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# A Novel, Highly Selective Anion-Exchange Column Prepared by Binding Pd$^2$ to an Immobilized Ligand

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# A Novel, Highly Selective Anion-Exchange Column Prepared by Binding $Pd^{2+}$ to an Immobilized Ligand

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## Abstract

A novel anion-exchange material was created by binding $Pd^{2+}$ to a neutral, bidentate ligand which was covalently bonded to silica gel. A two-site binding model was used to describe the anion binding. This anion-exchange material exhibits selectivities among anions which are generally orders of magnitude greater than those of classical ion-exchange resins because of the use of metal–ligand interactions. The ligand–$Pd^{2+}$–iodide complex is deeply colored. This fact was used to develop a simple colorimetric iodide analysis column. The iodide analysis column is convenient and simple, but it suffers from interferences and a small range of analyzable iodide concentrations.

## INTRODUCTION

For many years, scientists have studied anion separations on both analytical and preparative scales. Some needs, such as ultrapure chemicals, require removal of trace amounts of an anion from a matrix with a high salt content. Treatment of some water supplies necessitates removal of small amounts of nitrate ion from water containing large amounts of chloride ion (*1*). In these cases the separation system requires high selectivity. Even in analytical separations, more selective resins may prove useful. The analysis of organic acids in body fluids, for example, may require two chromatography columns to give the desired separations due to the lack of selectivity shown by the ion-exchange resins (*2*).

One of the oldest methods of anion separation is precipitation. Although this method is often quite selective, it can be expensive due to the cost of the precipitating agents. Ion exchange is used commonly, but the selectivity of classical ion-exchange resins for similarly charged anions is often quite low, usually less than 10 (*3*). The interactions of anions with cyclic polyamines or cyclodextrins have been studied (*4–7*). These complex molecules show selectivities between some anions of about 100, but selectivities are generally below 20. Because size and shape of the macrocyclic cavity are the main factors determining selectivity, ions of similar size and shape are difficult to separate. The difficulty of synthesizing these molecules with the resultant unfavorable economics may also prevent their widespread use.

Large differences are found among the interaction constants of metal cations with certain anions (*8*). For example, precipitation is often a highly selective physical separation tool because it uses the selective affinities of metals for specific anions. Interactions between macrocycle–metal complexes and anions have been studied, but the macrocycles used were three dimensional so the separation was based more on anion size than on the relative magnitudes of metal–ligand interactions (*9*, *10*).

Anion separations are described here which use palladium(II) bound to a neutral, bidentate ligand which is covalently attached to silica gel. Because of the large equilibrium constant for the formation of the immobilized ligand–palladium complex, most anions are incapable of removing the $Pd^{2+}$ from the ligand. Being bidentate, the ligand–palladium complex still has two coordination sites available for binding anions (see Fig. 1). Because the complex has a 2+ charge, anions must remain with the palladium to maintain electrical neutrality. This procedure thus combines the selectivity of anion–metal cation coordination chemistry with the convenience of col-

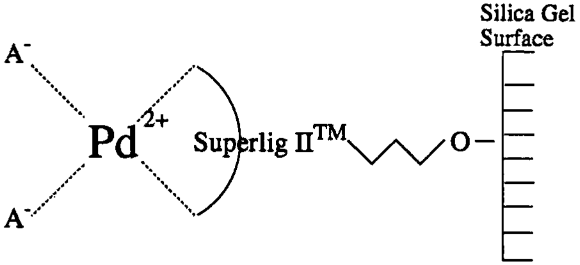

FIG. 1. SuperLig II–$Pd^{2+}$–anion ($A^-$) complex. SuperLig II may be obtained from IBC Advanced Technologies, Inc., Provo, Utah.

umnar separations. The column shows selectivities greater than 1000 among halide, hydroxide, and nitrate ions. Selectivity for hydroxide ion over nitrate ion is on the order of $10^8$. These high selectivities show the effectiveness of using coordination chemistry principles in designing anion separations. The ligand–$Pd^{2+}(I^-)_2$ complex is interesting because it has a deep purple color. A system is described here which uses the color of this complex as a basis for iodide analysis.

## EXPERIMENTAL

Anion binding columns were prepared by adding 1.0 g silica gel-bound ligand material (35–60 mesh SuperLig II, IBC Advanced Technologies, Provo, Utah, 0.3 mmol ligand per gram silica gel; worldwide composition of matter and process patents pending) to a 0.6-cm diameter column. Descriptions of some of the bound ligands which are tradenamed SuperLig have been given (*11*, *12*). The column was loaded with 50 mL of 0.01 *M* $Pd(NO_3)_2$ in 1 *M* $HNO_3$ and rinsed with 10 mL $H_2O$ to remove unbound $Pd^{2+}$. Next, a solution containing the anions of interest was pumped through the column until the inlet and outlet concentrations of the anions were equal. The column was then assumed to be in equilibrium with the loading solution. In some instances it was not possible to analyze for both anions in the load because of a large excess of one anion. In these cases the loading volume was increased by 50% from one replication to the next, and if the results did not differ by more than experimental error, the column was assumed to be in equilibrium with the loading solution. The column was stripped with 0.03 *M* NaOH because the $OH^-$ strongly coordinates with $Pd^{2+}$. The stripping solutions were then analyzed by ion chromatography (Dionex-AS6 column with potentiometric detection for $I^-$ and Dionex-AS4A column with conductivity detection for other anions). Before reuse, the columns were rinsed with 25 mL of 5 *M* $HNO_3$, loaded with 25 mL of 0.01 *M* $Pd(NO_3)_2$ in 1 *M* $HNO_3$, and rinsed with 25 mL of 5 *M* $HNO_3$ and 10 mL $H_2O$. In the nitrate/hydroxide experiments the column was rinsed with 1 L $H_2O$ before loading the column. The $HNO_3$ was used to make certain that the Pd was oxidized. The column was reloaded with $Pd^{2+}$ because a small amount of $Pd^{2+}$ was removed in the $OH^-$ strip. Other stripping agents, such as tartrate, may prove useful, but hydroxide ion is particularly convenient because it does not interfere with analysis. Loads were pumped through the column at about 10 mL/min, and strips were run under gravity flow (about 2 mL/min).

The $Pd^{2+}$–ligand system is somewhat different from traditional anion-exchange columns because two singly charged anions per exchange site are required to maintain electrical neutrality, as shown in Fig. 1. Thus, if two different anions, $A^-$ and $B^-$, are present in a system, the following equilibria must be considered:

$$\text{L–PdB}_2 + \text{A}^- = \text{L–PdAB} + \text{B}^- \tag{1}$$

$$\text{L–PdB}_2 + 2\text{A}^- = \text{L–PdA}_2 + 2\text{B}^- \tag{2}$$

where L is the silica gel-bound ligand which binds the Pd(II). The equilibrium constants ($\beta_n$) are

$$\beta_1 = \frac{[\text{B}^-][\text{L–PdAB}]}{[\text{A}^-][\text{L–PdB}_2]}, \quad \beta_2 = \frac{[\text{B}^-]^2[\text{L–PdA}_2]}{[\text{A}^-]^2[\text{L–PdB}_2]} \tag{3}$$

The fraction of sites on the $\text{L–Pd}^{2+}$ occupied by $A^-$ can be expressed as

$$f_{\text{A}^-} = \frac{[\text{L–PdAB}] + 2[\text{L–PdA}_2]}{2[\text{L–PdB}_2] + 2[\text{L–PdAB}] + 2[\text{L–PdA}_2]} \tag{4}$$

Substitution of the $\beta_1$ and $\beta_2$ expressions from Eq. (3) into Eq. (4) results in

$$f_{\text{A}^-} = \frac{\beta_1[\text{L–PdB}_2][\text{A}^-]/[\text{B}^-] + 2\beta_2[\text{L–PdB}_2][\text{A}^-]^2/[\text{B}^-]^2}{[\text{L–PdB}_2](2 + 2\beta_1[\text{A}^-]/[\text{B}^-] + 2\beta_2[\text{A}^-]^2/[\text{B}^-]^2)} \tag{5}$$

Rearranging yields

$$f_{\text{A}^-} = \beta_1(0.5 - f_{\text{A}^-})[\text{A}^-]/[\text{B}^-] + \beta_2(1 - f_{\text{A}^-})[\text{A}^-]^2/[\text{B}^-]^2 \tag{6}$$

Thus, to obtain $\beta_1$ and $\beta_2$, one can perform experiments at several ratios of the anions of interest and determine the fraction of sites occupied by $A^-$ in each experiment. Linear regression can then be used to calculate $\beta_1$ and $\beta_2$.

In the nitrate–hydroxide experiments, linear regression of the data gave negative values for $\beta_1$ and $\beta_2$. Three experiments at different ratios of nitrate and hydroxide ions yield three equations by substitution of the ratio of anions and $f_{\text{OH}^-}$ into Eq. (6). Two of the three equations were solved simultaneously. This yielded positive values for $\beta_1$ and $\beta_2$ in two of the three possible combinations of equations. The two sets of positive values for $\beta_1$ and $\beta_2$ were averaged to obtain final $\beta_1$ and $\beta_2$ values.

Because hydroxide ion is capable of binding to the ligand–palladium complex, pH must be controlled in all experiments. The column capacity was determined by loading the column with 0.02 *M* HBr and measuring the amount of $Br^-$ bound to the column. Because loading the column with 0.02 *M* HBr, 0.002 *M* HBr, 0.002 *M* HCl, or 0.002 *M* HI yielded approximately the same column capacity, it was assumed that an insignificant amount of $OH^-$ was binding to the palladium under these conditions. All of the experiments not concerned with binding $OH^-$ were performed in the ranges of acid and anion concentrations necessary to prevent hydroxide ion from binding to the column.

In some experiments, such as those involving hydroxide ion, only the other anion could be analyzed. The fraction of bound anions was calculated by using the column capacity determined in a separate run. In the experiments with a large excess of one anion in the loading solution, a 10-mL $H_2O$ rinse was used before stripping the column. The $H_2O$ rinse did not remove a significant amount of anions other than those in the column void volume. This was verified by experiments without the one anion in excess. Blank runs were performed by using a column which was not loaded with palladium so that effects of column void volume could be accounted for. All of the experiments were performed at least four times except for blank experiments which were done twice. The compositions of the loading solutions used to determine column selectivities were the following: 0.002 *M* HCl, 0.002 *M* HBr; 0.02 *M* HCl, 0.002 *M* HBr; 0.02 *M* HCl, 0.0002 *M* HBr; 0.001 *M* HI, 1 *M* NaCl; 0.25 *M* NaBr, 0.001 *M* HI; 0.5 *M* NaBr, 0.001 *M* HI; 0.02 *M* HBr, 0.0002 *M* HI; 0.001 *M* HCl, 1 *M* $HNO_3$; 0.001 *M* HBr, 1 *M* $HNO_3$; 0.01 *M* $HNO_3$ ($1 \times 10^{-13}$ *M* $OH^-$); 0.001 *M* $HNO_3$ ($1 \times 10^{-11}$ *M* $OH^-$); 0.04 *M* $HNO_3$ ($2.5 \times 10^{-13}$ *M* $OH^-$). All chemicals used were reagent grade and their sources were as follows: HCl (Fisher), HBr (Aldrich), HI (Mallinckrodt), $HNO_3$ (Mallinckrodt), $Pd(NO_3)_2$ (Aldrich), NaCl (EM Science), NaBr (Baker), and NaOH (Mallinckrodt).

An iodide analysis column was prepared by filling a 2.5-mm inside diameter polyethylene tube to a height of 1.5 cm with SuperLig II material which had 33% of its sites filled with $Pd^{2+}$. The SuperLig II material was loaded by stirring it in a solution with only enough $Pd^{2+}$ to load 33% of the column sites and was then screened so as to be 100 mesh. Solutions of iodide ion were then forced through the column by using a syringe (3–5 mL/min), and the length of the newly formed purple band was measured. Other anions were added to the iodide ion solution to test for possible interference.

## RESULTS AND DISCUSSION

Many metal ions form ion pairs selectively. Equilibrium constants for the ion pairing of Pd(II) with chloride, bromide, iodide, hydroxide, and nitrate ions are given in Table 1. Note that the constants for different anions involving the same reactions are usually orders of magnitude apart.

TABLE 1
Ion Pairing Constants for Halide, Hydroxide, and Nitrate Ion Interactions with Aqueous $Pd^{2+}$

| Equilibrium expression | Log *K* | Equilibrium expression | Log *K* |
|---|---|---|---|
| $K_1 = \frac{[PdCl^+]}{[Pd^{2+}][Cl^-]}$ | 4.47[a] | $K_1 = \frac{[PdBr^+]}{[Pd^{2+}][Br^-]}$ | 5.17[a] |
| $K_2 = \frac{[PdCl_2(aq)]}{[Pd^{2+}][Cl^-]^2}$ | 7.74[a] | $K_2 = \frac{[PdBr_2(aq)]}{[Pd^{2+}][Br^-]^2}$ | 9.42[a] |
| $K_3 = \frac{[PdCl_3^-]}{[Pd^{2+}][Cl^-]^3}$ | 10.2[a] | $K_3 = \frac{[PdBr_3^-]}{[Pd^{2+}][Br^-]^3}$ | 12.7[a] |
| $K_4 = \frac{[PdCl_4^{2-}]}{[Pd^{2+}][Cl^-]^4}$ | 11.5[a] | $K_4 = \frac{[PdBr_4^{2-}]}{[Pd^{2+}][Br^-]^4}$ | 14.9[a] |
| $K_4 = \frac{[PdI_4^{2-}]}{[Pd^{2+}][I^-]^4}$ | 24.5[a] | $K_1 = \frac{[Pd(OH)^+]}{[Pd^{2+}][OH^-]}$, | 13.0[b] |
| $K_1 = \frac{[Pd(NO_3)^+]}{[Pd^{2+}][NO_3^-]}$ | 0.08[c] | $K_2 = \frac{[Pd(OH)_2(aq)]}{[Pd^{2+}][OH^-]^2}$ | 25.8[b] |

[a] Data from Ref. *13*.
[b] Data from Ref. *14*.
[c] Data from Ref. *15*.

The order of binding strength will be $OH^- \gg I^- \gg Br^- > Cl^- \gg NO_3^-$. The silica-gel-bound ligand–palladium complex showed similar binding properties toward all of these anions as can be seen in Tables 2 and 3.

The constants in Tables 2 and 3 cannot be directly correlated with those in Table 1 because the complexes of interest contain a mixture of at least two types of ligands (Fig. 1). Perhaps the values for $\beta_2$ can be predicted by assuming that the anions add to the ligand–palladium complex as if they were the third and fourth anions of their kind adding to free $Pd^{2+}$. In this case, log $\beta_2$ would be predicted by the difference between log $(K_4/K_2)$ (see Table 1) for the different anions involved. In the case of the chloride–bromide system, this prediction method gives a value that is 0.4 log units too low (see Table 2). The predicted value is reasonably close to the actual value. Unfortunately, sufficient ion pairing data are not available to test this prediction method on the other systems studied.

The $\beta_2$ value might also be predicted by assuming that the anions add to the ligand–palladium complex as if they were the first and second anions adding to free $Pd^{2+}$. The predicted value for $\beta_2$ will be the ratio of the values of $K_2$ (see Table 1) for the anions of interest. The predicted value

TABLE 2
Selectivity Constants for the Interaction of SuperLig II[a] Ligand–$Pd^{2+}$ Complexes with Several Anions and Predictions for These Constants

| Anions | Log $\beta_1$ (Eq. 3) measured | Log $\beta_2$ (Eq. 3) measured | Log $\beta_2$ (Eq. 3) predicted by using $K_2$ data in Table 1 | Log $\beta_2$ (Eq. 3) predicted by using $K_4/K_2$ data in Table 1 |
|---|---|---|---|---|
| $A^- = Br^-$<br>$B^- = Cl^-$ | 1.3 ± 0.1 | 2.1 ± 0.1 | 1.7 | 1.7 |
| $A^- = I^-$<br>$B^- = Br^-$ | 2.6 ± 0.3 | 4.5 ± 0.2 | Not available | Not available |
| $A^- = OH^-$<br>$B^- = NO_3^-$ | 11.3 ± 1 | 19 ± 1 | 26[b] | Not available |

[a] Obtained from IBC Advanced Technologies, Inc., Provo, Utah; patents pending.

[b] The second nitrate constant was not available but was assumed to be approximately the value of the first constant.

for the chloride–bromide system is only 0.4 log units too low, but the value for the nitrate–hydroxide system is 7 log units too high. More data are needed before a good prediction procedure can be developed.

Although the selectivities of the ligand–$Pd^{2+}$ complex cannot be predicted quantitatively by the ion pairing constants in Table 1, it is obvious that the larger the difference between ion pairing constants for two anions, the larger the selectivity. Some of the systems studied were so selective that both $\beta_1$ and $\beta_2$ could not be determined. For the nitrate–chloride system, for example, even in 1000 times excess nitrate, the chloride filled about 70% of the column sites. An approximate value for $\beta_1$ was calculated

TABLE 3
Approximate Values[a] of $\beta_1$ (Eq. 3) for the Interaction of Several Anions with SuperLig II[b] Ligand–$Pd^{2+}$ Complexes in Highly Selective Systems

| | Log $\beta_1$ (Eq. 3) |
|---|---|
| $A^- = NO_3^-, B^- = Cl^-$ | −2.7 |
| $A^- = NO_3^-, B^- = Br^-$ | −3.1 |
| $A^- = Cl^-, B^- = I^-$ | −2.9 |

[a] Values are approximate because $\beta_2$ was assumed to be negligible.

[b] Obtained from IBC Advanced Technologies, Inc., Provo, Utah; patents pending.

by assuming $\beta_2$ to be negligibly small. Approximate values for $\beta_1$ in these cases are given in Table 3.

Selectivities for iodide over nitrate were not determined because the iodide ion is too easily oxidized in the large excess of nitrate ion which is necessary to determine selectivity. Halides versus hydroxide could not be studied because of the difficulty of maintaining the column pH above 3. Buffers could not be added because the anions in such buffers are capable of binding to $Pd^{2+}$.

Ion-exchange selectivities ($\alpha$) are defined as follows:

$$\alpha = \frac{A_{resin}\,[B]}{B_{resin}\,[A]}$$

where $A_{resin}/B_{resin}$ is the ratio of the amounts of A and B absorbed by the resin. The concentrations refer to the solution phase. There is no way to make a direct comparison between anion-exchange selectivities and the values of $\beta_1$ and $\beta_2$ given in Table 2 because selectivities for the ligand–palladium–anion complex are dependent on two binding constants. To compare selectivities of the ion-exchange and ligand–palladium–anion systems, selectivities were determined for the ligand–palladium complexes which are valid only in 1000-fold excess of one ion over another. This ratio of anions was dictated by the experimental conditions used to determine $\beta_1$. When only $\beta_1$ could be determined, the selectivity was taken directly from the $\beta_1$ experiment which was performed in 1000-fold excess of one anion. Comparisons of the selectivities using the two systems are given in Table 4. Generally, the ligand–palladium complex is more selective than ion exchange by several to many orders of magnitude. In some cases, even the order of selectivity is reversed. This high selectivity demonstrates how highly specific systems can be designed from a knowledge of the magnitude of the energy of intermolecular interactions. This information allows large recognition factors to operate compared to the simple charge–charge interactions present in ion exchange.

As can be seen in Tables 2 and 3, the ligand–palladium complex is highly selective for iodide ion over bromide and chloride ions. This, along with the fact that the $L\text{–}PdI_2$ complex is a deep purple color, suggested using a SuperLig II–$Pd^{2+}$ column for $I^-$ analysis.

Iodide analysis columns performed reasonably well, but they have some limitations. The length of the purple colored band is proportional to the amount of solution passed through the column, but it is somewhat concentration-dependent. This is shown in Fig. 2 where band length is seen to vary linearly with the amount of iodide ion added but the slope of the line is a function of iodide ion concentration. When iodide concentrations

TABLE 4

Comparison of Typical Ion-Exchange Selectivities with the Selectivities of SuperLig II[a] Ligand–$Pd^{2+}$–Anion Complexes[b]

| Selectivity | Ion-exchange selectivity[c] | SuperLig II–$Pd^{2+}$ |
|---|---|---|
| $Cl^-/NO_3^-$ | 0.263 | 2100[d] |
| $Br^-/NO_3^-$ | 0.737 | 3500[d] |
| $Br^-/Cl^-$ | 2.8 | 10[e] |
| $I^-/Cl^-$ | 8.7 | 2600[d] |
| $I^-/Br^-$ | 3.1 | 200[e] |
| $OH^-/NO_3^-$ | 0.024 | $1 \times 10^8$ [e] |

[a] Obtained from IBC Advanced Technologies, Inc., Provo, Utah; patents pending.

[b] Selectivity of the SuperLig II–$Pd^{2+}$–anion complex is valid only when the second anion listed is in a 1000-fold excess.

[c] Data from Ref. *3*.

[d] SuperLig II–$Pd^{2+}$ selectivity was determined experimentally.

[e] SuperLig II–$Pd^{2+}$ selectivity was calculated from the constants in Table 2.

drop below 1 ppm, there is no distinct end to the purple band. This limits the concentration range for useful application of the column to systems above 1 ppm $I^-$.

Other anions can interfere with the iodide ion determinations. Using 10 ppm $I^-$, nitrate interferes with the analysis at concentrations of about 0.01 *M*. This may be a kinetic effect or the $I^-$ may be oxidized by the nitrate ion. The selectivity of the column is high enough that nitrate ion should not compete for $Pd^{2+}$ sites at this concentration. Bromide and chloride ions at concentrations of about 0.01 *M* also begin to interfere with 10 ppm $I^-$ analysis. This interference may be due to competition for $Pd^{2+}$ sites or to kinetic difficulties or both.

The analytical column is convenient and easy to use, but it suffers from interferences which may render it impractical for most applications. The range of $I^-$ concentration which may be measured is also a limiting factor but this might be improved with changes in column diameter, mesh size, and flow rate.

The usefulness of the ligand–palladium complex for anion separations need not be limited to the anions discussed in this article. For example, many carboxylates of biological interest show significant differences in their ion pairing constants with metals (*13*) which may prove useful in analytical separations. The metal in the metal–ligand complex need not be palladium, but several factors need to be considered along with ion pairing when designing a ligand–metal complex which can bind anions of interest. First, the complex should have sufficient thermodynamic stability that the metal is not removed from the column by the anions. Even though $Hg^{2+}$ shows

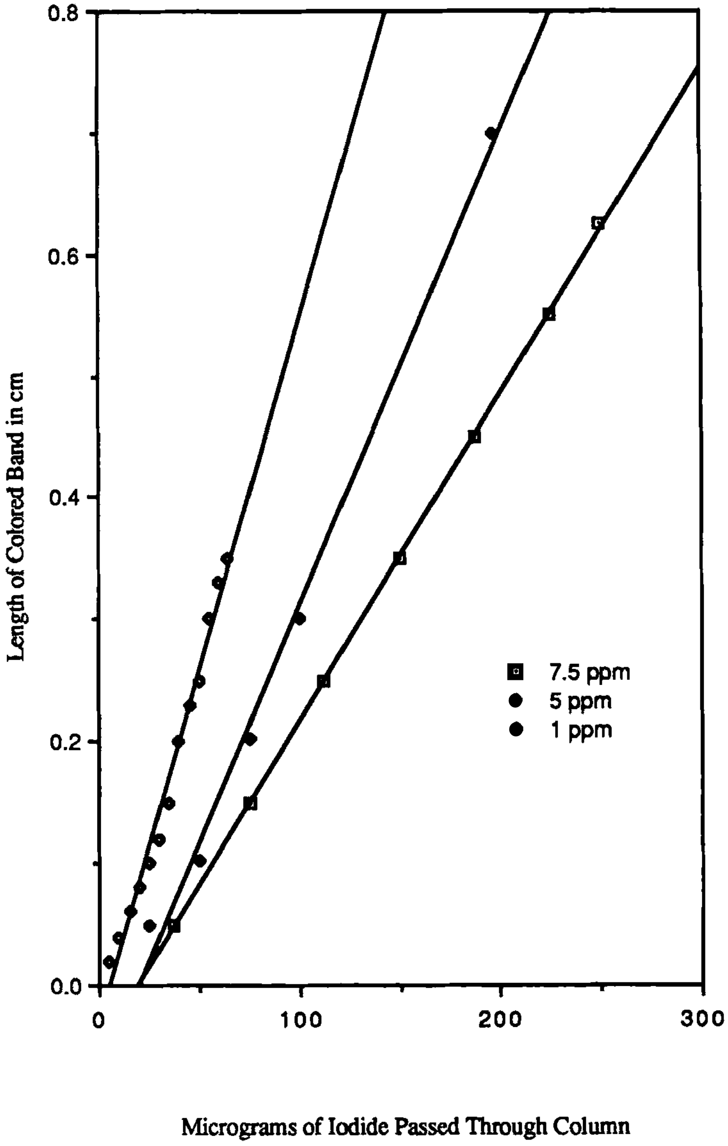

FIG. 2. Band length (length of column which is purple due to the SuperLig II–$Pd^{2+}$–iodide complex) versus amount of iodide ion added to a SuperLig II–$Pd^{2+}$ column at several iodide concentrations.

high selectivity in its ion pairing with halides, it cannot be used because halides are able to elute mercury from SuperLig II. Second, the pH of the system must be controlled because many metals will form hydroxide complexes even under mildly acidic conditions. In the case of the ligand–$Pd^{2+}$ complex, even in 0.01 *M* $HNO_3$, hydroxide ion occupies 45% of the column sites. Third, an appropriate regenerating reagent must be found. Strong acids may be slow regenerating agents because of the high selectivity of the column. In the case of the palladium column, 1 *M* $HNO_3$ will be slow in replacing halides. It is desirable to find a quick regenerating agent. The regenerant will need to bind strongly to the column, so it is useful to use a regenerant which can be protonated so it can be replaced easily in the presence of an acid which will prepare the column for reuse. In the case of the palladium column, hydroxide ion is not a good stripping reagent because it removes small amounts of palladium from the column and slowly dissolves silica. Other reagents such as carbonate ion and tartrate ion may prove to be useful regenerants. Further study is needed to develop regenerating agents, new ligand metal complexes, and chromatographic quality columns to fully demonstrate the usefulness of immobilized ligand– metal–anion complexes, but they do show good possibilities.

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