

## **Synthesis of a Material with Properties Suited for Chemical Sensing**

### **Introduction:**

Materials chemistry is a field of high priority internationally, both in terms of fundamental and applied science. Research contributions to the advancement of this field come from a wide range of scientists who develop the synthetic processes, design the blends to produce the desired properties, perform the fundamental characterizations, and employ them in a wide range of applications. One of the synthetic processes of great interest at present is sol-gel chemistry. The sol-gel process, which was discovered over 150 years ago, was originally a method for the production of ceramic materials. However, it was not until the 1960's that sol-gel research emerged as a major field of study. The reason for the prolonged delay before the resurgence of sol-gel chemistry was because initially xerogel drying time was greater than one year. With modern procedures, xerogel drying time decreased from a period of greater than one year to a few days. The glass-like material that is produced is no longer important only to ceramic science but instead finds widespread application. As a result, sol-gel chemistry is the subject of research in several areas of chemistry.

Chemists are exploring means of synthesizing xerogels with tailored properties. Among the properties of interest is the internal pore structure, which can be controlled in a manner that traps macromolecules such as enzymes while allowing small molecules to move in and out of the structure. Outcomes of new synthetic methods are formulations that are ideal for applications as diverse as chemical sensors, optical lenses, and electrodes for batteries and fuel cells.

### **Background:**

#### ***Formation of Xerogels by a Sol-Gel Process:***

There are a variety of sol-gel processes. Perhaps, the most common uses hydrolysis of a metal alkoxide to make the solid. A typical procedure used to synthesize a silica xerogel employs the following reagents: a silica precursor, a mixture of water and methanol as solvents, an acid or base for catalysis of the reactions, and a surfactant to reduce fracturing and cracking. In this report, tetramethyl orthosilicate (TMOS) is the source of silica that forms the backbone of the xerogel. The TMOS is dissolved in a mixture of water and methanol. The water is necessary to hydrolyze the TMOS as illustrated in reaction 1.

Condensation and polycondensation reactions occur to form the Si-O-Si network. Reaction 2 illustrates a condensation reaction of hydrolyzed TMOS.

The hydrolysis and condensation reactions occur in localized regions to form colloidal particles. A suspension of liquid containing these particles is called a sol. Sol formation is expedited by acid or base catalysis. Upon formation of the sol, the liquid can be molded or cast into various shapes and sizes. Gelation occurs as the silica and oxygen atoms bind to form a three-dimensional network. The process begins spontaneously when the sol is exposed in a manner that allows loss of volatile reaction products (water and alcohol). These particles react to form an oxo-bridged SiO<sub>2</sub> network which causes the viscosity to increase. Gelation of the sol is the point at which the sol forms a globally connected solid matrix.

Aging and drying of the xerogel occur as water and alcohol evaporate from the internal cavities. The volume of the xerogel shrinks to approximately one-eighth of the original volume of the sol. Large pores empty while smaller pores remain wetted with solvent, causing an internal pressure gradient. This stress may cause cracking and fracturing of large monoliths if the drying is too fast. High temperature heating of a xerogel leads to densification or the elimination of various pores within the matrix. Drying the gel under ambient laboratory conditions leads to formation of a xerogel. It should be noted that xerogels can still contain pore water. In recognition of the possibility of incomplete solvent loss under given drying conditions the term dried gel often is used to describe the solids.

***Merits of Sol-Gel Chemistry:***

One merit of sol-gel chemistry is that it offers a convenient method to synthesize a material for hosting chemical reactions. Many different types of chemical species can be impregnated or “doped” within the pores of a xerogel by adding them to the sol. Organics (1,2), organometallics (3), proteins (4), and enzymes (5) are just a few of the compounds that have been encapsulated in silica. The xerogel can be molded or cast into a variety of shapes (e.g., thin films, fibers, or monoliths).

The nature of xerogel synthesis allows researchers to investigate and control the pore size and to study the influence of pore size on the properties of the products. Some of the experimental variables of interest are drying and aging conditions (especially temperature) and the nature of the catalyst. As the drying time of gels is increased, more liquid is displaced from the pores making the solid network become more dense. Increasing the temperature at which gels are aged is, of course, a more direct means of drying.

Acid or base catalysis increases the rate of hydrolysis and condensation reactions which, in turn, increases the rate of water expulsion.

***Applications of a Sol-Gel Process:***

As mentioned above, sol-gel research has emerged as a major field of study. Currently, sol-gel chemistry is being investigated in many branches of chemistry. This experiment was developed to investigate a few representative aspects of this field. One topic being investigated is the role of certain experimental parameters in xerogel synthesis. The sol-gel process allows researchers to optimize the preparation method for a given application. Of special importance are the conditions that determine the reaction and drying rates (pH, temperature, gelation conditions). These factors, which influence the pore size and other properties of the solid product (xerogel), will be the focus of the experiment described herein.

Also, this experiment will focus on the encapsulation of reagents for the development of chemical sensors. One model for a chemical sensor is an analyte (the targeted chemical species), **A**, that reacts with a reagent, **R**, to form a colored product, **P**.



Photometric compounds (color-producing reagents) can be doped within the silica matrix. Many different types of analytes have been studied by this process (2). Typical cations and anions that have been detected and quantified include Pb(II), Fe(III), Cu(II), hydronium ion (pH),  $\text{SO}_4^{2-}$ , and  $\text{NO}_2^-$ . The result is a color change that can be observed either visually or spectrophotometrically. The color change in the xerogel typically is a result of either a change in pH or the formation of a colored complex. An example of an application to analysis involves doping a xerogel with dimethylglyoxime. The development of a color permits qualitative identification and, the “intensity” of the color is related to the concentration of Ni(II). The intensity is usually measured with an instrument, but may be estimated visually.

In a xerogel-based sensor, **R** is encapsulated and ideally does not leach into the sample. **A** originates in the sample. The rate at which it enters the xerogel and the position of the equilibrium between the liquid and solid are important parameters. Ideally, the formation of **P** is in the solid, not the external liquid. This results in an efficient optical sensor when, as suggested above, the leaching of the encapsulated reagent is restricted while the entry of analytes in the porous solid occurs. In the present experiment this colorimetric sensor design will be tested in terms of detectability, reproducibility, reusability, and response time. The sensors are semi-quantitative in that the colors are estimated visually.

Xerogels have been synthesized for application as biosensors. Biomolecules are known to denature outside of limited ranges of pH. The sol-gel process provides intrinsic merits by allowing the xerogel matrix to form under conditions compatible with the biomolecules and, upon encapsulation, protect them from an otherwise-hostile environment. The biomolecule can thus retain its normal stability and reactivity. Examples in the literature include using xerogels doped with hemoglobin, myoglobin, and glucose oxidase for the detection of oxygen, carbon monoxide, and glucose, respectively (6). In this experiment, glucose oxidase will be entrapped in a xerogel for the detection of glucose. Glucose oxidase is much larger than glucose, so the former is trapped in the xerogel whereas the latter can enter it via the porous structure. The signal is produced by quantifying the reacting product. Hence, the enzyme-doped xerogel serves as a colorimetric sensor for glucose. It is important to note that a major purpose of this experiment is to use the information from the sensor performance to draw conclusions about the pore structure of the xerogel.

In addition to possible sensor development, parameters that affect xerogel porosity are evaluated by performing leaching experiments. Xerogels are doped with salts of colored cations (e.g., salts of Ni(II) and Co(II)). Upon gelation, the silica xerogel is optically transparent and takes on the color of the doped cation. Xerogels are soaked in an aqueous solution, and the amount of leached cation is determined quantitatively. Varying amounts of cation from the xerogel leach, depending on how it is prepared. The external solution (leachate) is analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The amount leached is interpreted in terms of pore diameter of the xerogel.

Thermogravimetry is another technique used to indirectly investigate xerogel structure. A thermogravimetric analyzer (TGA) is used to measure the amount of residual liquid (primarily water) present in the xerogel. In this case, the entrapped water is determined from the decrease in the mass of the xerogel at temperatures well-above 100 °C. The amount of residual water is interpreted in terms of the pore volume.

In summary, a series of experiments is developed to give each group the opportunity to collect both quantitative and qualitative data. Groups obtain qualitative data regarding porosity by testing xerogels as colorimetric sensors. Quantitative data related to the porous nature of xerogels is provided by TGA and ICP-AES.

**Purpose of Experiment:**

The following sol-gel experiment is to emulate a research project. This project involves the preparation and characterization of a glass-like solid. Experimental conditions (e.g., temperature and pH) are altered to yield xerogels of various sizes, porosity, and resistance to fracturing.

Your six-member research group at work has been given a new project, the development of a group of sensors. A supervisor believes that sol-gel chemistry is an approach well-suited to this project. Nobody in your team has any prior knowledge of sol-gel chemistry directly related to this new project. Your research team decides that the most efficient way to address this new project is to subdivide into pairs. Each pair of researchers will work on different methods of xerogel preparation (week 1 of project). While xerogel formation is occurring (over Thanksgiving vacation), your research group will meet to develop a protocol for evaluating the supervisor's idea (week 2 of project). Your group will need to make collective observations, collate data, and draw appropriate conclusions. The results that you obtain will be discussed with other members of your group. You will need to study and review reports in the scientific literature to interpret the observations of your team (see references). The reporting format will allow the influence of synthetic conditions to be surmised at the completion of the experiment and hypotheses for future testing to be made.

**Procedure:**

***Reagents Involved:***

Alkoxysilane: Tetramethyl orthosilicate (denoted as TMOS) is a low molecular weight alkoxysilane that serves as a precursor to the sol-gel process. It is the source of silica used to form the Si-O-Si network.

Solvent: A mixture of methanol and water is the solvent because alkoxysilanes are not miscible in water alone.

Surfactant: Hexadecyltrimethylammonium bromide (denoted as CTAB) is the surfactant and is used to reduce the surface tension in the monoliths. The surfactant mitigates the tendency of the xerogel to fracture as the xerogels dry and/or are rewetted.

pH: The pH affects the pore size and the rate of the formation. Addition of an acid catalyst increases the rate of hydrolysis while retarding the condensation reaction. Adding base produces a rapid condensation reaction, increasing the rate of solid formation.

***Collaborative Study Plan (Week 1):***

Each pair of students will follow an assigned collaborative study plan (CSP). Each pair of students will be responsible for the preparation of twelve xerogels (4 different preparation procedures, each made in triplicate). The reagents will be mixed according to the conditions that were presented on their CSP. Each pair of students will have to prepare a solution containing the assigned surfactant. In a 50 mL beaker prepare a sol that serves as the precursor to the “blank” xerogel by combining 0.9 g of CTAB (F.W. 364.46 g/mol) with 10 mL of methanol. Into separate 50 mL beaker, pipet 2.5 mL of H<sub>2</sub>O, 2.5 mL of methanol, 2.5 mL of TMOS, and 0.5 mL of the prepared CTAB solution.

To prepare sols used as precursors for the “doped” xerogels, use the above method, except replace the 2.5 mL of H<sub>2</sub>O with 2.5 mL of an aqueous solution of the dopant. Prepare a  $1 \times 10^{-3}$  M stock solution, of the assigned dopant (a salt of either Fe(III), Co(II), Cr(III), Pb(II), or Ni(II)). Similarly to the metal cations, complexing reagents, either dimethylglyoxime (DMG) or thiocyanate ion, are included in the sol production. The DMG solution may require heat and/or sonication to dissolve, and the Fe(III) may require a drop of diluted HNO<sub>3</sub> to suppress hydrolysis. Save your stock solution for use in week two.

Thoroughly mix the components in the beaker. Use an Oxford pipet to transfer the sols into the labeled methacrylate cuvetts provided. Record the exact amount of sol placed into each cuvet. The cuvetts should be covered with Parafilm<sup>®</sup> to allow the xerogel to form under ambient (room temperature) conditions. Also, small amounts of acid and base will be added to selected sols to help catalyze the xerogel formation. Pore size is dependent on how fast the xerogel is formed; the influence of rate of formation on pore size will be investigated by varying the quantity of acid or base added.

The effect of drying temperature on pore size will be investigated. Three conditions will be used, namely room temperature, 40 °C, and 110 °C. At the highest temperature, the methacrylate cuvet will be softened and change shape. In addition, each pair of students will prepare a xerogel doped with an enzyme, glucose oxidase. Details are provided in a later section.

***Procedure (Week 2):***

**Leaching Experiment:**

In this series of experiments, the metal-doped xerogels are placed in water, and the amount of metal leached from the solid is determined. Each team will need ten 50-mL beakers. Place a blank xerogel into one of them, and a doped xerogel into each of the others. Add 5.00 mL of water to each beaker (warning: the addition of water may cause the xerogel to fracture). Preferably, allow two days for the

leaching (note: depending on the laboratory schedule, this step may need to be performed by an instructor). Transfer the liquid (leachate) into a clean test tube. If necessary, centrifuge the mixture to remove particles of fractured material.

Prepare standard solutions ( $1 \times 10^{-5}$  and  $5 \times 10^{-6}$  M) of the assigned cation by serial dilution of the  $1 \times 10^{-3}$  M stock solution prepared during week one. Each of the three solutions and the liquid recovered from the soaked xerogels will be analyzed by the ICP-AES to quantify the leaching of the analyte. Prepare a calibration curve using a spreadsheet to quantify the data. The instructor will direct you to a computer with a program for this step.

#### **Visual Sensor Experiment:**

Xerogels that have complexing reagents or enzymes doped internally can serve as visual sensors. The level of response of the visual sensor will depend on the concentration of the complexing reagent and the concentration of the dopant in the contacting solution. Here, the concentration of the complexing reagent is varied from 0.1 to 0.001 M in the water portion of the sol. Also, each group will vary the concentration of the cation or glucose in the contacting solution.

#### **Thermogravimetric Analysis:**

Thermogravimetric analysis (TGA) also will be performed to determine the amount of solvent (mostly residual water) that is present in the xerogels. The amount of solvent present will depend on the procedure used to prepare the xerogel. Each group will test a single sample. The different groups must then collaborate to develop a hypothesis about the factor(s) that control residual water. Conclusions based on the entire set of TGA data are incorporated into each report.

#### **References:**

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4. Avnir, D.; Braun, S.; Lev, O.; Ottolenghi, M. *Chem. Mater.* **1994**, 6, 1605.
5. Braun, S.; Shtelzer, S.; Rappoport, S.; Avnir, D.; Ottolenghi, M. *J. Non-Cryst. Solids* **1992**, 147&148, 739.
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## Collaborative Study Plan For Blue Pair #1:

Names of Partners:

Blue #1:

Basic Components for this  
Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Blue #1: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 1-1, 1-2, and 1-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with 0.001 M Co(II) salt solution. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 1-4, 1-5, and 1-6.

#### *Variation 2:*

Dope one batch of sol with a 0.01 M dimethylglyoxime (DMG) solution. These three gels will be dried under ambient conditions. Label the cuvetts as 1-7, 1-8, and 1-9.

#### *Variation 3:*

Dope one batch of sol with a 0.01 M dimethylglyoxime solution, and add 4 drops of 0.1 M hydrochloric acid to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 1-10, 1-11, and 1-12.

## Collaborative Study Plan for Blue Pair #2:

Names of Partners:

Blue #2:

Basic Components for this  
Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Blue #2: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 2-1, 2-2, and 2-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Co(II) salt solution and add 4 drops of 0.1 M hydrochloric acid to the basic sol components. One of these three gels will be dried under ambient conditions; one in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 2-4, 2-5, and 2-6.

#### *Variation 2:*

Dope one batch of sol with a 0.001 M dimethylglyoxime (DMG) solution. These gels will be dried under ambient conditions. Label the cuvetts as 2-7, 2-8, and 2-9.

#### *Variation 3:*

Dope one batch of sol with a 0.001 M dimethylglyoxime solution, and add 4 drops of 0.1 M hydrochloric acid to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 2-10, 2-11, and 2-12.

### Collaborative Study Plan for Blue Pair #3:

Names of Partners:

Blue #3:

Basic Components for this  
Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

#### **Procedure for Blue #3: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 3-1, 3-2, and 3-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Co(II) salt solution and add 4 drops of 0.1 M hydrochloric acid to the basic sol components. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 3-4, 3-5, and 3-6.

#### *Variation 2:*

Dope one batch of sol with a 0.01 M dimethylglyoxime (DMG) solution. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 3-7, 3-8, and 3-9.

#### *Variation 3:*

Dope one batch of sol with a 0.01 M dimethylglyoxime solution, and add 4 drops of 0.1 M sodium hydroxide to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 3-10, 3-11, and 3-12.

## Collaborative Study Plan For Yellow Pair #1:

Names of Partners:

Yellow #1:

Basic Components for this  
Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Yellow #1: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 1-1, 1-2, and 1-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Ni(II) salt solution. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 1-4, 1-5, and 1-6.

#### *Variation 2:*

Dope one batch of sol with a 0.01 M dimethylglyoxime (DMG) solution. These three gels will be dried under ambient conditions. Label the cuvetts as 1-7, 1-8, and 1-9.

#### *Variation 3:*

Dope one batch of sol with 0.01 M dimethylglyoxime solution, and add 4 drops of 0.1 M hydrochloric acid to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 1-10, 1-11, and 1-12.

## Collaborative Study Plan For Yellow Pair #2:

Names of Partners:

Yellow #2:

Basic Components for this

Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Yellow #2: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 2-1, 2-2, and 2-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Ni(II) salt solution, and add 4 drops of 0.1 M hydrochloric acid to the basic sol components. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 2-4, 2-5, and 2-6.

#### *Variation 2:*

Dope one batch of sol with a 0.001 M dimethylglyoxime (DMG) solution. These three gels will be dried under ambient conditions. Label the cuvetts as 2-7, 2-8, and 2-9.

#### *Variation 3:*

Dope one batch of sol with a 0.001 M dimethylglyoxime solution, and add 4 drops of 0.1 M hydrochloric acid to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 2-10, 2-11, and 2-12.

### Collaborative Study Plan For Yellow Pair #3:

Names of Partners:

Yellow #3:

Basic Components for this

Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

#### **Procedure for Yellow #3: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 3-1, 3-2, and 3-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Ni(II) salt solution, and add 4 drops of 0.1 M sodium hydroxide to the basic sol components. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 3-4, 3-5, and 3-6.

#### *Variation 2:*

Dope one batch of sol with a 0.01 M dimethylglyoxime (DMG) solution. One of these gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 3-7, 3-8, and 3-9.

#### *Variation 3:*

Dope one batch of sol with 0.01 M dimethylglyoxime solution, and add 4 drops of 0.1 M sodium hydroxide to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 3-10, 3-11, and 3-12.

## Collaborative Study Plan For Green Pair #1:

Names of Partners:

Green #1:

Basic Components for this

Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Green #1: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 1-1, 1-2, and 1-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with 0.001 M Ni(II) salt solution. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 1-4, 1-5, and 1-6.

#### *Variation 2:*

Dope one batch of sol with a 0.01 M dimethylglyoxime (DMG) solution. These three gels will be dried under ambient conditions. Label the cuvetts as 1-7, 1-8, and 1-9.

#### *Variation 3:*

Dope one batch of sol with a 0.01 M dimethylglyoxime solution, and add 4 drops of 0.1 M hydrochloric acid to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 1-10, 1-11, and 1-12.

## Collaborative Study Plan For Green Pair #2:

Names of Partners:

Green #2:

Basic Components for this

Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Green #2: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 2-1, 2-2, and 2-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Ni(II) salt solution, and add 4 drops of 0.1 M hydrochloric acid to the basic sol components. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 2-4, 2-5, and 2-6.

#### *Variation 2:*

Dope one batch of sol with 0.001 M dimethylglyoxime (DMG). These three gels will be dried under ambient conditions. Label the cuvetts as 2-7, 2-8, and 2-9.

#### *Variation 3:*

Dope one batch of sol with a 0.001 M dimethylglyoxime solution, and add 4 drops of 0.1 M hydrochloric acid to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 2-10, 2-11, and 2-12.

## Collaborative Study Plan For Green Pair #3:

Names of Partners:

Green #3:

Basic Components for this

Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Green #3: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 3-1, 3-2, and 3-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Ni(II) salt solution, and add 4 drops of 0.1 M sodium hydroxide to the basic sol components. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 3-4, 3-5, and 3-6.

#### *Variation 2:*

Dope one batch of sol with a 0.01 M dimethylglyoxime (DMG) solution. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 3-7, 3-8, and 3-9.

#### *Variation 3:*

Dope one batch of sol with a 0.01 M dimethylglyoxime solution, and add 4 drops of 0.1 M sodium hydroxide to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 3-10, 3-11, and 3-12.

## Collaborative Study Plan For Purple Pair #1:

Names of Partners:

Purple #1:

Basic Components for this

Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Purple #1: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 1-1, 1-2, and 1-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Pb(II) salt solution. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 1-4, 1-5, and 1-6.

#### *Variation 2:*

Dope one batch of sol with a 0.1 M thiocyanate ion (SCN<sup>-</sup>) solution. These three gels will be dried under ambient conditions. Label the cuvetts as 1-7, 1-8, and 1-9.

#### *Variation 3:*

Dope one batch of sol with a 0.1 M thiocyanate ion solution, and add 4 drops of 0.1 M hydrochloric acid to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 1-10, 1-11, and 1-12.

## Collaborative Study Plan For Purple Pair #2:

Names of Partners:

Purple #2:

Basic Components for this

Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Purple #2: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 2-1, 2-2, and 2-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Pb(II) salt solution, and add 4 drops of 0.1 M hydrochloric acid to the basic sol components. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 2-4, 2-5, and 2-6.

#### *Variation 2:*

Dope one batch of sol with a 0.01 M thiocyanate ion (SCN<sup>-</sup>) solution. These three gels will be dried under ambient conditions. Label the cuvetts as 2-7, 2-8, and 2-9.

#### *Variation 3:*

Dope one batch of sol with a 0.01 M thiocyanate ion solution, and add 4 drops of 0.1 M hydrochloric acid to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 2-10, 2-11, and 2-12.

### Collaborative Study Plan For Purple Pair #3:

Names of Partners:

Purple #3:

Basic Components for this

Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

#### **Procedure for Purple #3: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 3-1, 3-2, and 3-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Pb(II) salt solution, and add 4 drops of 0.1 M sodium hydroxide to the basic sol components. One of these three gels will be dried under ambient conditions; one in an oven at 40 °C; and one at 110 °C. Label the cuvetts as 3-4, 3-5, and 3-6.

#### *Variation 2:*

Dope one batch of sol with a 0.1 M thiocyanate ion (SCN<sup>-</sup>) solution. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C, and one, in an oven at 110 °C. Label the cuvetts as 3-7, 3-8, and 3-9.

#### *Variation 3:*

Dope one batch of sol with a 0.1 M thiocyanate ion solution, and add 4 drops of 0.1 M sodium hydroxide to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 3-10, 3-11, and 3-12.

## Collaborative Study Plan For Red Pair #1:

Names of Partners:

Red #1:

Basic Components for this  
Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Red #1: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 1-1, 1-2, and 1-3.

When preparing doped gels (variations 1,2,and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Cr(III) salt solution. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 1-4, 1-5, and 1-6.

#### *Variation 2:*

Dope one batch of sol with a 0.01 M thiocyanate ion (SCN<sup>-</sup>) solution. These three gels will be dried under ambient conditions. Label the cuvetts as 1-7, 1-8, and 1-9.

#### *Variation 3:*

Dope one batch of sol with a 0.01 M thiocyanate ion solution, and add 4 drops of 0.1 M hydrochloric acid to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 1-10, 1-11, and 1-12.

## Collaborative Study Plan For Red Pair #2:

Names of Partners:

Red #2:

Basic Components for this

Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Red #2: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 2-1, 2-2, and 2-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Cr(III) salt solution, and add 4 drops of 0.1 M hydrochloric acid to the basic sol components. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 2-4, 2-5, and 2-6.

#### *Variation 2:*

Dope one batch of sol with a 0.001 M thiocyanate ion (SCN<sup>-</sup>) solution. These three gels will be dried under ambient conditions. Label the cuvetts as 2-7, 2-8, and 2-9.

#### *Variation 3:*

Dope one batch of sol with a 0.001 M thiocyanate ion solution, and add 4 drops of 0.1 M hydrochloric acid to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 2-10, 2-11, and 2-12.

### Collaborative Study Plan For Red Pair #3:

Names of Partners:

Red #3:

Basic Components for this

Sol-Gel Process:

- 1) 2.5 mL H<sub>2</sub>O
- 2) 2.5 mL TMOS
- 3) 2.5 mL methanol (CH<sub>3</sub>OH)
- 4) 0.5 mL CTAB (0.9 gm CTAB/  
10.0 mL CH<sub>3</sub>OH)

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood!

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

#### **Procedure for Red #3: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, magnetically stir the components for 10 minutes, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 3-1, 3-2, and 3-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Cr(III) salt solution, and add 4 drops of 0.1 M sodium hydroxide to the basic sol components. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C, and one, in an oven at 110 °C. Label the cuvetts as 3-4, 3-5, and 3-6.

#### *Variation 2:*

Dope one batch of sol with a 0.01 M thiocyanate ion (SCN<sup>-</sup>) solution. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 3-7, 3-8, and 3-9.

#### *Variation 3:*

Dope one batch of sol with a 0.01 M thiocyanate ion solution, and add 4 drops of 0.1 M sodium hydroxide to the mixture. These three gels will be dried under ambient conditions. Label the cuvetts as 3-10, 3-11, and 3-12.

## **Formal Laboratory Report for Sol-Gel Experiment**

Comprise the laboratory report of the following sections:

### **Introduction:**

The introduction will contain background information on this laboratory report. Background information will include material that is covered in the pre-laboratory lectures, material on reserve in the library, and results of your own library search. Emphasize sol-gel chemistry in this section. Factors discussed will include theory on pore size, temperature, and concentration of doped species in the xerogel. Do not discuss results you obtained in this section, only theory. The estimated length of the introduction is 1 page (single spaced).

### **Experimental:**

The experimental section will **briefly** outline the procedure that your group (team) followed. Focus on the preparation steps and what reagents your group used in the experiment. Do not be repetitive for similar experimental procedures. The estimated length of the experimental section is 1/2 page (single spaced).

### **Results and Discussion:**

This section is the most important part of the report. You will discuss the results of your entire 6-member research group. Visual sensing results will address intensity of observed color and the effect of concentrations of the doped species and the test solutions. The discussion will focus on the effect of experimental factors such as acid or base catalysis and drying procedures on xerogel synthesis. Results regarding the percentage leaching of cation from the xerogel matrix will be discussed here. Calibration curve(s) and tables must be included. The estimated length of this section is 1-1 1/2 pages of text in addition to the calibration curve and tables (single spaced).

### **Conclusions:**

The conclusion section will compare predictions that are based on theory and published studies to your experimental observations. Discuss anything you found interesting or contrary to predicted behavior. What specific trends did you notice in your data? The estimated length of the conclusion section is 1/2 page (single spaced). After stating your conclusions from the experiment, also comment on the following questions: Did you find the laboratory exercise interesting? Is it too hard or too easy? Do you feel this experiment would be worthwhile to incorporate into the laboratory curriculum as a permanent chemistry experiment? These questions are to be addressed on a separate sheet. It is not necessary to provide your name with these comments. Include these comments with the questionnaire.

### **Enzyme Analysis:**

A one page summary on enzyme analysis must be included. This one page report will have two major focuses. First, address the introductory and background information that was provided on enzyme activity in xerogels. Make sure you cite literature references. Second, summarize and discuss the results. Relate this discussion to the goals of the enzyme analysis (stated on handout). Include discussion regarding retention of enzyme activity and the response of xerogels containing glucose oxidase to glucose at various concentrations.

**Note: Laboratory report must be typed/printed. It cannot be longer than 5 pages of text. This includes the enzyme analysis but not your calibration curve or tables. The report and the questionnaire are due by 12 p.m. on the last day of lab.**

### Calculation of Percentage Leaching Information for Laboratory Final

$$\% \text{ Leaching} = (\text{moles leached out of xerogel} / \text{total moles in xerogel}) \times 100$$

#### moles in:

Must know the following information:

- \* Concentration of cation containing salt ---- 0.001 M (told to make 1 mM solution)
- \* Amount (volume) you took of that salt ---- 2.5 mL (amount you took to mix with other components to make sol)
- \* Total amount of sol---- 8 mL
- \* Amount (volume) you put in each cuvet-- 1.5-2 mL (volume you pipeted into each cuvet)

Example:  $0.001 \text{ M} \times 0.0025 \text{ L} = \# \text{ of mols in sol}$

$\# \text{ of mols in sol} / 0.008 \text{ L} = \text{concentration of sol (M)}$

$\text{Concentration of sol (M)} \times \text{amount (volume) placed in each cuvet} = \# \text{ of mols in xerogel}$

#### moles out:

- \* Find out the y-int (b value) and slope (m value) from the regression analysis.
- \* You know that  $y = mx + b$
- \* Knowing m and b from the regression data, insert the proper intensity values and solve for the concentration or x value.
- \* Multiply the concentration from the above step by 0.005 L to yield the moles leached out. (remember the gels were soaked in 5.00 mL of water)

## How to use Lotus 1-2-3 Release 5

The software is available in most computer labs on campus on the IBM computers. Microsoft Excel offers a very similar approach.

Open up program, Lotus 1-2-3 Release 5.  
It will look like an empty spreadsheet.

### Step 1:

- 1) Label column A with x variable (concentration).
- 2) Label column B with y variable (intensity).
- 3) Insert data collected under corresponding labeled cells.

### Step 2:

To graph data:

- 1) Highlight data to be graphed.
- 2) Click on "**Chart**" window. The arrow of the mouse will change into an icon of a bar graph. Click on empty space in spreadsheet and enlarge graph. The position of the graph may be altered by clicking on the graph and when the arrow is a hand icon, move the graph with the mouse.
- 3) Select "**Chart**", select "**Type**", select "**XY**". Use the default setting of the "**XY**" graph.
- 4) Label axes and title the graph by double clicking on words to be replaced. Insert a new name in Line 1.
- 5) Click on the plotted line in graph.
- 6) Select "**Style**", select "**Lines and Color**", click on "**Style**", scroll up and choose "**None**". Press return, only the points now appear, no line will be present .

### Step 3:

Regression analysis:

- 1) Click anywhere on spreadsheet, other than the graph.
- 2) Select window labeled "**Range**", select "**Analyze**", select "**Regression**".
- 3) For X-Range:  
Click on arrow at right, highlight x variables on spreadsheet.  
For Y-Range:  
Click on arrow at right, highlight y variables on spreadsheet.  
For Output range:  
Click on arrow at right, click on cell D1.  
Press "**OK**".
- 4) Calculate predicted y variables using equation  $y=mx + b$ . (Let Lotus do the math for you)

In the data created under the Regression analysis:

slope = m = "**x-coefficient**" in cell F8  
y intercept = b = "**constant**" in cell G2  
x = x variables = in column A

To calculate predicted y values using Lotus:

1. click on cell C1
2. Enter " $=($F$8*A1 + $G$2)$ ". Make sure the dollar signs are in the right position.

3. Under windows, click on **copy** icon.
4. Highlight the remainder of column C (where there exists corresponding values of x and y values in column A and B).
5. Under windows, click on **paste** icon.

Values will appear in column C:

To enter values from column C into graph, select "**Chart**", select "**Ranges**", in set labeled "**Empty**", highlight set, spreadsheet will appear, highlight column C values. Press "**OK**". New line should appear on graph. Click on line with mouse. Select "**Style**" window, select "**Lines and Color**", select "**Symbol**", scroll up to "**None**". Press "**OK**".

**Step 4:**

1) Save working copy and then print out a copy including the spreadsheet data and graph.

## Sol-Gel Experiment Evaluation

Please remember your answers on this evaluation will in no way influence your grade in this course. Thank you for taking the time to complete this form.

Please answer the questions below based on the following scale:

1= strongly disagree 2= disagree 3= neutral 4= agree 5= strongly agree

1. The sol-gel experiment helped me to better understand the concepts discussed in class on qualitative analysis. 1 2 3 4 5
2. This experiment was written at the appropriate level for first-year B.S. students. 1 2 3 4 5
3. I would recommend this experiment be incorporated into the first-year B.S. chemistry curriculum. 1 2 3 4 5
4. I liked working in a group setting. 1 2 3 4 5
5. I thought my individual grade was too dependent on other people. 1 2 3 4 5
6. I liked being introduced to experiments that would be performed again in higher level chemistry courses. 1 2 3 4 5
7. I thought that being introduced to spreadsheets and writing a formal report were appropriate for the scope of this class. 1 2 3 4 5
8. What did you particularly like about the sol-gel experiment?
9. What did you particularly dislike about the sol-gel experiment?
10. Please make any additional comments on the back of this page.

## Procedure Handout for Week 2:

### Group Project:

#### 1. Metal Cation Leaching:

##### A. Analysis using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

- 1) Run standard samples of 0.001 M (metal stock solution) and  $1 \times 10^{-5}$  M and  $5 \times 10^{-6}$  M made from dilution of the stock. ICP-AES is a trace level method, it may be necessary to further dilute these samples.
- 2) Each group will then have 9 samples in addition to the standards to analyze. All samples were prepared under different conditions. Again, it may be necessary to dilute samples to make them fit the calibration curve.

##### B. Calculation of Percent Leaching

- 1) You can calculate how many moles of metal cation were placed in each xerogel.
- 2) By knowing the concentration (from ICP data) of the 5.00 mL solution, you can calculate how many moles leached out.
- 3) Percent leaching = (moles leached out / total moles in each xerogel) x 100
- 4) Draw conclusions as to how temperature and catalysis affected the leaching from specific xerogels.

#### 2. Visual Sensors:

##### A. Xerogels doped with complexing reagents or enzymes.

##### B. Visual sensors have 4 basic functions:

1. Selectivity- complexing reagent defines
- \*\*\* 2. Detectability
- \*\*\* 3. Reproducibility
- \*\*\* 4. Reusability
- \*\*\* 5. Response time

##### C. Experimental Results

- 1) Detectability- metal ion or anion solutions ranging over various molarities should be prepared. (Hint: borrow cation solutions from other groups)
- 2) Notice response times for color changes to appear from complex formation in monoliths.
  - a. Visually estimate intensities of colors from the complex formations.
- 3) Can monoliths be reused for another analysis?
  - a. Design experiments to reverse the complex formation.
- 4) What effect does temperature and acid/base catalysis have on the visual sensors: response time, sensitivity, or reusability?

a. Develop and test a hypothesis.

**3. Thermogravimetric Analysis (TGA):**

A. Each group is assigned one xerogel to be analyzed by thermogravimetric analysis.

B. Thermogravimetric analysis is a technique employed to analyze the percentage of residual solvent in xerogels. In this experiment, water is the major component of the residual solvent.

1) Each xerogel is prepared differently.

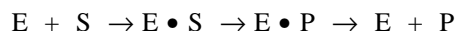
2) Notice that the percentage of residual solvent differs between groups.

a. What effect does the gel preparation procedure have on the remaining residual solvent?

## Enzymes

### Background:

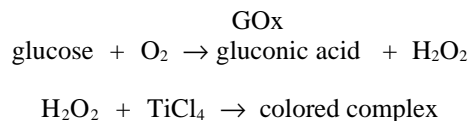
One of the major areas of interest in sol-gel research involves enzymes. Enzymes are biological catalysts that bind to a given substrate (reactant), perform a specific reaction, and then release the product (P). The enzyme (E) is then free to bind to another substrate (S) molecule.



Enzymes differ from most chemical catalysts in several ways. An enzyme catalyzed reaction has a rate that is  $10^6$  to  $10^{12}$  times greater than the corresponding uncatalyzed reaction. In chemical catalysis,  $10^3$  is a representative acceleration factor. Enzymes are active under a narrow range of experimental conditions; they can become irreversibly inactive due to changes in temperature or pH. Enzymes are known to have a much greater degree of specificity than typical chemical catalysts. This specificity will often greatly reduce or eliminate concern about possible interfering species. Because the specificity is so high for the binding, it is also rare to have undesired side products.

There are several reasons why the silica network obtained through sol-gel chemistry is an attractive host for enzymes. One is that silica xerogels physically protect hosted species from many components in the external environment. Through the addition of buffers or other chemical reagents to sols, internal parameters (such as pH) of the gels can be controlled that are important to the activity of the enzyme. Also, through controlling the porosity of the gel, the large enzyme can be blocked from leaching into the external solution. Because the substrate is generally much smaller than the enzyme, it can enter into the xerogel and react with the enzyme. The products, which are also small, can leach from the xerogel.

The goals of this experiment are to demonstrate the encapsulation of enzymes by sol-gel chemistry and to illustrate the role of pore size in an application. The experimental system is the encapsulation of glucose oxidase (GOx) in a silica xerogel. The role of the porosity is evaluated by the reaction between glucose and oxygen in the presence of glucose oxidase to form gluconic acid and hydrogen peroxide. The reaction is quantified by the formation of a colored complex between hydrogen peroxide and titanium(IV) chloride (as shown below).



The first part of the experiment is to verify that the immobilized enzyme is active and is accessible to the substrate present in the external liquid. A film of enzyme-loaded xerogel is formed on a glass slide. The slide is placed into a glucose solution. The molecular oxygen required for the reaction is present in the solution and replenished from the atmosphere. A second aspect of the experiment is to determine the reusability of an enzyme-loaded xerogel. Here, the enzyme is encapsulated in a larger piece of xerogel (a monolith). A given monolith is used in tests on a series of glucose solutions. The data obtained in these two steps can be interpreted using information gained in experiments on xerogel properties. Hypotheses can be made about how variation of the procedures for preparing the xerogel will influence the results of this means of determining glucose. Approaches to optimizing a xerogel-based sensor for glucose can be projected.

### **Determination of Enzyme Activity in a Xerogel**

#### **Week One, Enzyme Encapsulation:**

##### Preparation of the xerogel

1) In a 50 mL beaker containing a stir bar, combine the following reagents:

- 1) 4 mL TMOS (tetramethyl orthosilicate)
- 2) 4 mL deionized water
- 3) 4 mL methanol
- 4) 1 mL glucose oxidase enzyme solution (180 units)
- 5) 4 drops of Triton X-114

2) Mix for 15 minutes using a magnetic stirrer.

3) Apply 100  $\mu$ L of the resulting sol onto each of three glass microscope slides and place them into plastic petri dishes to dry.

4) Fill two methacrylate cuvetts with the resulting sol and allow two weeks at ambient conditions for drying (see earlier section for the exact drying procedure). Label the cuvetts as 13 and 14.

## **Week Two, Applications of the Enzyme-Loaded Xerogels:**

### Refresher

Each group coated slides with 100  $\mu\text{L}$  of sol and prepared monoliths in cuvetts.

The resulting silica xerogel contains the glucose oxidase enzyme.

The glucose will be added by the experimenter and the oxygen will be replenished in the solution from the atmosphere. (Hint: Do not cover your reaction vessel!)

### Goals

Address the following points:

- 1) Determine if the enzyme retained activity. Is there a reaction?
- 2) Was enzyme activity lost during the two-week period?
- 3) Over what concentration range does a color change occur?
- 4) How do the thin films compare to monoliths in terms of hydrogen peroxide yielded (e.g., color products)?

### How will we accomplish these goals?

- 1) Solutions of varying concentration of glucose will be contacted to the loaded xerogels.
- 2) For the thin films (on glass slides), place 7 mL of glucose solution directly into the petri dishes.
- 3) Use freshly prepared xerogels doped with enzyme (dried and aged for one day) on glass slides to investigate whether enzyme activity was lost during the two-week period. These slides may be prepared by the instructor. These xerogels are to be employed as described in Point 2 above.
- 4) For the monoliths, place the monolith into a beaker and add enough glucose solution to barely cover the xerogel.
  - A.) Allow one hour for the reaction between the glucose, oxygen, and the enzyme-loaded xerogel.
  - B.) Add 3 mL of previously prepared  $\text{TiCl}_4$  solution to the resulting solution. (Caution: the  $\text{TiCl}_4$  solution is in 6 M HCl! Perform this in the hood and wear safety goggles.) After 15 minutes, record your observations.
  - C.) Test these xerogels in a manner analogous to tests on xerogels doped with complexing reagents. Investigate sensitivity, reusability, reproducibility, and response time.

## Instructor's Notes

### Background Information:

The sol-gel process, which was discovered over 150 years ago, was originally a method for the production of ceramic materials. However, in the 1960's sol-gel research emerged as a major field of study. The renewed interest resulted from advances in synthetic procedures which decreased drying times from several months to a few weeks or days, depending upon the xerogel size and the specific preparation conditions.

There are a variety of sol-gel processes. Perhaps, the most common uses hydrolysis of a metal alkoxide to make the solid. For example, a typical procedure used to synthesize a silica xerogel includes the following: a silica precursor, a mixture of water and methanol as solvents, an acid or base for catalysis of the reactions, and a surfactant to reduce fracturing and cracking. In this experiment, tetramethyl orthosilicate (TMOS) is the source of silica which forms the backbone of the gel. The TMOS is dissolved in a mixture of water and methanol. The water is necessary to hydrolyze the TMOS as illustrated in reaction 1.

Condensation and polycondensation reactions occur to form the Si-O-Si network. Reaction 2 illustrates a condensation reaction of hydrolyzed TMOS.

Small colloidal particles, which comprise the sol, form as the Si-O-Si network expands. Sol formation is promoted by acid or base catalysis. Subsequently, the colloidal particles react to form an oxo-bridged SiO<sub>2</sub> network, which increases the viscosity. The resulting gel is then aged and dried to complete formation of the xerogel. Drying of gels can be done by a variety of methods, ranging from ambient conditions to high temperature. Because forming the xerogel at high temperatures eliminates pores and causes densification, the procedures used in the experiments described herein employ temperatures no greater than 110 °C. It should be noted that the term "xerogel" implies a dry material. While this describes the solid backbone material, pore water (including water sorbed on the surface) is still present.

Xerogels have been synthesized for application as biosensors. Biomolecules are known to denature outside of limited ranges of pH. The sol-gel process offers intrinsic merits of allowing the xerogel matrix to form under conditions compatible with the biomolecules and, upon encapsulation, of protecting them from an otherwise-hostile environment. The biomolecule can thus retain its normal stability and reactivity. In

this experiment, glucose oxidase will be entrapped in a xerogel for the detection of glucose. Glucose oxidase is much larger than glucose, so the former is trapped in the xerogel whereas the latter can enter it via the porous structure. Hence, the enzyme-doped xerogel serves as a colorimetric sensor for glucose. It is important to note that a major purpose of this experiment is to use the information from the sensor performance to draw conclusions about the pore structure of the xerogel.

In addition to possible sensor development, students examined parameters that affect xerogel porosity by performing leaching experiments. Students were required to determine the amount of metal cation that leached from a doped xerogel. Students doped xerogels with salts of colored cations (e.g., Ni(II) and Co(II)). Upon gelation, the silica xerogel was optically transparent but took on the color of the doped cation. Xerogels were soaked in an aqueous solution, and the amount of leached cation was determined quantitatively. Varying amounts of cation were leached from xerogels depending upon its preparation. The external solution (leachate) was analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The amount leached was interpreted in terms of pore diameter of the xerogel.

Thermogravimetric analysis was another technique used to indirectly investigate xerogel structure. A thermogravimetric analyzer (TGA) was used to measure the amount of residual liquid (primarily water) present in the xerogel. In this case, the entrapped water was determined from the decrease in the mass of the xerogel at temperatures well-above 100 °C. The amount of residual water was interpreted in terms of the pore volume.

In summary, a series of experiments was developed to give each group the opportunity to collect both quantitative and qualitative data. Groups obtained qualitative data regarding porosity by testing xerogels as colorimetric sensors. Quantitative data related to the porous nature of xerogels was provided by TGA and ICP-AES. The above mentioned were just a few of the applications of sol-gel research.

### **Lab Preparation and Equipment Needs:**

#### **First Week of Experiment: *Xerogel Preparation***

**Caution: All operations using TMOS must be performed in a fume hood. Protective eyewear must be worn at all times. Vapors of TMOS are an eye hazard.**

Each group of students was given a collaborative study plan (CSP) that outlined the experimental procedure for the first week. Typical group size was two students. A typical collaborative study plan was:

Collaborative Study Plan for Color (Green) Pair #1:

Names of Partners: (assigned by instructor)

Group Designation: Color (Green) #1

|  |   |
|--|---|
| Basic Components for this Sol-Gel Process: | 1) 2.5 mL H <sub>2</sub> O                                  |
|  | 2) 2.5 mL TMOS  |
|  | 3) 2.5 mL methanol  |
|  | 4) 0.5 mL CTAB (0.9 gm CTAB/<br>10.0 mL CH <sub>3</sub> OH) |

Proper eyewear is mandatory at all times! Gel preparation and all operations using TMOS must be done in a fume hood.

Make sure you properly label each cuvet using a waterproof marker that matches your group's designation. Make sure your glassware is properly cleaned before preparation of the sol.

### **Procedure for Green 1: (Make triplicates of each sample)**

In the basic procedure, mix the 4 components in a 50 mL beaker, and transfer 1.5 mL of the solution into each of 3 separate plastic cuvetts. Label the cuvetts as 1-1, 1-2, and 1-3.

When preparing doped gels (variations 1,2, and 3), substitute 2.5 mL of a solution of the dopant for the 2.5 mL of H<sub>2</sub>O.

#### *Variation 1:*

Dope one batch of sol with a 0.001 M Ni(II) salt solution. One of these three gels will be dried under ambient conditions; one, in an oven at 40 °C; and one, in an oven at 110 °C. Label the cuvetts as 1-4, 1-5, and 1-6.

#### *Variation 2:*

Dope one batch of sol with a 0.01 M dimethylglyoxime (DMG) solution. These three gels will be dried under ambient conditions. Label the cuvetts as 1-7, 1-8, and 1-9.

#### *Variation 3:*

Dope one batch of sol with a 0.01 M dimethylglyoxime solution, and add 4 drops of 0.1 M hydrochloric acid to the basic sol components. These three gels will be dried under ambient conditions. Label the cuvetts as 1-10, 1-11, and 1-12.

The CSP listed the reagents necessary for this experiment, namely tetramethyl orthosilicate (Aldrich); reagent grade methanol (Fisher Scientific); cetyltrimethylammonium bromide, CTAB, (Aldrich); and distilled/deionized water. The solution of CTAB was prepared by dissolving 0.9 grams in 10.0 mL of methanol. The four components (TMOS:H<sub>2</sub>O:CH<sub>3</sub>OH:CTAB) were combined in volume ratios (mL) of 2.5:2.5:2.5:0.5 in a 50 mL beaker. The mixture of components was magnetically stirred for 10 minutes and then transferred (1.5 mL) to three semimicro methacrylate cuvetts (Fisher Scientific). The cuvetts were covered with aluminum foil after addition of the sol. Methacrylate cuvetts were used as molds to allow the students to observe the xerogel at various stages of drying. As the monolith forms, it shrinks and pulls away from the side of the cuvet.

### ***Doping the Sol***

Preparing an impregnated or “doped” xerogel involved the addition of the dopant to the sol. Colored metal salts were selected so students could visually evaluate the homogeneity of the doped xerogel. Metal salts (Fisher Scientific) doped in xerogels included: iron(III) nitrate, chromium(III) nitrate, lead(II) nitrate, cobalt(II) nitrate, and nickel(II) nitrate. The concentration of the metal salt was 1.0 mM in the 2.5 mL aliquot of sol. Complexing reagents used as dopants were dimethylglyoxime (Acros) and sodium thiocyanate (Aldrich). The concentration of the complexing reagent in the sol was varied depending on the group’s CSP.

Students also prepared xerogels with glucose oxidase (Sigma) as a dopant. The sol, which was the same for all groups, comprised a mixture of 4 mL TMOS, 4 mL methanol, 4 mL distilled/deionized water, 1 mL of glucose oxidase enzyme solution (0.3 g/10 mL H<sub>2</sub>O) and 4 drops of Triton X-114 (Sigma). The components were stirred magnetically for 10 minutes in a 50 mL beaker. Cuvets were filled with the resulting sol and allowed to dry as described above. In addition, students spotted glass microscope slides (Fisher Scientific) with 100  $\mu$ L of the sol and allowed them to dry in plastic petri dishes (Fisher Scientific). Please note the earlier instructions regarding the safe handling of TMOS-containing solutions.

### ***Experimental Variables***

Experimental parameters (e.g., acid/base catalysis, drying temperature, choice of surfactant) were varied by group during preparation of the sol. Catalysis was achieved by the addition of either 4 drops of 0.1 M hydrochloric acid (Fisher Scientific) or 0.1 M sodium hydroxide (Fisher Scientific) to the sol. The drying temperature of the xerogels was room temperature, 40 °C, or 110 °C. Two drying ovens (Fisher Scientific) were preset to dry gels at elevated temperatures. Drying temperatures in excess of 110 °C resulted in severe damage to the methacrylate cuvet (even at 110 °C, some distortion of the cuvet occurs). Some xerogels were prepared with Triton X-114 (5 drops) in place of CTAB. Triton X-114 was used where there was concern about bromide ion from the CTAB as an interferent.

### ***Intersession: Cuvet Storage***

All cuvetts were labeled appropriately with permanent marker and were covered with aluminum foil. After two days, two pinholes were poked in the aluminum foil cover of each cuvet to facilitate drying. Xerogels were dried at the assigned temperature. Two days prior to the second laboratory period, the xerogels doped with metal salts were placed in a 50 mL beaker containing 5.00 mL (Oxford pipet) of distilled/deionized H<sub>2</sub>O and covered with Parafilm<sup>®</sup>. Because of the laboratory schedule, this was done by the instructor.

## **Second Week of Experiment: *Xerogel Interrogation***

The second week of the experiment focused on the investigation of the newly synthesized material. A thermogravimetric analyzer (Perkin-Elmer TGA 7) was used by each group to determine the amount of residual solvent (mostly water) that is present in the xerogels. Each of the samples examined by TGA was prepared differently (e.g., acid or base catalyzed, dried and aged at different temperatures, or use of a different surfactant). Each team placed a small fragment (milligram sample) of the designated xerogel on the platinum TGA pan. The temperature program for the TGA was as follows: begin at 25 °C and increase to 150 °C at 30 °C/minute. Finally, the temperature was held at 150 °C for 10 minutes. The temperature program allowed sufficient time for pore water to evaporate. Some of the weight loss was from evaporation of residual methanol, but independent experiments in our laboratory have shown this component to be negligible in these xerogels. If a TGA is not available, this experiment can be performed by drying xerogels in an oven, cooling in a dessicator, and weighing on an analytical balance.

The leaching of metal salts from the xerogel was used as a means of estimating the relative porosities of xerogels formed at different temperatures. Each group prepared a 1 mM stock solution of an assigned metal salt. Standard solutions over the range of  $1 \times 10^{-5}$  M and  $5 \times 10^{-6}$  M were prepared by serial dilution. These solutions were used to prepare a calibration curve. Subsequently, the quantity of metal ion leached into 5.00 mL of water from the nine doped xerogels (three from each of the three pairs of students in the group) was determined by fitting the signals obtained to the calibration curve. The metal concentrations were determined using a Varian Liberty 150 ICP Emission Spectrometer.

Because the samples are single metals rather than mixtures, ICP-AES was used over such alternatives as atomic absorption spectrophotometry, flame emission spectroscopy, or UV-VIS spectrophotometry as a matter of convenience. If facilities are available, the use of emission spectroscopy is recommended in curricula where this method logically can be presented as an extension of flame tests for qualitative analysis. Moreover, all cations other than those used in the preparation of the silica are candidates as dopants.

The student groups investigated xerogels as possible colorimetric sensors. This section of the experiment was somewhat discovery-based in that a detailed procedure was not given to the students. Xerogels containing DMG and thiocyanate ion were placed in solutions containing nickel(II) or iron(III). Here, the concentration of the complexing reagent is varied from 0.1 M to 0.001 M in the water component of the sol. The color intensity of the xerogel was estimated visually and used to determine the sensitivity of

these doped xerogels as optical sensors. The instructors guided the students to identify and evaluate properties other than sensitivity that are important in optical sensing. Examples are reusability, reproducibility, and response/recovery time. Hypotheses were developed by the students pertaining to the influence of pore size. They were guided to a literature file to see if their views were consistent with published information.

Xerogels containing glucose oxidase were tested similarly. They were immersed for one hour in 5-10 mL solutions (0.1 M to 1 mM) containing glucose (Sigma). After the enzymatic reaction, the released hydrogen peroxide was determined by adding 3 mL of a titanium(IV) chloride (Aldrich) solution to form a colored product with the hydrogen peroxide that is produced by the enzyme-catalyzed oxidation of glucose by dissolved oxygen. The solution of titanium(IV) chloride was prepared by the instructor. The titanium(IV) chloride (10 mL) was diluted to 1 L using a chilled mixture of 1:1 HCl. In addition to monoliths, thin films of xerogels doped with glucose oxidase were formed on glass microscope slides and used as “test strips” for glucose. Test strips were made by pipetting 100  $\mu$ L of sol onto glass microscope slides. In addition to student-prepared slides, the instructor also prepared films one day prior to the experiment, thereby permitting the students to compare the activities of glucose oxidase in gels dried for 1 and 14 days.

**Below is a condensed list of chemicals and equipment to complete this experiment:**

#### Equipment for Sol-Gel Experiment

| Equipment                         | Chemicals                 | CAS RN#      |
|-----------------------------------|---------------------------|--------------|
| polymethacrylate cuvetts (Fisher) | tetramethyl orthosilicate | [681-84-5]   |
| 50 or 100 mL beakers              | methanol                  | [67-56-1]    |
| 100 and 200 mL vol. flasks        | distilled water           |              |
| 1 mL pipets                       | CTAB                      | [57-09-0]    |
| small stir bars                   | Triton X-114              | [9036-19-5]  |
| permanent markers                 | sodium hydroxide          | [1310-73-2]  |
| stir plates                       | hydrochloric acid         | [7647-01-0]  |
| Oxford pipets                     | Fe(III) nitrate           | [7782-61-8]  |
| plastic petri dishes (Fisher)     | Co(II) nitrate            | [10026-22-9] |
| glass microscope slides           | Cr(III) nitrate           | [7789-02-8]  |
|                                   | Pb(II) nitrate            | [10099-74-8] |
|                                   | Ni(II) nitrate            | [13478-00-7] |
|                                   | sodium thiocyanate        | [540-72-7]   |
|                                   | dimethylglyoxime          | [95-45-4]    |
|                                   | glucose oxidase           | [9001-37-0]  |
|                                   | titanium(IV) chloride     | [7550-45-0]  |
|                                   | glucose                   | [50-99-7]    |

**Instrumentation Used:**

**Results and Discussion:**

Xerogel porosity was the key variable that students were investigating. Data collected to investigate porosity were both quantitative and qualitative. Students obtained quantitative data from ICP and TGA studies. Investigation of xerogels as optical (visual) sensors provided qualitative data related to sensor response time, reusability, reproducibility, and sensitivity. These results were correlated to the controlled variations in the sol-gel synthetic procedure.

**ICP results**

Students generated a calibration curve and obtained linear regression parameters for their assigned metal ion by running standard solutions. The ICP data were collected on the leachates from the nine samples of xerogels doped with a metal salt. Students calculated the concentration of the metal ion in the leachates from the linear regression data. From the concentration, students calculated the number of moles that leached out and converted this result to a leaching percentage. Students related the trends of results to the conditions, thereby illustrating that drying xerogels at higher temperatures or performing gelation in the presence of an acid catalyst decreased leaching. The decrease in leaching percentage suggested that the pore diameters were decreased by these conditions. Students constructed a table to interpret the data. Table I depicts actual data obtained by one student group. The calculated

Table I: Example of Student Reported ICP Data

| Cuvet | Preparation Conditions                        | Leaching Percentage |
|-------|---|---------------------|
| 1-4   | Fe <sup>3+</sup> and Room Temp. Drying        | 31.2 %              |
| 1-5   | Fe <sup>3+</sup> and 40 °C Drying             | 5.88 %              |
| 1-6   | Fe <sup>3+</sup> and 110 °C Drying            | 1.03 %              |
| 2-4   | Fe <sup>3+</sup> , HCl and Room Temp. Drying  | 17.2 %              |
| 2-5   | Fe <sup>3+</sup> , HCl and 40 °C Drying       | 1.44 %              |
| 2-6   | Fe <sup>3+</sup> , HCl and 110 °C Drying      | 0.20 %              |
| 3-4   | Fe <sup>3+</sup> , NaOH and Room Temp. Drying | 70.1 %              |
| 3-5   | Fe <sup>3+</sup> , NaOH and 40 °C drying      | 3.55 %              |
| 3-6   | Fe <sup>3+</sup> , NaOH and 110 °C drying     | 0.27 %              |

percentage of leached metal cation gave students a numerical value on which to base a discussion of the porous nature of the silica xerogel. Although reported percentages varied among groups, specific trends in the data were consistent. Acid/base catalysis of gelation and xerogel drying temperature had a significant

impact on pore size. A large decrease in leaching percentage was reported for xerogels dried above ambient temperature or prepared in the presence of an acid.

### ***Thermogravimetric Data***

Thermogravimetric analysis was not a new concept to the students. Previously, they used a TGA to determine the water of hydration of barium chloride. Each group ran one sample on the TGA, but the synthesis conditions varied among groups. Each group calculated the weight percent loss of water. The groups needed to compare results in order to interpret their data. Typical results reported by students are illustrated in Table II. Xerogels dried in ovens were re-equilibrated with the ambient atmosphere prior to

Table II: Student Collected TGA Data:

| Group  | Experimental Conditions | Drying Temperature | Initial wt. (mg) | Final wt. (mg) | % lost |
|--------|-------------------------|--------------------|------------------|----------------|--------|
| Purple | HCl Catalyst            | Room Temp.         | 1.03             | 0.77           | 25.2 % |
| Yellow | CTAB                    | Room Temp.         | 1.79             | 1.43           | 20.1 % |
| Blue   | NaOH Catalyst           | Room Temp.         | 2.14             | 1.57           | 26.6 % |
| Black  | Triton X-114            | Room Temp.         | 1.17             | 0.87           | 25.6 % |
| Red    | None                    | 110 °C             | 1.07             | 0.97           | 9.3 %  |
| Green  | None                    | 40 °C              | 0.97             | 0.82           | 15.5 % |

TGA analysis. These xerogels contained substantially less water than xerogels dried under ambient conditions. Students reported that drying temperature had a profound effect on water content, as expected. The water content was not a very useful parameter, suggesting that it is not related solely to pore volume.

Perhaps the most useful aspect of this experiment was the evaluation of xerogels as optical sensors. The xerogels for this portion of the laboratory were doped with a chromophoric complexing reagent or an enzyme. Students were instructed to test the doped xerogels for the following: response time, sensitivity, reusability, and reproducibility, but they were not given a detailed procedure to follow. Students tabulated results similar to those displayed in Table III. Students made numerous interpretations

Table III: Example of Student Reported Optical Sensor Data

| Sample | Variable                      | Drying Temp. | Iron Fe <sup>3+</sup> (M) | Results                  | Reusable? (Y/N) |
|--------|-------------------------------|--------------|---------------------------|--------------------------|-----------------|
| 1-7    | 0.1 M SCN <sup>-</sup>        | Room Temp.   | 0.1                       | Instant red color        | N               |
| 1-8    | 0.1 M SCN <sup>-</sup>        | Room Temp.   | 0.01                      | Slow color change to red | N               |
| 1-9    | 0.1 M SCN <sup>-</sup>        | Room Temp.   | 0.001                     | No response              | ~               |
| 2-10   | 0.01 M SCN <sup>-</sup> , HCl | Room Temp.   | 0.1                       | Slow color change to red | Y               |
| 2-11   | 0.01 M SCN <sup>-</sup> ,     | Room         | 0.01                      | Same, less intense       | Y               |

|      |                                  |               |       |                           |   |
|------|----------------------------------|---------------|-------|---------------------------|---|
|      | HCl                              | Temp.         |       |                           |   |
| 2-12 | 0.01 M SCN <sup>-</sup> ,<br>HCl | Room<br>Temp. | 0.001 | Very slow response        | ~ |
| 3-7  | 0.1 M SCN <sup>-</sup>           | Room<br>Temp. | 0.1   | Immediate blood red color | N |
| 3-8  | 0.1 M SCN <sup>-</sup>           | 40 °C         | 0.01  | Immediate blood red color | N |
| 3-9  | 0.1 M SCN <sup>-</sup>           | 110 °C        | 0.001 | Slow color change to red  | N |
| 3-10 | 0.1 M SCN <sup>-</sup> ,<br>NaOH | Room<br>Temp. | 0.1   | Instant red color         | N |
| 3-11 | 0.1 M SCN <sup>-</sup> ,<br>NaOH | 40 °C         | 0.01  | Slow change to red        | N |
| 3-12 | 0.1 M SCN <sup>-</sup> ,<br>NaOH | 110 °C        | 0.001 | No response               | ~ |

of the Table III results. They noted that xerogels dried at higher temperatures and prepared in the presence of acid tended to fracture when placed in solutions. Students attributed this to an increase in internal pressure when the water diffused into the smaller pores. The reaction between the complexing reagent and metal ion was affected by the preparation procedure because of the role of diffusion in the pores. Response times for acid-catalyzed gels were very slow (1-2 minutes). For the same reason, drying temperature and base catalysis were noted to have an effect on sensor response. Both an increase in drying temperature and the addition of base to the sol to catalyze gelation slowed the formation of the colored complex.

The enzymatic sensor for glucose was evaluated in an analogous manner. Students were surprised that the encapsulated enzyme maintained some activity after a two-week storage at room temperature; however, freshly prepared xerogels yielded a greater response to glucose. The optical (visual) detection limit reported by students was 1 mM glucose.

The students correlated their observations from the sensor portion of the experiment to those obtained from TGA and ICP-AES studies. Conclusions regarding the porosity of xerogels were drawn from the collected data and either supported or refuted from selected literature references.

## **Evaluation of Laboratory Experiment**

### ***Report and Grading Summation***

Students were required to write individual laboratory reports. The report included four sections: introduction, experimental, results and discussion, and conclusions. Each section was given a suggested length with a five-page maximum for the report. In addition to the text, data tables, spreadsheets, and calibration curves were included in the report. Students were given one week to interpret the data and write the report. The key element repeatedly stressed to students was to look for specific trends in their data (i.e. effects of synthesis, aging and drying conditions on the observations) and relate them to xerogel porosity.

The students used selected literature on reserve in the library to support or refute their interpretations. The quality of their analysis was the major component in the grading of the individual reports.

### ***Student Assessment***

Students were asked to assess the lab experiment by completing an evaluation form. Some questions asked in Fall 1997 were the following:

Please answer the questions below based on the following scale:

1 = strongly disagree, 2 = disagree, 3 = neutral, 4 = agree, and 5 = strongly agree

| Posed question:  | Avg. Student Response (33 students): |
|--|--------------------------------------|
| I would recommend this experiment be incorporated into the first-year B.S. chemistry curriculum.   | 3.8                                  |
| I liked working in a group setting.  | 3.8                                  |
| I thought my individual grade was too dependent on other people.                                   | 3.4                                  |
| I liked being introduced to experiments that would be performed in higher level chemistry courses. | 4.3                                  |

Students were also asked to comment on their “likes” and “dislikes” regarding the sol-gel experiment. Typical favorable comments on the experiment were the following:

“This experiment introduced us to more sophisticated equipment (i.e. ICP, TGA).”

“I liked that it was a real research project and how it was something that was more related to what some of us could be doing someday.”

“Learning to work in groups was a valuable experience.”

“Experiment imitated an actual research setting.”

“The idea that the experiment has practical uses in the real world.”

A few students mentioned this particular experiment helped them decide to stay in the B.S. chemistry program. The experiment was not “cookbook” in nature but more of a guided inquiry exercise. Students especially liked the opportunity to design some of the experimental procedures used for testing the xerogels on their own. Students felt they were introduced to the basic concepts of what a research project will entail, and they found the experiment challenging.

One issue that elicited both positive and negative comments from students involved group dynamics. Some students really enjoyed working in groups. Others felt they were “carrying” the group or that their grades were too dependent on others. Typical comments unfavorable to the experiment included:

“I disliked all the reading (research articles) that was necessary to complete the report....In the end my chemistry knowledge was expanded.”

“Working and depending on/with others was difficult.”

“The amount of time that had to be put into the experiment. Although the concepts we learned were very helpful, the spreadsheet analysis was confusing and took us some time. Also, we had to go to the science library to get journal articles which was a bit annoying.”

### ***Instructor Assessment***

This experiment was developed for first-year B.S. chemistry students. Two classes, each in excess of 30 students, have completed this experiment to date. Our intention in developing this experiment was to introduce students to a mini-research project. Students were given the description of the experiment one week in advance. The first week of the experiment ran extremely well. After a lengthy pre-laboratory lecture, students began the synthesis of their xerogels, including the incorporation of complexing reagents, colored metal salts, and enzymes. Also, students learned to construct spreadsheets in small groups with other classmates. The monoliths were dried and aged over the Thanksgiving break, thereby allowing two weeks to stabilize. Initially, problems arose at the beginning of the second week. Students were required to multitask and had to allocate duties among the newly formed group of six. Also, a detailed procedure was not given to the students. It was intriguing to watch each group and see who would emerge as the “team leader”. After several minutes of confusion followed by some suggestions on how to proceed by the instructor, each group began to accomplish its tasks. During the 4.5 hour lab period, each team of students got hands-on experience with the TGA and ICP, and evaluated the solids as optical sensors.

### **Troubleshooting and tips for success**

1. Carefully plan out what students make up a group or team. Try not to advantage or disadvantage one group over another. Evaluations have linked the enjoyment of the experiment to the group experience.
2. During gel preparation, enforce eyewear protection and work in fume hoods.
3. Calculation of percent leaching was difficult for the first-year students. Although not a difficult calculation, it involves many steps. Prior to the laboratory final, a handout was supplied to students so that all students understood the concept.

4. Fifteen collaborative study plans are included with this experiment. New or revised collaborative study plans can be developed easily.

5. Place selected literature references on reserve for the students. These references are cited on the student version of the laboratory experiment.

