A New Approach for Determining Stability Constants of Metal Ion Complexes in Aquatic Systems Based on Flow Injection-Ion Exchange-Flame Atomic Absorption Spectrometry Coupling

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A NEW APPROACH FOR DETERMINING STABILITY CONSTANTS OF METAL ION COMPLEXES IN AQUATIC SYSTEMS BASED ON FLOW INJECTION-ION EXCHANGE-FLAME ATOMIC ABSORPTION SPECTROMETRY COUPLING*

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A method based on ion exchange(IE)-atomic absorption spectrometry(AAS) coupled by flow techniques, allowing the determination of formation constants of, at least, the first species of complex systems, in aqueous solution, was developed.

The IE-AAS coupling reduces significantly the number of experimental steps in comparison with IE batch methods, resulting in an important increase in analytical rate. The method is simple both from experimental and computational points of view, making possible its utilization by workers without special expertise in the field of complex equilibria in solution. On the other hand, taking into account mainly the amount of hollow cathode lamps available to date, the developed procedure may be applied, within certain limitations, to the study of many systems whose features prevent the use of traditional approaches.

Keywords: ion exchange; absorption spectrometry; stability constants

INTRODUCTION

In concern with speciation of metal complexes in natural waters some authors advise determination of formation constants in identical experimental conditions

as those found in natural matrices[1]. In such conditions, the high dilution level severely limits the number of techniques that may be employed. Furthermore, metal concentrations of the order of $10^{-5} - 10^{-9}$ mol.L^{-1} demand very special cautions.

Workers in environmental chemistry need sometimes to determine stability constants for certain systems for which there is lack of data in the literature. On the other hand, they can find special situations where, for several reasons, traditional methods cannot be used. Thus, the search for new, simple and fast methodologies, including preconcentration techniques, always constitutes a necessity.

In view of all this, we decided to use an experimental device coupling ion exchange (IE) with atomic absorption spectrometry (AAS) by flow procedures, including a closed loop[2,3], as an interesting alternative considering the laboriousness of batch methods based on IE[4,5] and the number of metals that can be determined by AAS without any care with electrode reversibility, colour and/or heat evolution limitations. Thus, in the present work we developed such a device and tested it by determining formation constants for the first complex species of Cu (II) and Ni (II) complexes with some oxygen- and nitrogen-donor ligands. The obtained results are compared with those reported in the literature for the same systems.

The basic concept applied in this work lies mainly upon previously devised procedures concerning the determination of free Ni(II) and Cu(II) in natural and wastewaters[6-8] as well as for the evaluation of stability constants associated with metal-ion complexes through ion exchange-emission spectroscopy coupling[9].

EXPERIMENTAL

Solutions and Reagents

Polyethylene and class A volumetric glassware were employed throughout. All reagents were of analytical purity. As solvent, distilled and de-ionized water was used. Copper (II) and Nickel (II) nitrates were obtained by reaction of nitric acid with the corresponding basic carbonates. Stock solutions of these salts were standardized with EDTA, by using PAN and murexide as indicators.

Solutions of mineral acids (HNO_3, HCl and $HClO_4$) were standardized with sodium hydroxide solution (previously standardized with potassium hydrogen phthalate) and maintained in a polyethylene flask protected with a soda lime tube. The ligands solutions were used as buffer solutions, adjusted whenever possible to pH = 5.0 (to avoid metal ion hydrolysis) by adding sodium hydroxide solution (for lactic, malonic and oxalic acids) or nitric acid solution (for imidazole and ethanolamine). Stock solutions of $NaNO_3$ were standardized by evaporation of a known volume (at 120 °C) until constant weight.

As cationic exchanger, Dowex 50 W-X8 (100 mesh; Na^+ form) resin was used. After adequate washing, the resin was expanded in water for 24 hours, with subsequent elimination of fines, and sequentially treated in a glass column with 0.1 M EDTA, de-ionized water, 1 M HCl, de-ionized water, 4 M NaCl (up to pH ≈ 7) and de-ionized water until negative chloride test. The resin was stored under water in a closed polyethylene flask until use.

Resin column

Column characteristics are detailed in Figure 1. The resin conditioning before measurements must be made by repetition of the analyte injection-elution processes until reproducible AAS signals are obtained. The determination of the resin weight inside the column was carried out at the end of every study, after regeneration and suitable drying.
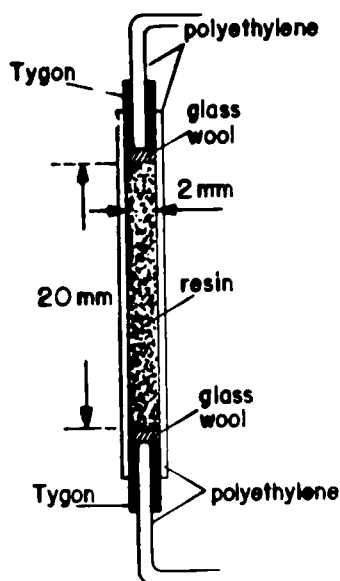

FIGURE 1 Resin column inserted within the flow device

Equipment

Potentiometric titrations were carried out with a "Metrohm" mod. 670 Titroprocessor. The volume measurements were made with "Metrohm" mod. 665 Dosimat

automatic burettes. Quantitation of Copper (II) and Nickel (II) eluted from the microcolumn were carried out with a Varian AA 1475 Atomic Absorption Spectrometer. For the flow circuit a six-way "Micronal" mod. B 332 - 11 peristaltic pump was used.

Calculation Procedure

For equilibria of mononuclear complex species formation,

$$Me + nL \leftrightarrow MeL_n$$
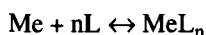
comprising a metal ion, Me, a ligand, L, and complex MeL_n, where $N \leq n \geq 1$ (the charges are omitted for simplicity), the corresponding overall stoichiometric formation constants of the MeL_n species (β_n) are defined as[5],

$$\beta_n = \frac{[MeL_n]}{[Me][L]^n} \tag{1}$$

where [ ] stands for molar concentration ($mol.L^{-1}$).

For the resin – metal – ligand equilibrium, the distribution coefficient of Me between the resin and the solution is defined as[4]:

$$K_d = \frac{\%Me \text{ in resin}}{\%Me \text{ in solution}} \cdot \frac{v}{m} \tag{2}$$

where v is the volume (ml) of sample solution in equilibrium with the resin and m is the weight (mg) of dry resin in equilibrium with the complex system solution. Thus if we know v, and C_{Me} (analytical metal ion concentration), m and the amount of metal retained by the column being determined, the corresponding K_d values may be calculated with eq. (2) for each metal ion-ligand mixture. Metal ion quantification can be made by comparison between solution absorbance (expressed as the corresponding peak height, if it is narrow enough) and the analytical curve, drawn from solutions of known concentrations, in identical experimental conditions.

It is assumed that the complex species are not adsorbed by the resin. This assumption has solid experimental basis[10]. On the other hand, the MeR species (formed by the resin's functional group and the metal ion) are in equilibrium with the metal ion solution. Thus, we shall have,

$$K_{d0} = \frac{(MeR)}{[Me]} \tag{3}$$

where K_{d0} is the metal distribution coefficient between resin and solution, in the absence of ligand. Here, (MeR) represents any quantity of MeR.

In the presence of a ligand, $K_{d0} = K_d$ and we shall have:

$$K_d = \frac{(MeR)}{[Me] + [MeL] + [MeL_2] + \ldots + [MeL_n]} \tag{4}$$

From eq. (1):

$$[MeL_n] = [Me]\beta_n[L]^n \tag{5}$$

By combining eqs. (3), (4) and (5):

$$\frac{(MeR)}{K_d} = \frac{(MeR)}{K_{d0}} + \frac{(MeR)}{K_{d0}}\beta_1[L] + \frac{(MeR)}{K_{d0}}\beta_2[L]^2 + \ldots + \frac{(MeR)}{K_{d0}}\beta_n[L]^n \tag{5}$$

If we multiply by $K_{d0} / (MeR)$ all terms of eq. (6), then,

$$\frac{K_{d0}}{K_d} = 1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n = F_0([L]) \tag{7}$$

where $F_0([L])$ is the well known Fronaeus' function[11]. The K_{d0} value may be determined by graphical extrapolation of the $1/K_d$ vs. C_L plot to $C_L = 0$, where C_L is the analytical ligand concentration. As, in principle, $[L]$ is unknown, preliminary β_n values may be computed from the $\{F_0([L]), C_L\}$ pairs, and then refined through iterative procedures[12].

Apparatus

The proposed flow device is schematized in Figure 2. The main idea is to introduce a closed loop including the resin column (column circuit) where the complex system solution once injected may attain physical and chemical equilibrium with the resin, before washing and elution. The device (detailed in Figure 3) contains two proportional commuters (CI and CII), made from acrylic resin, with three and two sections, respectively.
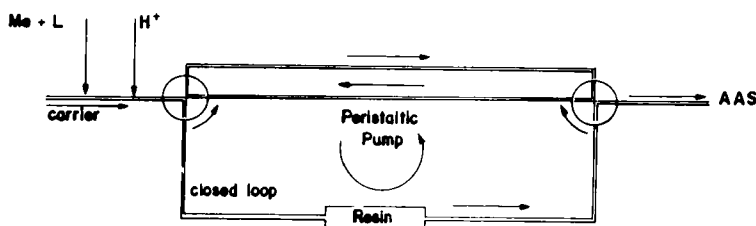

FIGURE 2 Flow Device: Simplified Diagram

The polyethylene tubing is 0,9 mm i.d.. The commuter CI has sampling and elu-
tion functions, whereas CII is used only to open and close column circuit. The
sampling loop (L1) and elution loop (L2) volumes are 0.653 mL and 2.732 mL,
respectively. These volumes as well as the column circuit one ($v = 1.968$ mL)
were determined by filling the respective loops with standardized sodium acetate
solution which, after carrying with de-ionized water for 5 minutes, was potentio-
metrically titrated with standard perchloric acid solution. Elution was carried out
with 1.5 M HNO_3 solution and carrying was performed with $NaNO_3$ solution of
the same ionic strength value as that of the complex system being studied.
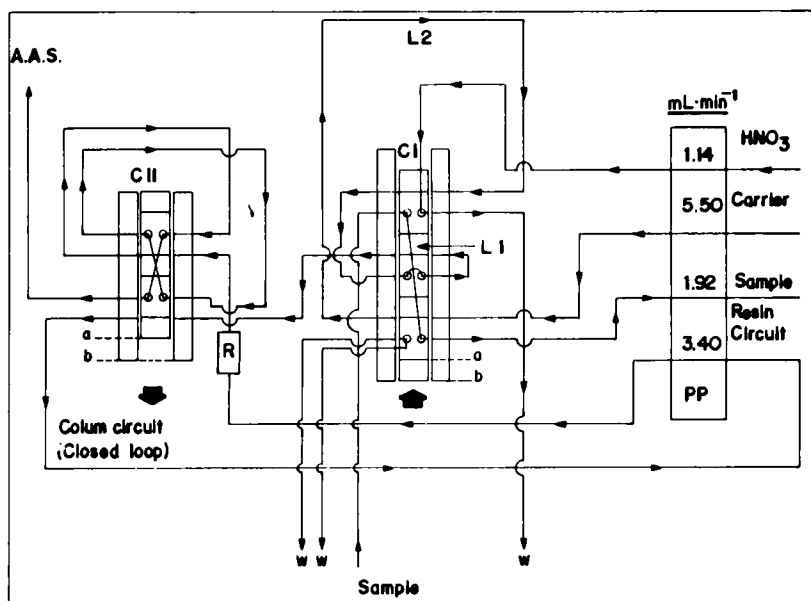
FIGURE 3 Detailed Flow Diagram. Each commuter has two possible positions L1, sample loop;
L2, eluent loop; R, resin column; W, waste; PP, peristaltic pump

Experimental Procedure

The necessary steps for obtaining the transient signal corresponding to each sam-
ple are described in Table I, along with the suitable positions of both commuters
and the corresponding times. The equilibrium time (between 2 and 4 minutes)
must be experimentally determined for each system. The measurements corre-
sponding to each sample were always performed in triplicate; the mean value
was generally considered for subsequent calculations. All operations were car-
ried out in a conditioned room at $25 \pm 1°C$.

TABLE I Flow Operation Steps

Step	Commuters' position	Time
1 - Carrying of L1 with sample solution and of L2 with carrier. Resin regeneration.	CI b and CII a	2 min.
2 - Sample injection (L1) in column circuit. Carrying of L2 with eluent	CI a and CII a	15 sec.
3 - Column circuit closing (for equilibrium attainment)	CI a and CII b	2-4 min.
4 - Resin washing with carrier	CI a and CII a	2 min.
5 - Resin elution (back to step 1)	CI b and CII a	2 min.

RESULTS AND DISCUSSION

Figure 4 shows the analytical signal for the calibration curve, obtained from standard $Cu(NO_3)_2$ solutions. A straight line was fitted to the h (peak height) *vs.* $[Cu^{+2}]$ points, as shown in the aforementioned figure, whose equation is:
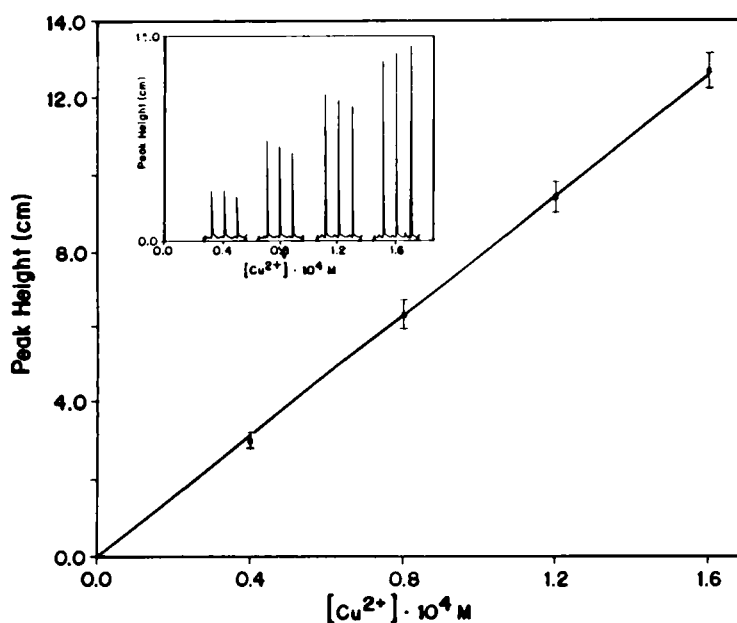
$h = 81,900 \, [Cu^{+2}]$ (8) (correlation coefficient = 0.995).

FIGURE 4 Calibration Curve Corresponding to $Cu(NO_3)_2$ Solutions. Inside Figure at upper left side: triplicate values for each of four Cu^{2+} concentrations. $I = 0.100$ M ($NaNO_3$), $t = 25 \pm 1°C$

The fiagram corresponding to metal-ligand mixtures (exemplified by the Cu^{2+}-lactate system) is represented in Figure 5. As we can see, there is a narrow-broad peak sequence. The broad ones (which were not used for quantitation purposes) correspond to total copper existent in solution, and the narrow ones, to total Cu^{+2} eluted from the column. By using eq. (8), $[Cu^{2+}]$ corresponding to each narrow peak may be determined.
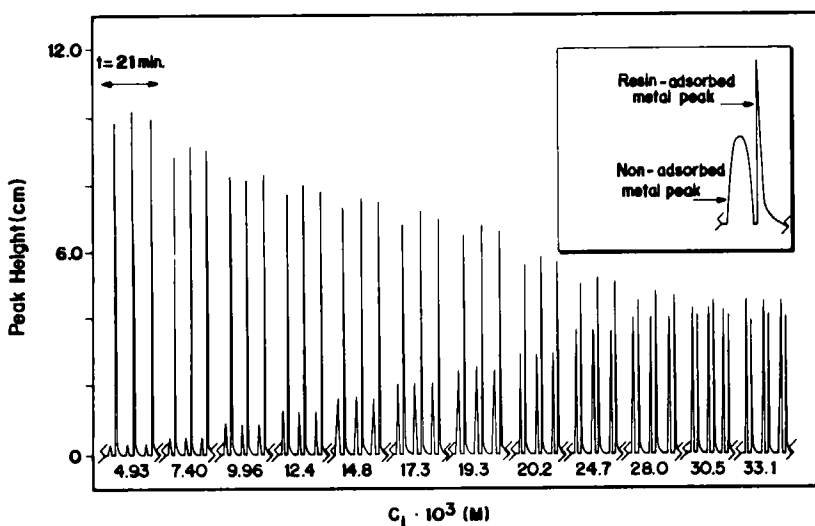

FIGURE 5 Fiagram for the Cu^{2+}-Lactate System. Each metal-ligand mixture was analysed in triplicate. $C_M = 1.60.10^{-4}$ M: I = 0.100 M ($NaNO_3$), t = 25 ± 1°C; pH = 5.5. Inside Figure at upper right side: expanded broad-narrow peaks couple

It is observed that as the total ligand concentration raises, the narrow peak heights decrease and those of the broad ones increase, making clearly apparent that competition between resin and ligand for metal ion[14] takes place. Detailed data for the Cu^{2+}-lactate system are found in Table II. The $1/K_{d0}$ value, extrapoled from $1/K_d$ *vs.* C_L plot is 0.45, so $K_{d0} = 2.2$. Knowledge of this value, leads to the $F_0(L)$ ones for each examined metal ion-ligand mixture via eq. (7).

From [F_0 ([L]), [L]] pairs, using a computer program based on iterative procedures, $\bar{n}$ (formation function) and [L] values were obtained, as well as the formation constants for the considered system:

$\log \beta_1 = 2.55 \pm 0.04$

$\log \beta_2 = 3.8 \pm 0.1$

Substituting these constants and the [L] values in eq. (7), the F_0 ([L])$_{calc.}$ ones, displayed in the last column of Table II, were obtained. As we see, there is a good agreement (compatibility) between experimental and calculated F_0 ([L]) data.

The other selected systems were studied in a similar way. In the present investigation we were only interested in the first complex species formation. Thus, sufficient ligand excess for the formation of all possible species in every system has not been introduced. For this reason, reliable data of formation constants were obtained only for β_1. The obtained results, together with those critically selected from the literature[13], are reported in Table III.

TABLE II Experimental and Calculated Data for the Cu (II) - Lactate System. I = 0.100 M (NaNO$_3$); t = 25 ± 1°C; pH = 5.5; C_{Me} = 1.60 × 10^{-4}mol.L^{-1} ; m = 7.9 mg; K_{d0} = 2.2; v/m = 0.25 ml.mg^{-1}

C_L (× 10^2 M)	h^* (cm)	% (MeR)	% (MeS)†	K_d	$1/K_d$	F_0 ([L])	$\bar{n}$ ‡	[L] (× 10^2 M)	$F_0([L])$ calc.
0.493	9.8	74.0	26.0	0.71	1.4	3.1	0.709	0.482	2.9
0.740	9.0	67.9	32.1	0.53	1.9	4.2	0.839	0.727	4.0
0.996	8.2	62.7	37.3	0.42	2.4	5.3	0.934	0.981	5.2
1.24	7.6	57.6	42.4	0.34	2.9	6.4	1.00	1.22	6.4
1.48	7.5	57.0	43.0	0.29	3.5	7.7	1.06	1.46	7.7
1.73	7.0	53.7	46.3	0.24	4.2	9.0	1.11	1.71	9.1
1.93	6.6	54.3	48.7	0.21	4.8	10.3	1.14	1.91	10.3
2.02	5.7	44.5	55.5	0.20	5.0	11.0	1.16	2.00	10.9
2.47	5.1	39.0	61.0	0.16	6.3	13.9	1.22	2.45	13.9
2.80	4.7	35.9	64.1	0.14	7.4	16.3	1.26	2.78	16.3
3.05	4.2	32.4	67.6	0.12	8.3	18.3	1.29	3.03	18.1
3.31	4.0	30.6	69.4	0.11	9.1	20.2	1.32	3.29	20.2

* mean values of triplicate determinations.
† stands for % Me in solution.
‡ formation function[5].

TABLE III Formation Constants for Binary Mononuclear Metal Ion Complexes. t = 25 ± 1°C; Ionic Strength (I) = 0.100 M (NaNO$_3$)

System	log $\beta_1{}^{abs.}$ ± σ^*	
	present work	literature[13]
Cu(II)-lactate	2.55 ± 0.04	2.54
Cu(II)-oxalate	4.79 ± 0.05	4.84 ± 0.01
Cu(II)-malonate	5.27 ± 0.04	5.04 ± 0.07
Cu(II)-ethanolamine	5.55 ± 0.05	5.7
Ni(II)-oxalate	3.65 ± 0.04	3.7‡
Ni(II)-malonate	3.30 ± 0.03	3.24 ± 0.06
Ni(II)-Imidazole	3.02 ± 0.04†	3.03 ± 0.04

* standard deviation.
† I = 0.200 M (NaNO$_3$).
‡ I = 1.00 M (NaClO$_4$).

The experimental values of conditional formation constants were converted to the corresponding absolute ones (independent of pH) through the following equation[15]:

$$\beta_1^{abs.} = \beta_1^{exp.}(1 + \beta_1^H[H] + \beta_2^H[H]^2 + ... + \beta_n^H[H]^n) \tag{9}$$

where β_n^H are the protonation constants for the ligands, taken from the literature[13].

In spite of good agreement between the present work and literature data, there are some limitations to the proposed method. First, the present method, being a competitive one, a reasonable compromise between the relative affinities of resin and ligand for metal ion should be maintained. The Dowex 50W-X8 resin used allows the study of complex systems only when log $\beta_1 < 6$. For this reason, it is necessary to choose suitable commercial resins or to synthesize them according to the actual necessities[16,17]. On the other hand, another limiting factor is the significant affinity of most cationic resins regarding the background electrolyte cation, present in the medium at high concentration as compared with that of the system's metal ion. Thus, only low ionic strength values can be fixed in these studies. A promising perspective seems to be the use of chellating type poly (dithiocarbamate) resins[18], able to adsorb ions like Fe(III), Cr(III), Ni(II), Cu(II), Pb(II), Co(II), Cd(II), Zn(II) and Mn(II), but not alkaline and alkaline earth metals, making their utilization possible in marine samples, among other applications.

Nonetheless, the method showed much higher analytical rate in comparison with the corresponding batch methods, described in the literature[4,5]. Furthermore, the device can be easily automated.

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