

SPECTROSCOPIC INVESTIGATIONS OF  
8-HYDROXYQUINOLINE-5-SULFONIC ACID-  
DOPED SOL-GEL DERIVED GLASSES

By

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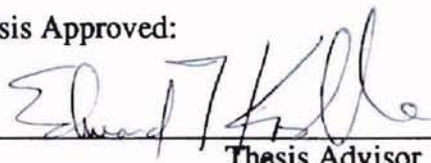
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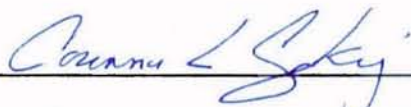
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DOPED SOL-GEL DERIVED GLASSES

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# CHAPTER 1

## INTRODUCTION AND BACKGROUND

### I.A. Introduction

This thesis is a product of three years of work toward the development of a fluorescence-based sensor material for the detection of aqueous heavy metal ions such as zinc, cadmium, and mercury. The actual development of a sensor material is far from complete. However, the work accomplished here is an exploratory study of the behavior of HQS-doped silica and aluminosilicate gels which may lead to the eventual development of such a system. Doped sol-gel derived materials have been studied as sensor materials in many different systems. If developed, a sensor for heavy metal ions such as this could be used in analyzing ground and surface water for metal ion contaminants. Also, marine environments could be inspected for poisoning from these metal ions. Another potential use is in industrial processes; for example, in the production of mercury cadmium telluride where chemical baths may need to be continuously investigated for these metals. These examples clearly show the necessity of finding processes for analyzing aqueous metal ions such as mercury, cadmium, and zinc.

Initially, silica gels that had been formed by sol-gel processing and doped with the organic ligand, 8-hydroxyquinoline-5-sulfonic acid (HQS) were used as sensor materials. The gels that were formed from this process were analyzed by fluorescence spectroscopy for their response toward zinc, cadmium, and mercury. Milli-, micro-, and nanomolar concentrations of metal ions were differentiated between by calculating internal complexation process rates. The optode behavior of HQS-doped silica gels is presented in Chapters 2 and 3.

HQS-doped aluminosilicate gels which were formed by sol-gel processing were also investigated. Aluminosilicate gels are especially useful in sensor systems that

require organic dopants because they are processed at more neutral pHs and have higher porosity relative to silica gels. These doped aluminosilicate gels showed an intense emission band which was theorized to be due to complexation between the HQS dopants and aluminum sites of the aluminosilicate precursor. Therefore, these gels were not used as optode materials, but the experiments performed on them are presented in Chapters 4 and 5 due to the novel nature of the fluorescent material which was formed.

In Chapter 2, the optode response of HQS-doped silica gels toward aqueous zinc and cadmium ions is presented. Luminescence characteristics of the doped gels are perturbed upon introducing the gels to aqueous zinc and cadmium solutions. Excitation and emission spectra are presented which show the optode response. The results of this study show that the bulk gels formed by the sol-gel technique have extremely long diffusion rates, since, it takes up to 3 hours for steady-state luminescence to be achieved.

In an effort to find a method for determining metal ion concentration on a faster time scale, Chapter 3 shows the results of a preliminary investigation of internal complexation (ICP) process rates. The ICP rate is the overall process rate associated with complex formation in the xerogel between HQS and aqueous cations. It is a function of concentration-dependent mass transport rates of the aqueous metal ions through the gel matrix and complexation kinetics between HQS and the aqueous analyte species. Time-evolution fluorescence spectroscopy was used, and the ICP rate for each metal ion concentration was calculated from the recorded spectrum. This new method then, made it possible to differentiate between concentration regimes of milli-, micro-, and even nanomolar metal ion species on the time scale of seconds to minutes. This chapter also presents mercury complexation behavior with the HQS-doped gels. Finally, gels used in this chapter were studied for leaching behavior of the dopant from the porous matrix. It was concluded that 18 hours of soaking in distilled water was required for any physisorbed HQS to be removed. This chapter concludes the work done on HQS-doped silica gels.

Chapter 4 is the first chapter to deal with the behavior of HQS within aluminosilicate gels. Since silica gels were determined in Chapter 3 to have leaching problems, new materials were sought. Therefore, HQS was doped into the aluminosilicate precursor, (di-*sec*-butoxyaluminoxy)triethoxysilane [DBATES], which had been used by other investigators of doped sol-gel materials. However, upon doping with HQS, the gels were found to have extremely interesting luminescence properties including an intense emission band and relatively high quantum yield and fluorescence lifetime. These fluorescence properties were theorized to be due to HQS binding with aluminum sites of DBATES.

Chapter 5 presents the results of preliminary experiments using solid state NMR to elucidate the structure of the HQS-doped aluminosilicate gels. Although some interesting results were found, including results which contradict published structures for aluminosilicate formed by DBATES, the structure of the doped gels was not determined and further studies are necessary to confirm the hypothesis that the HQS is binding with DBATES.

In Chapter 6, several potential experiments are discussed which will be necessary in the future in order to form materials which could be applied in sensor technology. Thin film formation, factors affecting leaching, reversibility, fluorescence decay processes, mixed-metal solutions, and marine environments will all need to be investigated just to name a few of the major topics which will need to be addressed. In the aluminosilicate system, the structure of the HQS adduct is still unknown, perhaps further NMR studies, as addressed in this chapter, could help.

Appendix A was added to this thesis to address the some question of whether a true silica polymer was actually be synthesized in the work done in Chapters 2 and 3. This appendix addresses this controversy and perhaps explains, at least in part, some of the problems with leaching.

Finally, the rest of this chapter (Chapter 1) will deal with background material on sensor materials. I will discuss why different aspects of this work such as sol-gel processing, HQS, and the chosen metal ions were used and the advantages and disadvantages of them. The work will be put into perspective of current sol-gel based sensor research.

## I.B. Background

The approach used in this research, i.e. doping of organic molecules into silica made by sol-gel processing, is not unique. Sol-gel derived media have been investigated as materials for making everything from dentures to lasers. Therefore, the background discussion will begin by putting the research into context. Then, the use of sol-gel processing and the advantages and disadvantages to this method will be discussed. Finally, selection of the ligand, HQS, and the metal ions will be described.

### Context of work

Many different types of molecules have been doped into sol-gel derived media in an effort to create sensor materials. In 1990, Braun and coworkers doped the enzyme alkaline phosphatase in sol-gel matrices and noted a 30% retention of activity of the enzyme (1). More recently, Zink et al have used the sol-gel method to encapsulate three large proteins into silica gel: bovine copper-zinc superoxide dismutase, cytochrome c, and myoglobin (2). The reactivity of the bound proteins was retained. Doped sol-gel derived materials have also been used in pH determination (3), glucose monitoring (4), and determination of gases such as oxygen (5) and nitric oxide (6). The field of doped sol-gel materials is huge, and an extensive review would require an entire book.



However, these examples clearly show that sol-gel derived materials are being used in a wide range of applications and have merit in the sensor area.

In the Knobbe research group, tetra(4-sulfonatophenyl)porphyrin, sodium salt, 12 H<sub>2</sub>O [TPPS] was used by Yates et al (7) and incorporated within sol-gel derived media as a fluorescent probe molecule for zinc and cadmium. This compound, shown in Figure 1, was incorporated into aluminosilicate gels and was shown to be a fluorescent probe for transition metal ions such as divalent zinc. TPPS-incorporated aluminosilicate gels were active towards zinc ions, but cadmium ions proved to be a problem, only complexing after extremely long periods, and even then not very strongly. It is known that the hydration sphere of cadmium is quite large. The comparatively large size of the solvated ion may be expected to slow diffusion through the gel matrix, thereby giving a lower ICP rate in a gel matrix than for the free porphyrin in solution. TPPS is also extremely pH sensitive and slight pH fluctuations can change the fluorescence spectra of both the parent and the complexed species (8). This porphyrin is not selective for transition metal ions. In fact, both sodium and potassium will complex with TPPS preferentially over zinc and cadmium. Another problem associated with the TPPS probe is the difficulty in detecting changes in fluorescence due to the high fluorescence of parent TPPS. The problems identified with TPPS by Yates suggests that other probe molecules needed to be investigated to find one less pH sensitive and more selective toward the metal ion analytes of interest.



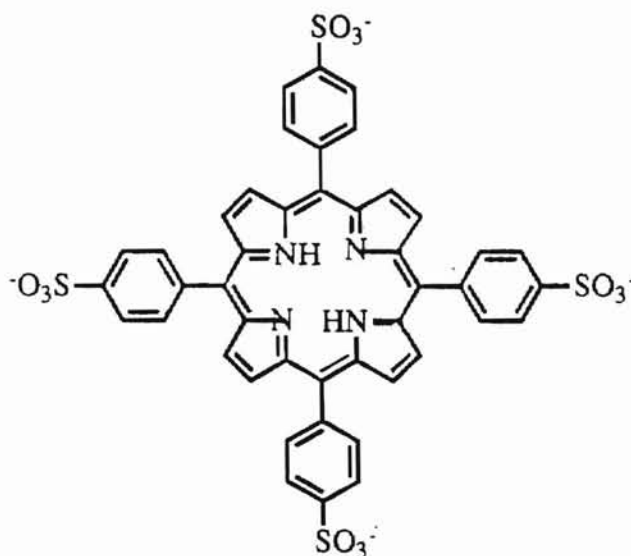


Figure 1: Tetra (4-sulfonatophenyl)porphyrin  
TPPS

The work presented here uses a much less pH sensitive probe molecule, 8-hydroxyquinoline-5-sulfonic acid (HQS), as a dopant in the sol-gel derived media. It was found that this compound had the advantage over TPPS of having weak fluorescence when not complexed and high fluorescence when complexed (9). Therefore, changes in fluorescence, as caused by metal ion complexation, are much more obvious than with TPPS. HQS is also selective for zinc and cadmium over monovalent cations such as sodium and potassium (10).

Another unique feature of this work is the use of internal complexation process (ICP) rates to determine metal ion concentration. This approach gives a means to determine concentration regimes of the metal ions, for example, milli-, micro-, or nanomolar. It also allows for these determinations to be made on a much faster time scale by measuring the rate at which fluorescence changes occur and correlating them to concentrations.

Upon doping DBATES with HQS and exciting with ultraviolet radiation, intense blue emission was observed. This emission was notable from the instant that HQS was added to the precursor and even in the solid state material. The aluminum site within the

DBATES precursor may act as a Lewis acid and bind with HQS. In comparison to the complex between 8-hydroxyquinoline and free aluminum ions [tris(8-quinolinolato)aluminum (III) {Alq<sub>3</sub>}], the quantum efficiency is more than doubled for the HQS-doped aluminosilicate gels, presumably from increased rigidity due to the gel matrix. Also, the fluorescent lifetime of these HQS-doped gels is longer than reported lifetimes for Alq<sub>3</sub>. In this work, solid state NMR studies of the gels were performed. Although the structure of the HQS-aluminum sites within the gels were not determined, these NMR results suggest that previously reported structures for the aluminosilicate gel formed by DBATES may be incorrect. In fact, the results reported in Chapter 5 indicate the exact opposite of the reported structure determined by Pouxviel et al.

### Sol-Gel Processing

The sol-gel method for making glasses has been used to prepare materials such as silica (11) and mixed metal-oxide glasses such as aluminosilicates (12). Gels are produced by reacting alkoxymetal precursors such as tetraethoxysilane (TEOS) and (di-*sec*-butoxyaluminoxy)triethoxysilane (DBATES) with water in a two-step reaction mechanism of hydrolysis followed by condensation. The sol-gel process for making silica and aluminosilicate was chosen for this project for several reasons.

First, the sol-gel method offers a low-temperature technique for making glassy materials such as silica and aluminosilicate. Since the high temperatures for making traditional silica glass are not required, organic molecules which would typically be destroyed by the glass-making process may be doped into sol-gel derived materials. This is important because silica is transparent to most visible light, so it is capable of transmitting both the excitation source to excite a fluorophore and the emission from it.

Second, sol-gel derived materials have a relatively high porosity, depending on the processing conditions, especially where stresses are low enough to allow for pore

formation. Porosity is important in sensor materials because the analyte species, in this case aqueous metal ions, must be able to enter the pores and come in contact with the probe molecule. Some precursors will produce gels with higher porosity than others; for example, aluminosilicate gels formed by DBATES have a higher porosity than silica gels formed by TEOS (13). This porosity can allow for flow of small molecules through the sol-gel matrix.

Finally, these gels are made through a room temperature, aqueous process which allows a wide variety of dopants to be incorporated. This feature makes it possible to introduce molecules which would decompose under other silica preparative methods. Sol-gel processing offers a simple way to prepare silica and aluminosilicate gels, requiring only a precursor, water, and a small amount of acid or base catalyst (no special instrumentation or catalysts are required).

However, there are some serious drawbacks to sol-gel derived materials. For example, leaching of molecules from the gels has been observed (14). This effect is especially problematic in the case of sensor materials. Since the probe concentration is constantly changing, determination of analyte concentration is problematic. However, there appears to be a size limitation to leaching. Large molecules, such as TPPS, are not readily leached from the gels. Therefore, the leaching problem may be solved through the use of larger probe molecules.

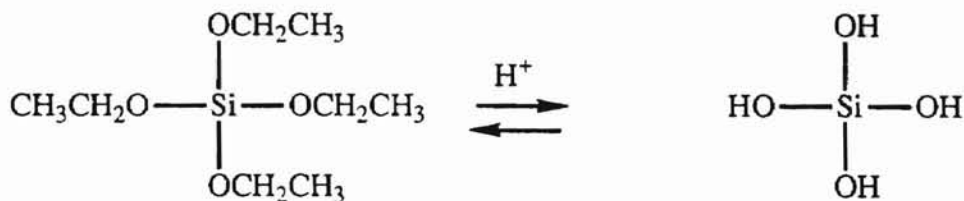
Another problem, reported by Harris (15) in thin films of silica, is the pore collapse observed when producing the films. Harris also found that once the film is formed, it can be unstable in aqueous solutions. Upon introduction to water or aqueous solutions, the structure of the film begins to change. The film will rearrange the gel network until it becomes extremely dense. This work was done on thin films, but it may have implications for bulk structures, especially on surfaces where stresses may be greater.

Finally, a major difficulty of working with sol-gel derived media is the lack of reproducibility. Since the precursors react with water, atmospheric conditions may affect the quality of gels produced from one day to the next. Also, once a bottle of precursor is opened, the contents within begin to alter so that it is nearly impossible to identically reproduce a batch of gels. This problem may, however, be compensated for by preparing large batches of samples at one time.

The sol-gel process, overall, shows real promise in the sensor area. Problems such as leaching, pore collapse, stability, and reproducibility may be compensated by choosing the right dopant and through engineering better precursors. The advantages of low-temperature processing, optical clarity, aqueous processing, and porosity far outweigh the present disadvantages of using sol-gel processing.

The general process for making silica glass via the sol-gel method is shown in Figure 2. Esquivias reports that either the addition of base or acid can be employed to initiate the reaction (16). He found that rates of hydrolysis as relative to condensation (i.e. amount of acid to base) produces physically different gels. Under basic conditions, step 2 (condensation) is the fast step. Therefore, base-catalysis tends to be produce extremely porous silica gels. However, these glasses are not extremely stable unless heat-treated and have a tendency to crystallize and disintegrate. Under acidic conditions, step 1 (hydrolysis) is the fast step. Therefore, acid-catalyzed silica gel is very strong when dry and less likely to crack than base-catalyzed silica. Porosity of silica gels produced through acid catalysis has been reported to be much lower than base-catalyzed, however.

### Step 1: Hydrolysis



### Step 2: Condensation

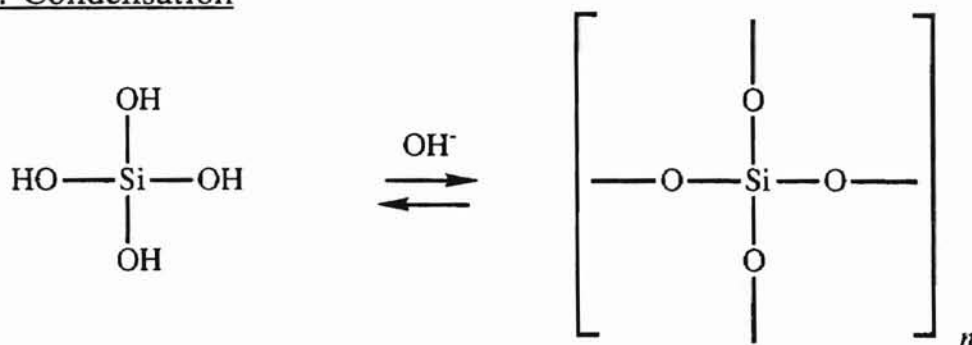


Figure 2: Sol-Gel Processing of Silica from TEOS

The use of both acid and base in a stepwise fashion has tended to produce gels with high porosity and strength (17). The acid is added to the reaction mixture first and catalyzes hydrolysis of the alkoxy groups. Subsequently, base is added slowly to neutralize the excess acid and catalyze the condensation step. Sols made by this process are then allowed to react for 2 or more hours before placing in a form or using for dip or spin coating. This two-step method produces high porosity in the gel structure because the acid is added first and, given ample time to react, will hydrolyze a majority of the alkoxy groups. The product of the acid hydrolysis is then subsequently catalyzed by base addition to form a highly condensed structure.

Another precursor which has been used for producing sol-gel derived glass is (di-sec-butoxyaluminoxy)triethoxysilane (DBATES) (12). As shown in Figure 3, the processing of DBATES is similar to that of TEOS except that no catalyst is required. This precursor reacts with water at much more moderate pHs (around 5 or 6). Thus,

DBATES-derived gels containing fluorescent dopants tend to maintain exceptional fluorophoric activity, as problems associated with chromophoric decomposition upon exposure to pH extremes are obviated. Aluminosilicate gels formed by DBATES are reported to have higher porosity than TEOS-derived silica gels. DBATES is an especially useful sol-gel precursor, as it represents a double alkoxide which can be used to synthesize compositionally novel alumina-silica gel “copolymers”. These factors make aluminosilicate an ideal materials for organic dopants which are sensitive to pH effects and for sensor materials that require high porosity.

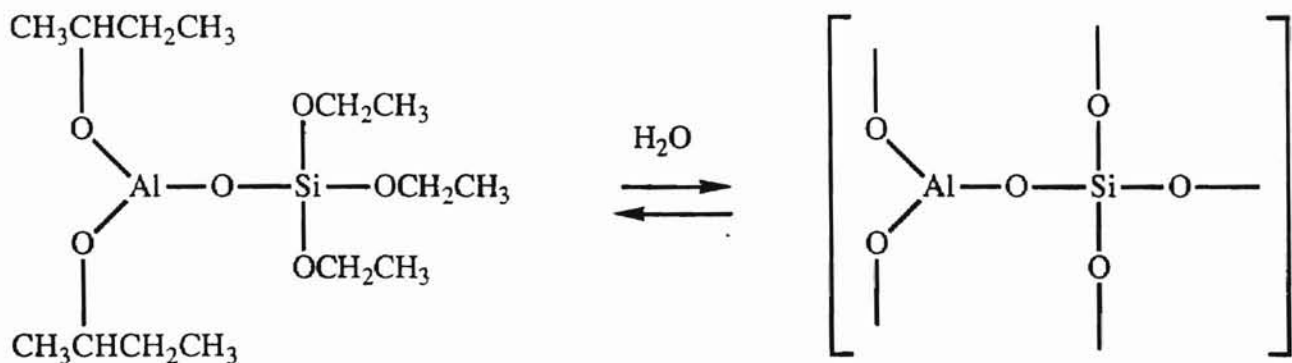


Figure 3: Sol-Processing of Aluminosilicate from DBATES

Pouxviel et al have reported that glasses formed by this method are mostly tetrahedral with respect to the alumina sites with some octahedral sites (12). Also, they report that since the aluminum sites in the aluminosilicate precursor hydrolyze their organic side chains much faster than the silica sites, there is a tendency of forming islands of high aluminosilicate concentration in the network itself. These properties have several important implications to the gels formed from this precursor, among which is the high porosity. Effects of this inhomogeneity on doped molecules may be important as well.

### 8-Hydroxyquinoline-5-sulfonic Acid (HQS)

As mentioned earlier, 8-hydroxyquinoline-5-sulfonic acid (HQS) was chosen as a probe molecule for this work because of its selectivity, low pH sensitivity, and known luminescence properties. The structure of HQS is shown in Figure 4. HQS has been shown to bind selectively with zinc and cadmium over sodium and potassium (10). Also, HQS is able to complex with metal ions at all pHs, although pHs between 4 and 8 yield the most stable coordination compounds based on the pKa values for the hydroxyl and amino positions on the ligand (18). Also, HQS and the related compound, 8-hydroxyquinoline, have been widely used in analytical ion exchange columns; therefore, the fluorescence properties of most of its metal ion complexes have been published (19).

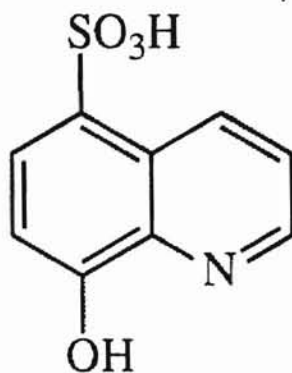


Figure 4: 8-Hydroxyquinoline-5-sulfonic acid (HQS)

As shown above, the HQS molecule is a bidentate ligand with three acidic protons. The sulfonato proton is the most acidic and is important in determining the solubility of the organic molecule in aqueous or alcoholic solutions. The second two protons exist in the coordination site of HQS and are important in complexation of metal ions. Much controversy exists over the pK<sub>a</sub>s of the various protonated sites on the HQS



molecule. It has been reported that a pH of  $\sim 4.5$  or greater is needed for metal ion detection (20). However, it has generally been agreed that the molecule has a first ionization point of approximately 2 pH units (for the sulfonato group). The second ionization point due to the deprotonation of the hydroxyl group is at approximately 4 pH units, and the third point due to the amino group is at approximately 8 pH units. These values have been considered accurate for the non-complexed HQS molecule. The second ionization point (involving the hydroxyl group), however, seems to affect complexation of metal ions. Upon complexation with various metal ions, protonation occurs at different pHs, depending on the metal ion which is coordinated. These values have been compiled by Dasgupta (20). Cadmium is reported to optimally complex at a pH of 7, zinc at a pH of 6. Therefore, it seems that the particular metal ion which is being analyzed can affect complexation behavior.

HQS has other desirable features as well. The parent HQS molecule is virtually non-luminescent. According to Schulman (21), the lowest excited state of HQS is the  $n \rightarrow \pi^*$  singlet, which generally possesses a very small radiative probability due, at least in part, to poor orbital overlap. The inherent structural flexibility of these molecules also tends to reduce the fluorescence yield. Upon complexation with species such as  $Al^{3+}$ , however, HQS-metal complexes become highly luminescent. Tris(8-hydroxyquinolinolato)aluminum(III) [ $Alq_3$ ], shown in Figure 5, has been shown to be a metalorganic complex which exhibits blue-green fluorescence and has a quantum efficiency of approximately 8% (22). The luminescence phenomenon in such chelates is reported to arise when the non-bonding electrons on the HQS molecule interact with the metal center, and the energy of these nonbonding levels is concomitantly lowered. Thus, the first excited state for the HQS molecule no longer results from a the  $n \rightarrow \pi^*$  singlet transition, but becomes instead a  $\pi \rightarrow \pi^*$  singlet transition as shown in Figure 6. The allowed  $\pi \rightarrow \pi^*$  singlet transition has a very large oscillator strength. Such transitions are typically associated with fluorophores exhibiting high quantum yields such as the



rhodamine and coumarin laser dyes (23). In addition, the rigidity of HQS-metal molecular complexes are greatly increased with respect to the noncomplexed parent structure. The combination of these effects frequently results in the development of vastly increased fluorescence activity subsequent to complexation, as in the case of Alq<sub>3</sub>.

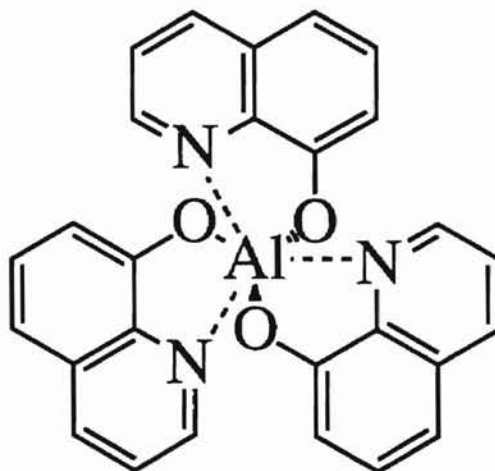


Figure 5: Tris(8-Hydroxyquinoline)aluminum(III)  
Alq<sub>3</sub>

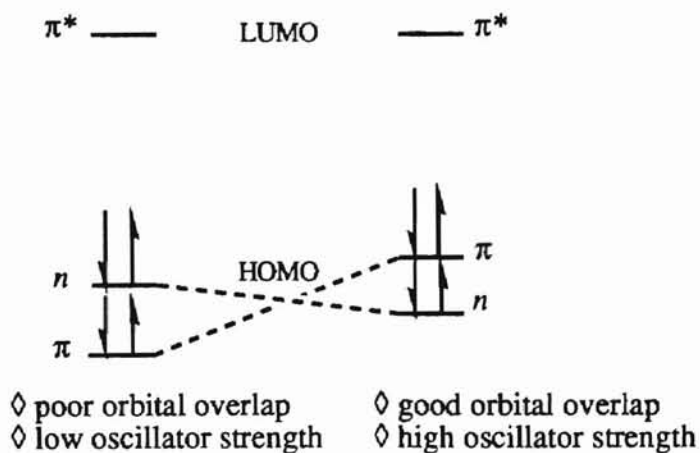


Figure 6: Jablonski-type diagram of electronic transitions of parent and complexed HQS

Although HQS binds selectively with aqueous transition metal ions such as zinc and cadmium over alkaline and alkaline earth ions, has desirable fluorescence properties, and is less pH sensitive than other ligands, it is not a perfect probe molecule for the purposes of doping into sol-gel derived media. First, the solubility of HQS in water, although better than 8-hydroxyquinoline from which it was derived, is still relatively low. The maximum concentration of HQS in water is 3 mM, and this is at neutral pH values (24). Also, the size of the molecule is small enough that leaching from porous gels can and does occur. This effect proved to be enough of a problem that preliminary studies in Chapter 3 were performed to try to determine the extent of leaching.

#### Metal Ions Studied

Distinguishing between electronically similar cations in solution is a problem. In this project, zinc and cadmium were chosen because they are in the same group and are typically similar in the complexes that they form, i.e. ligands that bind with zinc typically also bind with cadmium. This is problematic because it is often difficult to distinguish between these complexes using other conventional methods such as absorption. Since fluorescence has increased sensitivity to small fluctuations in signal over other spectroscopic methods such as infrared or visible light absorbance, it may be used as a technique for quantitation of similar cations which are complexed with a fluorophore. Fluorescent organic ligating molecules can be used to monitor metal ion analytes, as the luminescence characteristics of select probe molecules are distinctively perturbed in the presence of complexed ionic species. The use of continuous wave spectroscopy permits the study of complex formation on a time evolution basis. Differences between spectral features of metallorganic complexes containing closely related ionic species may allow specific ion quantitation to be performed.

These ions are also interesting because they are common contaminants in water supplies and in industrial processes. The project was funded by the Office of Naval Research as a result of their interest in the quantitation of these particular ions. Therefore, the determination of these ions is more intriguing due to the possibility of eventually pursuing the development of a sensor.

Zinc, cadmium, and mercury had the advantage of having well-studied complexation behavior with HQS (19). This fact made research of the gels much simpler since the luminescence bands were already known. Also, these ions all have salts that are soluble in water which made preparation of solutions of metal ions very simple.

However, there are some disadvantages of using these metal ions. First, zinc and cadmium complexes of HQS are extremely similar in their optical properties. Mixed metal solutions were not studied within the body of this work, but the effect of band mixing may be a problem for solutions containing more than one species of metal ion. Also, these complexes have relatively short fluorescence lifetimes and require violet or ultraviolet excitation which makes measurement by common instrumentation difficult. Finally, the greatest disadvantage is the toxicity of these ions, especially mercury and cadmium. It is important to take special precautions when handling and disposing of these solutions due to the high toxicity of the metal ions (25).

## CHAPTER 2

### OPTODE RESPONSE OF HQS IN SILICA GEL SYSTEMS

#### II.A. Introduction

This chapter focuses on the study of steady-state optode response characteristics of HQS-doped silica media. Silica-based gels, containing the HQS probe molecule, were prepared as sensor materials for aqueous analyte species such as  $Zn^{2+}_{(aq)}$  and  $Cd^{2+}_{(aq)}$ . The inorganic matrix which holds the organic probe molecule was synthesized by the acid catalyzed sol-gel preparation of silica gels, followed by addition of base to reach a pH of 4-5. As shown by Dasgupta et al., this pH range is desirable to obtain maximum deprotonation of the hydroxyl group on the HQS molecule at the binding site (20). Perturbations to the luminescence characteristics of the HQS probe molecules incorporated within these gels were seen upon complexation with metal ion species, as verified by peak intensity increases and band shifts. Differences in luminescence and absorbance spectra between the non-chelated HQS and its metal ion complexes were used to qualitatively identify the analyte species. Times required to achieve steady-state fluorescence for the different analyte species were measured and used in conjunction with specific band structure to differentiate between metal ions.

#### II.B. Experimental

##### II.B. 1. Materials Synthesis

Initial samples of HQS-doped silica gel were made by a modification of the sonogel method described by Esquivias and Zarzycki (16). A 1:4 molar ratio of tetraethylorthosilicate (TEOS) to water was created in the sol by mixing 13.4 mL of the

silica precursor to 6.6 mL of glass-distilled ultrapure H<sub>2</sub>O in a 250 mL polypropylene beaker. 0.0049 g of HQS were mixed into this biphasic solution to give an initial concentration of 1 mM HQS. Five drops of 0.4 N HCl were added to this solution to catalyze the hydrolysis. The beaker containing the reaction mixture of TEOS, water, HQS, and acid was placed in a water bath within a Bransonic model 3 ultrasonic source and sonicated for approximately 30 minutes or until a clear, monophasic solution was obtained. The beaker containing the solution was moved to a magnetic stirring plate and a stir bar was added. While stirring, the pH of the sol was increased to a value of  $4.8 \pm 0.1$  (monitored by colorphast pH paper produced by EM Science) by dropwise addition of a 2M NH<sub>4</sub>OH in ethanol solution prepared by dilution of NH<sub>4</sub>OH<sub>(aq)</sub> with ethanol. To prepare the solid gels, approximately 4 mL of the sol was cast into 4.5 mL polystyrene cuvettes, having the dimensions of 1 cm x 1 cm x 4.5 cm, and the cuvette was covered with parafilm. Gellation occurred in approximately 5 days at room temperature under ambient conditions. Following gellation, a pin was used to perforate the cover and allow slow evaporation of residual solvents. Xerogels were obtained within approximately 2 weeks. HQS-doped gel specimens made by this method were subsequently used for optode behavior characterization.

## II.B. 2. Spectroscopic Measurements

Complex formation within HQS-doped silica gels was observed by measuring analyte-induced perturbations to the absorption and luminescence features of the HQS molecule within the gels. These gels were soaked in 10 mM aqueous solutions of Cd<sup>2+</sup> and Zn<sup>2+</sup> ions and luminescence spectra were recorded. The time-evolution of complex formation between the ions and the gel-entrapped chromophore was monitored using continuous wave fluorescence spectroscopy. Following this analysis, the gels were removed from the aqueous solutions and dried under ambient conditions for 48 hours.

Metal-ion solution treated and non-treated HQS-containing gel specimens were then used to quantify changes to the absorbance band features of HQS probe molecules as a result of  $Zn^{2+}_{(aq)}$  and  $Cd^{2+}_{(aq)}$  treatment.

Excitation and emission features were measured using a Spex model F112A spectrofluorometer. 1.85 nm (excitation) and 0.86 nm (emission) band passes were used during the continuous wave luminescence measurements. Absorbance spectra of the solid state complexed and non-complexed HQS-doped gels were measured using a Cary 5 spectrophotometer (2.0 nm spectral band pass).

The degree of complex formation between HQS within the gels and aqueous group 12 analytes was observed by monitoring the emission intensity at 520 nm ( $\lambda_{max}$  for the complexed species) continuously for 240 minutes using an excitation wavelength of 400 nm.

## II.C. Results

Absorption spectra of HQS-doped xerogels are shown in Figure 7. The three curves correspond to the free parent (A), cadmium complexed (B), and zinc complexed (C) HQS-doped gels, respectively. In the case of the parent HQS, the absorption spectrum exhibits a maximum peak at 308 nm with a broad shoulder at 360 nm. The 360 nm band is observed to increase in amplitude, eventually dominating the absorption spectra upon  $Zn^{2+}$  and  $Cd^{2+}$  metal ion complexation. The absorbance bands for the parent, cadmium complexed, and zinc complexed HQS were deconvoluted into Gaussian peaks using Sigmaplot software. The deconvoluted bands associated with the parent HQS species are shown in Figure 8. Peak area ratios ( $A_{308nm}/A_{360nm}$ ) were found to be 0.723 for the free parent, 0.332 for the cadmium complex, and 0.231 for the zinc-HQS complex. For the parent HQS, a tail beyond 420 nm containing a smaller, third peak centered at approximately 450 nm was observed. This peak did not fit well with the

simple 2-peak Gaussian model and was ignored for the purpose of area ratio calculations. Upon complexation with the analyte ions, the small peak at 450 nm was no longer observed. These results indicate that comparison of the peak area ratios may be used to discriminate between isoelectronic cations such as zinc and cadmium.

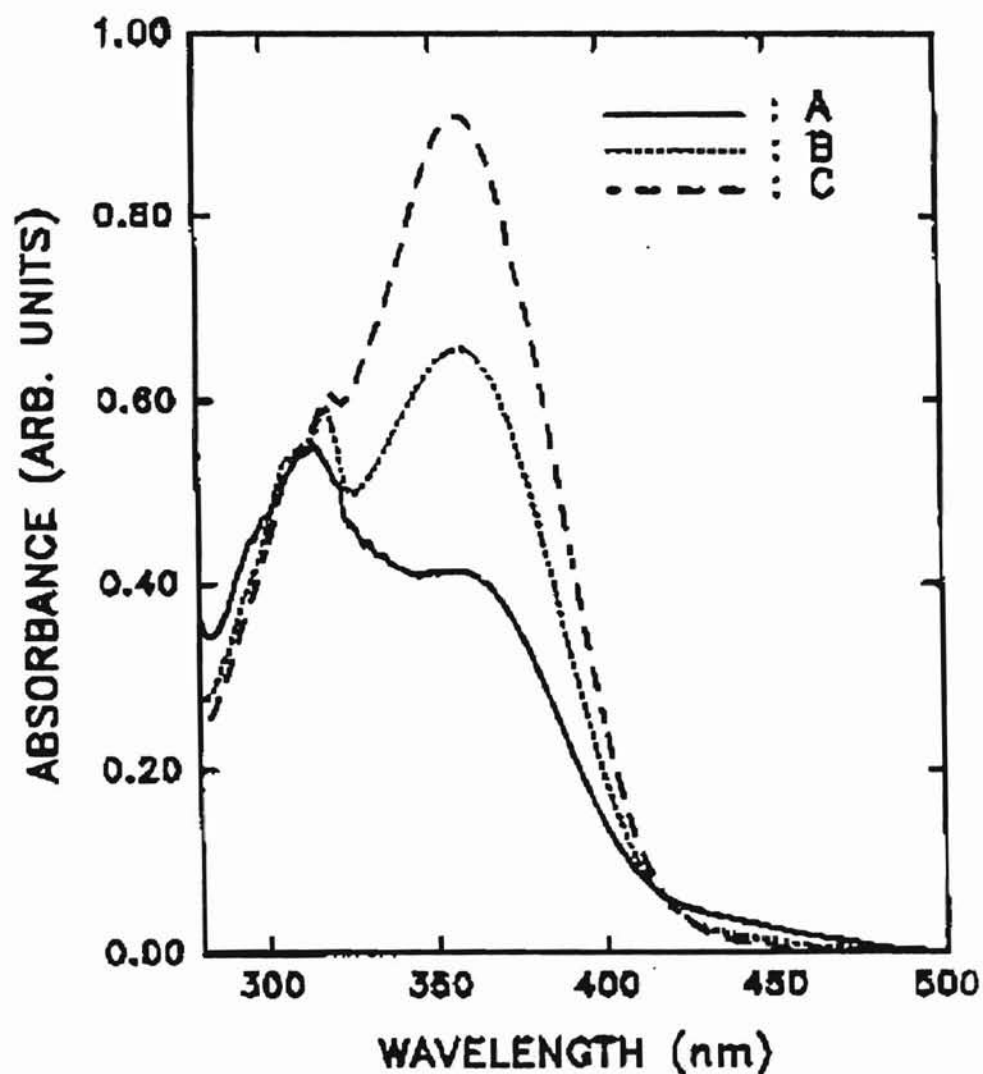


Figure 7: Absorbance spectra of parent (A), cadmium-complexed (B), and zinc-complexed (C) HQS-doped silica gels

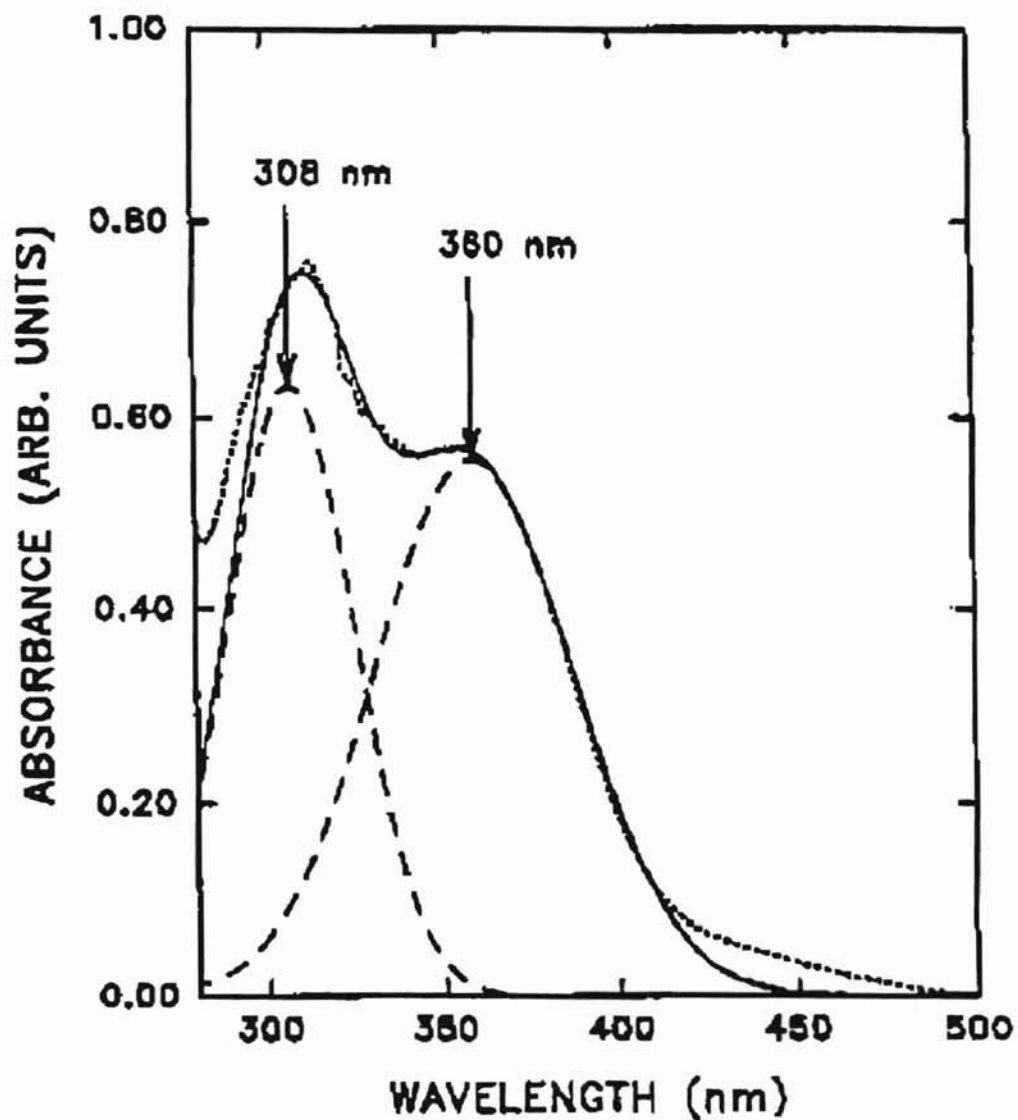


Figure 8: Absorbance spectrum of HQS showing the deconvoluted peaks at 308 and 358 nm (---), the fitted absorbance spectrum (—), and the measured absorbance (···)



The process of metalorganic complex formation was monitored by observing changes to both excitation and emission spectra of sol-gel confined HQS in the presence of aqueous transition metal ions. The time-evolution of the HQS emission spectra in the presence of 0.01 M zinc chloride are shown in Figure 9, where time = 0 corresponds to the emission spectrum of parent HQS prior to introduction of aqueous  $Zn^{2+}$  species. A broad emission band, centered at 535 nm, increased in intensity as complex formation proceeded. Red-shifting of the peak associated with the parent HQS (490 nm) was noted upon Zn-HQS complex formation. A similar behavior is observed upon introducing the HQS-doped gels to aqueous  $Cd^{2+}$ , as seen in Figure 10. Cd-HQS emission features were found to be substantially the same as in the  $Zn^{2+}$  case, although peak intensities for the  $Cd^{2+}$  complex were notably lower overall.

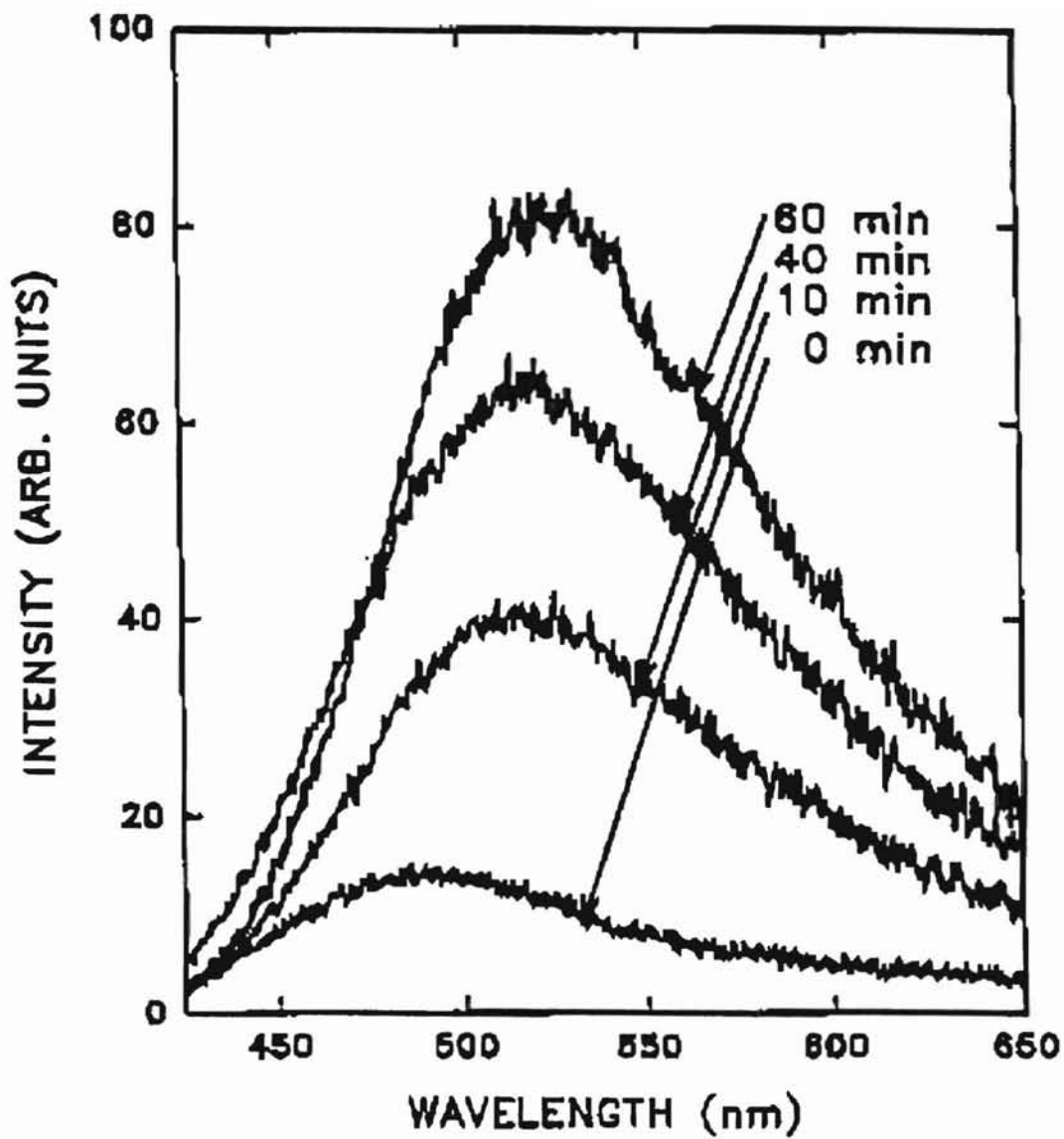


Figure 9: Time-evolved emission spectra of zinc-complexed HQS. Time 0 min. is the parent HQS, time 60 min. is the observably saturated zinc-HQS.

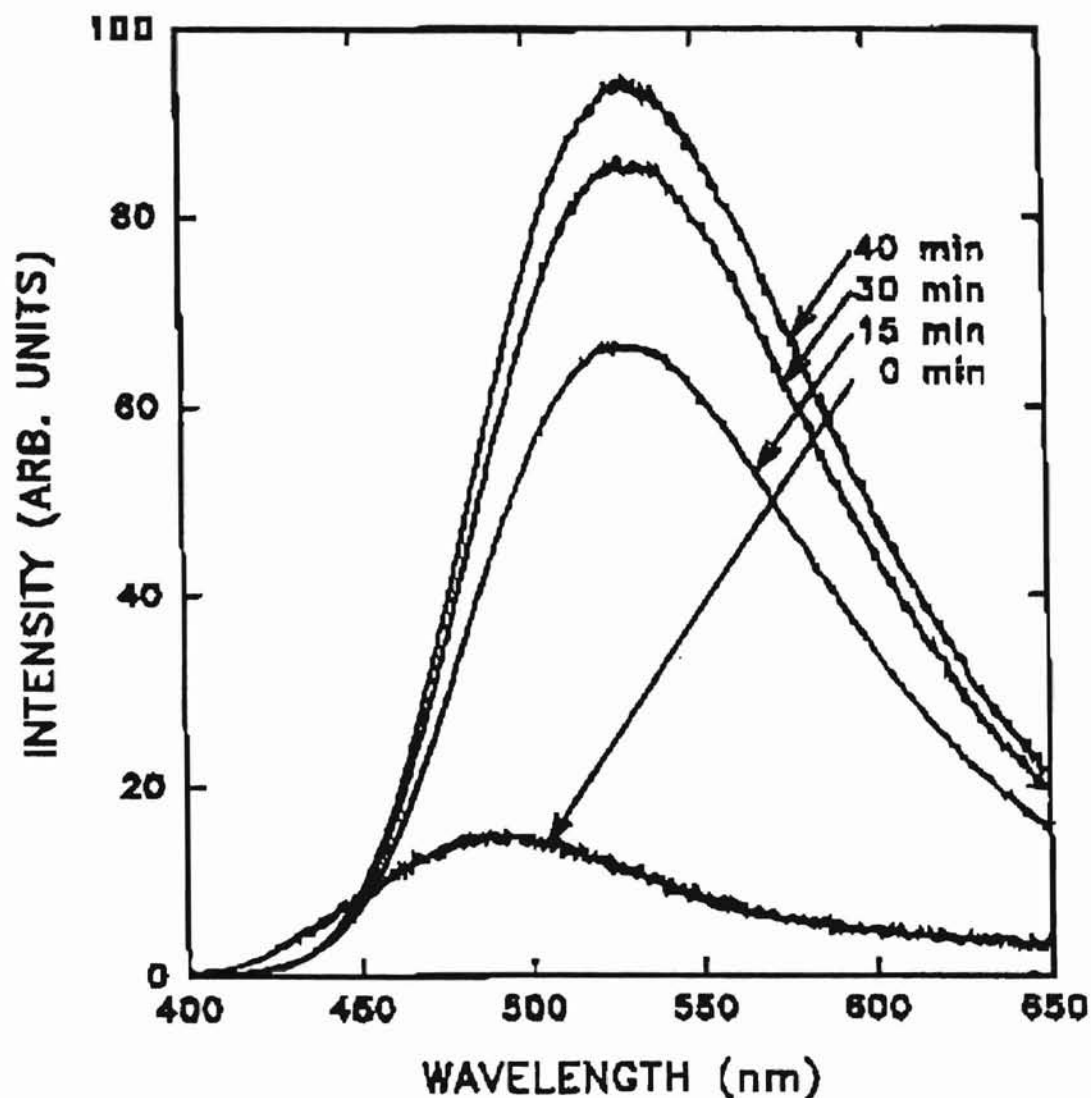


Figure 10: Time-evolved emission spectra of cadmium-complexed HQS. Time 0 min. is the parent HQS; time 40 min. is the observably saturated cadmium-HQS

Excitation spectra for the HQS complexes of  $Zn^{2+}$  and  $Cd^{2+}$  were observed by monitoring an emission wavelength of 535 nm, as shown in Figures 11 and 12, respectively. The spectrum for the  $Zn^{2+}$  complex indicates an excitation doublet at 325 nm and 365 nm. Blue-shifting of the complex peak with respect to that of the parent peak was observed, with concomitant intensity increases with time.

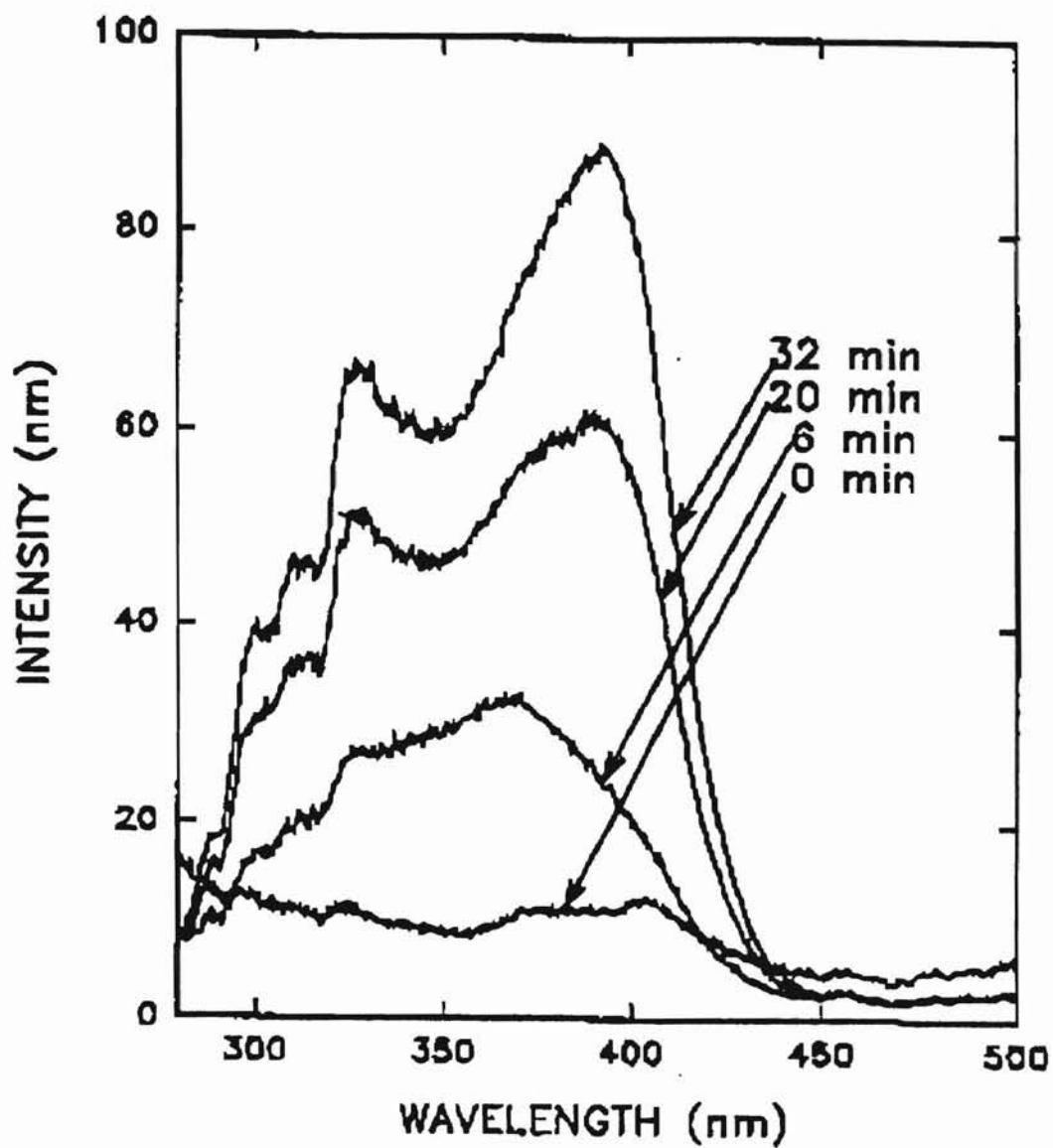


Figure 11: Time-evolved excitation spectra of zinc-complexed HQS. Time 0 min. is the parent HQS; time 60 min. is the observably saturated zinc-HQS.

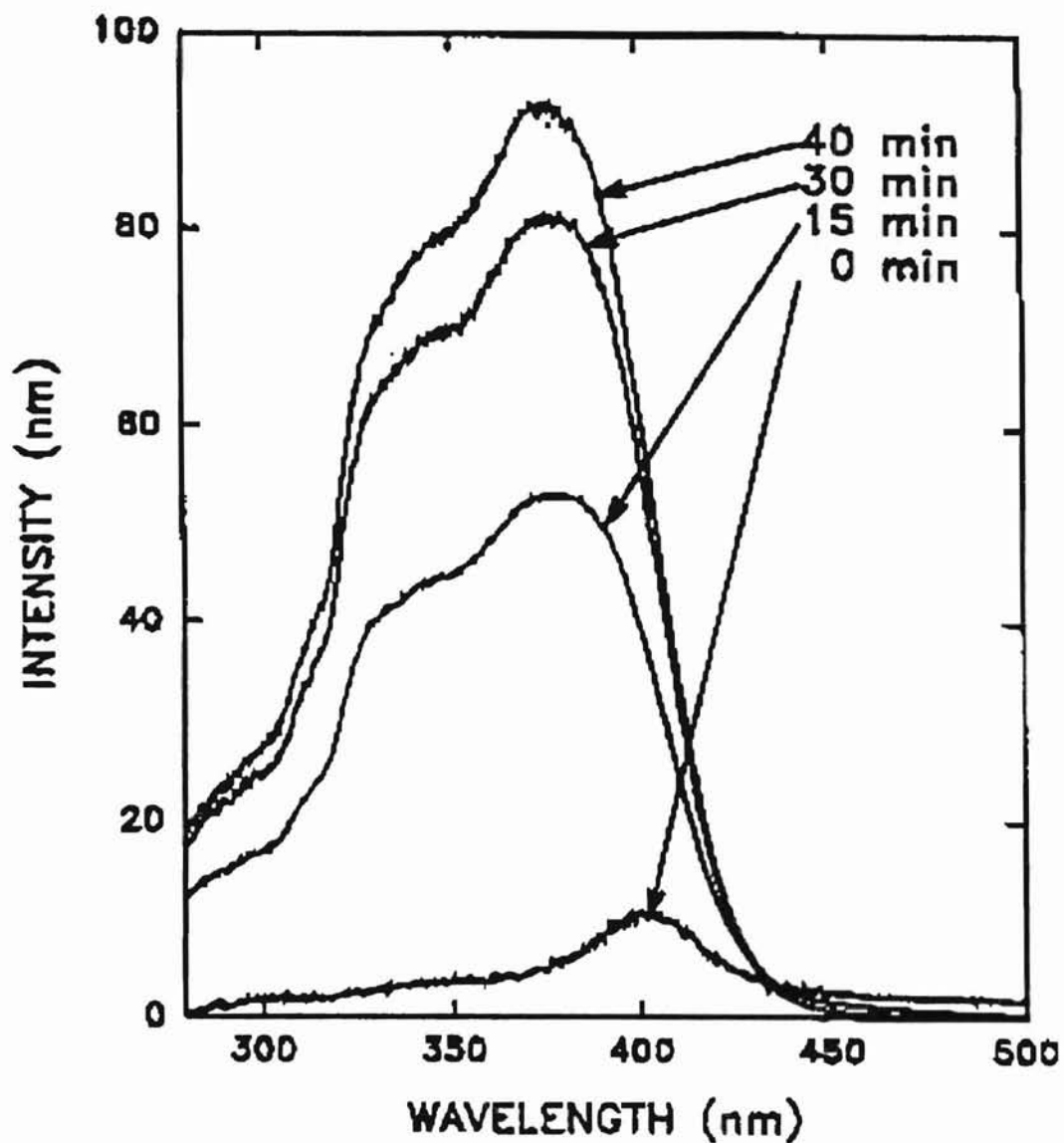


Figure 12: Time-evolved excitation spectra of cadmium-complexed HQS  
Time 0 min. is the parent HQS; time 40 min. is the observably saturated cadmium-HQS.

The changes in fluorescence of the HQS-doped gels due to metal ion complexation of the HQS molecule as determined by spectral changes in emission intensity, are indicated in Figure 13. As shown in this figure, zinc complexation requires approximately 150 min., whereas cadmium requires more than 210 minutes. This difference in time required to achieve steady state between the HQS-doped gels and the

analyte species may allow for specific ion detection when correlated to luminescence band features and area peak ratios of absorbance spectra.

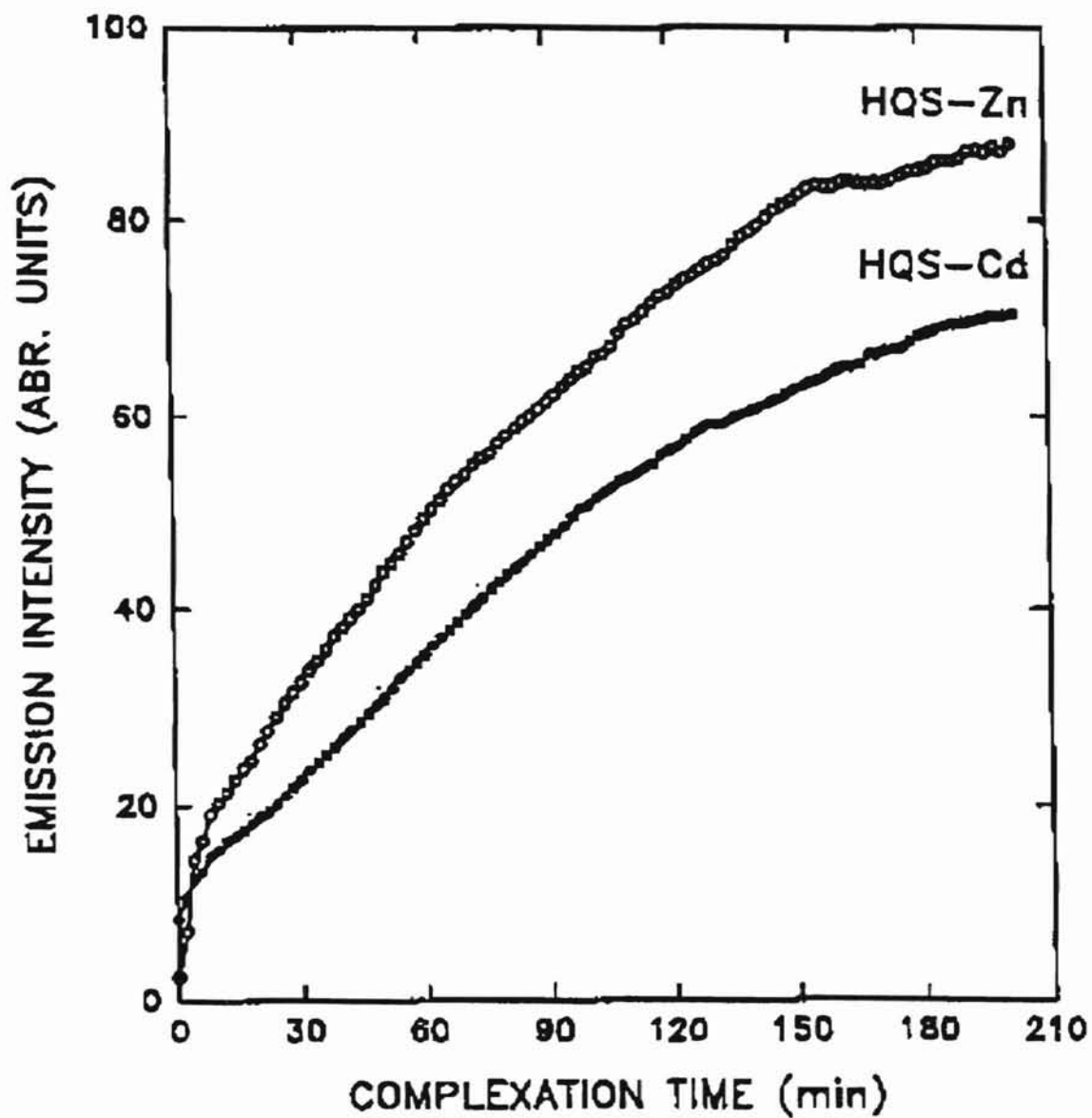


Figure 13: Complexation through the gel as a function of time HQS-doped silica gels with 0.01M  $\text{Cd}^{2+}_{(\text{aq})}$  and 0.01M  $\text{Zn}^{2+}_{(\text{aq})}$ .

## II.D. Discussion of Results

Variance in absorbance and luminescence spectra of parent HQS upon the introduction of aqueous IIB transition metal ions may be correlated to complex formation. Spectral changes in intensity of the doublet peaks of the emission and excitation bands of the zinc and cadmium treated gels have been attributed to this process. Following complexation, comparison of the integrated area peak intensities of absorption bands were made. These area ratios have been used to discriminate between parent HQS and the Zn (II) and Cd (II) complexes thereof. Thus, the comparison of area peak ratios of the maxima can provide a method by which to quantitate specific ionic complexes.

Fluorescence changes due to analyte treatment as a function of time can also be utilized to correlate the data with the appropriate ionic species. Results indicate that cadmium has a significantly longer complexation time than zinc. This event can allow for specific ion detection when correlated to absorbance and luminescence spectral band features.

## II.E. Conclusions

Silica gels made via the sol-gel process were doped with HQS and studied for potential use as optode sensor materials. These doped gels were treated with aqueous divalent zinc and cadmium solutions, and the internal complexation processes were studied through the use of continuous wave spectroscopy. Changes in fluorescence spectra with time were observed for the metal complexes, including a shift of the parent peak and a concomitant increase in the peak intensity. Although zinc and cadmium-complexes of HQS were observed to have substantially similar luminescence spectra, peak area ratios of their absorbance spectra are readily distinguishable. Absorbance

spectra of the parent and its complexed forms were recorded, and peak area ratios of the doublet were noted to allow for further differentiation between zinc and cadmium. HQS-doped sol-gel derived silica was found to be a good candidate for detection and differentiation of isoelectronic transition metal ions when coupled with absorbance and luminescence spectra, equilibrium achievement times, and area peak intensities.

Absorption, emission, and excitation spectroscopic techniques were used to monitor complex formation processes in the doped gels in the presence of aqueous divalent zinc and cadmium species. Metal complexation has been observed to perturb the optical characteristics of incorporated 8-hydroxyquinoline-5-sulfonic acid dopants, as observed via continuous wave spectroscopy. The time required to achieve steady state was used to differentiate between these isoivalent cations. Initial results from samples made by the present method were promising, but the time required to reach equilibrium conditions of HQS-metal complexation was slow, requiring more than 2 hours to stabilize. Therefore, samples made from another method were later used to study transient complexation rates between the incorporated probe molecule and a flowing solution of either zinc, cadmium, or mercury (see Chapter 3)



CHAPTER 3  
INTERNAL COMPLEXATION PROCESS RATE STUDIES  
OF HQS-DOPED SILICA WITH AQUEOUS ZINC (II), CADMIUM (II), AND  
MERCURY (II)

III.A. Introduction

HQS-doped silica gels reach complexation equilibria with metal ion analyte species after relatively long contact times (up to 4 hours), as described in Chapter 2. In this chapter, the effects of metal ion concentration on the internal complexation process (ICP) rates of the HQS-doped gels and aqueous solutions zinc (II), cadmium (II), or mercury (II) will be presented. The ICP rate is the overall process rate associated with complex formation in the xerogel between HQS and aqueous cations. It is a function of concentration-dependent mass transport rates of the aqueous metal ions through the gel matrix and complexation kinetics between HQS and the aqueous analyte species. HQS-doped gels were shown, by using time-evolution photoluminescence spectroscopy, to produce detectable optochemical response times in the range of seconds to minutes. Changes in fluorescence intensity of the entrapped probe species are described as a function of analyte activity over several concentration orders (milli-, micro-, and nanomolar levels).

One major factor which may limit the utility of the present system is the problem of leaching of the HQS from the silica gel network prepared by acid-base catalysis. It became apparent early in our research efforts that we were losing HQS from the matrix when we ran ionic solutions through the system. In order to alleviate the problem, gels have been pre-soaked in glass-distilled ultrapure water before using for spectroscopic analysis. It was noted, however, that relatively substantial losses were occurring. Therefore, leaching studies were carried out to investigate the extent of this problem.

## III.B. Experimental

### III.B. 1. Chemical Methods

Samples were prepared through the modification of the two-step acid-base catalysis of tetraethoxysilane (TEOS) as described by Brinker (17). 36 mL of TEOS (obtained from Aldrich) were mixed with 1.6 mL of 0.5 M aqueous HCl and 12 mL of water in a 250 mL polypropylene beaker resulting in an initial mole ratio of 1:4:0.005 (TEOS:H<sub>2</sub>O:HCl). This biphasic solution was then vigorously stirred using a magnetic stirring plate and stir bar until a clear, monophasic liquid was formed (approximately 30 minutes). 1.6 mL of 2.0M NH<sub>4</sub>OH in ethanol were added dropwise to this solution. Finally, 1.46 mg of HQS were added to yield an initial HQS concentration of 1 mM within the solution. The solution was then continuously stirred for 2 hours at room temperature.

Bulk specimens were prepared by pipetting one mL of this solution into one mL polystyrene cuvettes (1 cm x 0.5 cm x 2 cm), and covering the cuvette with parafilm. Gellation occurred within approximately 5 days at room temperature. The parafilm covers were then perforated using a pin to allow slow evaporation of the solvent from the wet gels. Dried gels were formed in approximately 3 weeks.

Experiments were performed to determine the period required to reach an equilibrium state of leached HQS from silicate gels. Silica gels containing 1mM of the host molecule were soaked in 5 mL of glass-distilled ultrapure water for 1 hour, 2 hours, 4 hours, 6 hours, and 24 hours. The solution was then decanted from the gels. A Beer's law standard curve was generated by preparing a solution of 1mM HQS in ultrapure water. This solution was then diluted to prepare standards of the following concentrations: 0.5mM, 0.1mM, 0.05mM, and 0.01mM HQS. Absorbances at 350 nm

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were recorded from a Cary 5 spectrophotometer and plotted against standard solutions' concentrations to prepare the curve. The absorbances of the leaching extracts were then recorded. These absorbances were used in conjunction with the Beer's law plot to determine concentrations by the following formula (Beer's Law):

$$A=kc$$

where A=absorbance, k=the slope of the Beer's law plot, and c=concentration (the value being determined). A separate plot of supernatant absorbance versus time of leaching was then made.

Based on the results of the leaching experiment, the doped dried gels were fully uncovered and placed into a 250 mL beaker of glass-distilled water for 24 hours to remove any physisorbed HQS from the porous gel specimens prior to spectroscopic analysis.

### III.B. 2. Spectroscopic Measurements

Experiments involving the complexation of zinc (II), cadmium (II), and mercury (II) with HQS in the gels were performed using a Spex Industries Model F112A spectrofluorometer. Excitation and emission band passes of 1.85 nm and 0.86 nm, respectively, were used, and all spectra were corrected for instrument response.

HQS-doped specimens were placed in a custom-designed quartz flow cell and introduced to a flowing solution of aqueous zinc chloride in one of the following concentrations: 10 mM, 1 mM, 100  $\mu$ M, 10  $\mu$ M, and 100 nM. Complex formation data between the HQS dopants and the analyte species were collected by monitoring the emission maximum at 522 nm of the HQS-Zn complex for a total of 1200 sec (20 minutes) using an excitation wavelength of 394 nm. Similar studies were carried out for aqueous cadmium nitrate; 10mM, 1mM, 100 $\mu$ M, 10 $\mu$ M, and 100nM concentrations of aqueous Cd(NO<sub>3</sub>)<sub>2</sub> were investigated. For the HQS-Cd complex, the same bands were

optically interrogated as for HQS-Zn. Mercury was used in the following concentrations from aqueous mercuric nitrate,  $\text{Hg(II)NO}_3$ : 10 mM, 1 mM, 100  $\mu\text{M}$ , 10  $\mu\text{M}$ , 1  $\mu\text{M}$ , and 100 nM. Mercury, however, delocalizes electrons from the  $\pi$  system of HQS, thereby creating a non-fluorescent complex. Consequently, the parent emission band at 480 nm was monitored for decreases in fluorescence intensity using an excitation wavelength of 408 nm.

### III.C. Results

#### III.C. 1. ICP Rates of aqueous Zinc, Cadmium, and Mercury with HQS-doped gels

The emission spectra for a bulk HQS-doped silica gel specimen prior to and after metal ion treatment are shown in Figure 14. Note the broad but weak emission band of the parent HQS at 410 nm. The intensity of the parent band has been magnified roughly 25 fold to scale it with the emission peak of the Zn-HQS complex. The emission peak shifts to 522 nm and increases in intensity during complexation with zinc or cadmium ions. Due to the spectral width of the parent HQS luminescence band there is some background signal at 522 nm from the uncomplexed probe molecule. At elevated concentrations of zinc (e.g. above 1 mM), this background signal was minimal compared to the intense fluorescence of the complex peak. In this case, changes to the fluorescence spectrum occur within seconds. However, as zinc concentrations were decreased, the intensity of the Zn-HQS peak was relatively weak and more difficult to distinguish from the broad parent band. This made it necessary to wait up to approximately 10 minutes to differentiate between micromolar and nanomolar analyte concentrations.

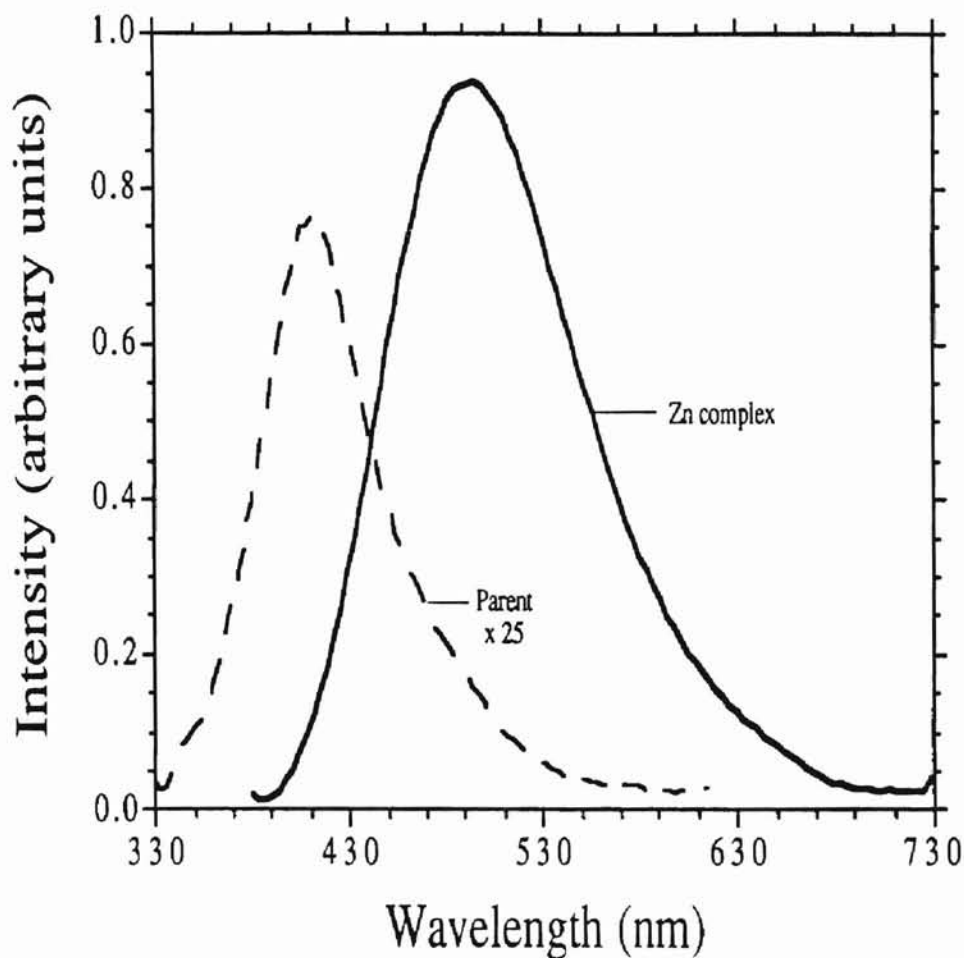


Figure 14: Parent (dashed line) HQS and Zinc-complexed HQS (solid line)  
 $\lambda_{ex} = 394 \text{ nm}$

The findings of the ICP measurements of divalent zinc are shown in Figure 15. As expected, the slope increases with increasing concentration, indicating that changes to the fluorescence are occurring more rapidly for higher concentrations of  $\text{Zn}^{2+}_{(aq)}$ . The slopes, derived as the best fit by linear least squares analysis, were found for 10 mM, 1 mM, 100  $\mu\text{M}$ , 10  $\mu\text{M}$ , and 100 nM respectively and are presented in Figure 18. These results are a large improvement over the previously reported results (see Chapter 2), in

which up to 3 hours were required for detection of 10 mM Zn<sup>2+</sup> by HQS-doped gels. Complexation behavior can now be seen on a seconds-minutes scale.

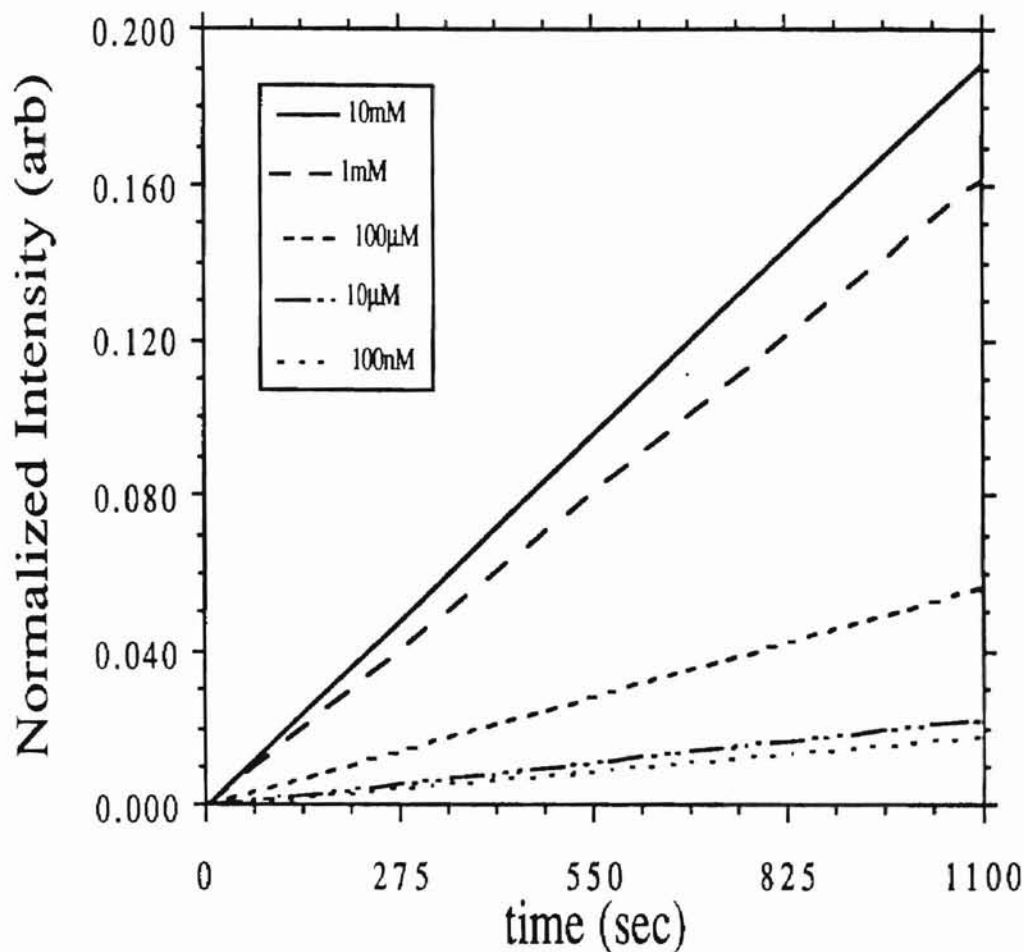


Figure 15: Complexation data of silica-incorporated Zn-complexed HQS A=10mM Zn, B=1mM Zn, C=100µM Zn, D=10µM Zn, and E=100nM Zn

Cadmium-complexation and mercury-complexation data were acquired in the same manner as for zinc. Results for cadmium complexation are shown in Figure 16, and results for mercury complexation are shown in Figure 17. ICP data for mercury-

complexed HQS was derived by monitoring the emission peak of the parent at 480 nm. Slopes of the complexation data are shown in Figure 18.

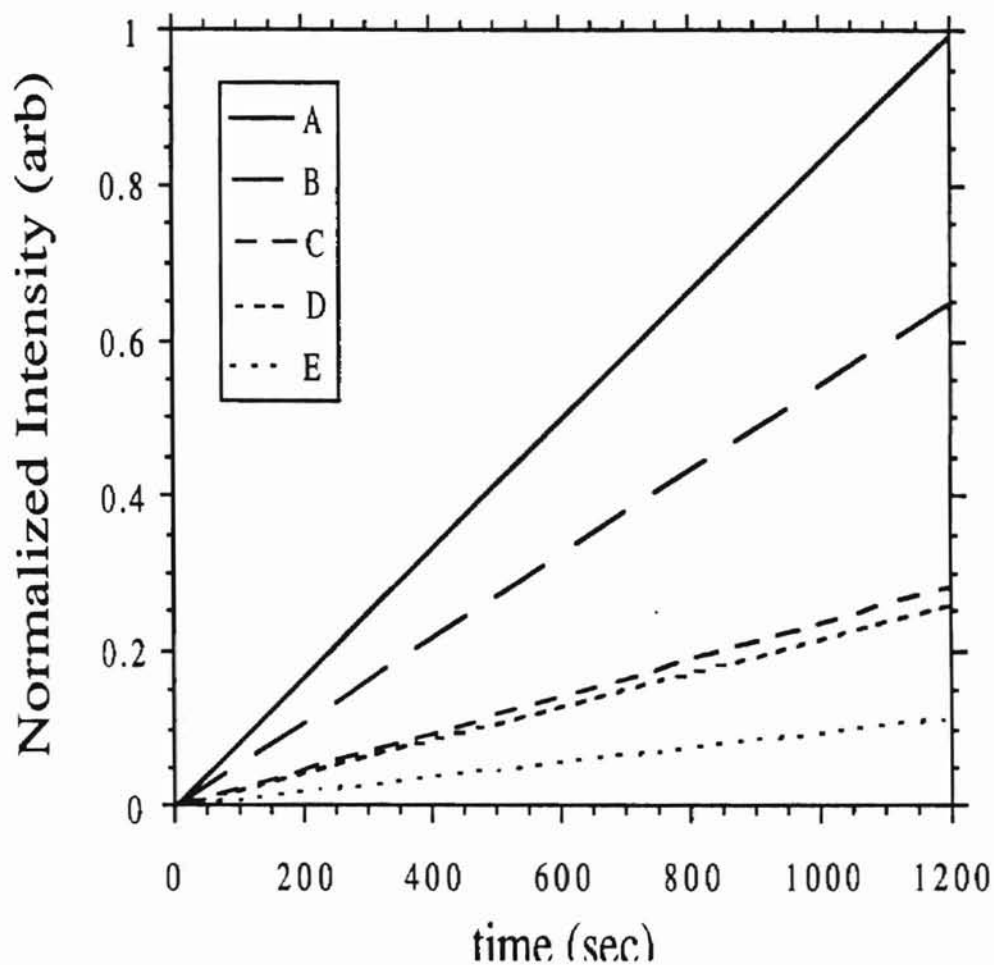


Figure 16: Complexation data of silica-incorporated Cd-complexed HQS  
A=10mM Cd, B=1mM Cd, C=100µM Cd, D=10µM Cd, E=100nM Cd

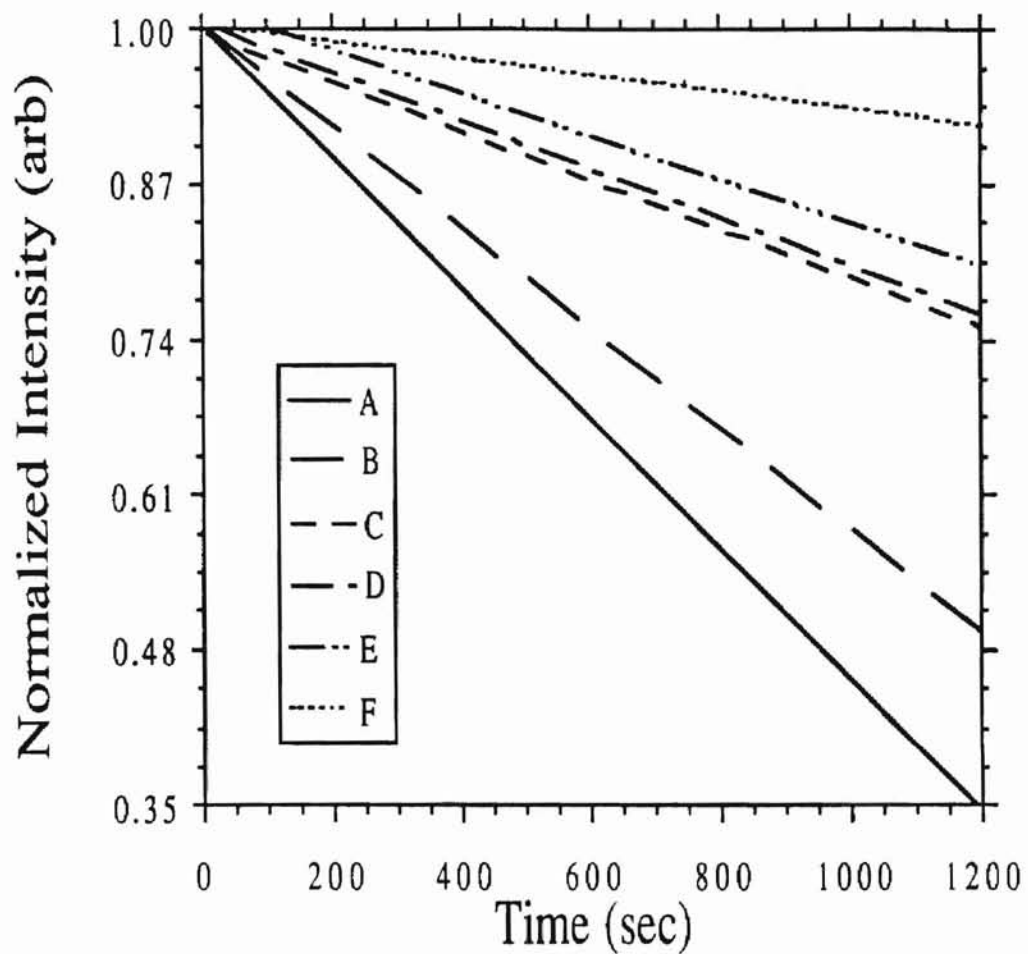


Figure 17: Complexation data of silica-incorporated Hg-complexed HQS  
 A=10mM Hg, B=1mM Hg, C=100μM Hg, D=10μM Hg, E=1μM Hg, F=100nM Hg



<u>Concentration</u>	<u>Metal Ion:</u>		
	<u>Zn</u>	<u>Cd</u>	<u>Hg</u>
100nM	$1.62 \times 10^{-5} \text{ s}^{-1}$	$9.64 \times 10^{-5} \text{ s}^{-1}$	$-6.99 \times 10^{-5} \text{ s}^{-1}$
1 $\mu$ M	-----	-----	$-1.81 \times 10^{-4} \text{ s}^{-1}$
10 $\mu$ M	$2.03 \times 10^{-5} \text{ s}^{-1}$	$2.16 \times 10^{-4} \text{ s}^{-1}$	$-2.03 \times 10^{-4} \text{ s}^{-1}$
100 $\mu$ M	$5.14 \times 10^{-4} \text{ s}^{-1}$	$2.37 \times 10^{-4} \text{ s}^{-1}$	$-2.05 \times 10^{-4} \text{ s}^{-1}$
1mM	$1.47 \times 10^{-4} \text{ s}^{-1}$	$5.42 \times 10^{-4} \text{ s}^{-1}$	$-4.23 \times 10^{-4} \text{ s}^{-1}$
10mM	$1.74 \times 10^{-4} \text{ s}^{-1}$	$8.29 \times 10^{-4} \text{ s}^{-1}$	$-5.48 \times 10^{-4} \text{ s}^{-1}$

Figure 18: Table of slopes for HQS complexation with  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$

### III.C.2. Results of Leaching Study

The Beer's law curve used in the leaching studies is shown in Figure 19. As shown in Figure 20, leaching was observed to occur for approximately 18 hrs. After 12 hrs, leaching effects no longer increased indicating that any physisorbed HQS and that in relatively large pores had been removed.

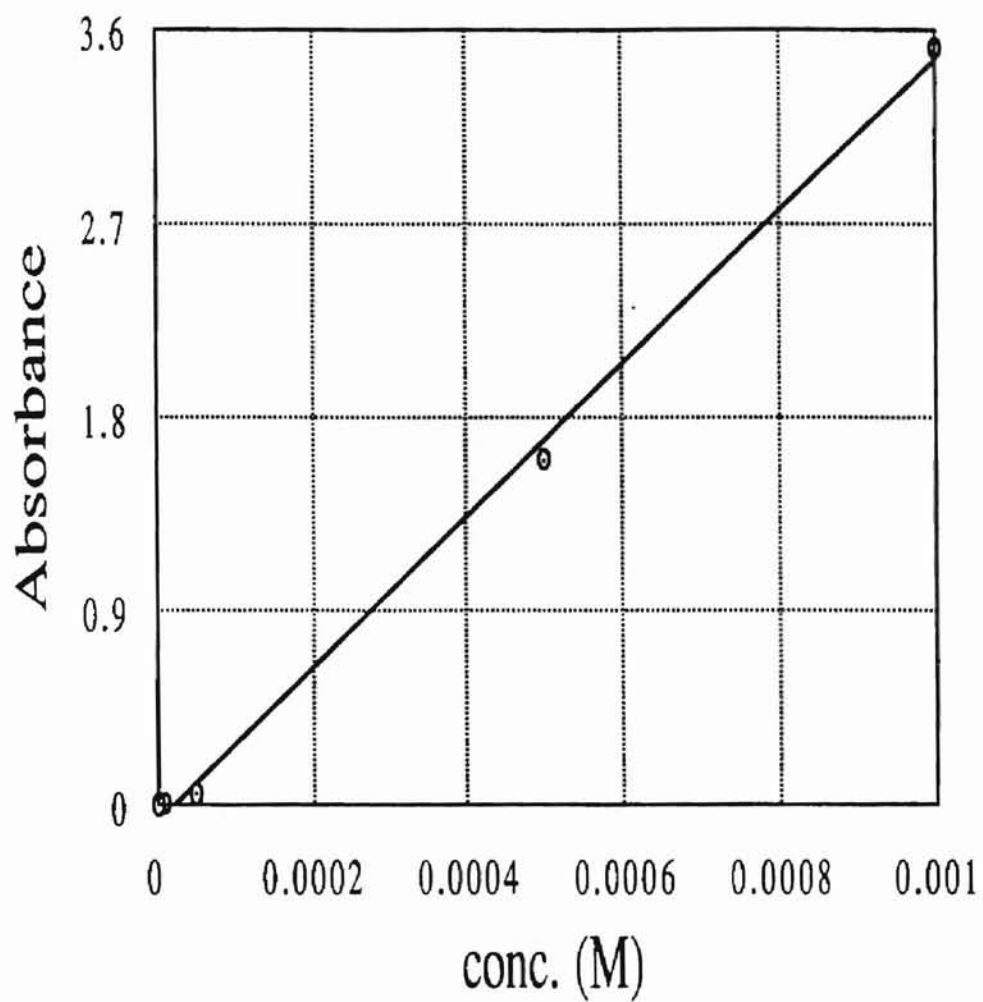


Figure 19: Beer's Law Plot of HQS in water

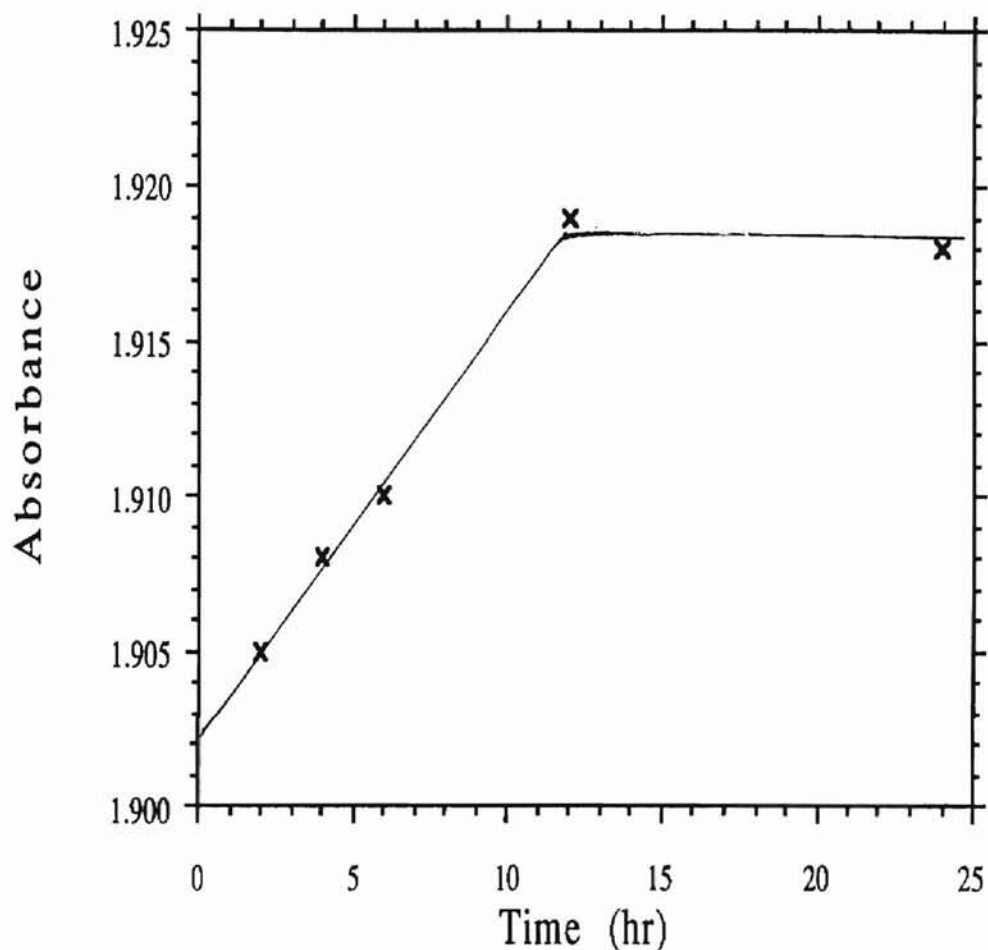


Figure 20: Absorbance versus time for leached gels

### III. D. Discussion of Results

Complexation behavior of ligand-doped sol-gel derived glasses toward  $Zn^{2+}_{(aq)}$  and  $Cd^{2+}_{(aq)}$  occurred rather slowly, as described in Chapter 2, only arriving at steady state conditions (as indicated by fluorescence measurements) between the HQS-doped gels and aqueous zinc or cadmium after approximately 3-4 hours of contact time with the ionic solutions. Measurement of the complexation process of comparable systems have

been utilized and reported by others to detect low concentrations within minutes (28). By monitoring the internal complexation process between analyte species and gel-confined HQS probe species, we have observed optode behavior within minutes after introducing the materials to aqueous analyte solutions. The results reported in this chapter show an improvement in determinable response time of complexation between HQS-doped gels with divalent zinc and cadmium over the results from Chapter 2. The internal complexation rate between the doped gels and divalent mercury has also been investigated and shows a quenching affect toward the fluorescence of HQS.

Preliminary results from this work indicate that HQS-doped gels have potential to be useful in the detection and differentiation of milli-, micro-, and even nanomolar concentrations of aqueous metal ions such as zinc, cadmium, and mercury. Such optode materials could be developed for the purpose of monitoring various transition metal ion analyte concentrations based on linear and non-linear fluorescence effects and internal complexation process rates between the HQS-doped gels and specific aqueous metal ions.

Leaching is seen to occur from the doped solid state specimens for approximately 18 hours. Therefore, any HQS which is on the surface of the gels after preparation, and that HQS which is in large pores is removed in this quantity of time. The HQS remaining in the gels is able, as seen through the fluorescence results of the ICP rate studies, to complex with metal ions.

### III.E. Conclusions

Silica gels derived by acid-base catalysis are relatively porous material. Organic probe molecules are susceptible to leaching from the matrix which can appear as a decrease in fluorescence intensity if monitored over time. Therefore, experiments were carried out to explore this problem. It was found that after 18 hours there is no further substantive leaching of the dopant from the matrix.

The present work supports the idea that porous, sol-gel derived materials incorporated with organic ligands such as HQS can show optode behavior toward transition metal ions on a real-time scale. The results show an important, novel path for semi-quantitative determination of concentrations of these ions by measuring the slope of ICP data. Coordination of the metal ion with the HQS ligand was observed fluorometrically within seconds to minutes of introduction of the solution to the doped gels. The present work supports the theory that complete saturation is not necessary to determine concentration range. Instead, concentration ranges (i.e. milli-, micro-, or nanomolar) can be determined based on the slope of the ICP rate line. These preliminary results have been reported down to nanomolar proportions of metal ion, showing that "real-time" detection of low concentrations using fluorescence spectroscopy is plausible.

## CHAPTER 4

### HQS-DOPED ALUMINOSILICATE GELS

#### V.A. Introduction

This chapter describes the preparation and spectroscopic characterization of 8-hydroxyquinoline-5-sulfonic acid (HQS) doped aluminosilicate gels. The precursor for aluminosilicate gels, di-sec-butoxyaluminum triethoxysilane (DBATES), was altered by the addition of HQS to form a novel, fluorescent modified precursor. The studies described herein arose from earlier attempts to prepare DBATES-based sensors using HQS dopant species. Experiments involving the characterization of the luminescent gels obtained from a suspected quinolinato-aluminoxysilane precursor were performed. Such precursors are of interest for the purpose of preparing luminescent media by the sol-gel approach.

The quinolinolato-aluminoxysilane precursor was observed to possess intense blue luminescence, which is believed to result from complexation of the bidentate ligand to the  $Al^{3+}$  center. The modified DBATES precursor was subsequently hydrolyzed and allowed to gel. The luminescence behavior of the modified alkoxide and the resultant gels was studied through the use of absorbance and fluorescence (continuous and time-resolved) spectroscopy. The results of those experiments are subsequently described. This is the first work known to the authors of a sol-gel precursor which exhibits efficient fluorescence behavior due to the formation of an internal metal-ligand complex.

## V.B. Experimental

### V.B. 1. Chemical Methods

HQS-doped aluminosilicate gels were formed through the hydrolysis and condensation of (di-*sec*-butoxyaluminoxy)triethoxysilane (DBATES) mixed with a dilute aqueous solution of HQS in the method shown in Figure 21. Nine milliliters of the DBATES precursor was placed in a 250 mL polypropylene beaker and diluted to form a 1:1 volume ratio with 9 mL of isopropanol (solution 1). In a separate polypropylene beaker, a solution of 1:3 volume ratio of 3 mL of water to 9 mL of isopropanol was prepared (solution 2). Solution 2 was then slowly added, in a dropwise fashion with constant stirring, to solution 1. 7.3 mg of HQS was added to the beaker containing solution 1 and 2 to provide a final dopant concentration of 1 mM HQS in the sol. Following 2 hours of hydrolysis during which the solution was continually stirred using a magnetic stirring plate and stir bar, the resultant sol was poured into 5 mL polystyrene cuvettes, covered with parafilm, and allowed to gel. Upon gelation, the parafilm was perforated to allow slow solvent evaporation. The gels were allowed to dry under ambient conditions for 2 weeks.

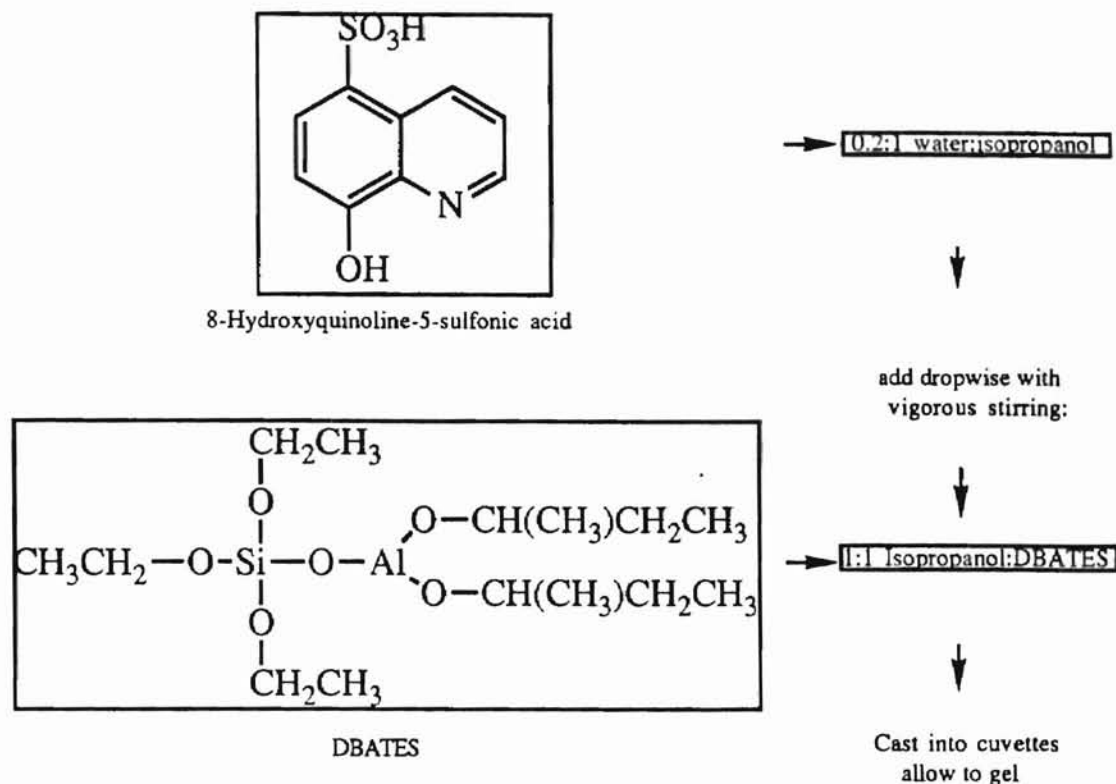


Figure 21: Preparation of HQS-doped Aluminosilicate

## V.B. 2. Spectroscopic Measurements

Optical characteristics of the precursor solutions and the dried xerogels were studied. No substantive spectroscopic differences between the precursor solution and the solid state xerogel specimens were observed. Absorbance spectra were determined using a Cary 5 spectrophotometer (2.0 nm spectral band pass). Continuous wave front face excitation and emission spectra were measured using a Spex Industries Model F112A spectrofluorimeter having 1.85 nm and 0.86 nm excitation and emission band passes, respectively. All luminescence spectra were corrected for instrument response.

Lifetimes were measured using a modified Lambda Physik LEXtra 210i model excimer laser oscillating at the fundamental XeCl output wavelength of 308 nm. The excitation pulse had a temporal width (FWHM) of 10 ns. The time-resolved



luminescence behavior of the HQS-DBATES complex at 488 nm was determined through the use of a 0.25 M double-grating monochromator, thermoelectrically-cooled R928 photon-counting photomultiplier tube (2 nsec rise time at the voltage used), and a digitizing storage oscilloscope (Tektronix model 2440, 500MHz multipulse bandwidth; 16 pulse averaging). Mathematical deconvolution was performed, via custom software, to remove artifacts which arise due to the excitation source pulse width and detector rise times.

Quantum efficiencies were determined from the absorbance and luminescence spectra in accordance with the reference method described by Demas and Crosby, using the optically dense sample approximation (26). Quinine bisulfate dissolved in 1.0 N sulfuric acid, which is reported by Demas and Crosby to have a quantum efficiency of 54.6%, was chosen to be the reference standard. Both the standard and the prepared specimens were excited at 365 nm using a "front face" sample orientation. Bandpasses of 0.4 nm (excitation) and 0.2 nm (emission) were employed. The integrated fluorescence emission signal was determined for the modified alkoxide and reference solution, and the overall quantum efficiency was determined from the relative ratio value. The following formula was used to calculate the quantum yield:

$$Q=(Q_r)(A_r/A)(S/S_r)$$

where  $Q_r$ =quantum yield of the reference,  $A_r$ =absorbance of the reference,  $A$ =absorbance of the sample,  $S_r$ =integrated emission intensity of the reference, and  $S$ =integrated emission of the sample.

## V.C. Results

### V.C. 1. Steady State Spectroscopy

Upon the addition of HQS to the aluminosilane alkoxide, a highly luminescent solution is observed to immediately result. The absorbance spectrum for the HQS-DBATES solution is presented in Figure 22 and shows a peak absorbance at 365nm. The excitation spectrum (Figure 23) of the HQS-DBATES gels ( $\lambda_{em} = 488$  nm) shows an excitation peak at 365 nm which, as expected, correlates to the observed absorbance maximum. Photometric measurements of the HQS-DBATES system indicate substantive spectral similarities between this species and reported data for metal-ion complexed HQS. Blanco and coworkers (27), for example, reported absorbance behavior for tris(8-quinolinolato)aluminum(III) (Alq<sub>3</sub>) that is comparable to the HQS-DBATES absorbance. A peak-position blue shift equal to approximately 25 nm was noted for the HQS-modified aluminosilicate gels with respect to the comparable tris Alq<sub>3</sub> complex described by Blanco.

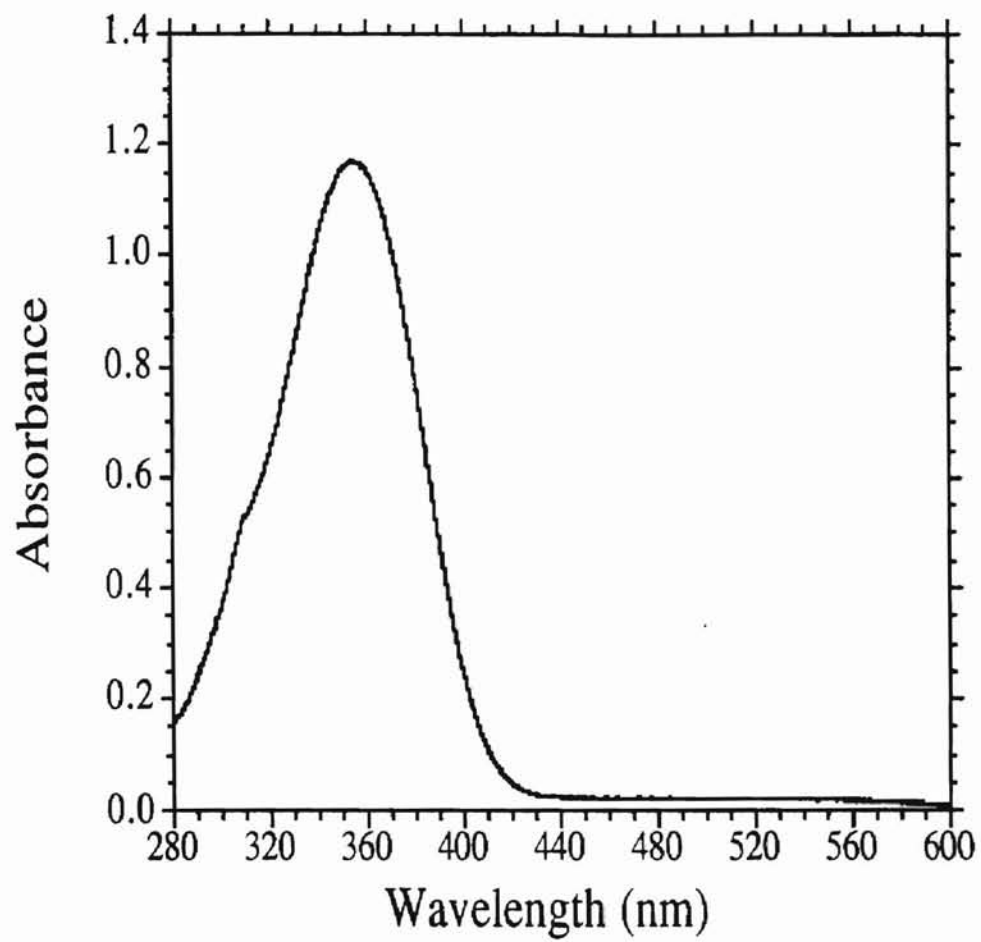


Figure 22: Absorbance spectrum of HQS-doped aluminosilicate gel

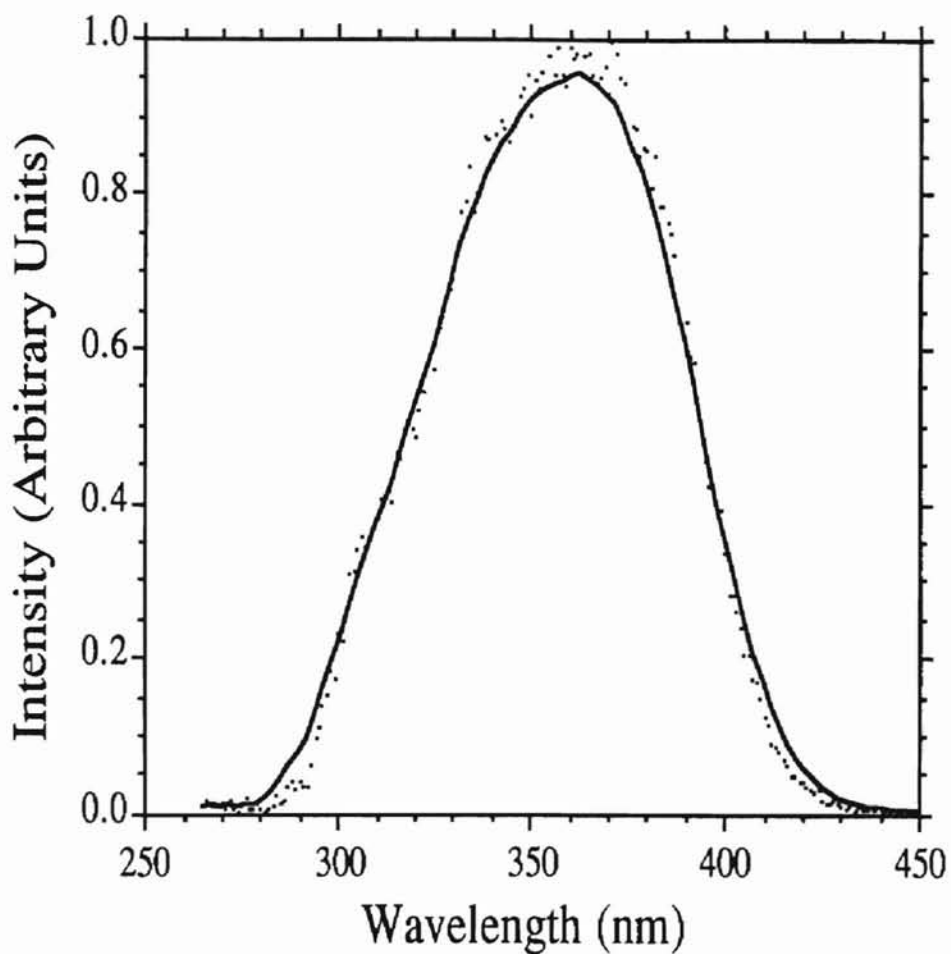


Figure 23: Excitation spectrum of HQS-doped aluminosilicate gel  
 (··· = data points, — = fitted curve)

The emission spectrum shown in Figure 24 was observed upon excitation at 365 nm; the peak emission intensity lies at 488 nm. This broad blue to blue-green emission is characteristic of complex formation between quinoline derivatives and  $Al^{3+}$ , as reported by Tang and co-workers (28). These observed spectra lead to the conclusion that HQS dopants are interacting with the aluminum sites of the aluminosilane precursor which are behaving as a Lewis acid.

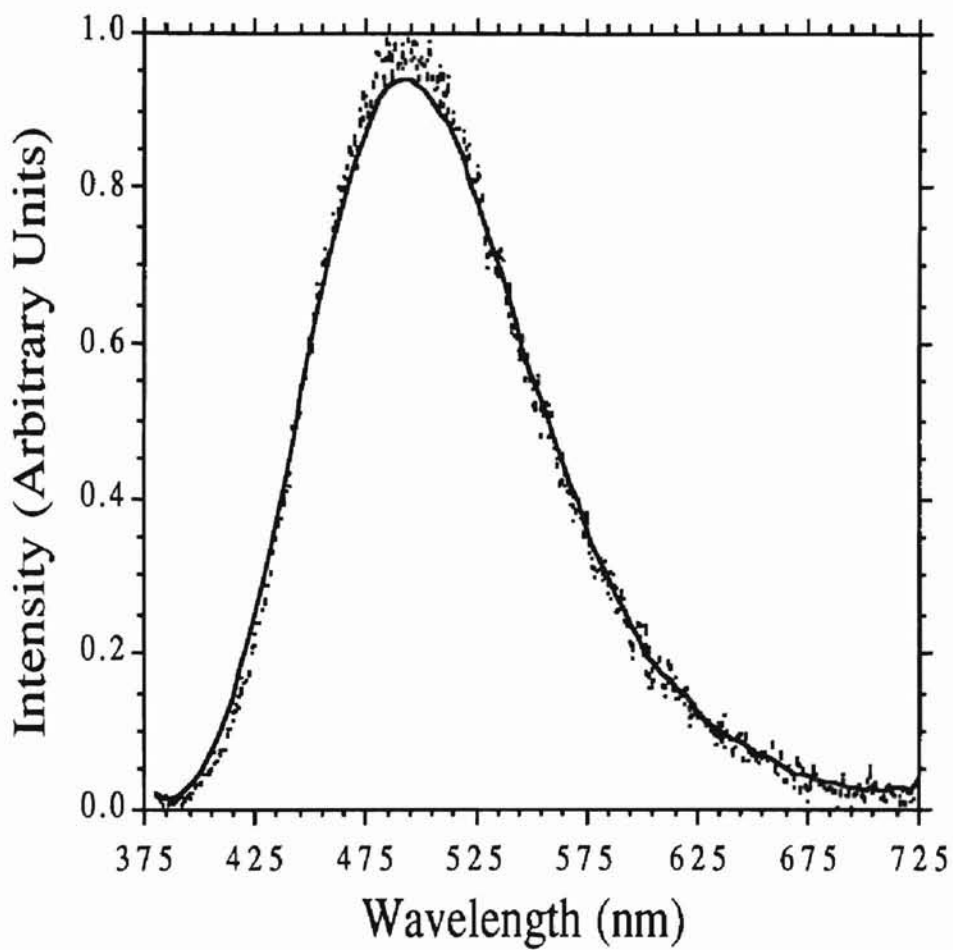


Figure 24: Emission spectrum of HQS-doped aluminosilicate gel  
(... = data points, — = fitted curve)

## V.C. 2. Radiative Decay Processes

Radiative lifetimes were taken for the HQS-DBATES gels at room temperature and at 77 K. Radiative lifetimes of 20 nsec for the room temperature gel (Figure 25) and 28 nsec for the gel at 77 K were calculated using deconvolution methods. These measurements compare well to Tang's reported value of 16 nsec in room temperature solution for tris(8-hydroxyquinolinolato)aluminum(III) (28).

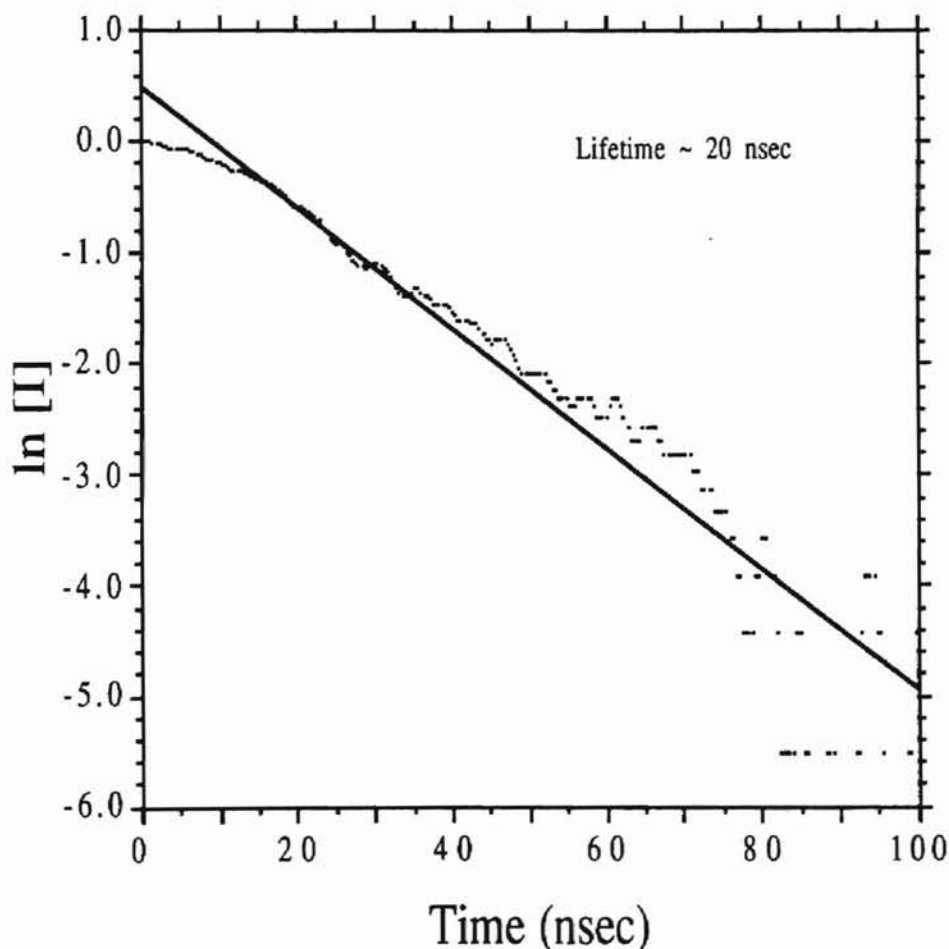


Figure 25: Radiative Decay of HQS-doped aluminosilicate gel at 298K.

### V.C. 3. Quantum Yield

The HQS-DBATES gel specimen was computed to have a quantum yield of 21% compared to the quinine bisulfate standard solution. This compares very favorably to the reported value by Tang of 8% for the  $Alq_3$  complex.

### V. D. Discussion of Results

At a pH value of 7, both the sulfonato and alcoholic protons of HQS are known to be mostly dissociated. Under these conditions, the quinolinato ion is highly reactive and readily forms complexes with various metallic cations. At the same time, the aluminum atom of the DBATES molecule behaves as a Lewis acid, and actively seeks excess electron density of the type presented by HQS under these conditions. Based upon these tendencies, it is reasonable to assume that the bidentate quinolinato species will interact with the aluminum centers present in the precursor sol.

The calculated quantum efficiencies, increased lifetime of the radiative decay process and observed emission/excitation spectra support the hypothesis that a fluorescent quinolinatoalkoxyaluminum(III) complex is formed upon the addition of HQS to DBATES. Free HQS is, by comparison, notably nonluminescent when dissolved into ordinary alcoholic or simple tetraalkoxysilane solutions. The onset of broad, intense luminescence bands upon the addition of HQS to the aluminoxy-containing alkoxides support the development of a highly allowed singlet state transition upon chelation. The short radiative lifetime, less than 30 nsec at 77 K, is also indicative of singlet state transitions rather than charge transfer or other types of luminescence mechanisms. Fluorescence emission and excitation of the HQS-doped gel is substantially similar to that reported for other  $Al^{3+}$  complexed quinoline species, indicative of complexation

between HQS and the aluminum center of the DBATES precursor. Increased rigidity of the system due to the gel network could account for the increased fluorescence yield compared to Alq<sub>3</sub> by allowing for better orbital overlap of the ligand and the aluminum species. Quantum efficiencies of the HQS-DBATES gels are approximately 20%, indicating a substantial and fundamental change in the energy levels and transition states of HQS. This value compares favorably to that of Alq<sub>3</sub> in toluene which has been reported to possess a quantum efficiency of 8%. This increase may be the result of the greater rigidity of the sol-gel matrix, thereby imparting a better overlap of the  $\pi$ -orbital system.

## V. E. Conclusions

8-Hydroxyquinoline and its derivatives have previously been reported to form highly luminescent complexes with cations such as aluminum(III). The development of an intensely fluorescent solution occurs upon addition of HQS to DBATES; this behavior has been associated with chelation between HQS and the aluminum center of the DBATES molecule. Continuous wave luminescence phenomena, absorbance, and radiative decay of the HQS-DBATES solution are substantially similar to reported values for quinolinolato-complexed trivalent aluminum ions, supporting the hypothesis that HQS forms a complex with the aluminum ion. These findings are significant, as the HQS-complexed double alkoxide undergoes hydrolysis and condensation reactions very much like those known to proceed for the unmodified DBATES precursors.

Xerogels prepared using the complexed alkoxide precursor were found to have a broad ultraviolet absorption band and intense blue emission characteristics. Quantum efficiencies of this material more than double the reported values for the complex of 8-hydroxyquinoline with trivalent aluminum in solution; this increase is postulated to be due to the increased rigidity that occurs upon gelation. The reported results indicate that



such media may be used in the development of efficient solid state sources which emit in the blue to blue-green portion of the spectrum.

## CHAPTER 5

### NUCLEAR MAGNETIC RESONANCE STUDIES OF HQS-DBATES SYSTEM

#### VI.A. Introduction

The interesting luminescent behavior including the increased quantum yield, increased radiative decay, and broad, bright emission of the HQS-DBATES adduct brought to question the exact interaction of the HQS with the aluminum centers within the sol-gel precursor. It was noted that luminescence behavior occurred before and after gellation with inconsequential differences. This same behavior was noted in the precursor before hydrolysis (i.e. HQS diluted in isopropanol mixed with DBATES--under anhydrous conditions). Attempts to identify the complex of HQS with the aluminosilicate gels through infrared spectroscopy and solutions  $^{13}\text{C}$  and  $^1\text{H}$  NMR (both 400MHz and 500MHz) were inconclusive, mainly due to the low solubility of HQS in  $\text{CCl}_4$ , isopropanol, or in the gels themselves (1mM HQS was the maximum dopant concentration without precipitation from any of the above). Finally,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  Solid State NMR was utilized in an attempt to discover information about the HQS-DBATES complex.

Pouxviel has reported that gels formed through the hydrolysis and subsequent condensation of DBATES precursor are mainly tetrahedral with respect to the alumina sites. He has investigated this precursor via 400 MHz solutions NMR after addition of water and isopropanol. However, results reported in this chapter show that the majority of sites within both the sol and gel forms of the aluminosilicate precursor have mainly octahedral sites, with tetrahedral sites being seen only in low numbers within the gelled specimens. The information obtained shows significant differences of the gel network over that reported by Pouxviel. However, information about the interaction of HQS with the matrix is still unresolved.

## VI. B. Experimental

Studies to investigate the nature of the HQS-DBATES complex were carried out by both  $^{27}\text{Al}$  and  $^{29}\text{Si}$  solid state nuclear magnetic resonance (NMR). First, undoped sols of the DBATES precursor were characterized, followed by investigation of the undoped gels. Subsequently, similar studies were carried out on the doped samples in both sol and gel form. Comparisons of unmodified and modified sols and gels were then possible.

Samples of undoped and HQS-doped DBATES derived sols and xerogels were prepared by similar methods as described in Chapter 5. Three different samples of the undoped samples were prepared. **Sample 1:** An alcoholic solution of undoped, unhydrolyzed DBATES was prepared by diluting 9mL of DBATES in 21mL of isopropanol. This solution was then poured in 5mL polystyrene cuvettes and covered with parafilm. **Sample 2:** Undoped, hydrolyzed DBATES sol was prepared by mixing 9mL of DBATES with 9mL of isopropanol. A separate solution of 9mL of isopropanol with 3mL of water was prepared and added to the first solution in a slow, dropwise fashion with constant stirring. The reaction was allowed to proceed for approximately 2 hours at which time, the final sol was cast into 5mL polystyrene cuvettes and covered with parafilm. These samples were analyzed as sols. **Sample 3:** The final undoped gels were prepared by taking sols prepared by the same method as the second samples just described, covering with parafilm and allowing to gel (approximately 2 days). At this time, the covers were perforated to allow slow evaporation of the solvent. Xerogels were obtained in approximately 2 weeks. These samples were analyzed as solid-state gels.

HQS-doped samples were prepared in the same methods as samples 2 and 3 above except that 0.0073 g of HQS was added to each to make sample 4 and 5, respectively. Therefore, two different samples of HQS-doped aluminosilicates were prepared: hydrolyzed, doped sols (sample 4) and hydrolyzed, doped gels (sample 5).

All five of the above samples were analyzed by single pulse  $^{27}\text{Al}$  NMR. The undoped and doped gelled samples were also analyzed by  $^{27}\text{Al}$  crosspolarized with  $^1\text{H}$  NMR and  $^{29}\text{Si}$  crosspolarized with  $^1\text{H}$  NMR.  $^{29}\text{Si}$  and  $^{27}\text{Al}$  and CP/MAS NMR spectra were obtained at 78.158 and 59.586 MHz, respectively, on a Chemagnetics 300 MHz Solid State Instrument. Samples were ground and packed into 5.0 and 7.5 mm rotors under ambient conditions. For  $^{29}\text{Si}$ , the number of scans ranged from 32 to 3200, contact times ranged from 5.0 to 20.0 ms, and repetition times varied from 1.0 to 15.0 s. For  $^{27}\text{Al}$ , the number of scans ranged from 16 to 3200, contact times ranged from 1.0 to 10.0 ms, and repetition times varied from 0.5 to 10.0 s.  $^{29}\text{Si}$  and  $^{27}\text{Al}$  chemical shifts are reported with respect to TMS and  $[\text{Al}(\text{OH})_6]^{3+}$ .

#### VI.C. Results

Figure 26, 27, and 28 show the single pulse  $^{27}\text{Al}$  spectra of DBATES sols without water or HQS (sample 1), with water but no HQS (sample 2), and with water and HQS (sample 4), respectively. The large peak centered at approximately 4ppm is consistent with Pouxviel's assignment of octahedral aluminum coordination (12). The small sideband at approximately 45 ppm in Figure 27 and 28 is consistent with tetrahedral coordination and is absent in Figure 26, suggesting that the tetrahedral coordination is formed under condensation conditions after reaction with water.

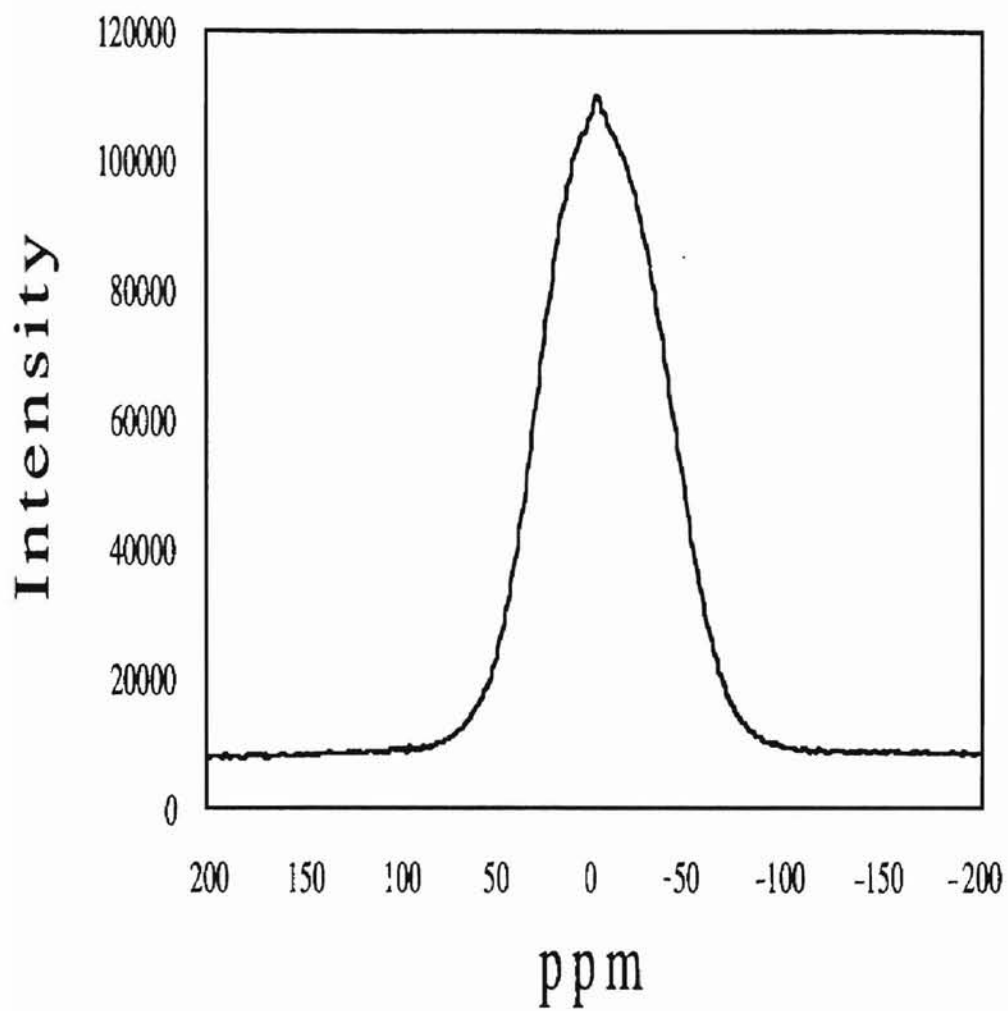


Figure 26: Single Pulse  $^{27}\text{Al}$  NMR of DBATES: no  $\text{H}_2\text{O}$  or HQS

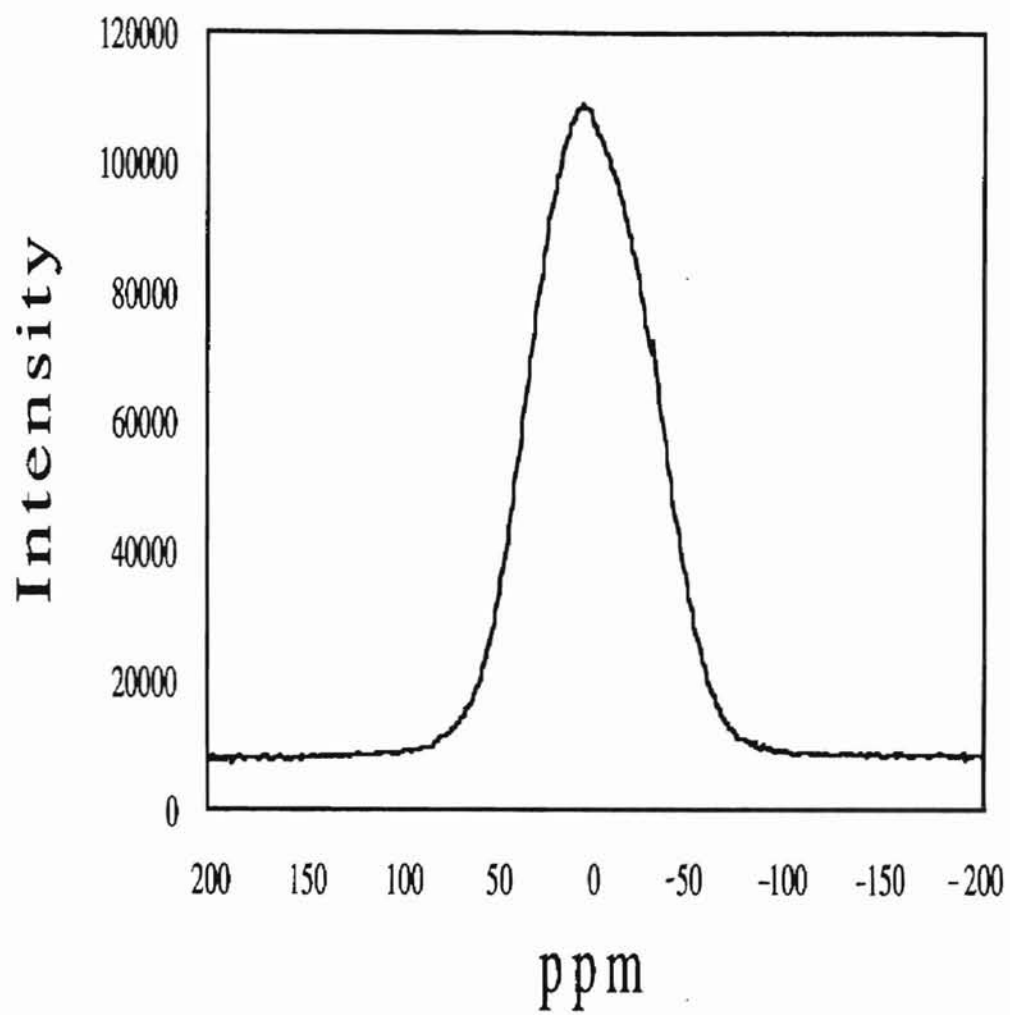


Figure 27: Single Pulse  $^{27}\text{Al}$  NMR of DBATES with  $\text{H}_2\text{O}$ : no HQS

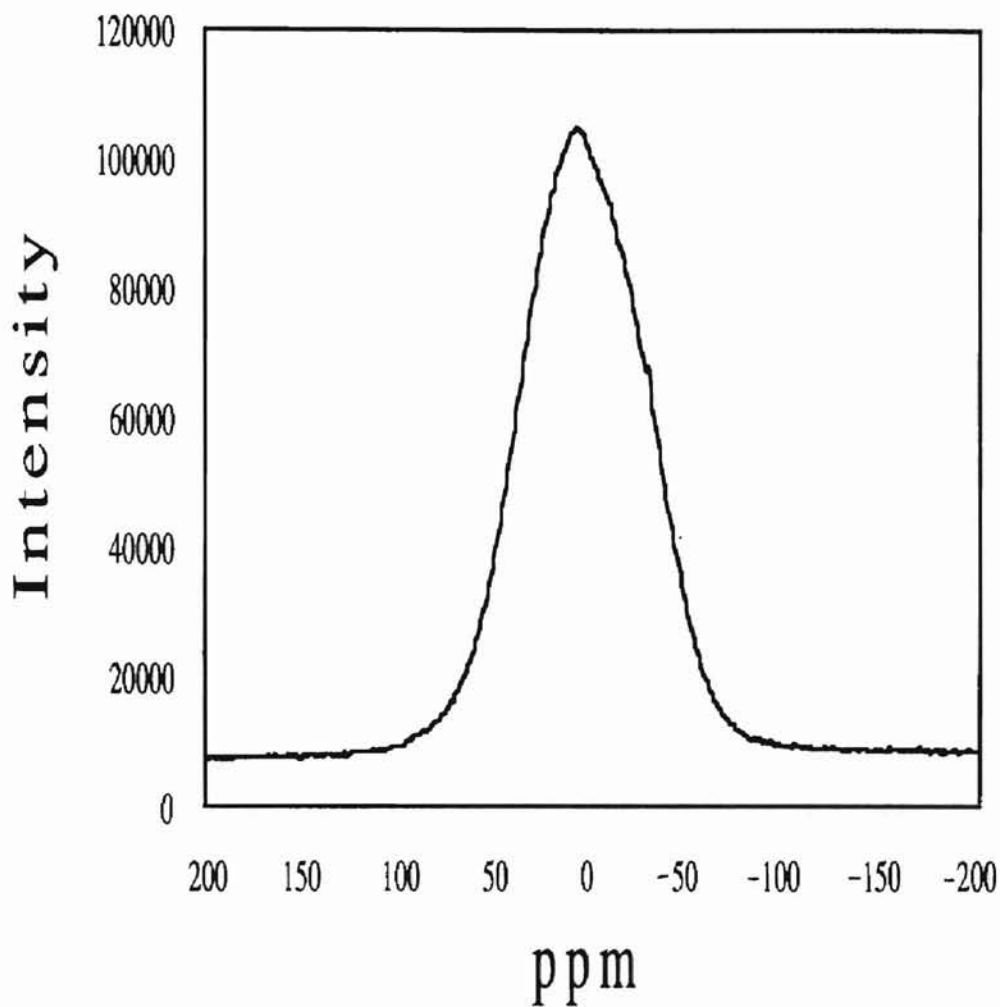


Figure 28: Single Pulse  $^{27}\text{Al}$  NMR of DBATES with  $\text{H}_2\text{O}$  and HQS

Figures 29 and 30 show the single pulse  $^{27}\text{Al}$  of DBATES gels without (sample 3) and with HQS dopant (sample 5), respectively. No substantial differences are notable between the two spectra. A large, broad peak at  $\sim 4\text{ppm}$  due to octahedral coordination of aluminum in both samples dominates the spectrum. Also, the sideband at 45 ppm is still present. This sideband has increased in breadth as compared to the sols, once again suggesting that condensation brings about more tetrahedrally coordinated sites.

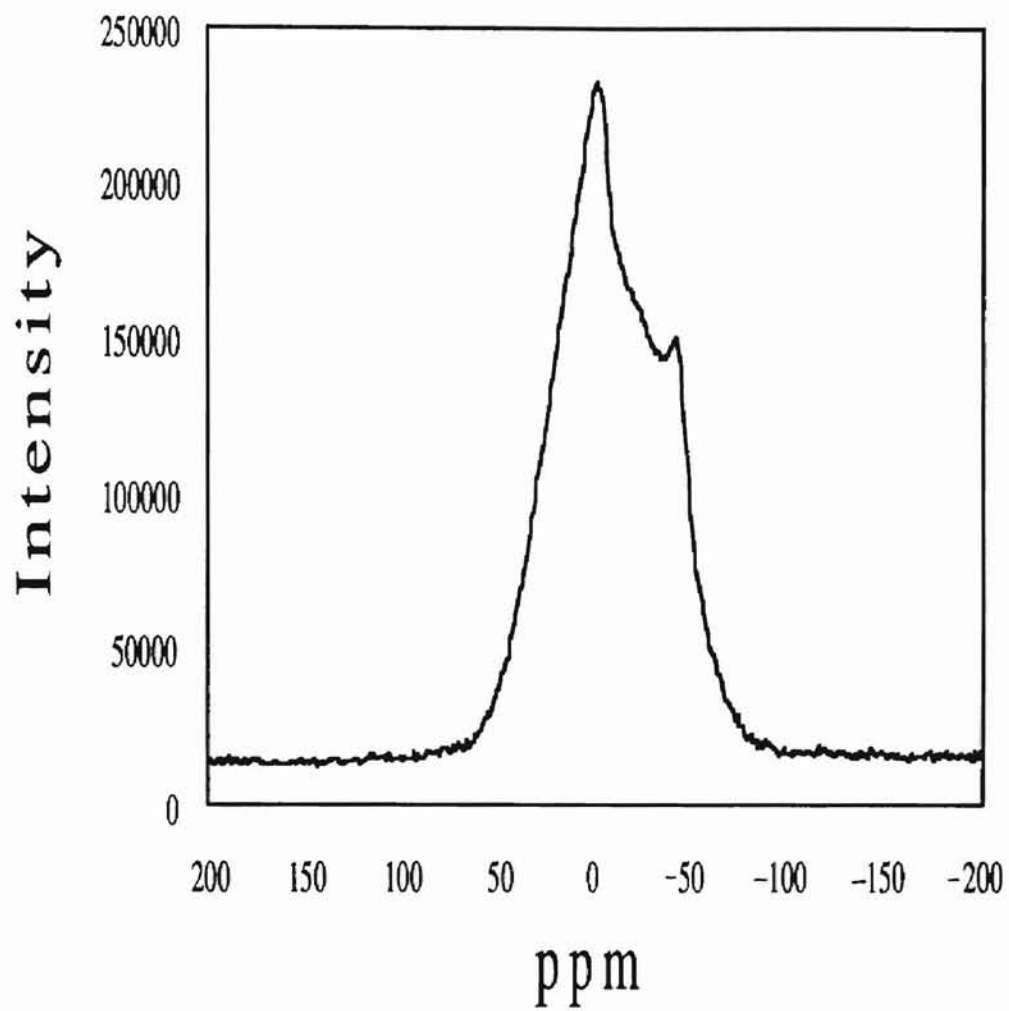


Figure 29: Single Pulse  $^{27}\text{Al}$  NMR of undoped DBATES xerogel



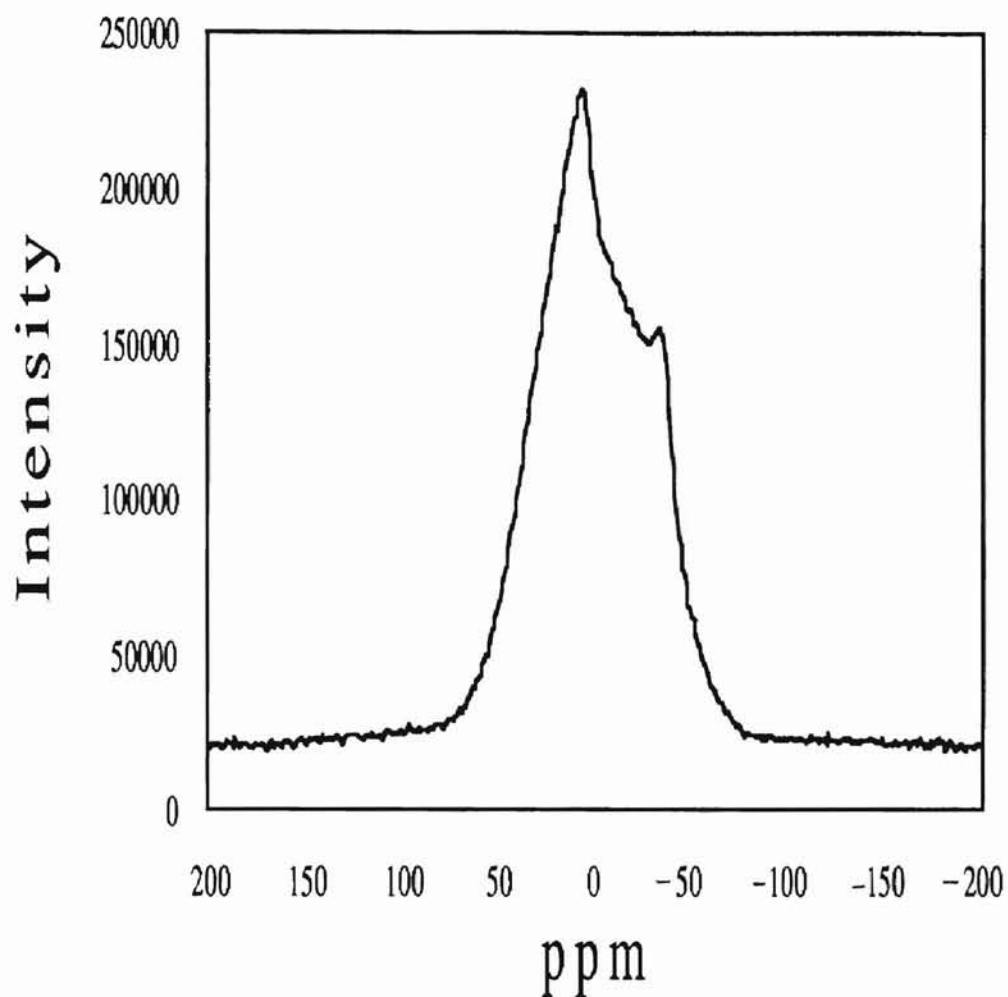


Figure 30: Single Pulse  $^{27}\text{Al}$  NMR of HQS-doped DBATES xerogel

Figures 31 and 32 show the  $^{27}\text{Al}$  crosspolarized with  $^1\text{H}$  NMR spectra of the undoped and doped aluminosilicate gels used for the previous two single pulse  $^{27}\text{Al}$  spectra above, respectively. Some differences are notable in the spectra, especially in the region between the two large peaks. Once again, octahedral coordination is noted to dominate the structure, with fewer tetrahedral sites apparent. The region between the octahedral and tetrahedral peaks is especially interesting and may prove to be important in determining the molecular interaction of the HQS with the DBATES-derived gels.

This area may be due to pentacoordinate aluminum complexes as reported in zeolite structures (29) or may be simply sidebands of the octahedral or tetrahedral sites, indicating several different octahedral or tetrahedral structures present within the matrix.

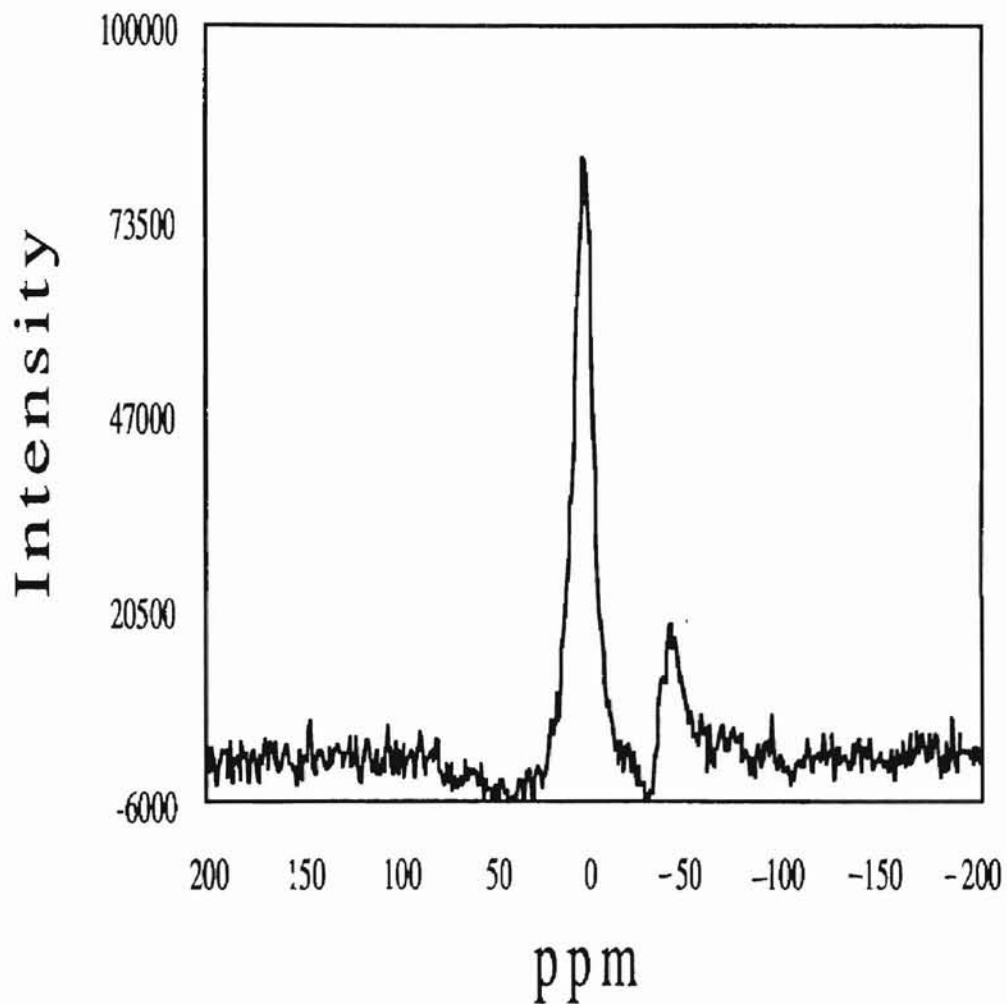


Figure 31: Cross-polarized  $^{27}\text{Al}$  NMR of undoped DBATES xerogel

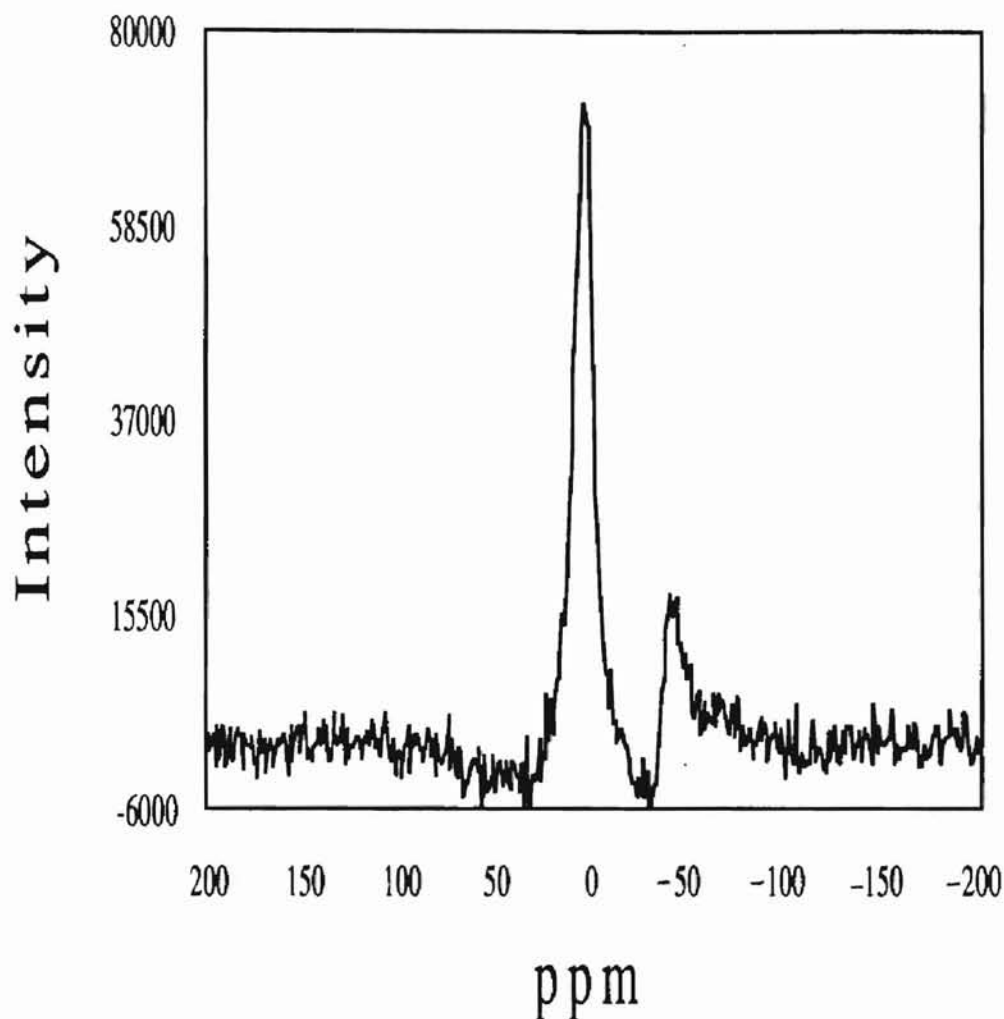


Figure 32: Cross-polarized  $^{27}\text{Al}$  NMR of HQS-doped DBATES xerogel

Results of the  $^{29}\text{Si}$  crosspolarized with  $^1\text{H}$  NMR experiments of the undoped and doped gels, respectively, are shown in Figures 33 and 34. The spectra indicate no substantive differences between the two gels. The main feature to note in these spectra is the large, broad band centered at approximately -85ppm, indicating "Q3" silica. "Q3" is defined to be a site containing 3 Si-O-M, bonds where M in this case is either aluminum or silicon, and 1 Si-OH bond. This feature proves that the majority of the siloxy groups have condensed to form a three-dimensional polymeric network of the silica sites.

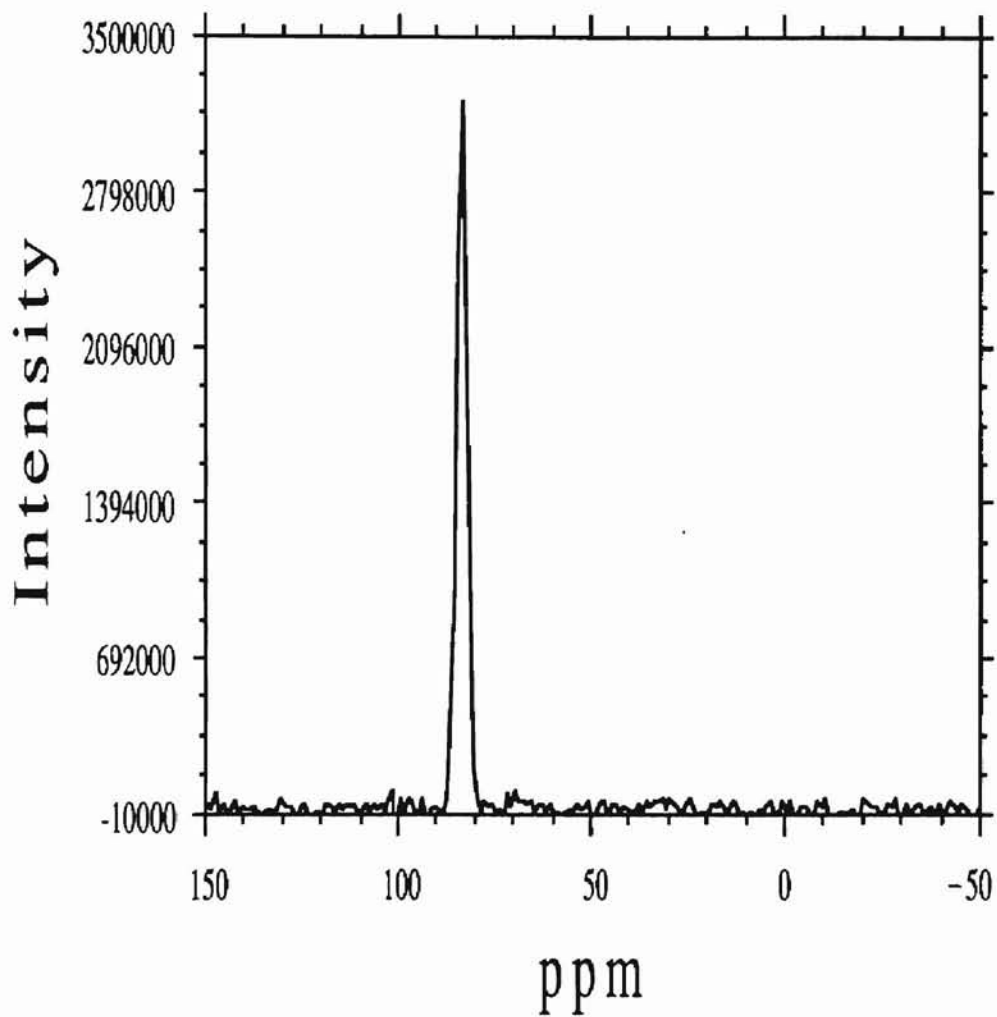


Figure 33: Cross-polarized  $^{29}\text{Si}$  NMR of undoped DBATES xerogel

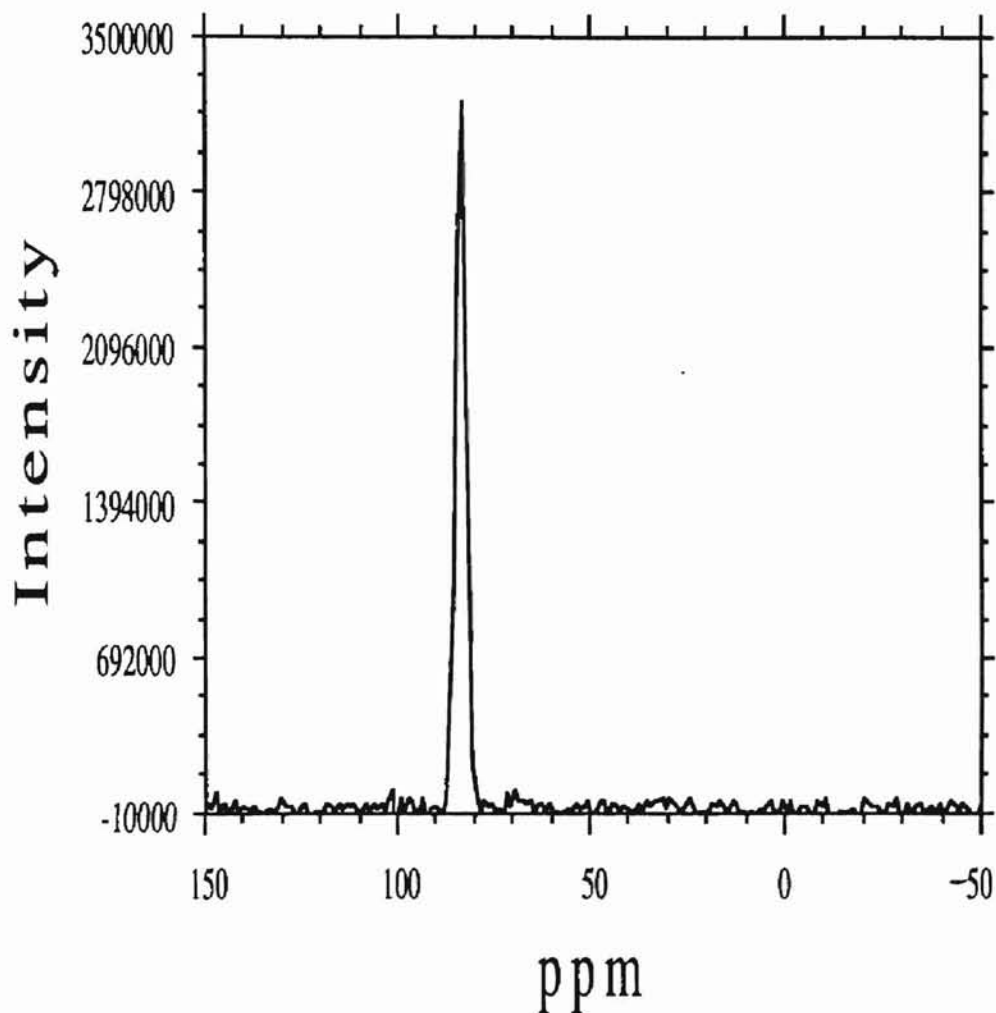


Figure 34: Cross-polarized  $^{29}\text{Si}$  NMR of HQS-doped DBATES xerogel

#### VI.D. Discussion of Results

Our results indicate that aluminosilicate formed by the hydrolysis and condensation of DBATES precursor in our method are mainly octahedrally coordinated both before and after gellation, even after xerogel formation. Pouxviel and coworkers have previously described sols and gels prepared by a similar sol-gel process using the same aluminosilicate precursor (12). However, their reported findings differ significantly

from our results. They report via 400 MHz solution  $^{27}\text{Al}$  NMR that gels formed by the hydrolysis and condensation of DBATES are mainly tetrahedral with respect to the aluminum sites with fewer octahedrally coordinated sites. Pouxviel also suggests that since the hydrolysis rate of the alkoxy groups from the aluminum sites occurs much more rapidly than the silica sites, aluminum "islands" are formed within the overall gel structure itself. However, the gels we have presently investigated resulted in much greater octahedral coordination of the aluminum sites within the network. Also, our results indicate that the precursor itself is mainly octahedrally coordinated, with little or no tetrahedral sites. This may be due to coordination with isopropanol solvent or the small amount of water present in the solvent as the precursor itself would be trigonal.

The main goal of these NMR experiments was to determine the exact molecular complex of the HQS molecule with the precursor. The cross-polarized (CP) aluminum spectra indicate that there may be differences between the structure of the undoped and doped gels. However, significant differences between the two spectra are not obvious. Several types of coordination between the HQS and the aluminum centers can be envisioned for the present system. As suggested in the previous chapter, the luminescence behavior of the HQS-DBATES adduct is consistent with other HQS-containing metalorganic complexes, such as Alq<sub>3</sub>, which are known to be octahedral complexes. However, 5- or even 4- coordinate complexes cannot be ruled out, especially due to the interesting CP  $^{27}\text{Al}$  spectra of the doped and undoped gels in the region between the octahedral and tetrahedral positions. Bertsch and co-workers have reported coordination of ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid, i.e. HQS with an iodo group in the 7 position) with aluminum in solution as being "representative of the tetrahedrally coordinated Al centralized in the cage-like structure composed of 12 octahedrally coordinated Al atoms grouped about each apex and interconnected by both their common edges" (30). These reported results indicate that many reaction paths for

complexation of HQS with aluminosilicate gels may be possible, and until further experiments are performed, no possibilities may be ruled out.

#### VI.E. Conclusions

The present NMR investigation of the HQS-DBATES sol-gel system has clarified the question of gel structure of the overall network. This work suggests that octahedral, not tetrahedral as reported by Pouxviel, coordination of the aluminum sites dominates the gel structure. These findings may be important in attempting to determine the nature of the HQS-DBATES coordination. No conclusive determinations can be made, however, with regard to the interaction of the HQS dopant with the aluminum centers. Future plans for this project include the use of DOR NMR in a further attempt to clarify this question.

## CHAPTER 6

### FUTURE WORK

#### VII. A. Thin Films and Fiberoptics

Presently, all work on this system has involved the utilization of bulk samples. Much improvement in the development of a fiberoptic sensor still needs investigation. Reactions involving the covalent attachment of HQS into the gel network has, as yet, been unsuccessful in creating a fluorescent material. Previous reactions reported by Mottola et al have involved the attachment of HQS to silica gel but yielded a non-fluorescent product. Due to the leaching effects seen in HQS-incorporated sol-gel processed silica gel, it will be necessary to achieve a method for attachment to the network before a fiberoptic system can be realized.

#### VII. B. Marine Environments

Another effect which will be necessary to study is the effect of marine environments on the complexation capability of HQS. HQS has been reported to be selective for transition metal ions over alkali and alkaline earth metal ions such as sodium and potassium which have high concentrations in ocean water. However, other factors such as ionic strength, turbidity, and pH within the waters may affect complexation rates. Therefore, studies need to be created and implemented which will evaluate the feasibility of this sensor material within marine environments.



### VII. C. Factors affecting leaching

Finally, since leaching from gel systems is a major problem with the present system, it will be important to study what factors affect leaching. Hydration sphere of the incoming metal ion has been hypothesized to be the major contributor for kinetics through the porous gel matrix. However, pores are substantially large enough that even hydrated zinc, cadmium, and mercury should readily complex at relatively fast rates. Other factors such as surface repulsion may be important in the leaching effects noted.

### VII. D. Reversibility

An important component of this project has been the necessity for reversibility of the sensor. One method which may be important to remove coordinated metal ions from the HQS probe molecules may be pH differences between the various complexed species (i.e. HQS complexed with zinc versus HQS complexed with cadmium, etc.). Work will be carried out first using pH gradients to removed complexed metal ion species from the probe molecule incorporated within the matrix. Another approach which may be considered if pH gradients are not successful is the utilization of photolysis which has been of some success in other, similar systems.

### VII. E. Time-resolved and Phase Resolved Radiative Decay Processes

Phase-resolved radiative decay processes may be utilized for the differentiation of metalorganic species of HQS with isoelectronic metal ions. Multi-component systems can be differentiated by differences in phase-shifting through the use of spectrofluorometric methods. Phase-resolved radiative-decay has several limitations for use in the present materials, however. First, the relative errors incurred with the

utilization of phase-resolved processes is relatively large in comparison to time-resolved data. Therefore, through the use of fast-pulse lasers, time-resolved radiative lifetimes of the HQS complexes will be determined and compared to phase-resolved data to verify the values obtained. Another limitation which may become important if other probe molecules are eventually utilized is the range of usefulness of phase-resolved spectroscopy (usually below 100psec). Time-resolved data can be obtained for ultrafast systems down to approximately 100 fsec through the use of a femtosecond laser. Through the utilization of both phase- and time-resolved spectroscopy, fluorescence lifetimes of metalorganic complexes of HQS will be determined and used to differentiate concentrations of isoelectronic metal ion species.

#### VII. F. Mixed-metal aqueous solutions

Unfortunately, in nature not everything is as neatly separated as it is in our lab. At present, we have only investigated zinc, cadmium, and mercury solutions separately from one another. Solutions involving more than one analyte species will need to be evaluated. Several spectroscopic methods may be utilized to determine which metal ions are present and in what quantity. First and second derivative synchronous fluorometry has been used by several groups to determine concentrations of more than one analyte species in HQS complexes. Also, phase-resolved radiative decay processes can be analyzed for multi-component systems. Assuming that the fluorescence spectra and the radiative lifetimes of the various complexes are substantially different from one another, quantitative determinations can be assigned.

## VII. G. DOR NMR

As described in Chapter 6, the exact nature of the HQS-DBATES adduct still needs to be determined. Infrared spectroscopy, solutions NMR, single pulse solid state NMR, and cross-polarized NMR have thus been inconclusive in determining the coordination and structure of the HQS within the aluminosilicate gels. DOR (double angle rotation) NMR may be useful, hopefully, in determining the complex structure. Efforts are also being taken to maximize the concentration of HQS within the gels.

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## APPENDIX A

### $^{29}\text{Si}$ NMR of HQS-Doped Silica Gels

Results of  $^{29}\text{Si}$  NMR on TEOS-derived gels used throughout the current work has been used to verify gel structure. Based on recent findings by another researcher within the investigative group, concerns were raised that the silica gels may not be fully condensed. Results of the cross-polarized  $^{29}\text{Si}$  NMR are shown below.

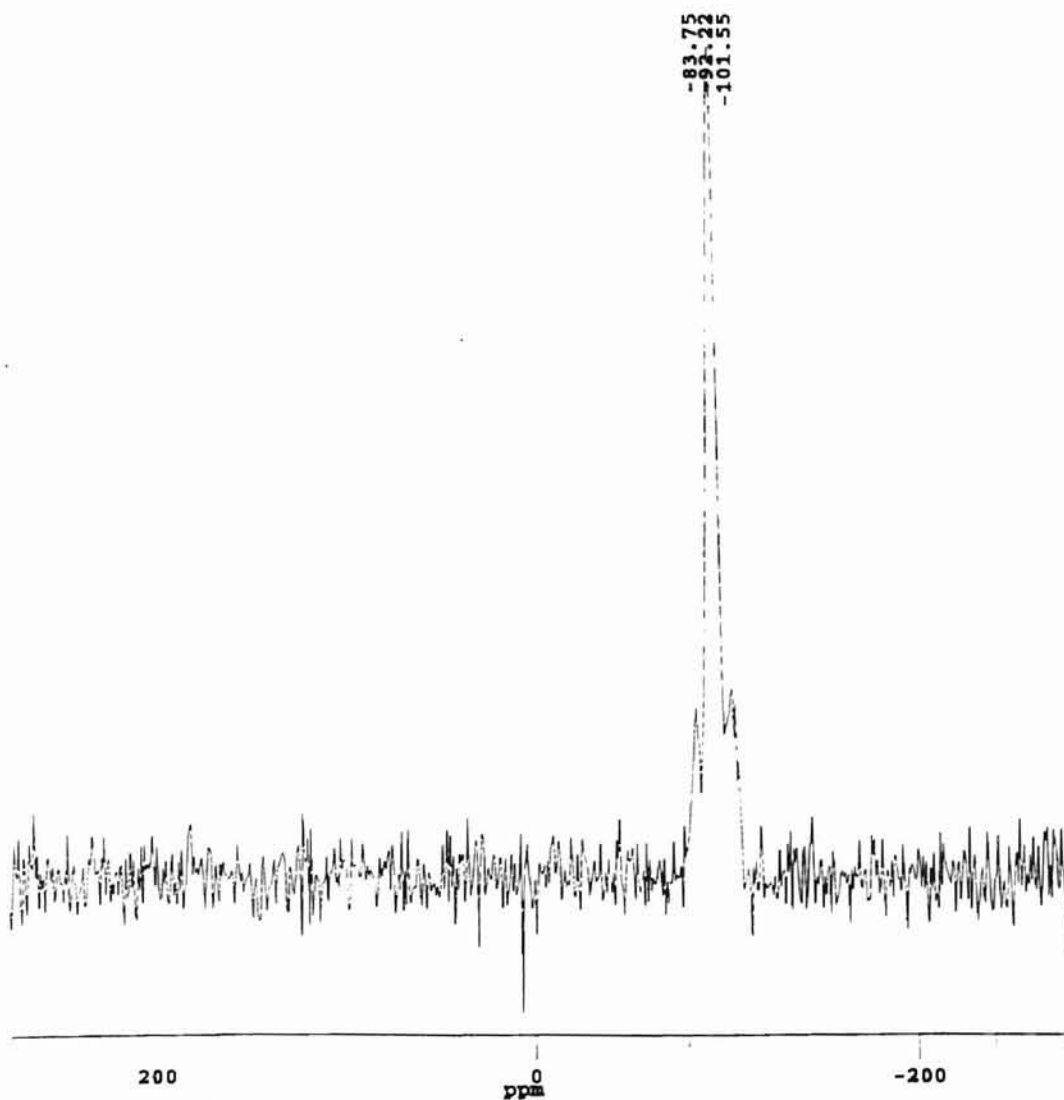


Figure A1: CP  $^{29}\text{Si}$  NMR of non-heat treated silica formed by the two step acid-base catalysis of TEOS

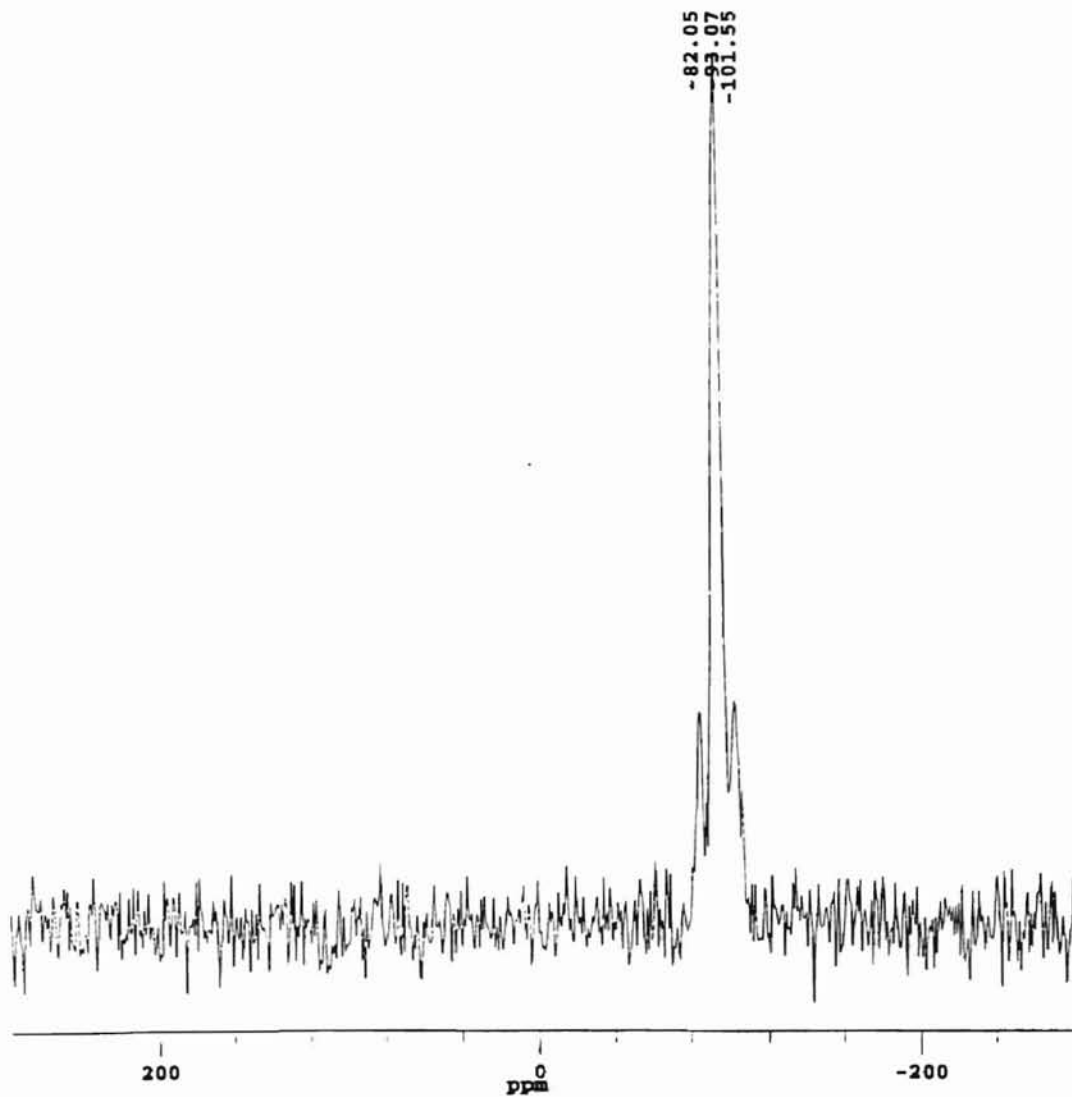


Figure A2: CP  $^{29}\text{Si}$  NMR of heat treated silica formed by the two step acid-base catalysis of TEOS

These results indicate that there are substantial amounts of Q3 and Q4 silica (along with some Q2 bands) within the xerogels used throughout the current research. These findings are important to the current project because they show that a porous network is being formed, and that HQS dopant molecules are not interacting to a substantial degree with the matrix.



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