of competitor ions, the alkali metal calcium was chosen. Since these studies were performed in pH = 5.0 and pH = 8.5 buffers, each

Table 4.3.5.1 Single-Shell Tank 241-AX-101

alkali metal ion	ppm
Na ⁺	1.6 x 10 ⁵
Ca ²⁺	750
K ⁺	1.3 x 10 ³
Sr ²⁺	0.38

buffer also contained either sodium or potassium. These three alkali metals competed with strontium. **Table 4.3.5.2** shows the concentration of the competitor metal ions compared to strontium. The concentrations were not the same as in waste storage tanks such as Hanford, but their concentration was still higher than the concentration of strontium.

For the competitive metal ion studies, 50 mg of FMMS material was weighed out and placed into a vial containing 10 mL of 25 mg/L Sr²⁺ and 40 mg/L Ca²⁺ concentration in either pH=5.0 or pH=8.5 buffer. The solution was allowed to stir for 5 hours. The sample was filtered and the filtrate was tested for Sr²⁺ and Ca²⁺ using atomic emission spectroscopy after dilution of samples so the signal would be on scale.

During this study, three different types of FMMS materials were used for the mono and bis phosphonates. They were nonimprinted (TMSBr treated), imprinted (no TMSBr treatment), and imprinted (TMSBr treated). The linked

Table 4.3.5.2 Concentration of alkali metal ions used in study

alkali metal ion	ppm
Na ⁺	1145
K ⁺	1950
Ca ²⁺	40 to 1500
Sr ²⁺	25

FMMS sorbent was not used because TMSBr breaks the glycol bridge, as mentioned in chapter 3, splitting the linked phosphonate into two mono phosphonate. Table 4.3.5.3 shows the results of the competitive loading of Sr²⁺ and Ca²⁺ by FMMS sorbents.

The nonimprinted (TMSBr treated) mono phosphonate FMMS material showed very little affinity for Sr²⁺ or Ca²⁺. As mention earlier in this chapter, this is from the coordination of the ligands on the surface of the mesoporous gel. The mono ligand, when grafted to the gel, is placed randomly and mono ligand has one binding site. There was significant improvement in the uptake of strontium with the imprinted samples. There was no selectivity between strontium and calcium. The imprinted mono phosphonate FMMS showed the same affinity for calcium and strontium. The same results are also seen with the linked phosphonate (TMSBr treated) FMMS material. The reason for this might be due to similar chemical properties of calcium and strontium and their similar sizes (Ca²⁺ 100pm; Sr²⁺ 118pm).^{2,49} As for the bis-phosphonate FMMS

Table 4.3.5.3 Competitive Loading of Sr(II) and Ca(II) by FMMS sorbents

Sorbent	Stock sol. Sr(II) (ppm) _a	Stock sol. Ca(II) (ppm) _a	% Sr(II) absorbed	% Ca(II) absorbed	K _d Sr(II) _b	K _d Ca(II) _b
blank	31.5	37.3	2 ± 3.0	0 ± 3.0	40	0
nonimprinted (mono)	26.0	40.7	2 ± 3.0	3 ± 3.0	10	10
imprinted (mono)	31.5	37.3	44 ± 3.0	57 ± 3.0	150	260
imprinted TMSBr (mono)	31.5	37.3	38 ± 3.0	57 ± 3.0	120	260
nonimprinted (bis)	26.0	40.7	24 ± 3.0	0 ± 3.0	60	0
imprinted (bis)	31.5	37.3	24 ± 3.0	2 ± 3.0	60	10
imprinted TMSBr (bis)	31.5	37.3	23 ± 3.0	3 ± 3.0	50	10
nonimprinted (linked)	26.0	40.7	45 ± 3.0	58 ± 3.0	170	280

a pH=5.0 (0.05M acetate buffer)

b K_d is in units of [μg Sr⁺² / g sol-gel]/[ppm Sr⁺² remaining]

material, the three different variations all showed the same results. The three samples had the same loading and had the same selectivity.

In conclusion, the imprinted mono phosphonate FMMS and the linked phosphonate FMMS material behaved similarly in competitor studies involving strontium and sodium. However, the imprinted mono-phosphonate FMMS material offers an advantage over the nonimprinted linked phosphonate FMMS

material. The mono-phosphonate ligand is cheaper and easier to produce than the linked phosphonate. As for the imprinted mono-phosphonate and the bis-phosphonate containing sorbents, the decision as to which is best, can be made based on the individual waste system. The imprinted mono-phosphonate material absorbs more strontium than the bis-phosphonate material. The mono phosphonate material also absorbs calcium, whereas the bis-phosphonate material does not absorb as much calcium.

4.4.1 Preliminary Binding Studies of Uranyl Using the Mono, Bis, and Linked FMMS material

Preliminary binding studies were performed first to determine if the FMMS material did bind divalent metal cations, such as Sr^{+2} and UO_2^{+2} , and what pH showed the largest metal cation uptake. As mentioned above, buffer solutions were used for the pH studies. The uranyl cation precipitates above $\text{pH} = 7.0$, so no pH studies were performed above $\text{pH} = 7.0$. All FMMS material samples for these studies were prepared in the same manner. It is necessary to have an adequate amount of gel per volume of divalent metal cation solution. A ratio of 200:1 metal solution to FMMS material was chosen in order to compare results with those reported in the literature.⁴⁷

For this study, blank gel, mono FMMS, bis FMMS, and linked FMMS were all studied to determine UO_2^{+2} uptake at three different pHs. All of these samples were treated with TMSBr as discussed in the previous chapter. Each

sample was weighed out to 50 mg and placed into a vial containing 10 mL 25mg/L UO_2^{+2} concentration in the appropriate buffered pH. The solution was allowed to stir for 5 hours. The solution was filtered and the filtrate was analyzed using UV/vis spectroscopy after dilution of samples so the signal would be on scale. Tables 4.4.1.1, 2, 3, 4 show the results of the preliminary binding at different pHs.

Table 4.4.1.1 Uranyl extraction by TMSBr treated blank sorbent

pH	Stock solution UO_2^{+2} (ppm)	Final Conc. of UO_2^{+2} (ppm)	% UO_2^{+2} absorbed	$K_d \text{UO}_2^{+2}_a$
pH = 2.0	106.5	106.5	0 ± 3.0	0
pH = 5.0	106.5	102.1	4 ± 3.0	10
pH = 7.0	106.5	102.3	4 ± 3.0	10

$a K_d$ is in units of $[\mu\text{g } \text{UO}_2^{+2} / \text{g sol-gel}]/[\text{ppm } \text{UO}_2^{+2} \text{ remaining}]$

Table 4.4.1.2 Uranyl extraction by TMSBr treated Mono sorbent

pH	Stock solution UO_2^{+2} (ppm)	Final Conc. of UO_2^{+2} (ppm)	% UO_2^{+2} absorbed	$K_d \text{UO}_2^{+2}_a$
pH = 2.0	106.5	100.4	6 ± 3.0	20
pH = 5.0	106.5	18.8	82 ± 3.0	1000
pH = 7.0	106.5	17.5	84 ± 3.0	1250

$a K_d$ is in units of $[\mu\text{g } \text{UO}_2^{+2} / \text{g sol-gel}]/[\text{ppm } \text{UO}_2^{+2} \text{ remaining}]$

Table 4.4.1.3 Uranyl extraction by TMSBr treated Bis sorbent

pH	Stock solution UO ₂ ⁺² (ppm)	Final Conc. of UO ₂ ⁺² (ppm)	% UO ₂ ⁺² absorbed	K _d UO ₂ ⁺² _a
pH = 2.0	106.5	90.2	15 ± 3.0	350
pH = 5.0	106.5	4.6	96 ± 3.0	4900
pH = 7.0	106.5	5.6	95 ± 3.0	4750

a K_d is in units of [μg UO₂⁺² / g sol-gel]/[ppm UO₂⁺² remaining]

Table 4.4.1.4 Uranyl extraction by TMSBr treated Linked sorbent

pH	Stock solution UO ₂ ⁺² (ppm)	Final Conc. of UO ₂ ⁺² (ppm)	% UO ₂ ⁺² absorbed	K _d UO ₂ ⁺² _a
pH = 2.0	106.5	93.8	12 ± 3.0	260
pH = 5.0	106.5	11.0	90 ± 3.0	2000
pH = 7.0	106.5	16.3	85 ± 3.0	1320

a K_d is in units of [μg UO₂⁺² / g sol-gel]/[ppm UO₂⁺² remaining]

Table 4.4.1.1 shows that the blank gel exhibit very little uptake of uranyl. The blank gel used was treated with TMSBr. This was performed to hydrolyze the silanol groups on the gel which would bind uranyl ions nonselectively. The small uranyl uptake observed at pH 5 and 7 (**Table 4.4.1.1**) is due to residual silanol groups that did not react with TMSBr. If the blank gel was not coated with TMSBr then the uptake of uranyl by the silanol groups would much higher. This will be shown later.

As for the mono, bis, and linked FMMS materials, there was very little uptake of uranyl at pH = 2.0. The reason for the low uranyl uptake is because the gels are protonated due to the low pH. At pH 5.0 and pH 7.0, there was significant uptake of uranyl. The mono and linked FMMS material had similar results. Both materials had much higher uptake of uranyl than strontium. The bis-FMMS material had the greatest uptake of uranyl. This is due to the close proximity of the two phosphonic acid groups. As for the mono and linked, the linked has slightly higher uptake of uranyl due to the two mono phosphonic acid ligands. Their close proximity provides for better uptake of uranyl.

4.4.2 Recyclability of FMMS Material after Uranyl Uptake

It previously shown that in a solution with 0.05M HCl/ KCl buffer at pH = 2.0, there was very little uptake of uranyl because most of the binding sites were protonated. Since 0.05 M HCl did not allow for much uranyl uptake, 1.0 M HCl was used for the removal of uranyl for FMMS materials. The 50 mg of FMMS material was allowed to stir for 5 hours in 25 ml of 1.0M HCl. After this time, the FMMS material was filtered and washed with water and then with pH 7.0 buffer. **Table 4.4.2** shows the recyclability of the bis-FMMS material after uranyl uptake. This table shows one sample that has gone through the process of uranyl uptake and acid wash three times.

After each acid wash, there was essentially no change in the uptake of uranyl when compared to the first cycle. Because the uranyl uptakes were

Table 4.4.2 Recyclability of bis-FMMS in pH = 5.0 solution

Cycle #	Initial Conc. of UO_2^{+2} solution	Conc. after UO_2^{+2} uptake	UO_2^{+2} conc. in acid wash
1	100.5 ppm	19.4 ppm	81.1 ppm
2	100.5 ppm	20.9 ppm	79.6 ppm
3	100.5 ppm	14.3 ppm	86.2 ppm

similar, this shows that 1.0 M HCl did remove uranyl for the FMMS material.

Due to the low acid concentration, this makes the acid waste easy to handle and store.

4.4.3 Imprinting Effects Using the Mono and Bis FMMS Material

As mentioned previously in this chapter, instead of simply grafting ligands to the surface of mesoporous silica, molecular imprinting may be used to try and enhance the metal ion affinity. For this study, the template was uranyl and the bifunctional ligands were the mono- and bis-phosphonic acids.

For a 1.0 g sample of FMMS material, 210 μL of functional ligand is needed to obtain 15% by weight coating assuming all added ligand binds to the surface of the mesoporous support. First, the phosphonate ligand undergoes transesterification using TMSBr followed by water. An appropriate amount of uranyl nitrate is dissolved in a small amount of ultra pure water so that there is a 1:2 metal to ligand ratio. The phosphonate ligand and the uranyl nitrate solution are mixed together. First, the water desilylates the TMS ester producing the

phosphonic acid group which then binds the uranyl ion. The solution was mixed for 5 minutes, and then added to a solution of 1.0 g mesoporous sol-gel in a 10% ethanol in water solution. The solution was stirred overnight at 60 °C. After cooling to room temperature, the ethanol was decanted and replaced with toluene. The toluene solution was then refluxed for another 6 hours, at which time the mixture was filtered and washed with 2-propanol, acetone, and water. The imprinted FMMS material was then dried to remove the excess water. 6M HCl was then added to the templated FMMS material to remove the uranyl ion. The solution was stirred for 5 hours. After two acid washes, the filtrate was tested for the presence of uranyl using UV/vis spectroscopy. There was no uranyl present in the filtrate, indicating that all of the templated uranyl had been removed.

All metal ion solutions were buffered to pH = 5.0 using 0.05 M sodium acetate/acetic acid. 50 mg of imprinted FMMS material was weighed out and placed into a vial containing 10 mL of 100 mg/L UO_2^{+2} . The solution was stirred for 5 hours. The solution was filtered and both the filtrate and the initial standard solutions were analyzed via UV/vis spectroscopy. **Table 4.4.3** shows the results comparing imprinted FMMS material to nonimprinted FMMS material.

When studying the imprinting effect of strontium with FMMS material, there was a significant increase of strontium uptake with the imprinted samples over the nonimprinted samples. As for uranyl imprinting, there was not as large increase in the amount of uranyl absorbed. There was a 14% increase in the

Table 4.4.3 Imprinting vs. Nonimprinted FMMS material

Sorbent	Stock sol. UO ₂ ⁺² (ppm)	% UO ₂ ⁺² absorbed	K _d UO ₂ ⁺² _a	K'
blank gel (no TMSBr)	106.5	46 ± 3.0	500	
blank gel	106.5	4 ± 3.0	10	
nonimprinted gel (mono)	106.5	82 ± 3.0	1000	
imprinted gel (mono)	106.5	96 ± 3.0	1850	1.8
nonimprinted gel (bis)	106.5	96 ± 3.0	1790	
imprinted gel (bis)	106.5	98 ± 3.0	2340	1.3
nonimprinted gel (linked)	106.5	90 ± 3.0	2000	

a = K_d is in units of [μg UO₂⁺² / g sol-gel]/[ppm UO₂⁺² remaining]

K' = k_{imprinted} / k_{nonimprinted}

uptake of uranyl with the mono-phosphonic acid material which shows the imprinting process was worthwhile. Very little effect of imprinting was observed with the bis-FMMS material.

4.4.4 Competitive Loading of Uranyl and Calcium Using FMMS Material

Most wastewater solution containing uranyl also contains many other metal cations such as calcium, potassium, sodium, and magnesium.^{1,42} These alkali metals are introduced into wastewater system primarily through tap water and acid treatment. Usually, the concentration of these alkali metals are several fold higher than uranyl. **Table 4.4.4.1** shows an average alkali metal

Table 4.4.4.1 Single-Shell Tank 241-AX-101

alkali metal	ppm
sodium ion	1.6×10^5
calcium ion	750
potassium ion	1.3×10^3
uranyl ion	2.48×10^3

concentration of a "high level waste" holding tank located at the Hanford, Washington.⁴²

For the study of competitor ions, the alkaline earth metal, calcium was chosen to compete with uranyl. These studies were performed in a pH = 5.0 buffer of 0.05 M sodium acetate/ acetic acid. Table 4.4.4.2 shows the concentration of the competitor metal ions compared to uranyl. The concentrations were not the same as in waste storage tanks such as Hanford, but their concentrations were still higher than uranyl.

For the competitive metal ion studies, 50 mg of FMMS material was weighed out and placed into a vial containing 10 mL of 100 mg/L UO_2^{+2} and 1200 mg/L Ca^{+2} concentration in buffer pH=5.0. The solution was allowed to stir for 5 hours. The sample was filtered and the filtrate was tested for UO_2^{+2} and

Table 4.4.4.2 Concentration of alkali metal ions used in study

alkali metal	ppm
Na ⁺	1145
Ca ²⁺	40 to 1500
UO ₂ ⁺²	100

Ca⁺² using UV/vis spectroscopy and atomic emission spectroscopy after dilution of samples so the signal would be on scale.

During this study, three different types of FMMS materials were used for the mono and bis phosphonates. They were nonimprinted (TMSBr treated), imprinted (no TMSBr treatment), and imprinted (TMSBr treated). Three different gels were not used for the linked phosphonate FMMS because TMSBr breaks the glycol bridge, as mentioned in chapter 3, splitting the linked phosphonate into two mono phosphonates. **Table 4.4.4.3** shows the results of the competitive loading of UO₂⁺² and Ca⁺² by FMMS sorbents.

As mentioned before, all samples were treated with TMSBr unless specified. The difference seen between the blank gel treated with TMSBr and the blank gel that was not treated is shown in **Table 4.4.4.3**. TMSBr causes silylation of the silanol groups of the mesoporous silica gel. Once the silanol groups have been silylated, the phosphonic acid ligands are the only groups that

Table 4.4.4.3 Competitive Loading of $\text{UO}_2(\text{II})$ and $\text{Ca}(\text{II})$ by FMMS sorbents

Sorbent	Stock sol. $\text{UO}_2(\text{II})$ (ppm) _a	Stock sol. $\text{Ca}(\text{II})$ (ppm) _a	% $\text{UO}_2(\text{II})$ absorbed	% $\text{Ca}(\text{II})$ absorbed	K_d UO_2 (II) _b	K_d $\text{Ca}(\text{II})$ _b
blank (no TMSBr)	100.8	1205.5	42 ± 3.0	6 ± 3.0	140	10
blank (treated)	100.8	1205.5	3 ± 3.0	1 ± 3.0	10	5
mono FMMS	100.8	1205.5	38 ± 3.0	0 ± 3.0	130	0
imprinted mono FMMS	100.8	1205.5	79 ± 3.0	1 ± 3.0	720	5
bis FMMS	100.8	1205.5	81 ± 3.0	2 ± 3.0	780	5
imprinted bis FMMS	100.8	1205.5	93 ± 3.0	2 ± 3.0	2420	5
linked FMMS	100.8	1205.5	39 ± 3.0	0 ± 3.0	130	0

a pH=5.0 (0.05M acetate buffer)

b K_d is in units of $[\mu\text{g } \text{UO}_2^{+2} / \text{g sol-gel}] / [\text{ppm } \text{UO}_2^{+2} \text{ remaining}]$

have an affinity for uranyl. The results of competitive binding studies are shown with the imprinted and nonimprinted samples in **Table 4.3.5.3**. Similar results were seen with the strontium uptake studies. All TMSBr treated samples showed very low affinity for calcium. There was a 12:1 ratio of calcium to uranyl. With no uptake of calcium and uptake of uranyl, there is selectivity in the FMMS material samples. This was not seen between calcium and strontium.

Nonimprinted mono FMMS material has the lowest uptake of uranyl. Once the same material has been imprinted as described above, there is significant uptake of uranyl. The reason for this is because two mono phosphonic acid bind to one uranyl before the ligands are grafted to the silica surface. Similar results are seen with the linked phosphonic acid. The linked phosphonate is broken into two phosphonic acid groups after treatment with TMSBr. The two functional groups are in close proximity with each other giving similar results to those of the imprinted mono FMMS material. The bis FMMS material overall showed the best result. The imprinted bis material showed a 12% increase in uranyl and lower uptake of calcium over the nonimprinted bis material.

In conclusion, the imprinted bis-phosphoric acid FMMS material showed the highest uptake of uranyl and the lowest uptake of calcium. The imprinted mono and linked FMMS materials showed similar results, but they had a 20% decrease in the uptake of uranyl compared to the bis-phosphoric acid FMMS. The imprinted mono material has one advantage over the linked material and that it takes less time and money to produce. The major advantage of these materials over methods such as solvent extraction is their recyclability; studies show that they can be used over at least 3 cycles with no loss of affinity for the target ions.

Chapter 5

Conclusions and Future Studies

5.1 Conclusions

The development of sol-gel materials containing bifunctional phosphonate ligands for the extraction of strontium(II) and uranyl(II) from solution has been reported in this thesis. The extraction technique proposed here utilizes mesoporous sol-gel containing functionalized monolayers (FMMS sorbents) of phosphonate bifunctional compounds. FMMS sorbents have been shown to absorb heavy metals from contaminated water, making this a promising tool for environmental cleanup applications.¹¹

Within the context of FMMS based sorbents, three ligands diethylphosphatopropyl-3-triethoxysilane (mono phosphonate ligand), 1,7-bis(triethoxysilane) 4,4 bis(diethylphosphato) heptane (bis phosphonate ligand), and bis(3-trimethoxy silyl propyl) glycol diphosphonate (linked phosphonate ligand) were chosen for grafting to the surfaces of mesoporous silicate supports. These ligands were chosen for two primary reasons. First, the ligand must contain a group which may be covalently tethered to the surface of a porous silicate based sol-gel. Second, the ligand must contain a functional group

such as a phosphonic acid. Phosphonic acid groups are well known for their affinity for divalent and trivalent metal cations such as strontium and uranyl.¹³⁻¹⁵

Phosphonate ester based FMMS sorbents were studied first. It was found that strontium and uranyl cations were not bound by phosphonate ligands in FMMS sorbents. Next, all of the FMMS sorbents were treated with TMSBr followed by water. This was performed to hydrolyze the esters to phosphonic acids and to silylate the residual silanol groups on the pore surface on the gel. The silanols on the silica matrix also have an affinity for divalent metal cations under basic conditions. However, once the silanols have been silylated, they no longer have the ability to bind to divalent metal cations. Only the tethered phosphonic acid ligands will bind metal cations because the silica surface has been neutralized with nonpolar trimethylsilane groups.

Initial studies of the new phosphonic acid ligand based FMMS sorbents exhibit affinities for strontium compared to the phosphonate based FMMS sorbents, but their affinity for strontium was low. For example the mono-FMMS sorbent showed little to no affinity for strontium while the bis and linked-FMMS sorbent only exhibited a 40-50% uptake of strontium. Because of the low affinity for strontium by the phosphonic based FMMS sorbent, molecular imprinting was attempted.

Instead of simply grafting ligands to the surface of mesoporous silica, the technique known as molecular imprinting was attempted to enhance the metal

ion selectivity. Molecular imprinting involves the formation of a templated complex involving a metal ion and the bifunctional ligand. The two are mixed together so that the metal binds to a set of ligands. The complex assembly is then grafted to the surface of mesoporous silica. Finally, the metal ion template is removed via acid. This leaves what may be referred to as an imprinted cavity composed of the ligands and possibly surface binding sites which reflect the size and electronic signature of the initial template.

The templates used in this study were strontium and uranyl and the bifunctional ligands used were the mono and bis-phosphonate ligands. The reason the linked phosphonate was not chosen was due to the fact that during transesterification and hydrolysis using TMSBr to form the phosphonic acid, the glycol bridge is broken forming two mono phosphonic acids. Imprinted phosphonic acid based FMMS sorbents did exhibit high affinities for both strontium and uranyl. The imprinted mono phosphonate FMMS and the linked phosphonate FMMS material behaved similarly in competitor ions studies involving strontium and sodium. However, the imprinted mono-phosphonate FMMS material offers an advantage over the nonimprinted linked phosphonate FMMS material in that it is cheaper and easier to produce than the linked phosphonate. As for the imprinted mono-phosphonate and the bis-phosphonate containing sorbents, the decision as to which is best can be made based on the individual waste system. The imprinted mono-phosphonate material absorbs

more strontium than the bis-phosphonate material. The mono phosphonate material also absorbs calcium, whereas the bis-phosphonate material does not absorb as much calcium. These imprinted phosphonic FMMS sorbents could be regenerated and were selective over competitive ions such as calcium and sodium.

Concentrating pollutants is an important factor in the management of waste. A contaminant that has been concentrated is generally much easier and more economical to handle than one that is dispersed in a large quantity of water or soil. The use of FMMS sorbents allows large quantities of water that is contaminated with waste to be cleaned up and the waste to be placed into smaller, more, maintainable containers. These FMMS sorbents offer fast kinetics, selectivity, solid support, and sensitivity in dilute systems making them ideal for environmental cleanup applications.

5.2 Future Studies

One area of this research that needs further study is selectivity. During the competitive ion studies between strontium and calcium there was little to no selectivity between the two. Selectivity was much higher between uranyl and calcium, but their size and chemical properties are different. As for calcium and

strontium, their size and chemical properties are similar which makes them more difficult to separate using phosphonic acid ligands which have an affinity for both.

Bis(3-trimethoxy silyl propyl) glycol diphosphonate (linked phosphonate ligand) was first designed to cage metal ions. However, it was later discovered that the linked phosphonate during transesterification and dealkylation using TMSBr to form the phosphonic acid, the glycol bridge was broken forming two mono phosphonic acids. Once the glycol bridge was broken, it no longer had the ability to cage the metal ions.

The linked phosphonate ligand does have one important feature that the mono and bis phosphonate ligands do not possess and that is chirality. During the Arbuzov reaction, two chiral centers are formed on the glycol bridge. In the future, a phosphonate ligand could be created that is chiral and is stable under mild dealkylation process such as the use of TMSBr. It is known that TMSBr will not cleave the carbon-oxygen bond on an aromatic alcohol, so a new ligand can be created in which the ethylene glycol bridge is replaced by a catechol (1,2-dihydroxybenzene) bridge. Research has been attempted with the synthesis of a catechol linked phosphonate ligand but the ligand has not yet been isolated. Another possibility for future research is the replacement of the catechol with a chiral sugar molecule or chiral cyclohexanes such as *trans*-1,2-

cyclohexane diol. This enables the ligand to bind to chiral substrates or show higher selectivity properties for metal cations than does the glycol linked phosphonate ligand.

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