

Molecularly Imprinted Polymers for the Selective Sequestering and Sensing of Ions

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A variety of polymeric materials were developed as the basis for sequestering and sensing ions in aqueous solution. Polymers were made that can act as selective ion exchange resins. The selectivity can sometimes be made to approach exclusivity and allow the simultaneous removal and purification of a variety of chemicals. This approach can be used to turn waste streams of hazardous chemicals into resources of valuable materials. In addition, some of the polymers were used to construct ion selective electrodes for sensing ions in aqueous solution. Similar polymers were constructed with complexing monomers that possess chromophores, allowing for the construction of chemically selective optical ion sensors. The result of these studies is a general approach for the construction of selective ion sequestering and sensing polymers.

(Keywords: Ion exchange, Molecularly imprinted polymer, Sensors.)

INTRODUCTION

An ideal reagent for use in constructing ion selective sequestering agents and sensors would be one for which only a specific ion would be complexed. An ideal ion selective separation or measurement technique would take place in a simple single-stage operation involving no elaborate apparatus, be rapid, require little or no pretreatment of the aqueous phase (required for *in situ* measurements), involve an agent that is insoluble in the aqueous phase, and entail minimal cost. This research is aimed to develop polymeric complexing agents that meet these criteria.

In nature, selective complexing agents are made by the immune system. Molecularly imprinted polymers (MIPs) are synthetic materials designed by emulating the way the immune system generates the selective complexants known as antibodies. Specifically, MIPs trace their origin to suppositions about the operation of the human immune system by Stuart Mudd in the

1930s and Linus Pauling in the 1940s. Mudd's contribution to understanding the immune system was to propose the idea of complementary structures.¹ This supposition states that the reason that a specific antibody attacks a specific target or "antigen" is because the shape of the antibody provides an excellent fitting cavity for the shape of the antigen. The description is very similar to the "lock and key" analogy used to explain the action of enzymes, the molecules responsible for hastening and directing biochemical reactions. Enzymes form a lock for a particular chemical key to fit, and as the "key" is turned, the enzyme directs and hastens the production of desired products from the chemical target.

Pauling's contribution to the development of MIPs was to explain the source of the complementary shape exhibited by antibodies.² He postulated how an otherwise nonspecific antibody molecule could be

reorganized into a specific binding molecule. He reasoned that shape specificity was obtained by using a target antigen to arrange the complementary shape of an antibody. Thus, a nonspecific molecule can be shaped to the contours of a specific target, and when the target is removed, the shape is maintained to give the antibody a propensity to rebind the antigen. This process is known as molecular imprinting or "templating."

The target or template molecule directs the positioning of the encapsulating antibody by the interactions that occur between certain sites on the target and complementary sites on the antibody. The sites that allow complementary associations are certain arrangements of atoms that exhibit an electrostatic attraction of a specific kind. These localized atomic arrangements are called "functional groups" by chemists. The functional groups on a molecule help to define the molecule's overall chemical properties. Functional groups may form attachments to their complements by covalent, ionic, or hydrogen bonding. In the context of ion-exchange materials, the association is through ionic bonds.

The early work in molecular imprinting was based on silica gels,^{3,4} which showed some retention or memory of structure but were limited in application. The synthesis and characterization of molecularly imprinted organic polymers were first reported by Wulff and Sarhan⁵ in 1972. Their investigations, and later those of Shea and others,^{6,7} and Damen and Neckers,⁸⁻¹⁰ indicated that polymers with specific cavities can be produced.

To be useful, Wulff and Sarhan⁵ indicated that these polymers must exhibit the following characteristics:

- The cavity geometry and the binding group arrangement should be preserved after the removal of the template molecule. This may be accomplished by high degrees of cross-linking, that is, use of a structural monomer that links chains together.
- The cavities must retain enough flexibility to permit rapid uptake and release of the template molecule. This property decreases with increasing cross-linking, so a balance must be sought.
- A large fraction of the template molecules should be removable after polymerization. This implies good accessibility of the cavities, which requires polymers with large surface areas.
- The polymeric materials should be chemically and mechanically stable to permit regeneration and reuse.

Wulff and Sarhan⁵ and the others⁶⁻¹⁰ also suggested two basic approaches to the preparation of site-specific polymers: (1) polymerize monomers that contain binding groups with set geometries by virtue of attachment to a template molecule, and (2) produce binding groups located on a flexible polymer chain, and then fix them

in a definite geometry by attachment to a template molecule followed by cross-linking.

The production of polymers with selective binding for a specific cation is achieved by providing polymers with cavities lined with complexing groups or "ligands" arranged to match the charge, coordination number, coordination geometry, and size of the target cation. Anion complexing polymers are made in a similar manner, but typically employ a trapped metal ion that has a large affinity for the anion in question. These cavity-containing polymers are produced by using a specific ion as a template around which monomeric complexing ligands will be self-assembled and later polymerized.

The complexing ligands are ones containing functional groups known to form stable complexes with the specific ion and less stable complexes with other ions. The process is outlined in Fig. 1. We have extended and amended previous methods in our work, as detailed later, by changing the order of the steps, by the inclusion of sonication, by using higher template complex loading, and by the selection of functional groups with better complexation constants. Further, we have used the imprinted polymers as selective extractants and in fabricating selective ion sensors.¹¹⁻¹³

POLYMER PRODUCTION

The key step in making a molecularly imprinted polymer is to form a complex that will survive the polymerization process and leave behind a suitable set of binding sites when the templating species is removed. To form such a complex, ligands must be chosen that exhibit sufficiently large affinities to resist dissociation. The polymerization process must provide sufficient rigidity to effect structural "memory" but be sufficiently flexible to allow removal of the template ion. In the case of sensors, the ligating monomers must provide a means of signal transduction. The success of the end product hinges on the selection of the ligating monomer.

Ligand Monomer Selection

Initially, monomeric ethylene, propylene, and styrene derivatives with substituted coordinating groups (X), both acidic and neutral ($H_2C=CH-X$, $H_2C=CH-CH_2-X$, and $H_2C=CH-C_6H_4-X$), were evaluated as specific ion complexing agents. Some were purchased and others were synthesized. Preparations for those compounds not available commercially are well known and readily available in the literature. Ligands were selected on the basis of the thermodynamic affinities for the specific metal ion (maximum affinity) versus the affinities for competing metal ions (maximum difference in affinities). Affinity data are readily available

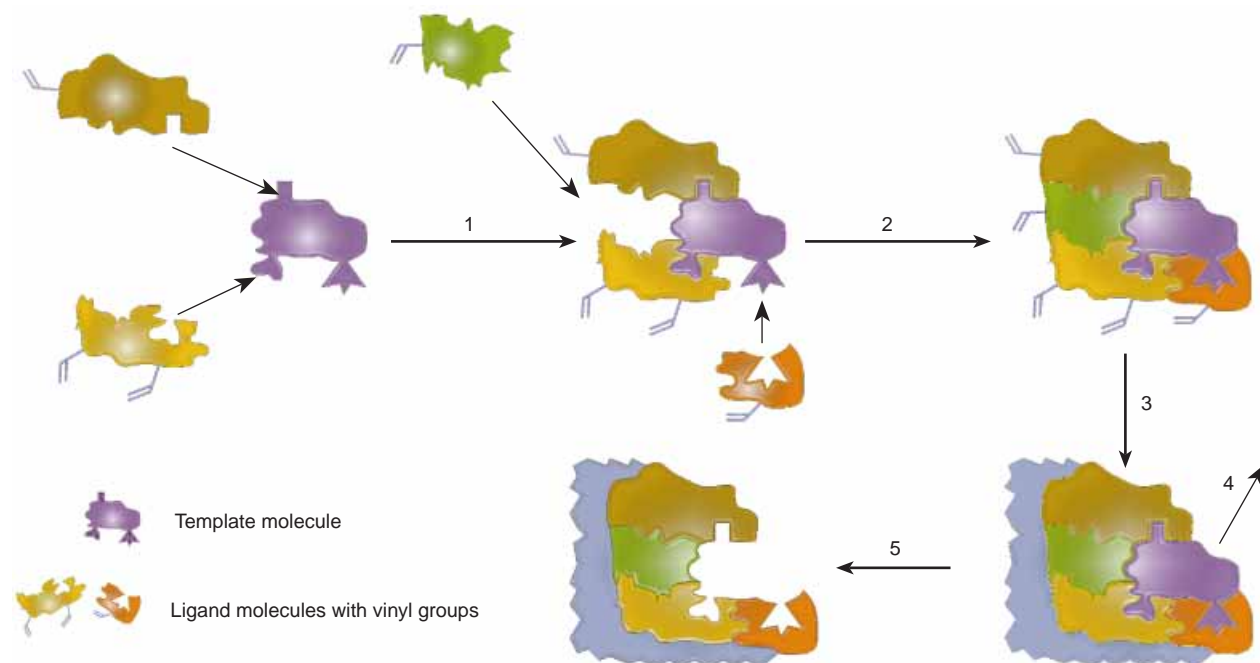


Figure 1. Schematic representation of molecular imprinting. 1,2: Self-assembly of the templates and ligand molecules; 3: incorporation of the ligand–template complex into the polymer matrix; 4: removal of the template molecule; 5: formation of the templated cavity.

from the chemical literature, for example, the tables of complexation constants in the *CRC Handbook*, *Gmelin*, and other sources.^{14,15}

On the basis of the affinities information, vinylbenzoic acid was chosen as the first candidate ligand for lead(II) ion complexation. Although vinylbenzoic acid is commercially available, we found that it required extensive purification before use. Therefore, it was synthesized in-house by the Wittig reaction. Several other vinyl-substituted ligands were also used. Methyl-3,5-divinylbenzoate was synthesized by the method of Shea and Stoddard.¹⁶ The divinyl compound was prepared primarily to give greater structural integrity to the coordination site by providing each ligand with two possible connections to the polymer network. It was anticipated that the methyl-esterified compound would eliminate the pH dependence, characteristic of the vinylbenzoic acid carboxyl functionality. 5-Vinylsalicylaldoxime was synthesized by a method adapted from Wulff and Akela¹⁷ and tested as a selective agent for both lead(II) and uranyl ions.

Synthesis of Complexes with Polymerizable Ligands

With a careful choice of complexing ligands, metal complexes were synthesized by mixing stoichiometric amounts of a metal salt and the complexing ligand in aqueous solution and evaporating to near dryness. Our experience with making complexes has shown that water or alcohol/water mixtures of the metal and ligand in stoichiometric ratios, evaporated to dryness, result in

near quantitative yield of the desired complex compound. The stoichiometry of the complexes was verified by determining the mass percent of metal ion using inductively coupled plasma atomic emission spectroscopy (ICP-AES). To make complexes that contain target anions, it was necessary to make mixed ligand complexes that have a one-to-one stoichiometric ratio of target anion to complex. This was done by synthesizing metal ion complexes with the proper coordination number of tightly binding ligands such that a single target analyte could bind by replacing a very weakly bound substituent. This step can be difficult if insufficient care is taken in selecting the appropriate ligands.

Synthesis of the Copolymers

Here and elsewhere in this article, cross-linking is defined as the mole percent content of the cross-linking agent, divinylbenzene. The polymer matrix was initially formed at a relatively high cross-link level to enforce the retention of the cavity “memory” upon the removal of the metal ion. Experience with templated resins for metal ions that exhibit directed bonding has since revealed that relatively small amounts of cross-linking result in more selective resins. This may be a result of the bulk of the polymer possessing metal ion-to-ligand ionic and dative bonds as well as covalent cross-links.

The introduction of microporosity for increased reagent accessibility was achieved through the addition of a noncoordinating monomer (styrene). Solutions of the monomeric complex (metal ion complexed with polymerizable ligands), styrene, initiator, and cross-

linker (divinylbenzene) in various amounts of a suitable solvent (0–20 weight percent of pyridine) were prepared. The dissolution of the complex/monomer mixture has historically been a difficult step. We have found that this step can be simplified if the copolymerization is carried out using ultrasonication. The sonication has the serendipitous effect of maintaining the temperature at about 60°C, which is the recommended temperature for chemically initiated free-radical polymerization using azobisisobutyronitrile. Lead vinylbenzoate copolymers were produced with and without sonication, and it was determined that the sonication results in a more homogeneous product but with only a slight increase in capacity over the polymers obtained by heating in an oil bath. On the other hand, examination of some uranium-containing copolymers has shown larger improvements (greater than 10-fold) in capacity due to sonication. The expectation was that in addition to improving solubility, the sonication would result in more complete incorporation of the metal ion complex in the copolymer. It is apparent that the effectiveness of sonication varies with the choice of metal ion complex and may or may not be simply a function of miscibility.

When the polymerization was completed, the cross-linked polymer was washed, cryogenically ground to a uniformly fine powder, and extensively eluted with nonpolar solvents to remove unreacted complex. A grinding step was necessary to maximize surface area and allow for access by the various reagents and samples. It required freezing the polymer in liquid nitrogen and using a ball mill employing a stainless steel capsule. This freezing made the polymer brittle enough to be ground and prevented distortions of the polymer by the heat of friction. Sieves were used to obtain the uniformly sized particles. Polymers used in the construction of optical sensors were prepared *in situ* on the distal end of an optical fiber whose surface was prepared by binding a polymerizable agent on the surface.

Acetone or another organic solvent was used to swell the polymers, allowing greater access to the coordinated metal ions. This step was necessary since, unlike commercial resins whose large amount of functionalization (ionogenic sites) causes the resin to swell most in polar solvents, the templated resins have a relatively low amount of functionalization and are primarily nonionic matrices. The template molecule can be removed in a variety of ways. For example, for metal ion templated resins, subsequent to the removal of unreacted monomer, a 1 N aqueous acidic solution was mixed into the acetone washes, with increasing aqueous acidic phase in each sequential wash, to remove the metal ions from the cavities by mass action. A significant fraction of the cations (but not all) was removed, thus leaving cavities that were cation-specific. Those cations that were not removed even after

swelling were locked inside the polymer in inaccessible sites. Cations can be removed from fiber-bound polymers with the aid of a chelating agent such as ethylenediaminetetraacetic acid (EDTA) after swelling in an appropriate solvent. Acidity is avoided in this case so that the polymer-to-silica bond is not hydrolyzed. Anions may also be removed by mass action with acidification when the anion can be protonated, leaving in its place the conjugate base of a strong acid such as chloride or nitrate.

ANALYTICAL APPLICATIONS OF THE METAL ION TEMPLATED POLYMERS

The ion templated polymers are being used in a variety of analytical applications. Lead selective resins were applied to the analysis of seawater in a head-to-head experiment with three other ion selective resins. A fast sensitive method for determination of lead in seawater was developed. Lead(II) and uranyl ion selective membrane electrodes were fabricated using ground polymer particles as sensing elements. Numerous selectivity studies were conducted to characterize the selectivity of the sensors. A fluorescent lead templated polymer is being developed as an optical sensor (optrode) for determination of the lead(II) ion concentration in aqueous solutions. And finally, a polymer templated for the hydrolysis product of the nerve gases sarin and soman has been developed as the basis of a portable sensor for these significant chemical threats.¹⁸

Templated Polymers as Sequestering Agents

The first application was a comparative study of ion exchange materials for the extraction and preconcentration of the lead(II) ion prior to analysis by ICP-AES and inductively coupled plasma mass spectrometry (ICP-MS). The lead(II) ion was extracted from seawater by employing four different ion exchange resins: Chelex-100, a proprietary NASA resin, our lead templated vinylbenzoic acid resin, and a commercial thiol-based ion exchange resin. Seawater is one of the most challenging matrices for chemical analysis and was chosen because of the difficulty it poses in chemical analysis. Measurement of the lead(II) concentrations, as well as the concentrations of possible interfering species, was performed first with ICP-AES and later with ICP-MS. Recoveries of lead(II) were determined to evaluate the suitability of the various resins as sequestering agents and to show the advantage in selectivity of the templated ion exchange material.

The results of this experiment exceeded expectations. The preconcentrated lead extracts obtained using the templated resin were found to be exceedingly pure. Because of the relative purity (absence of significant

amounts of interferents) of the seawater extract obtained from the templated resin, it was tested for lead by a simple photometric method that normally requires significant purification and preparation. This quantitative analysis was performed using dithizone complexation with spectrophotometric detection (measuring absorbance at 522 nm). Dithizone is a colorimetric reagent that forms colored complexes with a wide range of metal ions. The results of the photometric analysis agreed with the ICP-AES data. The use of the templated resin in this manner provides an inexpensive assay for the lead(II) ion in aqueous solutions with a detection limit of <100 ppb and a linear range from 100 ppb to 2.00 ppm. The use of the resin with larger volumes of analyte would allow for preconcentration and much lower limits of detection. The detection limit of 100 ppb is already better than the normal ICP-AES detection limit of about 1 ppm.

The limitation on the use of the templated resins fabricated by the preceding methods is the relatively small exchange capacity. The low capacity is due to the bulk of the ionogenic sites being buried in the polymer particle and thus being unavailable for exchange. In part, this handicap is overcome by the selectivity of the resin. Since the resin is so selective for the metal of choice, few of the available sites are occupied by interferents, and so less capacity is required for most applications. Another consequence of the activity of the resin being restricted to the surface of the particle is the rapidity of ion extraction, which allows for higher flow rates for extractions and is particularly attractive for analytical preconcentration.

Templated Polymers in Ion Selective Electrodes

After analyzing the sorbent properties of the metal ion templated polymers, the polymers were used to fabricate ion selective electrodes. Ground polymer of an appropriate size, 60 mesh, was cast in a polyvinyl chloride membrane. The membrane was adhesively bonded to a polyvinyl chloride support tube and assembled into a standard polymer membrane electrode. The selectivity and stability of the templated polymer give this electrode advantages over traditional ion selective electrodes. An extensively used electrode does not display a loss of function resulting from solubility of the active ingredient, and the electrodes are immune to the chemical poisoning that occurs with crystal-based electrodes. A typical response curve for the templated polymer electrode for the lead(II) ion is shown in Fig. 2.

The potential responses of the electrode to a variety of common interference ions are shown in Fig. 3. As expected, the electrode based on the lead(II) ion imprinted polymer membrane showed a strong preference for lead(II) ions. Membranes based on a 3 mole percent equivalent vinylbenzoic acid polymer and on benzoic

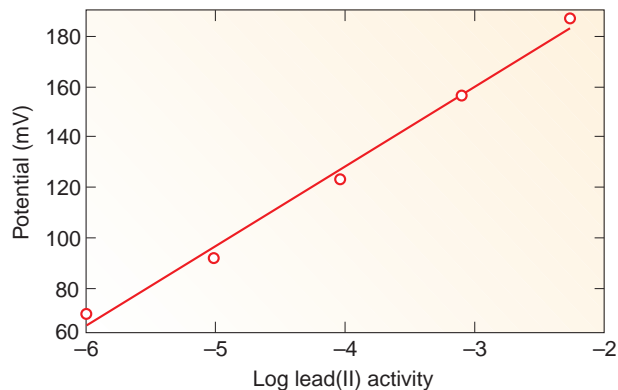


Figure 2. Calibration curve for a lead(II) ion selective electrode constructed with a templated polymer cast in a polyvinyl chloride membrane (slope = 31.7, correlation coefficient = 0.996).

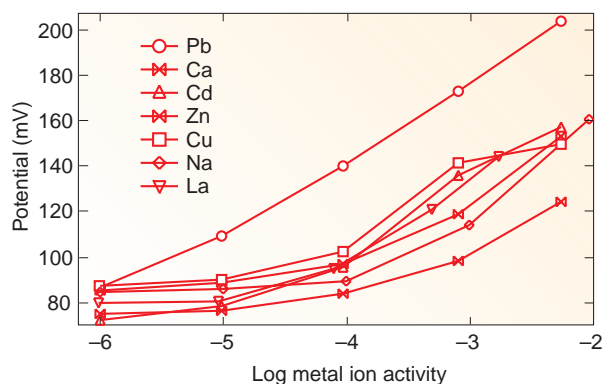


Figure 3. Response of a lead(II) ion templated electrode and the most likely interferent ions.

acid were also prepared and examined. The membrane based on the lead templated polymer was found to be more sensitive than either the membrane based on the untemplated polymer or the one prepared with dissolved benzoic acid.

The production of polymers for use with other metal ions has begun with templating a polymer for the uranyl ion. Figure 4 shows the response of a membrane prepared with a uranyl ion templated polymer. In this case, the result was astounding in that no interference has yet been detected. It was thought that the unique shape of the uranyl ion would make it a prime candidate for the template process. This expectation has been realized. The influences of unique shape and other factors are currently being investigated for uranyl templated polymers.

Templated Polymers in Optical Sensing

Lead Ion Optical Sensor

During the initial screening of coordinating monomers for possible ion selective electrode enhancements,

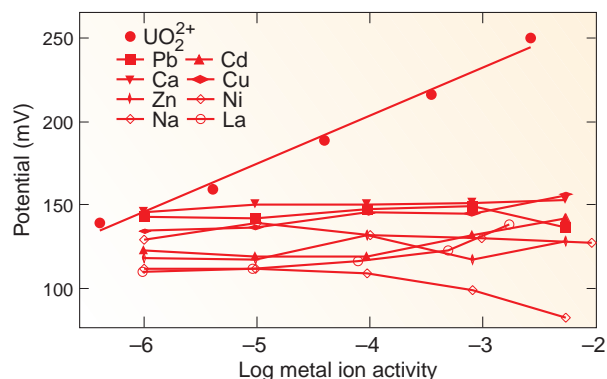


Figure 4. Response of a uranyl ion templated electrode (slope = 29.0, correlation coefficient = 0.995) and the most likely interferent ions.

it was observed that methyl-3,5-divinylbenzoate (DVMB) luminesces blue, and that the luminescence becomes yellow-green when a lead(II) complex is formed. This observation suggests phosphorescence due to an external heavy atom effect. Since the lead(II)-DVMB complexes rapidly polymerize in solution, it was decided to investigate the optical properties of the ligand precursor, methyl-3,5-dimethylbenzoate. The lead(II) complex was prepared by the method outlined previously and dissolved in hexane to prevent complex dissociation. Luminescence spectra of the lead(II) complex and free ligand were obtained with a spectrofluorimeter using a 467-nm excitation wavelength. Serial dilutions were used to obtain analytical figures of merit for a solution assay of the lead(II) complex in hexane. The calibration curve was linear for four decades of concentration from 70 to 7.0×10^5 ppb complex with a limit of detection of 50 ppb complex (equivalent to 20 ppb lead), having a correlation coefficient of 0.997.

These observations, along with similar results obtained with a variety of complexing ligands, presented convincing evidence that a lead sensing optrode could be made. The 3% lead(II)-DVMB complex (2% divinylbenzene) was bound by *in situ* copolymerization on a vinylized 400- μm optical fiber surface. The fiber was then used in the setup schematically presented in Fig. 5. The luminescence spectrum of the polymer-coated optical fiber showed the characteristic band of the lead(II) complex, virtually identical to the one displayed in Fig. 6. The lead(II) ion was then removed from the polymer by first swelling it in a mixture of methanol and water and then soaking it in a stirred solution of EDTA; each process took about 1 h. The luminescence spectrum of the cleaned polymer no longer exhibited the characteristic lead(II) complex luminescence band.

The standard curve generated by the first prototype optrode is given in Fig. 7. The luminescence was excited by the 488-nm line of an argon ion laser at a power of about 10 mW. The device is being tested for longevity and interference effects and is to be applied to field trials in an environmental project aimed at identifying sources of wastewater seepage into streams.

Counter-Terrorism Nerve Gas Sensor

The sensor system being developed has been designed to measure the primary hydrolysis products of sarin and soman. This is the process by which the agents degrade upon exposure to moist air, and the products of hydrolysis are relatively innocuous. This design allows preconcentration of the analyte at the sensor surface by enhancing analyte-to-sensor affinity. Also, the use of a hydrolysis product of the nerve agent obviates the need for exposing personnel to toxic chemicals during the development of the device.

The laboratory prototype for the sarin/soman fiber-optic sensor (Fig. 8) consists of an optical fiber onto which the polymer has been coated. The fibers were prepared by terminating one end of a 400- μm optical fiber with a standard optical fiber connector and removing the cladding from the distal end. The vinyl-silanized end of the fiber was then dip-coated with a viscous polymer solution, leaving a uniform coating on the fiber. The polymer was then cured under a handheld UV lamp overnight. Once cured, the polymer on the fiber was cleaned using the swelling and removal procedure described previously.

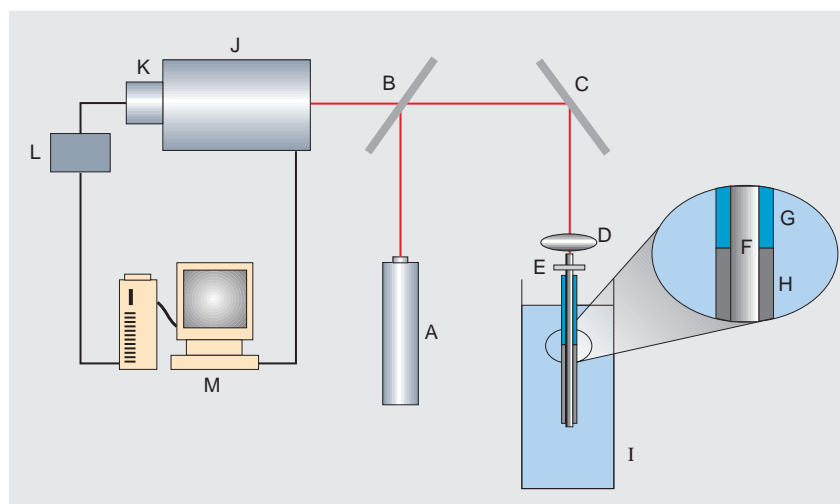


Figure 5. Prototype of a lead(II) ion measuring optrode system. (A) argon ion laser, (B) dichroic mirror, (C) mirror, (D) lens, (E) fiber mount, (F) optical fiber core, (G) fiber cladding, (H) templated polymer coating, (I) sample, (J) monochromator, (K) detector, (L) analog-to-digital converter, (M) computer.

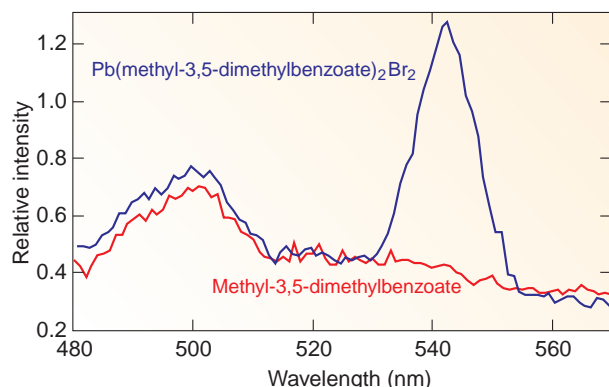


Figure 6. Luminescence spectra of a free ligand (methyl-3,5-dimethylbenzoate) and its lead(II) complex excited at 467 nm.

The prototype sensor coated with the 3 mole percent complex polymer is currently being tested. Luminescence is being excited using the 488-nm laser line with the response carried to the monochromator through the

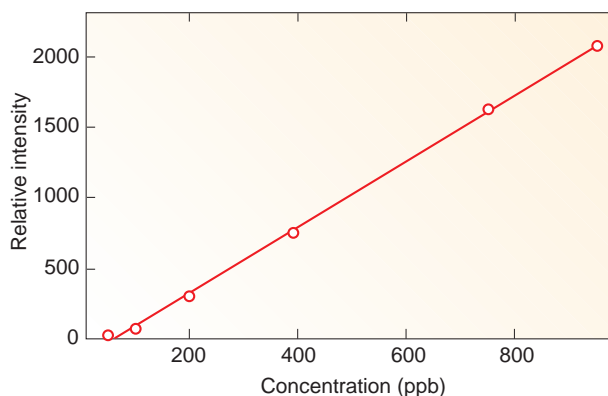


Figure 7. Calibration curve obtained for the first prototype lead(II) optrode (slope = 2.34, correlation coefficient = 0.9994).

fiber. Thus far, the sensor has been able to detect the hydrolysis product at levels from 150 ppm to 1 ppb with a linear response (Fig. 9). The limit of detection for this initial sensor is 125 parts per trillion of pinacolyl methyl phosphate in 0.1 M sodium hydroxide. The response time of the sensor is typically less than 1 min. Studies on limit of detection and interferences are currently being performed.

Once the preliminary testing is completed, the working end of the sensor will be enclosed in a semi-permeable membrane with an alkaline solution using a solvent such as polyethylene glycol to prevent evaporation. (The alkaline solution is necessary to catalyze the hydrolysis of the nerve agents to their respective hydrolysis products.) Once the prototype is completed, it will be subjected to testing with the actual nerve agents at an approved site. The portable device will be designed using a small photosensor module for detection, with the output going to a gated integrator. An optical multiplex switch will be incorporated into the design so that many sensors can be coupled to one control system. This setup should allow monitoring of a large building, subway station, or airport.

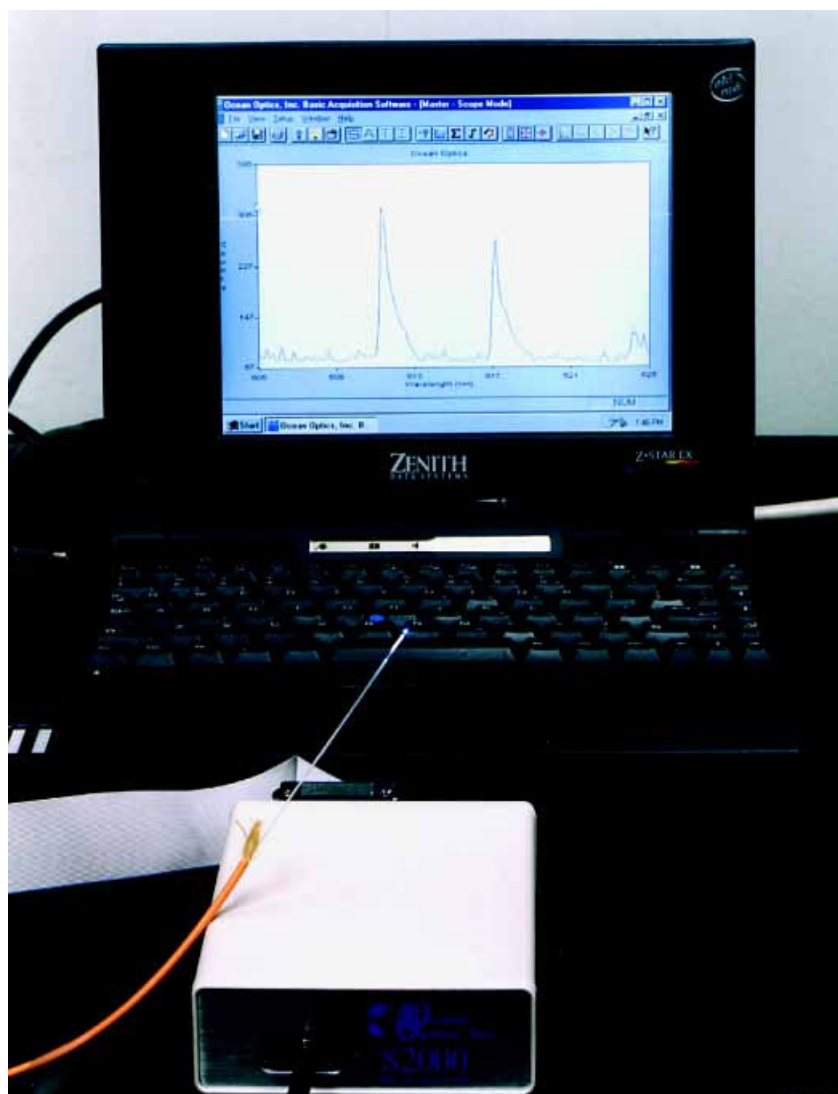


Figure 8. Laboratory prototype for the sarin/soman fiber-optic sensor.

CONCLUSIONS

Molecular templating is an emerging technology for the creation of selective binding sites in

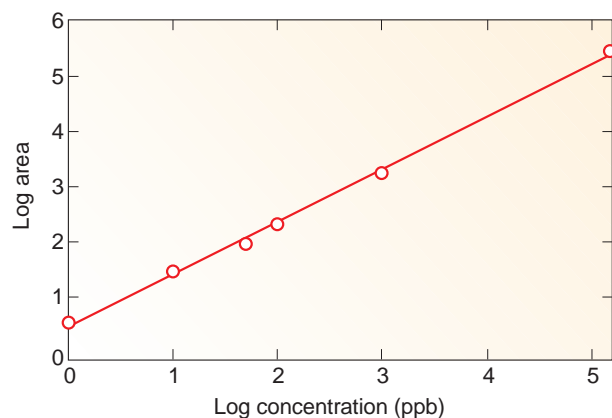


Figure 9. A log-log calibration plot for the sarin/soman sensor (correlation coefficient = 0.999).

synthetic polymers. Ion selective sensors have the advantages of being simple, rapid, and inexpensive. This research explores the utilization of metal ion templated polymers as selective sequestering agents and as components of electrochemical and optical sensors. Results from the characterization of the metal ion templated electrodes for lead(II) and uranyl ions demonstrate a broad linear range of measurement with a near-Nernstian response (the theoretically expected response according to the Nernst equation) and a strong preference for the templated metal ion over the other metal ions tested. The lifetime of the electrode is relatively long, which is one of the advantages rendered by templated polymers with the functional groups covalently attached to the polymer matrix. Optical sensors based on templated polymers have been shown to determine the lead(II) ion and a nerve gas hydrolysis product in the parts per billion range. The information obtained from these studies will be used to produce a variety of new ion selective polymers and to fabricate additional sensors.

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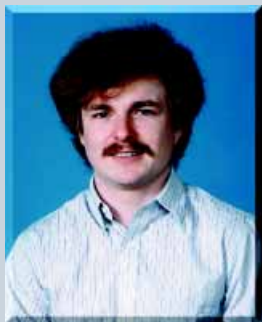
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