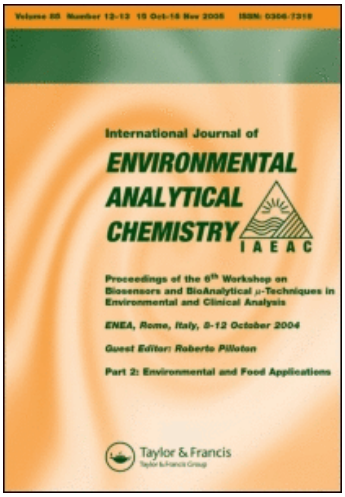

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SPECIATION OF CADMIUM(II) USING DONNAN DIALYSIS AND DIFFERENTIAL-PULSE ANODIC STRIPPING VOLTAMMETRY IN A FLOW-INJECTION SYSTEM

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A flow-injection/Donnan dialysis/differential pulse anodic stripping voltammetry system was developed for the determination of free cadmium concentrations, $[Cd^{2+}]$, in solutions containing organically complexed Cd(II). A small dialysis cell with a strong cation-exchange membrane separating the sample and the receiver channels, was equilibrated in a flow-injection system. The ionic strength of sample and receiver solutions was 0.1 M, with $NaNO_3$ as the bulk electrolyte. By determining a constant fraction of the Cd^{2+} associated with the membrane phase, $[Cd^{2+}]$ of the samples could be measured.

Experimentally determined $[Cd^{2+}]$ corresponded well with those calculated, using tabulated stability constants, when citric acid, nitrilotriacetic acid, and oxalic acid were added as ligands. Thus, negatively charged and uncharged complexes were excluded from the membrane. Using the experimental design presented, $[Cd^{2+}] > 5 \times 10^{-8}$ M could be determined, but there is a great potential for increasing the sensitivity of the method.

In solutions containing 1.0 μM Cd(II) and 200 mg fulvic acid/l, the inorganic fraction ($Cd^{2+} + CdNO_3^+$) decreased from 57% to 10% when the pH increased from 4.04 to 5.51. In a soil solution from an orthic podzol, having a high concentration of dissolved organic carbon (22.4 mM), the inorganic fraction constituted 53% of the total Cd(II) concentration.

KEY WORDS: Cadmium, speciation, organic ligands, fulvic acids, soil solutions.

INTRODUCTION

Metal speciation has been defined by Florence and Batley[1] as "the determination of the individual concentrations of the various chemical forms of the metal which together make up the total concentration in a sample". In natural waters, the free (hydrated) ion is often the most significant species, due to its biological availability[2,3] and its central role in e.g. solubility equilibria. Humic substances (HS), a series of acidic, yellow- to black-coloured polyelectrolytes originating from microbial and chemical transformation of plant material,[4] are generally the most important ligands in natural waters.[5] Due to the complexibility and the variability of these substances, the use of equilibrium calculations is very difficult. There is, consequently, a great need for sensitive and selective analytical speciation methods.

Differential-pulse anodic stripping voltammetry (DPASV) is a very attractive

speciation method because of its sensitivity. There are, however, also serious disadvantages. Firstly, surface-active compounds, like HS, may be adsorbed on the mercury electrode, thereby altering the deposition and stripping current in a complex way,[6] even when medium exchange is used.[7] Secondly, not only the initial free metal ion concentration is measured, because of a dissociation of complexes during the deposition step. A significant dissociation of Cu- and Pb-fulvic acid complexes has been reported.[8]

Recently, interest has been focussed on the possibility of using permselective cation-exchange membranes for metal speciation purposes (Donnan dialysis). Donnan dialysis was used by Cox and co-workers for enrichment and matrix normalization prior to analysis using atomic absorption spectroscopy[9–11] and DPASV.[12] A receiver solution of a high ionic strength was separated from a sample by a cation-exchange membrane, the initial transport rate of an ion being proportional to its concentration in the sample.[13] The dialysis was normally terminated after 30 min. The major disadvantage with this approach for metal speciation purposes is that only a kinetic discrimination between labile and non-labile species is possible. For example, a considerable dissociation of glycine and nitrilotriacetic acid (NTA) complexes with Cd(II), Cu(II), Pb(II) and Zn(II) has been reported.[14]

Not only anionic complexes (e.g. HS complexes) will be excluded by the membrane used in the present study, but also positively charged complexes like CuL_2^{2+} (L = ethylenediamine).[15] A study where the triphenyltin$^+$ ion and the Pb-phthalate^0 complex were excluded from a similar membrane supports these findings.[16] The high selectivity of this kind of membrane is thus based on both charge and size exclusion. Using a suitably designed analytical system it is possible to avoid the dissociation of labile complexes if cation-exchange equilibrium is attained between the sample and the receiver solutions. The distribution of cations at cation-exchange equilibrium has been described theoretically and verified experimentally by Blaedel and Haupert.[17] However, only a few studies using this approach have been published. Recently, Bourque and Guy[16] evaluated the possibility to use a tubular Nafion 811X cation-exchange membrane for metal speciation. In order to avoid adsorption to the membrane, 0.30 M $NaNO_3$ had to be added to the sample and receiver solutions.

The objective of this paper is to develop a speciation technique which takes advantage of the selective adsorption of the Cd^{2+} ion by a cation-exchange membrane. A small dialysis cell with a cation-exchange membrane separating the sample and the receiver channels was equilibrated in a flow-injection system. Since fresh sample was pumped through the dialyzer until no change in its composition occurred, the final equilibrium was related to the initial speciation of Cd(II) in the sample. Consequently, dissociation of labile complexes was avoided. The Cd^{2+} ions were detected by DPASV. The effect of electrolyte concentration on the distribution of Cd^{2+} between membrane and solution phases, and on the equilibration time of the dialyzer, was studied. The validity of the system was evaluated by measuring the Cd^{2+} concentration in samples containing well defined ligands such as citric acid, oxalic acid, and NTA. Finally, the Cd^{2+} concentration in spiked soil solutions was measured.

MATERIALS AND METHODS

Theory

If a sample solution containing Cd^{2+} and Na^+ is separated by a cation-exchange membrane from a solution containing Na^+ only (receiver), Cd^{2+} will permeate through the membrane to establish cation-exchange equilibrium. At cation-exchange equilibrium, the Cd^{2+} concentration, $[Cd^{2+}]$, will be the same on both sides of the membrane, provided Na^+ is present at an equal concentration in both sample and receiver, and $[Na^+] \gg [Cd^{2+}]$.[17] The heterogeneous equilibrium that represents the exchange between Cd^{2+} in the aqueous phase and Na^+ in the membrane phase (indicated by subscript *m*) exist on both sides of the membrane:

$$Cd^{2+} + 2Na_m \rightleftharpoons Cd_m + 2Na^+. \tag{1}$$

The thermodynamic equilibrium constant (K_{Na}^{Cd}) for the exchange reaction is:[18]

$$K_{Na}^{Cd} = \frac{(Cd)_m (Na^+)^2}{(Cd^{2+})(Na)_m^2} \tag{2}$$

where the parentheses represent activities of the ions in the two phases. Since the activities of Cd^{2+} and Na^+ must be identical throughout the membrane at cation-exchange equilibrium, Eq. (2) will have the same numerical values at both sample and receiver sides. By approximating activities in Eq. (2) by concentrations and single ion activity coefficients (γ), and rearranging, we obtain:

$$[Cd^{2+}] = \left(\frac{[Na^+]^2 \gamma_{Na^+}^2 \gamma_{Cd_m}}{[Na]_m^2 \gamma_{Na_m}^2 \gamma_{Cd^{2+}} K_{Na}^{Cd}} \right) [Cd]_m. \tag{3}$$

If the following conditions are fulfilled:

(i) $[Na^+]_{sample} = [Na^+]_{receiver}$;

(ii) $[Na^+] \gg [Cd^{2+}]$;

(iii) $[Na]_m \gg [Cd]_m$

and single ion activity coefficients can be considered as constants (constant ionic strength), then:

$$[Cd^{2+}]_{sample} = [Cd^{2+}]_{receiver} = \beta [Cd]_m \tag{4}$$

where β is a conditional constant related to a given Na^+ concentration. A prerequisite is that a third ion in the sample does not significantly compete with Na^+ and Cd^{2+} for the exchange sites.

If a sample is "swamped" with a simple electrolyte, e.g. $NaNO_3$ ($NaNO_3$ added in excess), to give the same concentration as in the receiver solution, it is possible to determine $[Cd^{2+}]$ in the sample in two different ways: either by determining $[Cd^{2+}]$ in the receiver solution or by determining all or a constant fraction of $[Cd]_m$. The cation-exchange membrane must exclude other Cd(II) species, if present. The first method was applied by Bourque and Guy,[16] using a Nafion 811X tubular cation-exchange membrane; 0.30 M $NaNO_3$ was the supporting electrolyte. The second method, which is adopted in the present study, was used by Cantwell and co-workers.[19–21] They swamped samples with 0.10 M $NaNO_3$ and equilibrated them with a Na^+-saturated strong acid cation-exchange resin. The amount of metal absorbed by the resin was assumed to be proportional to the free metal ion concentration. This method has also been used for samples containing natural 'swamping electrolytes', like soil extracts[22] and sea waters.[23]

The Flow-Injection System

A sample was pumped through the dialyzer on one side of the cation-exchange membrane in a flow-injection system (Figure 1a) using a flow rate of 1.1 ml/min. On the opposite side, there was a receiver solution with the same ionic strength (I) as the sample, but with a stopped flow. During the equilibration of the dialyzer, the 10 μl loop was filled with a standard solution (receiver solution spiked with 10 μM $Cd(NO_3)_2$). The content of the loop was subsequently pumped through the flow cell (0.17 ml/min) and Cd^{2+} ions were plated into the mercury film electrode (Figure 1b). Stripping was made into the receiver solution at a higher flow rate (0.9–1.0 ml/min).

The sample flow was stopped at cation-exchange equilibrium, e.g. after 31 min at an ionic strength of 0.1. Receiver solution was then pumped with a low flow rate (0.17 ml/min) through both channels (Figure 1c). The equilibrated solution from the receiver channel together with the receiver solution that had passed the equilibrated cation-exchange membrane was passed through the electrochemical cell, where the mercury film electrode was kept at a sufficiently negative voltage for plating of the Cd^{2+} ions. The amount of Cd^{2+} originating from the receiver channel normally constituted a very small fraction of the total amount of Cd^{2+} plated.

In order to avoid stripping into a solution contaminated with Cd^{2+} leached from the membrane, the valves were switched into the position of Figure 1d at the end of the plating step. Stripping was finally made into the receiver solution at a flow rate of 0.9–1.0 ml/min.

After the sample had been analyzed, another standard was injected. The response of the sample was related to the mean response of the two standards. Between two samples, the cation-exchange membrane was cleaned on-line by pumping a washing solution (flow rate, 1.1 ml/min) through the sample channel of the dialyzer for 10 min (same as Figure 1b, except that washing solution was used instead of sample).

The cation-exchange membrane was a sulphonated fluorocarbon (Teflon) membrane (RAI P-1010) obtained from RAI Research Corp., Hauppauge, NY, U.S.A.

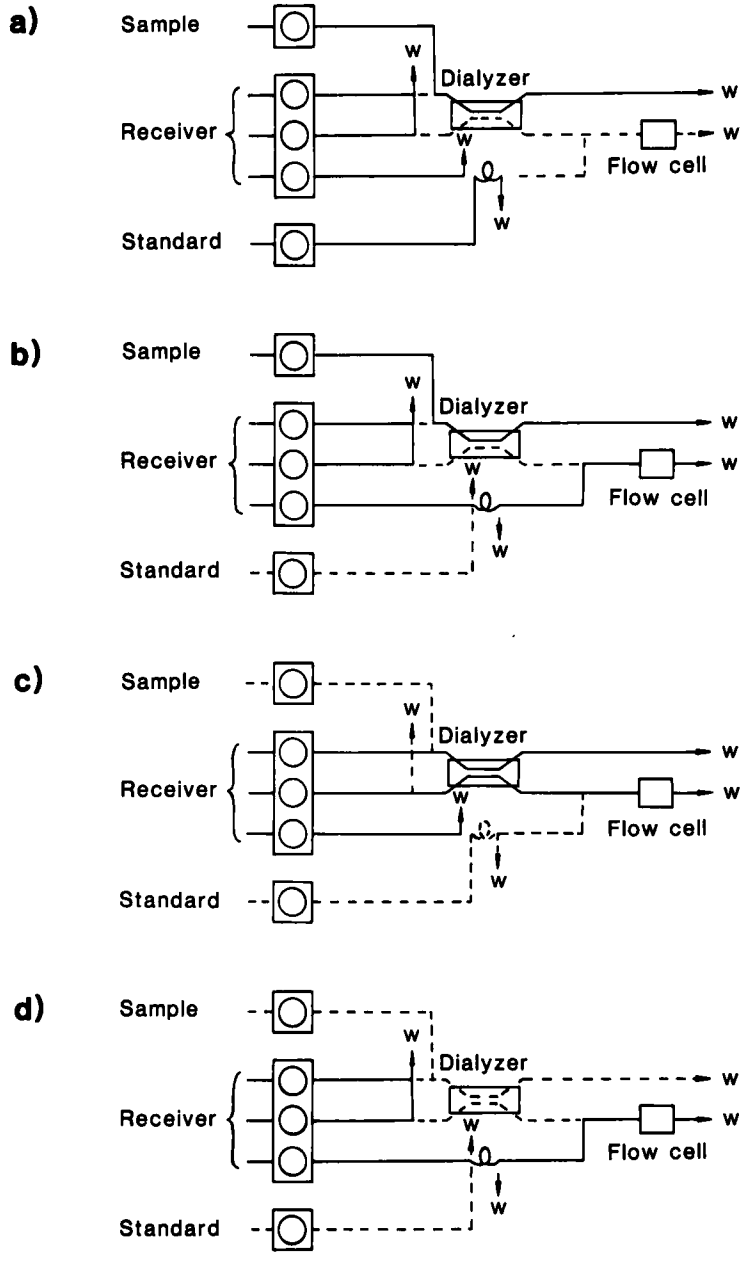

Figure 1 Switching sequence for the flow-injection/Donnan dialysis/DPASV system. Solid and broken lines represent active and inactive connections, respectively. (a) Equilibration of the dialyzer (1.1 ml/min) and filling of the standard loop (10 μl); (b) Plating of the content in the loop at a low flow rate (0.17 ml/min) followed by stripping into the receiver solution at a higher flow rate (0.9–1.0 ml/min); (c) Plating of Cd^{2+} in the equilibrated receiver channel and in the receiver solution that passes the equilibrated membrane; (d) Final stripping into an uncontaminated receiver solution. w = waste.

Dry thickness of the membrane was about 35 μm.[15] Before they were installed in the dialyzer, membranes were pretreated by leaching in 2 M HCl for 10 min followed by a rinse in deionized water and exposed to the washing solution for another 10 min. After a second rinse with deionized water, the membrane was mounted into the dialyzer and equilibrated on-line for at least 30 min with the receiver solution (Figure 1c). The membrane was changed every day.

The dialyzer, described in detail by Risinger *et al.*,[24] was made of plexiglass with rectangular channels of the same size (1.5 × 50 mm with a height of 0.17–0.20 mm) on both sample and receiver sides. Both channels contained half-sphere elements which functioned as an effective membrane support and also, to some extent, decreased mass transfer resistance in the channels. The small channel height was, however, the main cause of the high mass transfer efficiency of this dialyzer.[24]

The flow cell consisted of a confined wall-jet glassy carbon electrode assembled in a plexyglass holder.[25] A reference electrode of Ag/AgCl 0.15 M KCl was built into the flow cell. Preparation of the mercury film electrode followed the procedure described by Yang *et al.*[7]

The polarograph was a Princeton Applied Research instrument (model 174A). Plating of Cd^{2+} was done at a potential of −800 mV vs. Ag/AgCl. The scan rate was 10 mV/sec. Other components of the flow-injection system were three peristaltic pumps, three pneumatic three-way valves (Cheminert, LDC/Milton Roy) made of Kel-F, and Teflon tubings (0.3 or 0.5 mm I.D.).

Receiver solutions were purged with nitrogen in order to remove dissolved oxygen. The head of the receiver pump, valves, standard loop, and dialyzer were all enclosed in a thick-walled plastic box with a flow-through of nitrogen.[7] The nitrogen escaped coaxially with the tubings to the cell. The samples needed only a brief deoxygenation (ca. 10 min of nitrogen bubbling) before it was pumped through the dialyzer.

Chemicals and Solutions

The system behaviour, such as effect of bulk electrolyte concentration on the equilibration time, effect of plating time on the response, and linearity of the response, was studied using sample solutions containing Cd(II) and $NaNO_3$ as the bulk electrolyte (pH 4.07). The composition of receiver solutions was identical with that of samples, except that no Cd(II) was added.

In experiments with citric acid, NTA, oxalic acid, and fulvic acids (FA), two different receiver solutions were used: 0.100 M $NaNO_3$, pH 4.07 and a 0.099 M $NaNO_3$–1.0 mM CH_3COONa mixture having a pH of 5.56. Ionic strength of the samples was adjusted to 0.100 by adding $NaNO_3$. The NTA samples were buffered with 0.50 mM CH_3COONa. Appropriate Cd(II) concentrations were achieved by dilution of a 0.100 M $Cd(NO_3)_2$ stock solution. In order to calibrate the system, receiver solutions spiked with 1.00 μM $Cd(NO_3)_2$ were processed at least in duplicate. These solutions were prepared fresh every morning.

The washing solution used for leaching of new membranes and for on-line washing between samples, contained either 0.500 M $NaNO_3$ or a 0.495 M $NaNO_3$–5.0 mM CH_3COONa mixture. The former was used when the receiver

solution pH was 4.07 and the latter when pH was 5.56. In order to maintain the proportion of Na^+ and H^+ on the cation-exchange membrane, the quotient $[Na^+]/[H^+]$ in the washing solutions was about the same as in the receiver solutions.

All chemicals were of analytical-grade quality. No further purfication was necessary. Samples and standards were stored in polyethylene or polypropylene bottles cleaned by leaching in 10% concentrated HNO_3 overnight.

Fulvic acids, isolated from a surface water in a bog area (Bersbo),[26] were obtained from Dr. Hans Borén, Department of Water and Environmental Studies, Linköping University, Sweden. Number-average and weight-average molecular weights of 1750 and 2650, respectively, and an acid capacity (aqueous) of 4.65 meq/g were reported.[26] Soil solutions were collected from a dystric cambisol and an orthic podzol, using 15 and 50 cm deep percolation lysimeters.[27] Before use, soil solutions were filtered through acid-washed 47-mm-diameter cellulose acetate/nitrate filters (0.45 μm) (Millipore Corp.). The ionic strengths were estimated using the empirical relationship with electrical conductivity[28] and adjusted to 0.100 M by adding $NaNO_3$ salt. The soil solutions were subsequently spiked with $Cd(NO_3)_2$ and the pH was readjusted to the original value.

Total Na, K, Ca, Mg, Mn, Al and Fe concentrations were measured with ICP-ES (Perkin-Elmer, Plasma II), and dissolved organic carbon (DOC) was analyzed with a Beckman model 915-B total carbon analyzer. The Cd(II) concentration was determined with flameless atomic absorption spectroscopy (AAS) (Varian AA-475 spectrophotometer and GTA-95 graphite tube atomizer). Chloride, NO_3^-, SO_4^{2-} were analyzed by ion chromatography.

Batch Experiments

In the batch experiments, a piece of pretreated membrane (6.3 cm^2) was equilibrated with 250 ml solution in a polypropylene beaker by gentle shaking for 15 h. The solution contained 0.010, 0.050, 0.100, or 0.500 M $NaNO_3$ together with 1.0 or 100 μM Cd(II). In addition, two solutions, 0.500 M and 1.00 M $NaNO_3$, without Cd(II) were used. The Cd(II) concentration was determined on an aliquot of the solution. After a rinse in deionized water, the Cd^{2+} and Na^+ adsorbed on the membrane were displaced with 2 M HCl. Concentrations were determined using flame AAS (Varian AA6).

RESULTS AND DISCUSSION

System Behaviour

The time needed to attain equilibrium in the dialyzer was shorter at a higher bulk electrolyte concentration (Figure 2). Batch experiments showed that the amount of Cd^{2+} in the membrane was inversely related to $[NaNO_3]$ (Table 1). One way of explaining the relationship between $[NaNO_3]$ and equilibration time is, simply, that a longer time to reach equilibrium is required when more Cd^{2+} must diffuse into the membrane. Since fresh sample solution was pumped through the dialyzer,

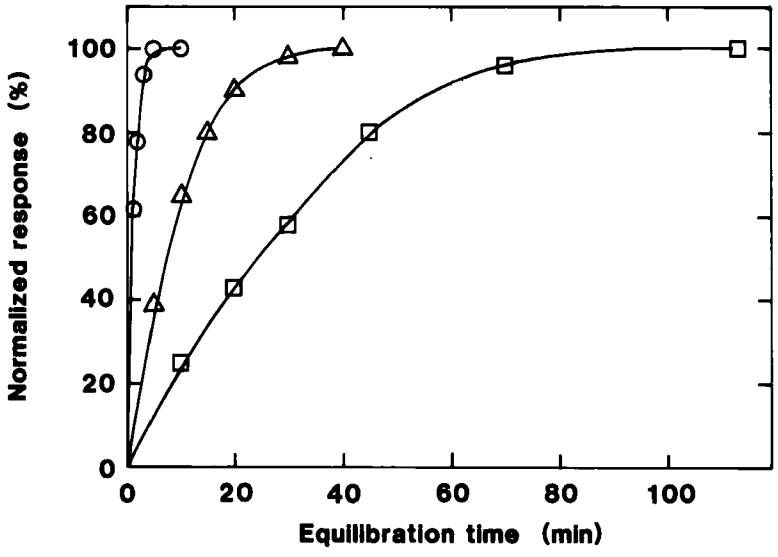

Figure 2 Relative DPASV signal for a 1.00 μM Cd(II) solution as a function of equilibration time, at a constant flow rate (1.1 ml/min). (○), (△) and (□) denote a sample and receiver [$NaNO_3$] of 0.500, 0.100 and 0.050 M, respectively; pH 4.07.

Table 1 Results from the batch experiments. A piece of cation-exchange membrane (6.3 cm^2) was equilibrated with 250 ml solution. The cation-exchange capacity of the membrane was 5.90 $\mu eq\ cm^{-2}$; relative standard deviation, 5.5% ($n = 9$)

$[NaNO_3]$ (M)	$[Cd(II)]^a$ *solution* (μM)	$[Cd(II)]^b$ *membrane* ($nmol\ cm^{-2}$)	$\frac{[Cd(II)]_{membrane}}{[Cd(II)]_{solution}}$ ($ml\ cm^{-2}$)
0.010	0.649	13.0	20.2
0.050	0.818	7.54	9.22
0.050	80.1	591	7.38
0.100	0.961	2.29	2.38
0.100	89.9	194	2.16
0.500	96.1	9.45	0.0983

[a] $[Cd(II)] = [Cd^{2+}] + [CdNO_3^+]$. The proportion of $CdNO_3^+$ increased from 1% to 23% when the $[NO_3^-]$ increased from 0.010 to 0.500 M.
[b] Cd(II) probably mainly associated with the membrane phase as Cd^{2+}.

the final equilibrium was related to the initial composition of the sample (as different from the batch experiments). It is thus possible to determine $[Cd^{2+}]$ in solutions containing labile complexes.

An alternative approach involved connecting the receiver channel directly to the nebulizer of a flame atomic absorption spectrophotometer and pumping the sample through the other channel. When equilibrium was attained, a constant fraction was dialyzed over the membrane into the receiver channel. Since the flow

rate in both channels was 4.0 ml/min, the time needed to reach equilibrium was about one-fourth of those shown in Figure 2. However, the relationships between the different [$NaNO_3$] were almost the same. The equilibrium times (Figure 2), could thus be lowered substantially by increasing the sample flow rate.

Subsequent experiments were performed at an ionic strength of 0.1, with $NaNO_3$ as the supporting electrolyte, using an equilibration time of 31 min. The time needed to equilibrate the dialyzer for samples buffered, as regards Cd^{2+}, was shorter. If the sample is swamped with $NaNO_3$ to give an ionic strength of 0.1, the conditional constant (β) in Eq. (4) will be rather independent of sample composition, when low ionic strength samples are analyzed. For example, forest soil solutions from Southern Sweden, have an ionic strength of $(0.5–3) \times 10^{-3}$ (D. Berggren, unpublished data). An even higher bulk electrolyte concentration would be desirable to satisfy the conditions of Eq. (4), but since the ionic strength affects existing equilibria in a sample, it should be kept at a minimum. A [$NaNO_3$] of 0.500 M instead of 0.100 M also resulted in a lower sensitivity, due to a lower membrane concentration of Cd^{2+} (Table 1). Also for validation of the method an ionic strength of 0.1 would be preferable, since many stability constants are reported for this ionic strength.

When the receiver solution passed the equilibrated membrane, Cd^{2+} diffused into the receiver solution and subsequently transferred to the electrochemical cell (Figure 1c). The response was a linear function of the plating time up to 360 sec (Figure 3). Using a plating time of 180 sec and an ionic strength of 0.1, a linear response in the interval 10^{-7}–10^{-6} M Cd(II) was obtained (Figure 4). These conditions were used in the speciation experiments.

The stripping peak current (i_p) obtained for a standard injected with the loop may be expressed in A (mole Cd(II))$^{-1}$. By comparing i_p of a receiver solution which has passed the equilibrated membrane with that of the loop, it is possible to calculate the number of moles of Cd(II) that has been plated. The same fraction of Cd(II) is assumed to be plated into the mercury film in both cases. Using data from the batch experiments, it was shown that the amount of Cd^{2+} diffusing from the membrane during the plating step was about 10% of $[Cd]_m$ at equilibrium, at a plating time of 180 sec (0.17 ml/min).

Speciation of Cd(II) in the Presence of Different Organic Ligands

In order to test the validity of the system for speciation studies, [Cd^{2+}] was determined in solutions containing different well-defined organic ligands: citric acid, NTA, and oxalic acid. The obtained results were compared with equilibrium calculations. All stability constants used are listed in Table 2.

Since $NaNO_3$ was used as a swamping electrolyte, some $CdNO_3^+$ was formed. This complex may adsorb to and permeate through the membrane. Because of a low [NO_3^-] in the membrane (due to the high concentration of fixed negative charges) and the higher valency of the Cd^{2+} ion, the amount of $CdNO_3^+$ in the membrane may be neglected compared to the amount of Cd^{2+}. As long as the sample and the standard solution have the same [NO_3^-], 0.10 M, the ratio [$CdNO_3^+$]/[Cd^{2+}] is constant (0.075). Correct results will consequently be

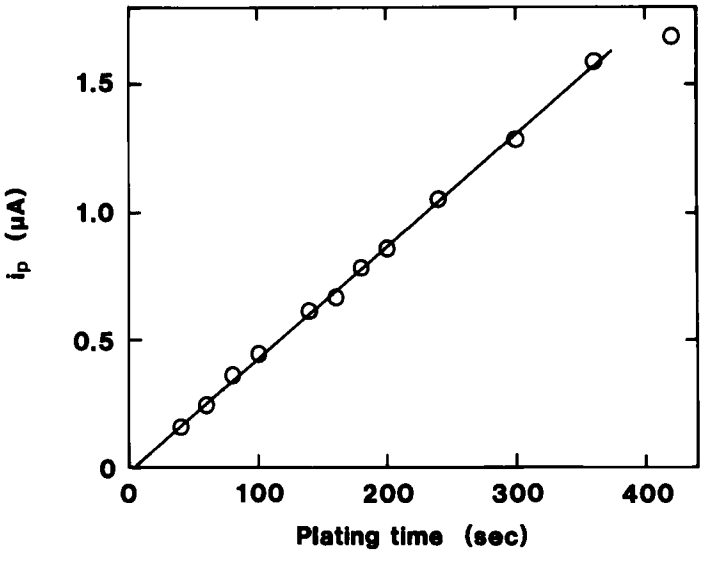

Figure 3 Stripping peak current (i_p) as a function of plating time using an equilibrated dialyzer. Sample: 1.00 μM Cd(II)–0.100 M $NaNO_3$, pH 4.07; Receiver: 0.100 M $NaNO_3$, pH 4.07.

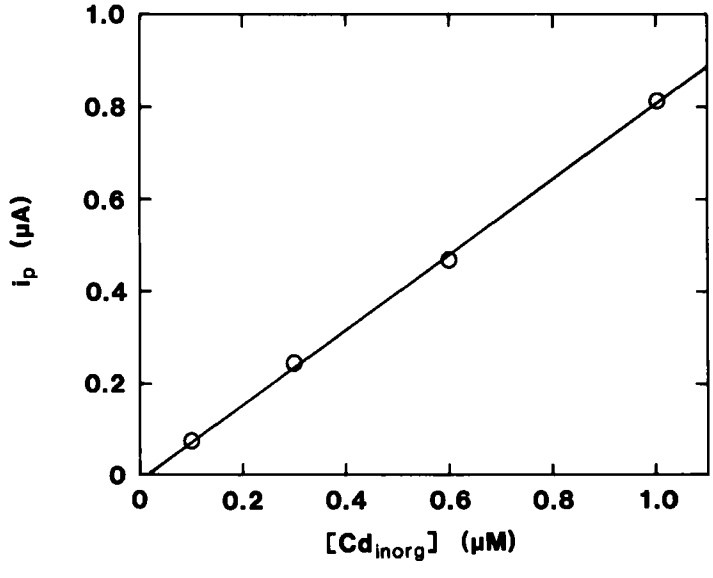

Figure 4 Stripping peak current (i_p) as a function of $[Cd_{inorg}]$ ($[Cd^{2+}]+[CdNO_3^+]$). Plating time was 180 sec. $[NaNO_3]$ of sample and receiver was 0.100 M; pH 4.07. Plot: $y=0.818x-0.008$; $r^2=0.999$.

Table 2 Stability constants used in the equilibrium calculations. Values refer to an ionic strength of 0.10 and to 20 or 25 °C

Ligand	*Equilibria*	*log K*	*References*
Acetic acid (HL)	HL/H.L	4.55	Sillén and Martell[29]
	CdL/Cd.L	1.61	
Citric acid (H_3L)	HL/H.L	5.68	Sillén and Martell[29]
	H_2L/HL.H	4.38	
	H_3L/H_2L.H	2.96	
	CdL/Cd.L	3.75	
	CdHL/Cd.HL	2.20	
	CdH_2L/Cd.H_2L	0.97	
NTA (H_3L)	HL/H.L	9.81	Ringbom[30]
	H_2L/HL.H	2.57	
	H_3L/H_2L.H	1.97	
	CdL/Cd.L	10.1	
Nitrate (L)	CdL/Cd.L	−0.12[a]	Lindsay[31]
Oxalic acid (H_2L)	HL/H.L	3.82	Martell and Smith[32]
	H_2L/HL.H	1.04	
	CdL/Cd.L	3.03[a,b]	

[a]Correction for ionic strength was made using single ion activity coefficients calculated by the extended Debye–Hückel equation. Ionic size parameters reported by Kielland[33] were used in the calculation.
[b]Temperature, 18 °C.

obtained for the sample, no matter how the response is related—to the $[Cd^{2+}]$ or to the sum of $[Cd^{2+}]$ and $[CdNO_3^+]$ in the standard solution. In subsequent experiments, it was convenient to relate the response of a sample to the sum of $[Cd^{2+}]$ and $[CdNO_3^+]$ ($=[Cd_{inorg}]$) in the standard. This value was compared with the $[Cd_{inorg}]$ calculated for the sample. By using $NaClO_4$ as swamping electrolyte and receiver solution, the undesirable complexation can be avoided.

In the experiments with citric acid, NTA and FA, at pH 5.56, buffering of the receiver by adding 1.0 mM CH_3COONa, did not significantly affect the Cd(II) speciation (Cd-acetate$^+$ = 3% of Cd_{inorg}). Since the ligand concentration in all samples was much less than the ionic strength, condition (i) of Eq. (4) could be fulfilled. The least satisfactory case was in the experiment with 2.0 mM citric acid, when $[Na^+]$ in the sample was 0.097 M.

A constant fraction of $[Cd]_m$ could be determined with a good reproducibility, using the flow-injection system. In speciation experiments, the standards (receiver solution spiked with 1.00 μM $Cd(NO_3)_2$) used to calibrate the system showed a range $\leqq 4\%$ (expressed as per cent of the mean) for duplicate analyses.

Using citric acid as ligand, the experimental results agreed well with the calculated values, if the receiver solution pH was the same as the sample pH (Table 3). A lower pH in the receiver than in the sample resulted in an overestimation of Cd_{inorg}, probably because of a shift in the equilibrium towards the inorganic forms as a result of a lower pH at the membrane surface.

An experiment with oxalic acid, indicated that the Cd-oxalate^0 complex did not permeate through the membrane (Table 3). This is in accordance with a study,

Table 3 Experiments with samples containing citric acid (CA) or oxalic acid (OA), and 1.00 μM Cd(II), having an ionic strength 0.100 (bulk electrolyte: $NaNO_3$). Two different receiver solutions were used: 0.100 M $NaNO_3$, pH 4.07 and 0.099 M $NaNO_3$–1.0 mM CH_3COONa, pH 5.56; L = ligand

Sample			*Receiver pH 4.07*	*Receiver pH 5.56*	*Calculated speciation*			
Ligand	*Ligand conc.* (*mM*)	*pH*	$[Cd_{inorg}]^a$ (μM)	$[Cd_{inorg}]$	$[Cd_{inorg}]$	$[CdL^-]$	$[CdHL^0]$	$[CdL^0]$
CA	0.50	5.56	0.62	0.56	0.50	0.48	0.02	—
CA	1.00	5.56	0.44	0.37	0.33	0.64	0.03	—
CA	2.00	5.56	0.30	0.23	0.20	0.77	0.03	—
CA	1.00	6.05	0.42	0.28	0.22	0.71	0.01	—
OA	0.30	4.07	0.84	—	0.85	—	—	0.15

$^a[Cd_{inorg}] = [Cd^{2+}] + [CdNO_3^+]$.

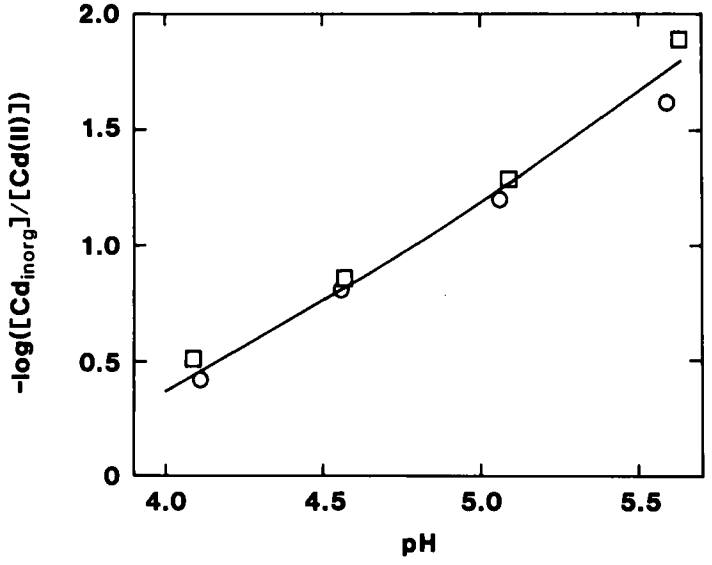

Figure 5 Speciation of 1.00 μM (pH 4.1 and 4.6) or 5.00 μM (pH 5.1 and 5.6) Cd(II) in 100 μM NTA as a function of sample solution pH. $[Cd_{inorg}] = [Cd^{2+}] + [CdNO_3^+]$. Sample ionic strength was 0.100 with $NaNO_3$ as the bulk electrolyte. Two different receiver solutions were used: (○) 0.100 M $NaNO_3$, pH 4.07 and (□) 0.099 M $NaNO_3$–1.0 mM CH_3COONa, pH 5.56. The solid line through the points was calculated using stability constants in Table 2.

where a similar membrane proved to be impermeable to the uncharged Pb-phthalate^0 complex.[16] This seems to be the main difference between the present method and the method of Cantwell and co-workers,[19–21] where uncharged complexes interfered by being adsorbed to the cation-exchange resin.[21]

The experimental results with NTA as a ligand corresponded very well with the calculated speciation (Figure 5). A problem with the use of equilibrium calculations for validation purposes is that different sets of stability constants are

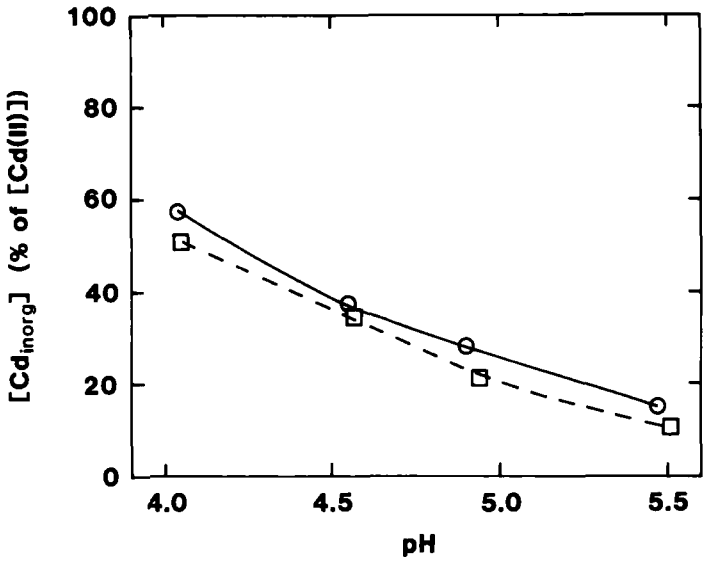

Figure 6 Speciation of 1.00 μM Cd(II) in 200 mg FA/l as a function of sample solution pH. $[Cd_{inorg}] = [Cd^{2+}] + [CdNO_3^+]$. Sample ionic strength was 0.100 with $NaNO_3$ as the bulk electrolyte. Two different receiver solutions were used: (○) 0.100 M $NaNO_3$, pH 4.07 and (□) 0.099 M $NaNO_3$–1.0 mM CH_3COONa, pH 5.56.

reported in the literature. For example, if the stability constants tabulated by Martell and Smith[32] had been used, the calculated line in Figure 5 had been 0.09–0.15 units lower. On the other hand, the set of stability constants used in Figure 5 also fitted the experimental data of Bourque and Guy,[16] obtained with both Donnan dialysis and differential pulse polarography. In contrast to the experiment with citric acid, the effect of the receiver solution pH seemed to be less important. One explanation may be that NTA forms kinetically more stable complexes with Cd^{2+} than does citric acid. Using e.g. differential pulse polarography, the Cd–NTA complex behaves like a totally inert complex during the time of measurement.[16,34]

The complexation between FA and metals is pH dependent, increasing with pH (Figure 6) (see, e.g., ref. 35). The small difference between the two receiver solutions may be ascribed to a dissociation of the Cd–FA complex when receiver solution pH $\ll$ sample pH and to an enhanced complexation when receiver solution pH $\gg$ sample pH. Metals and humic substances form complexes with a great range of labilities.[36] The most labile sites could thus be more sensitive to pH differences between the sample and the membrane surface. A receiver solution pH as close as possible to that of the sample is recommended, so as not to perturb the existing equilibria.

Speciation of Cd(II) in Soil Solutions

The content of both DOC and inorganic ions varied considerably between the different soil solutions used (Table 4). The receiver solution pH was close to that

Table 4 Chemical composition of the soil solutions. OP = orthic podzol; DC = dystric cambisol

Soil type	*Sampling depth (cm)*	*[Na]*[a]	*[K]*[a]	*[Ca]*[a]	*[Mg]*[a]	*[Mn]*[a]	*[Fe]*[a]	[Al][a]
		(μM)						
OP	15	256	203	50.9	13.6	1.1	37.1	37.1
DC	15	63.5	197	504	130	95.6	1.3	99.7
DC	50	50.5	126	179	44.4	34.8	<0.9	45.6
Soil type	*Sampling depth (cm)*	[DOC][b] (μM)	$[Cl^-]$	$[NO_3^-]$	$[SO_4^{2-}]$	[Cd][a] $\times 10^3$		*pH*
OP	15	22400	105	125	88.0	8.45		4.22
DC	15	833	82.1	1730	88.9	21.2		4.15
DC	50	242	40.6	571	134	6.58		4.56

[a]Total concentration determined either with flameless AAS (Cd) or ICP-MS (other metals).
[b]DOC = dissolved organic carbon.

Table 5 Experiments with soil solutions from an orthic podzol (OP) and a dystric cambisol (DC), and 0.100 M $NaNO_3$ solutions containing Al(III) (samples 1 and 2). Ionic strength of the soil solutions was adjusted to 0.100 by adding $NaNO_3$. In analyzing the soil solutions, a 0.0995 M $NaNO_3$–0.5 mM CH_3COONa mixture, pH 4.33, was used as receiver solution, whereas 0.100 M $NaNO_3$, pH 4.07, was used in the other two cases

Soil type/ sample no.	*Sampling depth (cm)*	$[Cd_{added}]$[a]	$[Cd_{inorg}]$[b]	*[Al]*[c]	*[DOC]*	*pH*
		(μM)				
OP	15	1.00	0.52	37.1	22400	4.22
OP	15	0.50	0.27	37.1	22400	4.23
DC	15	0.50	0.45	99.7	833	4.15
DC	50	0.25	0.25	45.6	242	4.56
1	—	1.00	0.97	19	—	3.90
2	—	1.00	0.94	190	—	3.90

[a]Cd(II) concentrations were originally $\leq 4\%$ of Cd_{added}.
[b]$[Cd_{inorg}] = [Cd^{2+}] + [CdNO_3^+]$.
[c]Total concentration (see Table 4).

of the sample (± 0.2 pH units). The ionic strength of the soil solutions was $\leq 3.0 \times 10^{-3}$, i.e., $[Na^+]$ was close to that of the receiver solutions.

The soil solution containing the highest [DOC], 22.4 mM, was coloured dark brown, due to a high content of humic substances. When samples were spiked with 1.00 and 0.50 μM Cd(II), 52 and 54% were recovered as Cd_{inorg}, indicating a high complexing capacity of this soil solution (Table 5). No organic complexes were formed in the sample with a [DOC] of 0.242 mM. Using the anion composition in Table 4 and stability constants from Lindsay,[31] it can be concluded that $CdSO_4^0$ and $CdCl^+$ did not significantly contribute to the inorganic speciation of Cd(II) in the soil solutions.

An experiment with standards spiked with 19 or 190 μM Al(III) was also

performed (Table 5; samples 1 and 2). Since the sample pH was 3.90, ca. 98% of the added Al(III) was present as Al^{3+}.[31] The Al^{3+} ion will compete efficiently with the Cd^{2+} and Na^{+} ions for anionic membrane sites due to its high valency. The sample with 190 μM Al(III) showed a somewhat lower response than the unspiked standard (Table 5). On the other hand, [Al^{3+}] found in natural waters, such as forest soil solutions and stream waters is generally less than 100 μM.[37]

The activity coefficients of the ionic species will be affected by the addition of a supporting electrolyte to samples and standards, and the equilibria involving the Cd^{2+} ion will therefore be altered. The effect can be illustrated using the Cd(II)–NTA equilibrium. At pH 3.84 and a total [NTA] of 10^{-4} M, 50% of the Cd(II) will be present as Cd^{2+} at an ionic strength of 0.10. If the ionic strength decreases to 0.010 there will be a decrease to 30% in the proportion of Cd^{2+}. A further decrease in the ionic strength to 0.0010 will decrease it to 20%. Single ion activity coefficients were calculated by the Davies equation.[38] However, since humic substances (predominately FA) generally are the most important ligands in natural waters,[5] the effect of the increased ionic strength on the Cd(II)–FA equilibrium is the key question. A recent investigation[39] using two independent methods, ultrafiltration and ion-exchange distribution, showed that the Cd(II)–FA equilibrium was insensitive to variations in ionic strength in the range 0.010–0.100. The addition of a swamping electrolyte to a natural water, having humic substances as the predominant ligand, may thus not alter the existing equilibria to the extent expected from the influence on single ion activity coefficients in a simple model system, like Cd(II)–NTA.

CONCLUSIONS

Using the experimental design presented [Cd^{2+}] $> 5 \times 10^{-8}$ M can selectively be determined in the presence of negatively charged and neutral organic Cd(II) complexes. There is a great potential for increasing the sensitivity of the method. Using a higher ionic strength of and/or a complexing agent in the solution that passes the equilibrated membrane it is possible to measure a greater proportion of the membrane-bound Cd(II). It is also possible to increase the membrane surface. If the exchange behaviour of Cd^{2+} is the same, an extension of the analytical range at least down to 10^{-9} M will be possible.

The method was rather time-consuming (total cycle time for one sample, including equilibration, detection and washing, was 55 min), but the total cycle time can be lowered substantially by increasing sample flow rate during the equilibration and by a careful optimization of the washing procedure.

The method has a potential of being applicable for metal speciation in natural waters, such as soil solutions and fresh waters, which have low ionic strengths, Al^{3+} concentrations of less than 100 μM, and organic compounds as the major ligands.

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