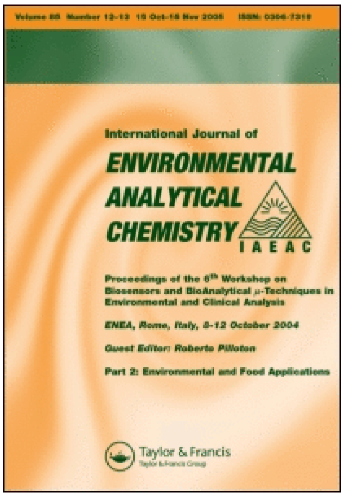

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Characterizing the Lead-Complexing Properties of Polyphosphate Water Treatment Products by Competing-Ligand Spectrophotometry Using 4-(2-Pyridylazo)Resorcinol

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CHARACTERIZING THE LEAD-COMPLEXING PROPERTIES OF POLYPHOSPHATE WATER TREATMENT PRODUCTS BY COMPETING-LIGAND SPECTROPHOTOMETRY USING 4-(2-PYRIDYLAZO)RESORCINOL

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A spectrophotometric titration method for characterizing Pb complexation by drinking-water-treatment chemicals has been developed. The colorimetric reagent is 4-(2-pyridylazo)resorcinol (PAR). The total PAR:total Pb ratio is kept low to allow measurable competition for Pb^{2+} between PAR and the polyphosphates. The data are analyzed by nonlinear regression involving the solution of the chemical equilibrium problem for each experimental point. Accurate results were obtained for both the concentration of nitrilotriacetic acid (NTA) (a test ligand) and the stability constant of PbNTA. The accuracy of the method is a function of the ligand concentrations and the stability constants. Estimates of the accuracy of the experimentally determined values of Log *K* and Log (total ligand concentration) as functions of the values of the parameters are presented.

Drinking water has been estimated to contribute from 5 to 30 percent of the total human exposure of the toxic metal Pb.[1] Lead is mainly introduced into drinking water through corrosion of solder, brass plumbing fixtures, and Pb pipes (in older buildings).[2] Regulations have been proposed[1] to minimize Pb solubility by controlling the pH and alkalinity of drinking water, thereby limiting the solubilities of Pb carbonates and hydroxide-carbonates. However, Pb solubility in domestic plumbing systems may be affected by other water-treatment practices. Polyphosphate-based water treatment products are added to potable waters by many water utilities to alleviate aesthetic water quality problems, including "red water" (oxidation of Fe(II) and precipitation of $Fe(OH)_3$)[3] and scale deposition (precipitation of $CaCO_3$ and other slightly soluble salts). Polyphosphates may also form strong complexes with toxic metal ions, including Pb^{2+}. Complexation may enhance the solubility of Pb introduced by corrosion and, therefore, increase the amount of Pb consumed through drinking water. The method described in this paper was developed to characterize Pb^{2+} complexation by commercial polyphosphate water-treatment products to predict their potential effects on Pb solubility in domestic plumbing systems.

It was necessary to study Pb^{2+} complexation under typical drinking water conditions, including pH ($7<pH<9$), major ion concentrations ($1\,mM\,Ca^{2+}$), product dose (typically $1\,mg\,L^{-1}$ total P), and total Pb concentration (less than

$200\,\mu g\,L^{-1}$ or approximately $1\,\mu M$ in corrosion situations). Under these conditions many methods for Pb speciation are not applicable. For example, the Pb ion-selective electrode only shows a Nernstian response for total Pb concentrations greater than 1×10^{-5} M. Anodic stripping voltammetry (ASV) is sensitive enough to determine Pb speciation under these conditions. However, the shift in ASV peak potential is a function of the product of the ligand concentration and the stability constant. ASV cannot be used to determine both parameters. When both the ligand concentration and the stability constant are unknown, ASV is most useful in confirming the results of independent speciation methods. ASV titrations were performed as part of the present research.

Competing-ligand spectrophotometry (CLS) using 4-(2-pyridylazo)resorcinol (PAR) has been used to study Eu(III) complexation by CO_3^{2-}.[4] PAR is one of the few water-soluble colorimetric reagents for the determination of Pb. The intense color of the reagent and of its Pb^{2+} complexes[5] suggest that a colorimetric method may have the necessary sensitivity to work in the Pb concentration range of interest. The stability constants of PAR-Pb^{2+} complexes are well known.[6] For these reasons it was felt that competing-ligand spectrophotometry may be feasible for the characterization of Pb^{2+} complexation by commercial water treatment products.

THEORY

The characterization of the Pb^{2+}-complexing properties of the commercial water treatment products entailed fitting the experimental results to a model that included two discrete ligands. The discrete ligand model has been used to describe metal complexation by natural waters.[7] The products tested may contain many ligands. However, the two-ligand model *describes* Pb^{2+} speciation (i.e., bound to polyphosphates or not bound) under the conditions of the experiment. The model parameters are not true thermodynamic stability constants or concentrations of actual species. The parameters are only applicable under the conditions under which the experiments were performed, including pH, ionic strength, and range of total Pb concentrations. Therefore, calculations of Pb speciation are only strictly valid under these conditions. However, such calculations are useful in estimating the effects of the water treatment products on Pb solubility.

The absorbance at wavelength λ is the sum of the absorbances of $HPAR^-$, $PbHPAR^+$, and $Pb(HPAR)_2^0$ (Eq. 1). The polyphosphates and their

$$A_\lambda = \varepsilon_{\lambda,\mathrm{HPAR}}[HPAR^-] + \varepsilon_{\lambda,\mathrm{PbHPAR}}[PbHPAR^+] + \varepsilon_{\lambda,\mathrm{Pb(HPAR)_2}}[Pb(HPAR)_2^0] \quad (1)$$

Pb^{2+} complexes are transparent in the wavelength range of interest. In Eq. 1, A and ε stand for absorbance and extinction coefficient, respectively. At the pH of the experiments (8.0) the predominant form of PAR is $HPAR^-$. Two complexes are formed with Pb^{2+}, $PbHPAR^+$ and $Pb(HPAR)_2^0$. Subscripts besides λ (e.g. $HPAR^-$) indicate species. For example, $\varepsilon_{\lambda,\mathrm{HPAR}}$ is the extinction coefficient of $HPAR^-$ at wavelength λ. Square brackets indicate concentrations. The extinction coefficients are determined as described in the experimental section. The concentrations of the various species are computed as described in the rest of this section.

The mass balance equations are given by Eqs. (2–5).

$$L_{1,\mathrm{tot}}=[L_1]+[PbL_1] \qquad (2)$$

$$L_2,\mathrm{tot}=[L_2]+[PbL_2] \qquad (3)$$

$$PAR_{\mathrm{tot}}=[PAR^{2-}]+[HPAR^-]+[H_2PAR^0]+[PbHPAR^+]+[Pb(HPAR)_2^0] \qquad (4)$$

$$Pb_{\mathrm{tot}}=[Pb^{2+}]+[PbOH^+]+[Pb(OH)_2^0]+[PbHPAR^+]$$
$$+[Pb(HPAR)_2^0]+[PbNO_3^+]+[PbL_1]+[PbL_2]. \qquad (5)$$

In Eqs. (2)–(5), L_1 and L_2 are the model ligands, while PbL_1 and PbL_2 are their Pb^{2+} complexes. $L_{1,\mathrm{tot}}$ and $L_{2,\mathrm{tot}}$ are the total concentrations of these ligands. The charges of the model ligands and their Pb^{2+} complexes are unknown. The mass action equations are given by Eqs. (6)–(12).

$$K_1=\frac{[PbL_1]}{[Pb^{2+}][L_1]} \qquad (6)$$

$$K_2=\frac{[PbL_2]}{[Pb^{2+}][L_2]} \qquad (7)$$

$$*\beta_1=\frac{[PbOH^+][H^+]}{[Pb^2]} \qquad (8)$$

$$*\beta_2=\frac{[Pb(OH)_2^0][H^+]^2}{[Pb^{2+}]} \qquad (9)$$

$$K_{PbHPAR}=\frac{[PbHPAR^+]}{[Pb^{2+}][HPAR^-]} \qquad (10)$$

$$K_{Pb(HPAR)_2}=\frac{[Pb(HPAR)_2^0]}{[Pb^{2+}][HPAR^-]^2} \qquad (11)$$

$$K_{\mathrm{PbNO_3}}=\frac{[\mathrm{PbNO_3^+}]}{[\mathrm{Pb^{2+}}][\mathrm{NO_3^-}]} \tag{12}$$

In Eqs. (6) and (7), K_1 and K_2 are the stability constants for PbL_1 and PbL_2, respectively. The other symbols have their usual meanings.

To fit the experimental data to the model, Eqs. (2)–(12) are solved and the resulting concentrations are substituted into Eq. (1). The model ligand concentrations and stability constants are treated as adjustable parameters. To test the method, a single well characterized ligand was used. In this case, Eqs. (3) and (7) were omitted. To include a mixed complex, Eq. (1) was modified by adding the term $\varepsilon_{\lambda,\mathrm{PbLHPAR}}[\mathrm{PbLHPAR}]$. The term [PbLHPAR] was added to Eqs. (2), (4), and (5). A mass action for the formation of the mixed complex was added to the system [Eq. (13)].

$$K_{\mathrm{PbLHPAR}}=\frac{[\mathrm{PbLHPAR}]}{[\mathrm{Pb^{2+}}][\mathrm{L}][\mathrm{HPAR^-}]}. \tag{13}$$

EXPERIMENTAL SECTION

Reagents

The pH was buffered at 8.0 using N-(2-hydroxyethyl)piperazine (HEPES), a noncomplexing weak acid.[8] The ionic strength was adjusted to 0.1 eq L^{-1} using $NaNO_3$. Lead concentrations in reagents were reduced below the detection limit of square-wave anodic stripping voltammetry (1 nM) by MnO_2 sorption[9] or ion exchange using Chelex-100 (Bio-Rad). Samples of the polyphosphate-based water treatment products Aqua-Mag®, CalciQuest®, and C-5® were obtained from, respectively, Kjell Water Consultants, Inc., Beloit, WI; Waltron Ltd., Whitehouse, N.J.; and Calgon Corp., Pittsburgh, PA.* These products contain orthophosphate and linear polyphosphates ($Na_{n+2}P_nP_{2n+2}n\geqq 3$).

Procedures

Volumetric flasks were cleaned with chromatic acid cleaning solution, rinsed with deionized water, cleaned with 6 *N* HCl, and rinsed again. Occasionally the cleaning had to be even more rigorous as indicated by erratic absorbance readings. When necessary, the flasks were cleaned with a 3:1 mixture of concentrated H_2SO_4 and HNO_3, rinsed, filled with hot (80 °C) 6 *N* HCl, allowed to stand for 15 minutes, and rinsed.

The procedure for determining the complexing properties of water treatment products is as follows. A solution containing PAR (10 μM for Aqua-Mag and C-5, 2.5 μM for CalciQuest), 0.001 M $CaCl_2$, 0.1 M $NaNO_3$, 0.01 M HEPES, and the water treatment product diluted to its typical dose (1×10^{-5} for Aqua-Mag and

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*The use of trade names does not imply endorsement by the Illinois State Water Survey.

C-5, 2.5×10^{-6} for CalciQuest) was prepared and the pH adjusted to approximately 5.0. The solution was then sparged for one hour to reduce the dissolved CO_2 concentration. The pH was then adjusted to 8.0 ± 0.02 using CO_2-free NaOH. This procedure has been shown to reduce the total inorganic carbon concentration to less than 1 μM,[10] thereby avoiding interference from Pb carbonate complex formation. The solution was immediately added to 50 mL volumetric flasks, filling to the mark. Lead standard solutions were added to produce Pb concentrations in the range of zero to twice the PAR concentration (i.e. a batch titration). Each set of 14 solutions included duplicates of three Pb concentrations. The contents of the flasks were mixed and at least 15 minutes was allowed for equilibration. Absorbances were read at 410 nm and 510 nm, the wavelengths of maximum absorbance for $HPAR^{-1}$ and its Pb^{2+} complexes, respectively.[5] For 10 μM PAR, 1-cm cuvettes were used. For 2.5 μM PAR, 4-cm cuvettes were used.

The procedure for determining the extinction coefficients of $PbHPAR^+$ and $Pb(HPAR)_2^0$ was the same as the general procedure except that there was no polyphosphate in the solution. To determine the extinction coefficients of $HPAR^-$, the solution contained no Pb^{2+} or polyphosphates and it was not sparged. The total PAR concentration was varied systematically in successive determinations.

The procedure for the differential-pulse ASV experiments was essentially that of Van den Berg.[11] The total Pb concentration was 1×10^{-7} M to avoid precipitation of $Pb(OH)_2$.

Data Analysis

The extinction coefficients of $HPAR^{-1}$ were computed using linear regression. To determine the extinction coefficients of $PbHPAR^+$ and $Pb(HPAR)_2^0$, the concentrations of $HPAR^-$, $PbHPAR^+$, and $Pb(HPAR)_2^0$ were first computed for the Pb-PAR solutions using the chemical equilibrium program TITRATOR.[12] The extinction coefficients were then computed using multilinear regression.

The complexation parameters of the polyphosphate products were determined by minimizing χ^2 in Eq. (14) using the simplex method.[13]

$$\chi^2 = \sum_i [(A_{410,i} - A_{410,i,\mathrm{comp}})^2 + (A_{510,i} - A_{510,i,\mathrm{comp}})^2] \tag{14}$$

In Eq. (14), the subscript "comp" indicates a computed quantity. The summation is over all data points. Standard deviations of the complexation parameters were estimated from the final simplex by the method of Phillips and Eyring.[14,15] The chemical-equilibrium subroutine was based on the method outlined by Taylor *et al.*[16] Routines for solving linear systems and inverting matrices were taken from Press *et al.*[17] Precipitation of $Pb(OH)_2$ could be either allowed or disallowed. The curve fitting program was written in Turbo Pascal (Borland) to run on an IBM PC. Stability constants were taken from Martell and Smith.[6,18]

RESULTS AND DISCUSSION

The method described in the present work differs from that of Thompson and

Table 1 Extinction coefficients of PAR and its Pb complexes

	Wavelength (nm)	
	410	*510*
	Extinction coefficient $(cm^{-1}\,M^{-1})$	
$HPAR^-$	28026	970
$PbHPAR^+$	3261	29238
$Pb(HPAR)_2^0$	32519	30941

Table 2 Complexation parameters determined for a test case (10 μM NTA)

	Concentration		*PbNTA⁻ Stability constant*		*Mixed complex Stability constant*	
	Log NTA_{tot}	*SD*[a]	*Log K*	*SD*[a]	*Log K*	*SD*[a]
True or accepted value[b]	−5.00		11.34			
Experimental values	−5.03	0.01	11.85	0.90	18.95	0.97
	−5.01	0.01	11.51	0.14	18.24	0.17

[a] Standard deviation.

[b] True value of concentration. Accepted value of stability constant (6).

Byrne[4] in several respects. Thompson and Byrne[4] used PAR concentrations that were orders of magnitude higher than the Eu concentrations to prevent precipitation of Eu. Under these conditions the concentration of $HPAR^-$, the predominant form of PAR at neutral pH values, would be essentially constant. For typical doses of water treatment products, there may not be significant competition between the polyphosphates and PAR for Pb^{2+} ions under high PAR solution concentration conditions. Therefore, in the present work, PAR concentrations similar to the polyphosphate ligand concentrations were used. The Pb concentrations were varied from one tenth to twice the PAR concentration. The relative concentrations of $HPAR^-$, $PbHPAR^+$, and $Pb(HPAR)_2^0$ changed considerably over the course of a titration. As a result, the data analysis procedure of the present work differs from that of Thompson and Byrne.[4]

The extinction coefficients of $HPAR^-$ and its Pb^{2+} complexes are listed in Table 1. The values agreee with values inferred from spectra of PAR and Pb-PAR complexes.[5] The spectrum of $Pb(HPAR)_2^0$ in reference 5 is for a fairly narrow range of wavelengths centered around the peak at 510 nm. The $Pb(HPAR)_2^0$ complex actually has a higher extinction coefficient at 410 nm, the maximum wavelength for free $HPAR^-$, than $HPAR^-$.

The method described in the present communication was tested by titrating a 1.0×10^{-5} M nitrilotriacetic acid (NTA) solution. The results are shown in Table 2. Duplicate titrations gave ligand concentrations and stability constants that agreed well with the true values. It was necessary to include a mixed complex to fit the data.

A titration of one of the polyphosphate water treatment products (Aqua-Mag®)

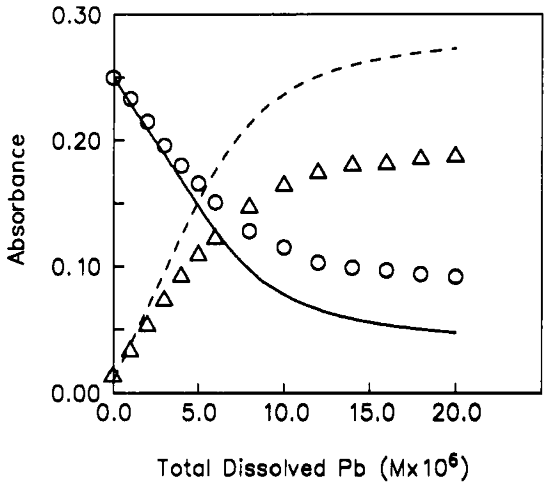

Figure 1 Comparison of titration of 1×10^{-5} M PAR and 1×10^{-5} M PAR+Aqua-Mag® diluted 1:10^5. Titrant is Pb^{2+}. —— 410nm, PAR. ○ 410nm PAR+Aqua-Mag. --- 510nm, PAR. △ 510nm PAR+Aqua Mag.

Table 3 Parameters for formation of lead complexes for polyphosphate water treatment products determined by competing ligand spectrophotometry

Product	*Dilution* ($\times 10^5$)	*Stability constants*				*Ligand concentrations*			
		Log K_1	*SD*[a]	*Log K_2*	*SD*[a]	*Log L_1*	*SD*[a]	*Log L_2*	*SD*[a]
Aqua-Mag	1.0	9.22	1.15	5.55	0.23	−6.49	0.24	−4.61	0.17
CalciQuest	1.0	10.07	0.21	4.94	0.13	−6.09	0.01	−3.95	0.12
	1.0	10.15	0.28	5.16	0.25	−6.01	0.06	−4.20	0.19
	0.1	9.78	0.42	7.41	0.37	−6.20	0.07	−5.98	0.07
C-5	1.0	10.47	0.08	6.68	0.07	−5.51	0.02	−4.64	0.05
	1.0	9.83	0.33	7.01	0.58	−5.34	0.15	−4.90	0.28

[a] Standard deviation.

is shown in Figure 1. The product was diluted by a factor of 1×10^{-5}, a value typically used to treat potable water according to promotional literature from Kjell Water Consultants. The pH (8.0) and Ca concentration (1 mM, 40 mg L^{-1}) were typical of potable water. The PAR concentration was 1.0×10^{-5} M. A titration of PAR under the same conditions (pH, Ca concentration, ionic strength, PAR concentration) is shown for comparison. In the solutions containing Aqua-Mag, absorbances at 410 nm were greater and absorbances at 510 nm were less than in the solutions containing no polyphosphates. The data shown in Figure 1 are consistent with successful competition of the polyphosphates with $HPAR^-$ for Pb^{2+} ions. Similar results were obtained for the other products. The results of the curve fitting for the three products are listed in Table 3. The results were

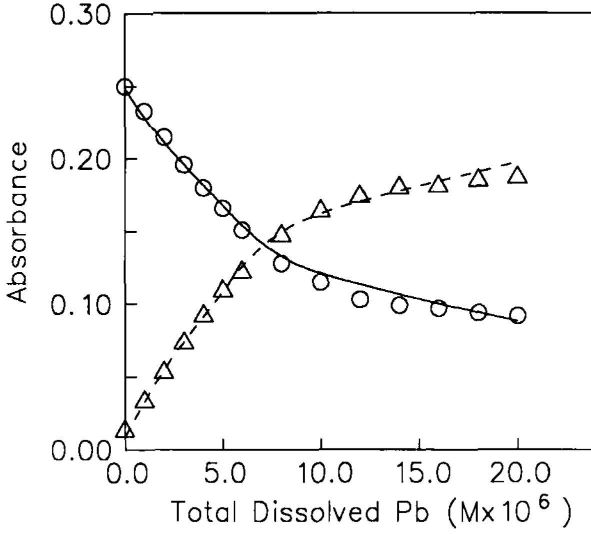

Figure 2 Comparison of titration of 1×10^{-5} M PAR + Aqua-Mag® diluted 1:10^5 with two-ligand model of the titration. ○ 410 nm observed, —— 410 nm model, △ 510 nm observed, --- 510 nm model.

reproducible. Some of the standard deviations of the parameters may seem large. However, the parameters were often highly correlated ($r \sim -1$). Therefore, propagated errors in computed species concentrations are smaller than may be expected from the standard deviations. The two-ligand model of the titration shown in Figure 1 is shown in Figure 2. The model fits the data very well. There was no apparent mixed complex formation in the polyphosphate-PAR solutions.

The ASV experiments confirmed that the polyphosphate water treatment products form complexes with Pb^{2+}. The titration curves had some of the features predicted by ASV theory. At low ligand concentrations (high product dilutions) the peak potential was constant. At high ligand concentrations the peak potential decreased linearly with the logarithm of the product dilution (ligand concentration). However, the slopes of the linear parts of the titration curves were significantly less (95% confidence level) than the theoretical value of -29 mV (log dilution factor)$^{-1}$. The reason for this may have been adsorption of the polyphosphates on the Hg electrode.

For the present method to work, there must be significant competition between a ligand or set of ligands and $HPAR^-$ for Pb^{2+} ions. That is, there must be measurable changes in absorbance. The accuracy of the method therefore depends on the total PAR concentration and the concentrations and stability constants of any other ligands in the sample. The limits of applicability of the method were tested by generating titration curves for a single ligand. The concentrations of the absorbing species $HPAR^-$, $PbHPAR^+$, and $Pb(HPAR)_2^0$ were computed using TITRATOR.[12] PAR concentrations of 1×10^{-5} M and 1×10^{-6} M were used. Ligand concentrations equal to, ten times, and one-tenth the PAR concentrations were used. Absorbances were calculated using the extinction coefficients from

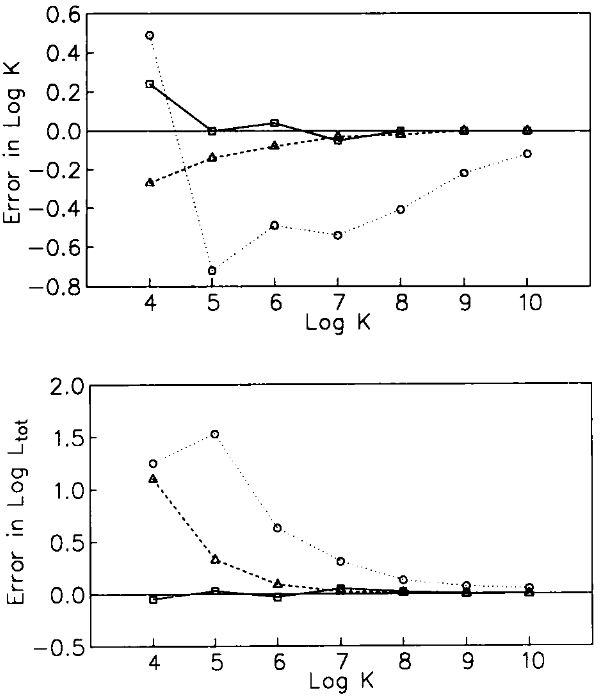

Figure 3 Dependency of errors in model parameters on the actual values of the parameters. PAR concentration is 1×10^{-5} M. (a) Error in stability constant. (b) Error in ligand concentration. –□– $L_{\mathrm{Tot}} = 1 \times 10^{-4}$ M, ---△--- $L_{\mathrm{Tot}} = 1 \times 10^{-5}$ M, ····○···· $L_{\mathrm{Tot}} = 1 \times 10^{-6}$ M.

Table 1. The path lengths were 1 and 10 cm for 1×10^{-5} M and 1×10^{-6} M PAR, respectively. The data were "ideal," i.e. no noise was added to the computed absorbances. The data were fit to a one-ligand model. The results are shown in Figures 3 and 4. In most cases the stability constant was underestimated and the ligand concentration was overestimated. Therefore, when computing Pb speciation, the effects of these errors may cancel to some extent. The greater the product of the stability constant and the total ligand concentration (L_{tot}), the greater the accuracy of the determination of both $\log K$ and $\log L_{\mathrm{tot}}$.

The values of the stability constant and ligand concentration needed to produce an error of less than a factor of two (0.3 log units) in both parameters at pH 8.0 are shown in Figure 5. The two lines on Figure 5 are for different total concentrations of PAR. A point on the graph represents a combination of stability constant and ligand concentration values. For a point below the line for 1×10^{-5} M PAR, the CLS method would yield a value of log K or log L_{tot} (or both) that differs from its true value by at least 0.3. For a point above the line, the errors in both parameters would be less than 0.3. For points between the 1×10^{-6} M and 1×10^{-5} M lines, CLS using 1×10^{-6} M PAR would produce results that are more accurate than CLS using 1×10^{-5} M PAR. For points below the 1×10^{-6} M line, CLS using PAR as the indicator ligand cannot accurately characterize Pb complexation.

In an actual titration the apparent ligand concentration should be approxima-

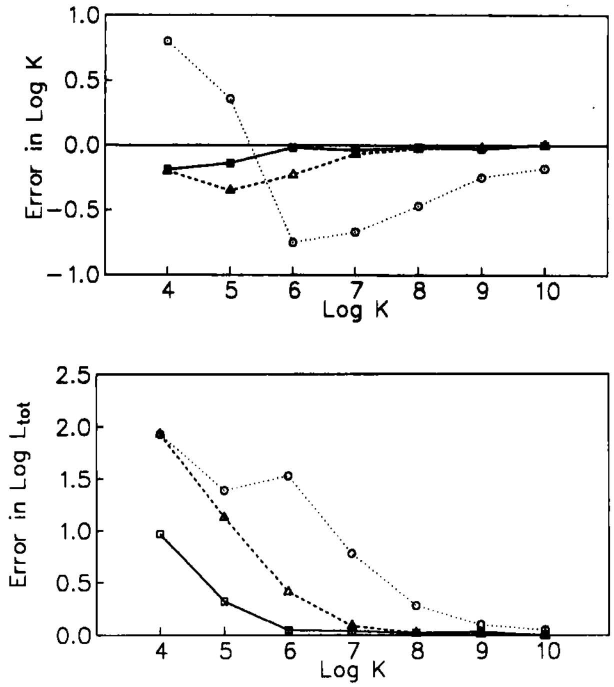

Figure 4 Dependency of errors in model parameters on the actual values of the parameters. PAR concentration is 1×10^{-6} M. (a) Error in stability constant. (b) Error in ligand concentration. -□- $L_{Tot}=1\times10^{-5}$ M, ---△--- $L_{Tot}=1\times10^{-6}$ M, ····○···· $L_{Tot}=1\times10^{-7}$ M.

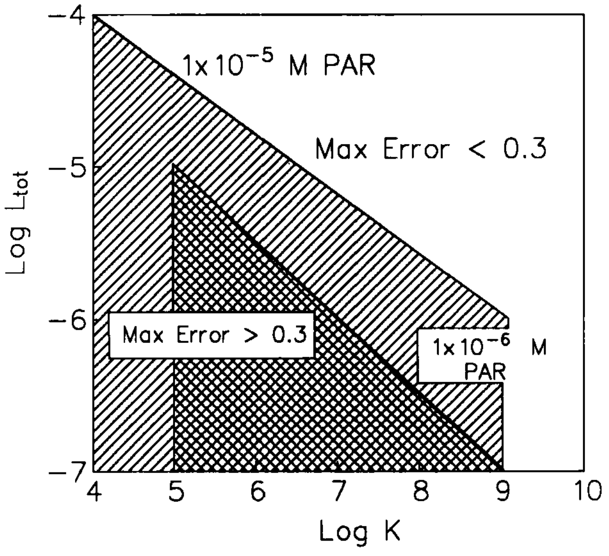

Figure 5 Values of stability constant and ligand concentration that give maximum errors in both Log K and Log L_{Tot} of 0.3.

tely equal to or greater than the PAR concentration for the greatest accuracy. If the model ligand concentration is found to be smaller than the PAR concentration by more than a factor of 10, another experiment should be performed using a lower PAR concentration.

Competing-ligand spectrophotometry using low PAR concentrations as described in the present work has many positive features when compared with other speciation methods. Unlike ion exchange or liquid–liquid extraction, it is a one-step procedure. Due to the large extinction coefficients of PAR and its metal complexes, the method is sensitive. For strong complexation, ligand concentrations as low as 1×10^{-7} M can be determined with fairly good accuracy. The instrumentation is simple. (Most laboratories have a UV-visible spectrophotometer.) PAR forms strong complexes with many metals, so the method is potentially applicable to many metals.

There are some possible disadvantages to the PAR-CLS method. Because PAR forms complexes with many metals, there may be interferences. For example, some polyphosphate water-treatment products contain Zn^{2+}. PAR-CLS cannot be used to study Pb^{2+} complexation by Zn-containing products because of the formation of Zn-PAR complexes. PAR-CLS would not work in anoxic natural waters having high Fe or Mn concentrations. PAR may form mixed complexes with other ligands in a water sample. Titration data must be checked for any evidence of mixed complex formation. If there is no competition from metal ions other than the one of interest and if mixed complex formation does not overwhelm complexation by the ligand of interest, then PAR-CLS may be a useful method for studying metal speciation in a variety of aqueous matrices.

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