Preparation of Ion Exchange Films for Solid-Phase Spectrophotometry and Solid-Phase Fluorometry

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March 2000
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PREPARATION OF ION EXCHANGE FILMS FOR SOLID-PHASE SPECTROPHOTOMETRY AND SOLID-PHASE FLUOROMETRY

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SUMMARY

Atomic spectroscopy has dominated the field of trace inorganic analysis because of its high sensitivity and selectivity. The advantages gained by the atomic spectroscopies come with the disadvantage of expensive and often complicated instrumentation. Solid-phase spectroscopy, in which the analyte is preconcentrated on a solid medium followed by conventional spectrophotometry or fluorometry, requires less expensive instrumentation and has considerable sensitivity and selectivity. The sensitivity gains come from preconcentration and the use of chromophore (or fluorophore) developers and the selectivity is achieved by use of ion exchange conditions that favor the analyte in combination with speciative chromophores. Little work has been done to optimize the ion exchange medium (IEM) associated with these techniques. In this report we present a method for making ion exchange polymer films which considerably simplify the solid-phase spectroscopic techniques. The polymer consists of formaldehyde-crosslinked polyvinyl alcohol with polyacrylic acid entrapped therein. The films are a carboxylate weak cation exchanger in the calcium form. They are mechanically sturdy and optically transparent in the ultraviolet and visible portion of the spectrum, which makes them suitable for spectrophotometry and fluorometry.

INTRODUCTION

During the past few decades, at least 6 review articles (refs. 1 to 6) and over 100 papers have appeared in the literature on the subjects of solid-phase spectrophotometry (SPS) and solid-phase fluorometry (SPF). In both SPS and SPF, the analyte is preconcentrated on a solid medium and separated from the original sample matrix, thus enhancing sensitivity and selectivity. Preconcentration is typically done on ion exchange resins, and the subsequent analytical finish uses the ion exchange material as the spectroscopic medium. Both SPS and SPF suffer from scattering and either absorption or emission from the ion exchange material because of the size of the beads (collected by filtration) and the material itself. These problems are minimized or eliminated by the introduction of ion exchange films (refs. 7 and 8), which are transparent throughout the visible and most of the UV region of the spectrum. The background luminescence from the films can be minimized by temporal discrimination for analytes that are long-lived fluorophores or phosphors.
The ion exchange material (IEM) in film form is a spinoff of a marginal space battery separator developed by NASA in the late 1970's (refs. 9 to 15). In those earlier experiments, a researcher was washing a separator and serendipitously discovered that this material had ion exchange properties. He noticed that washing the film with distilled water caused it to pick up a blue cast, a coloration that was traced to a corroding copper line in the still. This effect was later exploited for the SPS determination of Cu$^{2+}$ in tap water. To date, the SPS and SPF papers appearing in the literature (with the exception of our earlier report) used commercial resins, but no effort has been made to improve the spectroscopic properties of the ion exchange matrices. Herein, we present details to optimize the production of ion exchange films because they are excellent spectroscopic media and considerably simplify the SPS and SPF techniques.

EXPERIMENT

Apparatus

Max-Series Electronic Digital Calipers were used to make measurements for area determinations. A Perkin Elmer model 3100 flame atomic absorption spectrometer, equipped with a PC Craft workstation, was used in the normal mode of operation. The pH meter, a Corning model 130 equipped with combination pH and automatic temperature compensating electrodes, was used for all pH measurements. A Shimadzu UV 160 recording spectrophotometer, equipped with standard 1-cm$^2$ quartz cells and 9-mm quartz spacers, was used to record the visible spectra of nickel, cobalt, and copper ions on ion exchange films. The fluorescence spectrum of gadolinium ions on ion exchange film was taken on a Baird Atomic model FC 100 Fluorichord Spectrofluorometer with slits manually adjusted to optimize signal intensity and resolution. Spectra of films were taken in a triangular cell filled with deionized water such that the film was at a 45° angle with respect to the excitation and emission slits for the Fluorichord and the cell windows were normal to the entrance and exit of light from the cell.

Chemicals

Polyvinyl alcohol (PVA, molecular weights of 25 000, 78 000, 108 000, and 133 000) was obtained from Polysciences Inc., and polyacrylic acid (PAA, molecular weights of 250 000, 450 000, 750 000, and 3 000 000) from Aldrich Chemical Company. Solutions of polyacrylic acid (25% w/w in water with molecular weight of 90 000 and 50% w/w with molecular weight of 5000) were also purchased from Aldrich. AR grade formic acid, propionaldehyde that was further diluted to a 25% v/v solution with water, and a 25% w/w solution of glutaraldehyde in water were obtained from Aldrich, and a 37% w/w solution of AR grade formaldehyde from Fisher Scientific. All metal salts and acids were AR grade chemicals from Fisher Scientific or Mallinckrodt. All solutions were prepared with deionized water.

PROCEDURES

General Film Casting Procedure

The film of a 1:1-weight ratio of PVA to PAA was studied. An aqueous polymer solution (10 percent solids) was prepared from stock solutions of PAA (10 percent solids) and PVA (10 percent solids) by stirring in a beaker for 15 min by hand to ensure complete mixing. The solution was then transferred to a vacuum flask, and a vacuum was pulled over the solution to remove trapped air bubbles. The degassed polymer was then cast onto a lightly waxed, glass-topped table with a 12-in. doctor blade (Gardner Film Casting Knife, AG-4300 series, BYK Gardner, Inc.) set to the desired thickness. The solution was allowed to sit overnight for the water to evaporate. The next day, the dried film was then removed from the glass and cut into smaller easier to handle pieces (approx. 10 by 10 cm).
Molecular Weight Studies

The solubilities of each powdered polymer were studied to determine the optimum starting material. A 10-percent-solids solution of either PVA or PAA was prepared by mixing 10 g of the powder in a beaker with the correct volume of water. The beaker was heated in a hot water bath on a hot plate until all the solid dissolved. A 25% w/w solution in water (molecular weight, 90 000) and a 50% w/w solution of polyacrylic acid in water (molecular weight, 5000) were also investigated as potential starting materials and were used as received without dilution to 10 percent solids. This study concluded with the selection of the highest molecular weight PVA or PAA that dissolved easily, did not precipitate upon cooling, and remained viscous enough to be easily poured but not run off the casting plate. The optimum film determined from these studies was a 10-percent-solids, 1:1-ratio film of PVA (molecular weight, 180 000)-PAA (molecular weight, 450 000). In the remainder of this report, “films tested” refers to this optimum variation unless specified otherwise.

Salting Agents

Salting agents were used to prevent the polymer from dissolving in the aqueous crosslinking reagent prior to the occurrence of the crosslinking reaction. Four solutions were investigated as salting agents (table I). The salting agents were tested by placing approximately 6- by 6-cm films in a 600-ml beaker and adding 350 ml of the salting solution and 150 ml of a crosslinking solution. Formaldehyde was used with salting solutions 1 and 2 and glutaraldehyde with solutions 3 and 4. After the films were heated in a hot water bath at 70 °C for 2 hr, they were removed and tested to determine the extent of crosslinking. This testing is described in the section Extent of Crosslinking Study.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Salt</th>
<th>Weight of salt, g</th>
<th>Catalyst</th>
<th>Volume of catalyst, ml</th>
<th>Water, ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CaCl₂·2H₂O</td>
<td>300</td>
<td>HCl</td>
<td>50</td>
<td>500</td>
</tr>
<tr>
<td>2</td>
<td>(NH₄)₂SO₄</td>
<td>250</td>
<td>H₂SO₄</td>
<td>15</td>
<td>500</td>
</tr>
<tr>
<td>3</td>
<td>Na₂SO₄</td>
<td>100</td>
<td>Formic acid</td>
<td>125</td>
<td>500</td>
</tr>
<tr>
<td>4</td>
<td>CaCl₂·2H₂O</td>
<td>60</td>
<td>Formic acid</td>
<td>25</td>
<td>100</td>
</tr>
</tbody>
</table>

Crosslinking Reagents

After the best salting agent was determined, several chemical crosslinking reagents were tested. Formaldehyde, propionaldehyde, and glutaraldehyde were examined as potential crosslinking agents and were tested by using approximately 6- by 6-cm films that were placed in 600-ml beakers containing 300 ml of the salting solution and 150 ml of the crosslinking reagent. Table II lists the salting agent-crosslinking reagent combinations that were tested. The beakers were placed in a hot water bath at 70 °C and were heated for 1 hr. Afterwards, the films were removed and tested to determine the extent of crosslinking (see the section Extent of Crosslinking Study). In table II, the salting solution numbers refer to the reagents listed in table I. Hereinafter, the term “crosslinking reagent” refers to the combination of the salting agent and the chemical crosslinker at the concentrations given in table II.

<table>
<thead>
<tr>
<th>Salting agent</th>
<th>Salt solution number</th>
<th>Salt solution volume, ml</th>
<th>Crosslinker</th>
<th>Volume of crosslinker, ml</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂/HCl</td>
<td>1</td>
<td>300</td>
<td>Formaldehyde</td>
<td>150</td>
<td>A</td>
</tr>
<tr>
<td>CaCl₂/HCl</td>
<td>1</td>
<td>300</td>
<td>Propionaldehyde</td>
<td>150</td>
<td>B</td>
</tr>
<tr>
<td>CaCl₂/HCl</td>
<td>1</td>
<td>300</td>
<td>Glutaraldehyde</td>
<td>150</td>
<td>C</td>
</tr>
<tr>
<td>CaCl₂/formic acid</td>
<td>4 (a)</td>
<td></td>
<td>Glutaraldehyde</td>
<td>50</td>
<td>D</td>
</tr>
</tbody>
</table>

*Entire solution from table I.
Crosslinking Reagent Concentration Optimization

Several experiments performed to optimize the crosslinking reagent concentration used a 6- by 6-cm piece of film and exposed it to 300 ml of salt solution 1 (table I) and to either 50, 150, or 200 ml of formaldehyde in a 600-ml beaker. The samples were heated in a hot water bath at 70 °C for 1 hr and were then removed and tested to determine the extent of crosslinking.

Crosslinking Temperature

Various hot water bath temperatures used for crosslinking were examined to identify the one that yielded the optimum crosslinked film. Those investigated were 60, 70, and 80 °C and room temperature (approx. 20 °C). The 6- by 6-cm films were exposed to crosslinking reagent A (table II) and were placed in a hot water bath of the specified temperature for 1 hr. The film exposed to the crosslinking reagent at room temperature was allowed to sit for 24 hr rather than 1 hr. The films were then removed and tested to determine the extent of crosslinking. Their mechanical strength was also tested by pulling and stretching slightly to determine if they would tear.

Crosslinking Time

Various time increments of exposure to crosslinking reagent A (table II) were investigated to identify the optimum crosslinked film that was clear. Nine films, approximately 6 by 6 cm and separated by Teflon film, were exposed to the crosslinking reagent in a 600-ml beaker for 30, 60, and 90 min. The beaker was placed in a hot water bath at 70 °C. After each time increment had passed, three films were removed from the beaker, rinsed with deionized water, and stored in 10-percent NaOH. After the films were removed from the NaOH and rinsed with water, physical properties such as clarity, mechanical strength, and extent of crosslinking were tested. A similar beaker of reagent A with three films was set aside and allowed to sit for 24 hr at room temperature. These films were then removed, stored in 10-percent NaOH, and tested as just described. Similar procedures were followed using the propionaldehyde and the glutaraldehyde solutions, reagents B and C, respectively (table II).

Extent of Crosslinking Study

After the films were exposed to potential crosslinking reagents, they were tested to determine the extent of crosslinking. After each step in the crosslinking procedure, the 6- by 6-cm films were dried with a Kim Wipe and the final dimensions measured with the digital calipers to determine if swelling had occurred. The films were tested for acceptable mechanical strength by pulling and stretching to determine if they would tear. They were then placed in beakers of water and were boiled on a hot plate for 1 hr. Afterwards, the film dimensions, clarity, and mechanical properties were observed again. The goal was to produce a film that would withstand a minimum of 24 hr continuous stirring with a stir bar. Many of the earlier films prepared using unoptimized conditions deteriorated significantly under prolonged stirring.

Film Thickness Study

The wet polymer solution for the IEM film was cast at different wet thicknesses to determine the optimum thickness. The doctor blade used had a height adjustment capability that altered the wet thickness of the material being cast. The various wet thicknesses examined were 0.5, 1.0, and 2.0 mm. The dried films were then crosslinked by using reagent A for 45 min at 70 °C, after which they were tested for the extent of crosslinking, clarity, and mechanical strength as described in the previous section.

Conversion to Different Forms

Three forms of the film (calcium, sodium, and acid) were examined for their effectiveness in removing metal ions. Because the crosslinking takes place in an acidic solution, the film was already in the acid form after the
crosslinking procedure was completed. The film was placed in a solution of 10-percent NaOH to be converted to the sodium form. Likewise, that film was placed in a solution containing excess suspended Ca(OH)₂ to be converted to the calcium form. A second method for conversion to the calcium form was also investigated. Faintly ammoniacal CaCl₂ (1000 ml of 0.5 M CaCl₂ and 100 ml concentrated NH₄OH) was placed in a beaker, and the films were added. The pH of the solution was monitored over several hours to maintain a pH greater than 9 so that the acid groups on the film would be removed completely. If the pH dropped below 9, more NH₄OH was added. The system was monitored until a stable pH (above 9) was achieved.

**Calcium, Sodium, and Acid Forms**

All three forms of the film were tested for their effectiveness in removing Cu²⁺ ions from a standard solution of 15-ppm Cu²⁺. For each test, 60 mg of dry-weighed film was placed in a widemouthed glass jar containing 200 ml of 15-ppm Cu²⁺ solution in water. A 4-ml sample of the initial solution was acidified with a drop of concentrated HNO₃ and set aside for a later determination of the initial concentration of Cu²⁺ ions. The pH of the solution was adjusted with dilute HNO₃ or NaOH until the pH stabilized at 5.0. The jars were capped, placed on electronic stirrers, and mixed for 24 hr at 200 rpm with a Fisher 1/2- by 5/16- in. stirring bar. After the full 24 hr of mixing, the films were removed, and the solutions were acidified with 0.1 ml of concentrated HNO₃ and were analyzed along with the initial solution by flame atomic absorption spectroscopy (AAS). For each new variation of film (i.e., different wet film thickness or different chemical crosslinking reagents), all three forms of the resin were prepared and tested for their ability to remove Cu²⁺ ions from solution as just described (see ref. 7 for further details on the Cu²⁺-IEM system).

**Solid-Phase Spectroscopy**

The films used were cut to approximately 1 by 4 cm (60 mg) from the optimum film formulation and formaldehyde (reagent A) crosslinking process used on 6- by 9-cm pieces of uncrosslinked film. To cover larger pieces of film, it was necessary to increase the volume of formaldehyde to 200 ml in the crosslinking solution. The procedures for sorption of the metal ions on films for SPS and SPF are detailed in the literature (ref. 7). Briefly, the solution containing the metal ion of interest was pH adjusted and an appropriately sized piece of film equilibrated by gentle stirring. The film was then mounted in the spectrometer cell and the spectra acquired according to conditions given in the captions for the appropriate figures. Absorption and fluorescence emission spectra were acquired on films as described in the text.

**RESULTS AND DISCUSSION**

**Film Preparation**

This project involved the development of a water-insoluble, ion exchange polymer film from two water-soluble materials, PAA and PVA. The film desired for this application was required to be optically clear, consistent, mechanically strong, and thermally stable. The film produced was obtained through numerous optimization experiments. As each experiment was performed, the optimum result was then selected and combined with other optimum results to create such a film.

The components of this new material are two water-soluble polymers (an active ingredient, PAA, and a support polymer, PVA) that were obtained in the powdered form. A solubility study was performed on each powder to determine the ideal starting material. This initial material consisted of a water-based solution of the two ingredients. Since a film was to be cast from this solution, it had to be fluid enough to cast the film but viscous enough to prevent flow after casting on the glass surface. The solubility study of the different molecular weight polymers resulted in the selection of the highest molecular weight polymer that easily dissolved in a solution that was slightly viscous. The higher molecular weight was desirable because it provided a stronger support (PVA) or the active ion exchanger was less likely to leach from the final product (PAA). The wet casting thickness study revealed that 0.5 mm was too thin to cast the solution and caused tearing of the dried film and difficulties in removing the film from the casting surface. The casting surface was lightly waxed to allow the removal of the dried film that adhered strongly to glass. Attempts to cast the film on Teflon sheet did not produce films because the surface energy of the Teflon was so low that the cast liquid beaded. The 2-mm wet thickness was too thick for this analytical purpose. The optimized mixture
was a 1:1-weight ratio of 10-percent PVA (molecular weight of 108 000) and 10-percent PAA (molecular weight of 450 000) that was cast at a wet thickness of 1 mm.

The two polymers used in the ion exchange material (IEM) are naturally water soluble and therefore must be rendered insoluble. Originally, to be crosslinked, the films were radiated (refs. 9 to 15). However, the next step in the development of the films was creating a chemical method to crosslink them so as to facilitate manufacturing in common chemical facilities. The addition of calcium chloride as a salting agent was selected as the best method because the film did not dissolve in water after exposure to the salting agent. The film exposed to solution 2 (ammonium sulfate, sulfuric acid, formaldehyde) did not remain intact when placed in water, which indicated that negligible crosslinking had occurred. The film exposed to solution 3 (sodium sulfate, formic acid, glutaraldehyde) became very brittle, indicating too much crosslinking had occurred. Formaldehyde was chosen as the crosslinking agent because suitable crosslinking was achieved along with desirable physical properties. The propionaldehyde solution achieved little crosslinking and the glutaraldehyde, too much crosslinking. The maximum volume of formaldehyde tested (200 ml) was selected in conjunction with the 300 ml of calcium chloride salting agent because, in addition to producing strong, clear films, this mixture could be filtered and reused. The hot water bath temperature used for the crosslinking procedure was optimized, and a 70 °C bath was selected because it provided the best crosslinked film. Higher temperature baths resulted in cloudy, brittle films. In comparison, lower temperatures, especially room temperature, extended the time for the films to crosslink, with little or no improvement in the physical properties of the film over those reacted at 70 °C. The time exposed to the crosslinking solution was also a factor in the production of a clear film. A clear film that was produced in 30 min was not very mechanically durable, whereas those produced after 1 hr of exposure were stronger but cloudy. Therefore, the optimum time of exposure to the crosslinking reagent was determined to be 45 min.

The crosslinking process using formaldehyde is presented in figure 1. The acetal formation involves two alcohol functional groups. Adjacent alcohol functional groups on the same PVA can become involved (path a), and bridging between intermolecular alcohol functional groups (path b) is also feasible. The film is insoluble because the formed polyvinyl acetal is less soluble than the PVA and intermolecular bridging increases the molecular weight. The film may become more insoluble by the proper choice of an activation cation. The calcium polyacrylate is much less soluble than the corresponding sodium salt or the initial PAA.

![Crosslinking mechanism diagram](image-url)
Two methods for converting the film to the calcium form were studied. Both were successful; however, the method employing excess calcium hydroxide in water was preferred because it was simpler to use. With the calcium chloride-ammonium hydroxide method, the pH of the solution had to be monitored continuously and more ammonium hydroxide added if the pH of the solution dropped below 9. This process was time consuming and therefore less desirable. With an excess of suspended calcium hydroxide, the pH did not have to be monitored. Conversion of the film to the sodium form caused swelling and led to a deterioration of the mechanical strength. The calcium form actually shrank, which suggested that calcium acts to further crosslink the film at the acid functional groups of the PAA. This type of metal crosslinking may be inter- or intramolecular and is reversible.

SPS and SPF on IEM Films

Using IEM films rather than powder offers a considerable advantage because the powder must be recovered by filtration, packing it into small cells is problematical, and the refractive indices must be matched to achieve appreciable transmission. The IEM films have a long shelf life. We recovered colored cations on IEM films 6 years ago and with the exception of Cr\textsuperscript{3+}, they do not appear to have degraded during storage. The SPS spectra of Cu\textsuperscript{2+}, Ni\textsuperscript{2+}, and Co\textsuperscript{2+} appearing in figure 2 were run versus Ca-exchanged IEM film (60 mg film, 100 ml of approx. 15 ppm of various ions). These cations were collected on 1- by 4-cm strips of film equilibrated at pH 5 to 6. Colored photocopies of these films and of Fe\textsuperscript{3+} and Cr\textsuperscript{3+} are available through reference 7. Another advantage is that traditional SPS chromophore development reactions can be done on the IEM films. Figure 3 presents the spectrum of the neocuproin (2,9-dimethyl-1,10-phenanthroline) complex from 100 ml of 0.1-ppm Cu\textsuperscript{2+} extracted on the IEM.

Figure 2.— Solid-phase spectrophotometry spectra (SPS) of Cu\textsuperscript{2+}, Ni\textsuperscript{2+}, and Co\textsuperscript{2+} extracted on IEM at pH 5.5.

Figure 3.— SPS spectrum of Cu(neocuproin)\textsubscript{2} complex formed according to literature (ref. 16) and extracted on IEM.
This spectrum clearly demonstrates the enhancement in sensitivity gained by color development as the absorbance at the analytical wavelength for the complex (490 to 500 nm) is almost twice as great as that of Cu$^{2+}$ (710 nm) in figure 2. Preliminary data indicate that it is just as feasible to extract Cu$^{2+}$ onto the IEM followed by reduction to Cu$^+$ with subsequent color development as it is to form the complex in solution and then extract the cationic complex onto the IEM. An interesting system is the complex of S-diphenylcarbazone (DPC) with Hg$^{2+}$, in that the complex is a water-insoluble neutral species. Figure 4 shows the spectrum of the complex formed by adding alcoholic DPC to a film containing Hg$^{2+}$. The uncharged complex is retained within the polymer framework which, relative to the aqueous solvent, is hydrophobic and acts as an organic medium. The Hg(DPC)$_2$ complex can also be precipitated from water and extracted to the IEM, yielding similar spectra. Figure 5 shows the spectra of a holmium oxide glass calibration filter and Ho$^{3+}$ extracted from 100 ml of 30-ppm standard onto 61 mg of IEM at pH 5.3. The

![Figure 4.—SPS spectrum of Hg(DPC)$_2$ complex formed on IEM.](image)

![Figure 5.—Spectra of Ho$^{3+}$. (a) Holmium oxide filter. (b) SPS of Ho$^{3+}$ on IEM.](image)
basic features of the Ho$^{3+}$ are apparent in the IEM but some of the fine structure is missing due to the difference in Ho$^{3+}$ coordination between the polymer and glass. Because of the reproducibility of the film and spectra of extracted Ho$^{3+}$, it should be possible to use this system to prepare inexpensive, disposable wavelength calibration standards.

Figure 6 is the SPF fluorescence emission spectra of Gd$^{3+}$ in solution (1000 ppm) and on IEM (approx. 100 ml of 15-ppm equilibrated with 60 mg of IEM at pH 5.5). Both fluorescence spectra were collected using identical instrument settings, excitation wavelength (275 nm), excitation and emission spectral slit widths, photomultiplier gain, and so forth to demonstrate the gain in sensitivity associated with preconcentration on IEM films.

CONCLUSION

This report presented a method for making optically transparent, mechanically strong ion exchange films for solid-phase spectrophotometry (SPS) and solid-phase fluorometry (SPF). The optimized film composition was formed by evaporating a 10-percent-solids aqueous solution, 1:1-ratio of polyacrylic acid (PAA, molecular weight of 450 000) and polyvinyl alcohol (PVA, molecular weight of 180 000) cast to a wet thickness of 1.0 mm. The final optimized crosslinking procedure follows: Cut the films to be crosslinked to a size that will fit in a 600-ml beaker (approx. 6 by 9 cm). Place the films in the beaker, separating each film by a piece of 0.4-mm-thick Teflon film of the same size. The purpose of the Teflon is to prevent the films from sticking together during the crosslinking reaction. To 200 ml of formaldehyde, add 300 ml of a solution prepared from 300 g of CaCl$_2$, 50 ml of HCl, and 500 ml of water. Completely immerse the IEM films and Teflon in the solution, place the beaker in a 70 °C hot water bath, and heat for 45 min. Remove the films from the crosslinking solution and rinse them with deionized
water. The crosslinking solution can then be reused after filtering out any solid matter. The films are then activated by placing them in the appropriate solution for conversion to the desired form, either a 10-percent NaOH solution for the sodium form or excess suspended Ca(OH)$_2$ for the calcium form. The calcium form is preferred because the equilibrium solution concentration of analyte over the calcium resin is always lower for multivalent ions in combination with its being a more durable material.

REFERENCES

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Atomic spectroscopy has dominated the field of trace inorganic analysis because of its high sensitivity and selectivity. The advantages gained by the atomic spectroscopies come with the disadvantage of expensive and often complicated instrumentation. Solid-phase spectroscopy, in which the analyte is preconcentrated on a solid medium followed by conventional spectrophotometry or fluorometry, requires less expensive instrumentation and has considerable sensitivity and selectivity. The sensitivity gains come from preconcentration and the use of chromophore (or fluorophore) developers and the selectivity is achieved by use of ion exchange conditions that favor the analyte in combination with speciative chromophores. Little work has been done to optimize the ion exchange medium (IEM) associated with these techniques. In this report we present a method for making ion exchange polymer films, which considerably simplify the solid-phase spectroscopic techniques. The polymer consists of formaldehyde-crosslinked polyvinyl alcohol with polyacrylic acid entrapped therein. The films are a carboxylate weak cation exchanger in the calcium form. They are mechanically sturdy and optically transparent in the ultraviolet and visible portion of the spectrum, which makes them suitable for spectrophotometry and fluorometry.