

Solution Studies of Systems with Polynuclear Complex Formation: Copper(II) and Cadmium(II) D-Gluconate Systems

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Gluconate (HG = D-gluconic acid) is widely used as an efficient masking reagent for cations in strongly alkaline solutions. The complex formation with Cu^{2+} and Cd^{2+} has been studied by means of combined pH and pM measurements (25 °C, 0.5 mol/L KNO_3). Dimeric species of the composition $\text{M}_2\text{H}_{-4}\text{G}_2^{2-}$ seem to form in solutions containing an excess of the ligand. The evaluated stability constants are presented. A diagram is given which compares the masking ability of EDTA, tartrate, citrate, and gluconate for cupric ions.

Naturally occurring hydroxycarboxylic acids belong to the oldest complex-forming agents applied by mankind. Important members of this class of reagents are citric and tartaric acids, as well as the sugar acids. An example of the last group is D-gluconic acid, which is extensively used as a masking reagent for cations in alkaline solutions. Numerous practical and industrial applications have been reported for such systems (1).

When comparing the complexing ability of the mentioned hydroxycarboxylic acids, we note that citrate and tartrate carry a larger negative charge than gluconate because there are more carboxyl groups present in the ligand. The stability of the "normal" 1:1 metal:ligand complexes will therefore follow the order: citrate > tartrate > gluconate.

Investigations of metal-gluconate systems (1) indicate that two or more hydroxyl groups of the anion may ionize at high pH values (ionization of the hydroxyl group in α -position to the carboxyl group is a well-known phenomenon, the following dissociable protons may come from the ligand and/or from coordinated water molecules). This property makes the reagent a powerful chelating agent in alkaline solutions. The gluconate anion contains a greater number of hydroxyl groups than tartrate and citrate. Consequently, in ternary metal-OH-hydroxycarboxylate systems gluconate may be a better sequestering agent than citrate (and even tartrate) for cations with a strong polarizing power in order to dissociate protons.

We have an interest in the formation of basic metal hydroxycarboxylate complexes (2-4). Our main concern is the alkaline pH region where an ionization of the ligands occurs. The deprotonated alcoholic group has bridge-bonding ability (like the OH^- ion in metal hydrolysis reactions) and we may expect to find polymeric species present in solution. The formation of such species has, however, to a large extent been overlooked in the literature and most of the investigators explain their experimental data in terms of only mononuclear complexes (5).

We wanted to reinvestigate the cupric- and cadmium-gluconate systems in order to compare the complex-forming ability of a monohydroxycarboxylate (citrate) and a polyhydroxycarboxylate ligand. The study was carried out with the aid of combined pH and pM ($=-\log [\text{M}^{2+}]$) measurements as an ion-selective electrode is available for both cations. The theory for the evaluation of the data has been outlined previously (2, 4).

Dimeric complex species have been proposed earlier in the cupric and cadmium gluconate systems (1). Of other met-

al-OH-gluconate systems we note that dimeric species seem to be formed by manganese(II) (polarography, ESR, and magnetic susceptibility) (6), and by lead(II) (emf work with a lead amalgam electrode) (7). The species proposed in the latter study were $\text{PbH}_3\text{G}^{2-}$ ($\text{Pb}(\text{OH})_3\text{G}^{2-}$), $\text{Pb}_2\text{H}_5\text{G}^{2-}$, and $\text{Pb}_2\text{H}_4\text{G}_2^{2-}$, where HG denotes D-gluconic acid.

EXPERIMENTAL SECTION

All chemicals were of reagent grade and were used as received. The experiments were carried out at 25 ± 0.1 °C in solutions of ionic strength $0.5 \text{ mol L}^{-1} \text{ KNO}_3$.

The potentiometric measurements were carried out with two Orion Model 801 pH/mV meters. A Radiometer metal-ion selective Selectrode was used for the pCu and pCd measurements. The linearity of the electrode response was tested by using various metal buffers and was found to be good. The E_M° value of the Selectrode was measured in the metal ion solution before the addition of the ligand and was checked after the titration. A glass electrode was used for the pH measurements and the hydrogen ion concentration was calculated from the pH readings using the relationship $-\log [\text{H}^+] = \text{pH} - 0.14$.

All the calculations were performed with the aid of a programmable pocket calculator of the type HP-41 CV.

RESULTS

Gluconic acid forms weak complexes with potassium ions and the protonation constant was determined in the same ionic medium. The result is given in Table II.

The data required to analyze the equilibria in a system containing polynuclear species must involve variables measured over a wide concentration range. We have chosen to use combined pH and pM measurements as variables, since in emf work the response signal is a logarithmic function of the variable and it is possible to cover several decades of the concentration range.

The evaluation of the stability constants follows the theory outlined earlier (2, 4, 8). A short presentation of the methodology and theory is given below (all charges of the species are omitted):

Solutions containing the metal ion (M) and the ligand (L) are mixed in an appropriate ratio and the acidic solution is gradually neutralized with potassium hydroxide. The used $C_M:C_L$ ratio (C denotes total concentration) depends on which kind of complex species are predominantly formed (mononuclear, dinuclear, monoligand, diligand, etc.). From the measured pH and pM values the constants can be calculated provided the stoichiometry of the complexes is known. The amount of base consumed at the neutralization could be used in the evaluation procedure, but usually this variable is used only for checking (and refining) the results.

The stability constants of a mononuclear monoligand complex can thus relatively simply be determined by performing a series of combined pH and pM measurements on a well pM-buffered solution, i.e., a solution containing the ligand in excess. Let us further assume that not more than two protons or hydroxide ions can be taken up by the complex ML, thus forming MHL , MH_2L , MH_1L (MOHL), and MH_2L ($\text{M}(\text{OH})_2\text{L}$). The pM value of the solution will be governed by the conditional constant (8)

$$K_{(\text{ML})}^{\text{ML}} = [(\text{ML})]/([\text{M}][\text{L}']) = K_{\text{ML}}^{\text{ML}} \alpha_{\text{ML}(\text{H},\text{OH})} / \alpha_{\text{L}(\text{H})} \quad (1)$$

where

$$[(ML)'] = \sum_{i=-2}^2 [MH_iL] = [MH_{-2}L] + [MH_{-1}L] + [ML] + [MHL] + [MH_2L] \quad (2)$$

$$[L'] = \sum_{i=0}^t [H_iL] = [L] + [HL] + [H_2L] + \dots + [H_tL] \quad (3)$$

$\alpha_{L(H)}$ and $\alpha_{ML(H,OH)}$ denote distribution or side-reaction coefficients and have their usual definitions (9)

$$\alpha_{L(H)} = [L']/[L] = 1 + [H]K_{HL}^H + [H]^2K_{H_2L}^{2H} + \dots \quad (4)$$

$$\alpha_{ML(H,OH)} = [(ML)']/[ML] \quad (5)$$

Substitution of the mass balance equations into eq 1 yields (8)

$$\log K_{ML} + \log \alpha_{ML(H,OH)} = pM + \log \alpha_{L(H)} + \log \{(C_M - [M'])/(C_L - C_M + [M'])\} \quad (6)$$

$[M']$ is the concentration of uncomplexed metal ion. If $[M']$ differs from $[M]$, it is mostly a question of metal hydrolysis.

The left-hand side of eq 6 contains the unknown constants of the chelates, whereas all the terms on the right-hand side are calculable. The pM value of the solution can be measured at different pH values and $\log \alpha_{L(H)}$ can be calculated from the known protonation constants of the ligand. A plot of $\log K_{ML} + \log \alpha_{ML(H,OH)} = \log K_{(ML)}^{ML}$ as a function of pH will show the chelates formed in solution. The plot will indicate the species formed and will provide good estimates of the unknown stability constants. The values of the constants can then be refined by nonlinear regression analysis with the conditional constant as error variable (8).

Let us now assume that a condensation reaction will give predominating dimeric species in solution. The dimers have a 2:2 stoichiometry of the composition $M_2H_iL_2$, i.e., a stepwise protonation or deprotonation of the dimer is allowed. The free metal ion concentration of the solution will be determined by the conditional constant (2)

$$K_{(M_2L_2)}^{2M_2L_2} = \frac{[(M_2L_2)']}{[M]^2[L']^2} = K_{M_2L_2}^{2M_2L_2} \alpha_{M_2L_2(H,OH)} / (\alpha_{L(H)})^2 \quad (7)$$

Insertion of the mass balance equations yields

$$\log K_{M_2L_2} + \log \alpha_{M_2L_2} = 2pM + 2 \log \alpha_L + \log (C_M - [M']) / \{2(C_L - C_M + [M'])^2\} \quad (8)$$

The equation shows that dilution experiments can be used to test the existence of dimeric (or higher polymeric) species in solution. In most cases $[M'] \ll C_M$ and a dilution by a factor of 10 will diminish the pM value by 0.5 units (at constant pH value and for fixed $C_M:C_L$ ratio). On the other hand, if a monomer predominates, the pM value will remain constant on dilution (see eq 6).

This means that a wrong assumption of the degree of polymerization of the chelate will give an "apparent" constant depending on the total concentration of the reactants. A comparison of eq 6 and 8 (with the assumptions given above and at a fixed pH value) yields for the reaction



the following relationship between the constant for the dimer and the "apparent" constant K_{ML}^{app} obtained when assuming monomers in solution:

$$K_{M_2L_2} = (K_{ML}^{app})^2 / (2C_M) \quad (10)$$

This means that K_{ML}^{app} will be proportional to $C_M^{1/2}$.

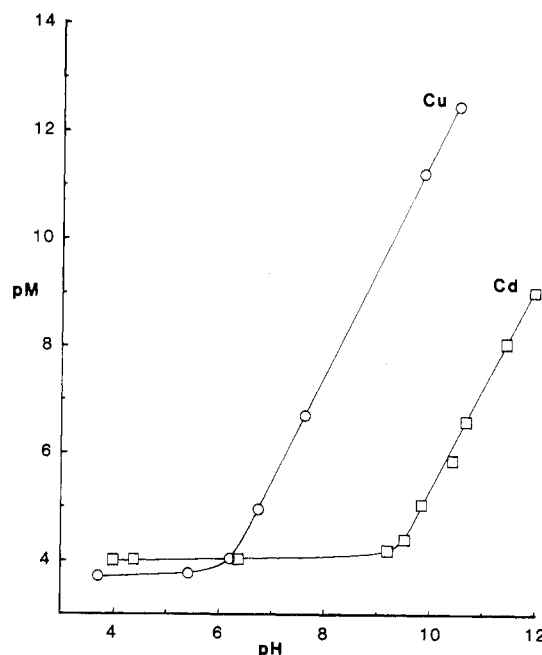


Figure 1. The figure shows recorded pM values vs. pH for solutions with a $C_M:C_G$ ratio of 1:3, $C_{Cd} = 0.1$ mmol/L, and $C_{Cu} = 0.2$ mmol/L, respectively.

Table I. Dilution Experiments Probing the Dimeric Nature of the Formed Complexes

A. Calculated Values of $K_{CdH_2G}^{app}$ as a Function of C_{Cd}			
C_{Cd}	C_G	$\log K_{CdH_2G}^{app}$	
3×10^{-4}	9×10^{-4}	-14.62	
2×10^{-4}	6×10^{-4}	-14.70	
1×10^{-4}	3×10^{-4}	-14.76	
B. Experiment at Constant pH Values ^a			
pH	$\log C_{Cu}$	emf reading	$dpCu/dpC_{Cu}$
10.544	-4.000	-66.1	
10.544	-4.405	-59.3	-0.61
10.543	-4.812	-51.7	-0.63

^aThe potential (in mV) is recorded vs. calomel.

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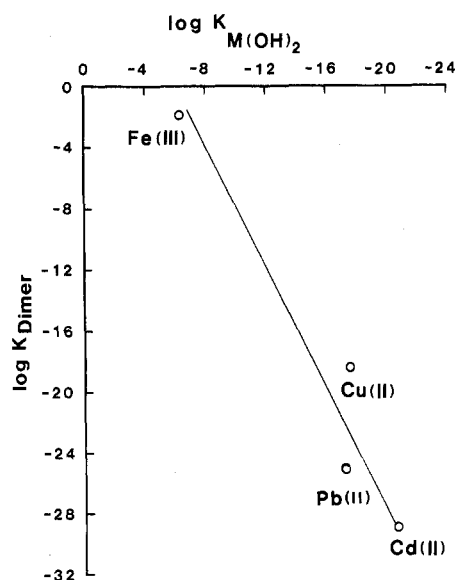
Combined pH and pM measurements have been used in the study of the copper(II)- and cadmium(II)-gluconate complexes. The solutions were mixed in a $C_M:C_G$ ratio of 1:3 in order to avoid the formation of 2:1 metal:gluconate complexes. The results of two experiments are given in Figure 1 as a plot of pM vs. pH. The M:G ratio in the chelates is 1:1 and the slopes of the plots are +2 at alkaline pH values. Consequently, the composition of the chelates is $(MH_2G)_n^{n-}$ in this pH region.

Dilution experiments can be used to determine the value of n . Experiments have been carried out with C_M values of 0.1, 0.2, 0.3, and 0.5 mmol/L and $C_M:C_G = 1:3$ (and 1:2). The results show that the "apparent" constant K_{ML}^{app} goes with the square root of C_M or that the spacing (2), dpM/dpC_M , is ca. -1/2.

Table IA shows three of the titrations performed in the cadmium-gluconate system indicating that K_{ML}^{app} is proportional to $C_{Cd}^{1/2}$. Table IB gives emf readings obtained in a dilution experiment at pH 10.54 in the cupric gluconate system. The calculated spacing (-0.62) slightly exceeds the theoretical value for a dimer (-0.50), but the performed titrations are in accordance with predominating dimeric species and not higher polymerized ones.

Table II. Stability Constants of Complexes $M_pH_qG_r$ Formed in Metal D-Gluconate Solutions (25 °C, 0.5 mol/L KNO_3)

<i>p</i>	<i>q</i>	<i>r</i>	reaction	$\log \beta_{pqr}$ ($\pm 3\sigma$)
0	1	1	$H^+ + G^- \rightleftharpoons HG$	3.56 ± 0.03
2	-4	2	$2Cu^{2+} + 2G^- \rightleftharpoons Cu_2H_4G_2^{2-} + 4H^+$	-13.7 ± 0.1
2	-4	2	$2Cd^{2+} + 2G^- \rightleftharpoons Cd_2H_4G_2^{2-} + 4H^+$	-25.9 ± 0.1

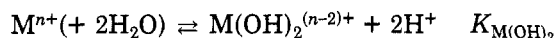
**Figure 2.** The ionization constant of basic metal-gluconate formation as a function of cation hydrolysis reaction. The definitions of the reaction equilibria are given in the text.

Consequently, dimeric species of the composition $M_2H_4G_2^{2-}$ predominate in alkaline solutions. The obtained stability constants are presented in Table II.

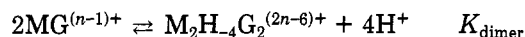
Intermediate species of the type $M_2H_iG_2^{(i-2)-}$ ($i = 1, 2, 3$) are not observed in the experiments of this study. The reason for this may be due to the dilute solutions used in the experiments (there is a solubility problem at higher metal ion concentrations, especially in the cadmium gluconate system).

DISCUSSION

The polarizing power of the cation is operative in the ionization process of metal hydroxycarboxylate complexes. In Figure 2 we compare the constants of the reactions



and



{Estimates (10) of the hydrolysis constants and literature values (5, 7) for the $MG^{(n-1)+}$ complexes have been used ($\log K_{CuG} \approx 2.4$, $\log K_{CdG} \approx 1.5$). The value for the ferric complex (5) is based on an assumption of dimeric species and not mononuclear ones predominating in solution and on eq 10.}

The figure shows that to a first approximation the two ionization constants are linearly dependent of each other (as illustrated by a straight line with a slope of -2).

We may also compare the formation of basic citrate and gluconate complexes in reactions not involving the ionization of protons. Such a comparison is made in Table III (estimates of the appropriate hydrolysis constants of the cation are taken from literature values (10)). It is found that the stability of the citrate and gluconate complexes as defined by the reactions given in the table is of the same order of magnitude (for lead(II) the corresponding values amounted to 11.8 and 12.1, respectively). The high value of the gluconate complexes is

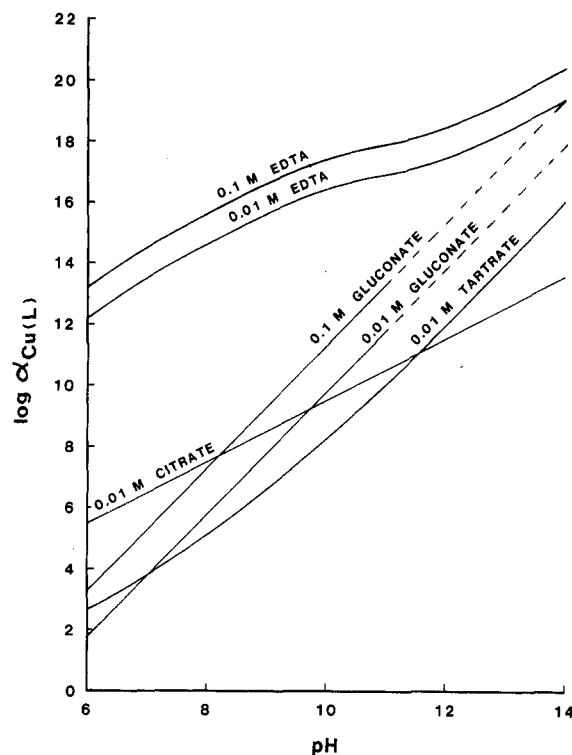
Table III. Stability of Basic Citrate and Gluconate Complexes According to the Reactions Given Below^a

reaction	$\log K$	
	Cu(II)	Cd(II)
$2MOH^+ + 2Ci^{3-} \rightleftharpoons M_2H_2Ci_2^{4-} (+ 2H_2O)$	21.2	15.4
$2M(OH)_2 + 2G^- \rightleftharpoons M_2H_4G_2^{2-} (+ 4H_2O)$	21.6	15.6

^a Values as far as possible valid at 25 °C, $\mu = 0.5$. ^b H_3Ci = citric acid.

Table IV. Formation Constants for Copper(II) and Proton Interactions with EDTA, Citrate, and D(+)-Tartrate Used in the Calculation of Figure 3

<i>p</i>	<i>q</i>	<i>r</i>	interaction	$\log \beta_{pqr}$
0	1	1	protonation of EDTA	10.23
0	2	1		16.41
0	3	1		19.07
0	4	1		21.08
1	0	1	Cu(II)-EDTA	18.86
1	-1	1		7.4
0	1	1	protonation of citrate	5.65
0	2	1		9.95
0	3	1		12.74
2	-1	2	Cu(II)-citrate	10.82
2	-2	2		5.80
0	1	1	protonation of tartrate	3.72
0	2	1		6.36
2	-2	2	Cu(II)-tartrate	0.1
2	-3	2		-7.0
2	-4	2		-17.3

**Figure 3.** $\log \alpha_{Cu(L)}$ as a function of pH in the presence of the complexing agents citrate, D(+)-tartrate, gluconate, and EDTA (L denotes the ligand). The plots are made for $C_{Cu}:C_L = 1:10$.

surprising and may indicate a rather special stereochemical structure in the complex species.

The stability of the reactions given in Table II clearly shows the good masking effect of citrate, and especially gluconate, toward cation hydrolysis reactions. The usefulness of an organic reagent for various masking purposes can be expressed by means of α -coefficients (9). In Figure 3 the α -coefficients

for cupric ions and the complexing agents EDTA, citrate, D(+)-tartrate, and gluconate are presented ($C_{Cu}:C_L = 1:10$). The formation of dimeric species is accounted for (the formation constants used in the calculations are given in Table IV).

The figure shows the ability of gluconate to mask copper(II) efficiently in alkaline solutions, whereas citrate is a poorer masking agent. At neutral pH values citrate forms stronger complexes with copper(II) due to its higher negative charge.

EDTA is able to mask copper more efficiently than the mentioned hydroxycarboxylate ligands in neutral and weakly alkaline solutions. A comparison of the Cu-EDTA and Cu-gluconate log α curves for the two total concentrations shows the greater dilution effect occurring in systems containing dimeric species.

Registry No. Cu^{2+} , 15158-11-9; EDTA, 60-00-4; tartaric acid, 87-69-4; citric acid, 77-92-9; gluconic acid, 526-95-4.

LITERATURE CITED

- (1) Sawyer, D. T. *Chem. Rev.* **1964**, *64*, 633.
- (2) Still, E. R.; Wikberg, P. *Inorg. Chim. Acta* **1980**, *46*, 147.
- (3) Grenthe, I.; Wikberg, P.; Still, E. R. *Inorg. Chim. Acta* **1984**, *91*, 25.
- (4) Blomqvist, K.; Still, E. R. *Inorg. Chim. Acta*, in press.
- (5) Sillén, L. G.; Martell, A. E. "Stability Constants of Metal Ion Complexes"; The Chemical Society: London, 1964 and 1972; Special Publications Nos. 17 and 25.
- (6) Bodini, M. E.; Willis, L. A.; Riechel, T. L.; Sawyer, D. T. *Inorg. Chem.* **1976**, *15*, 1538.
- (7) Coccioli, F.; Vicedomini, M. J. *Inorg. Nucl. Chem.* **1978**, *40*, 2103, 2106.
- (8) Still, E. R. *Anal. Chim. Acta* **1980**, *116*, 77.
- (9) Ringbom, A. "Complexation in Analytical Chemistry"; Wiley-Interscience, New York, 1963.
- (10) Baes, C. F., Jr.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley-Interscience: New York, 1976.

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High-Sensitivity Spectroelectrochemistry Based on Electrochemical Modulation of an Absorbing Analyte

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When a laser beam passes parallel to an electrode surface, the light diffracted by the electrode samples the solution within less than 10 μ m of the surface. If an absorber is generated electrochemically, the diffracted light is attenuated rapidly (<50 ms) and the attenuation is related to absorber concentration by Beer's law. A modulated potential was used to generate and remove absorber, leading to a modulated diffraction intensity which is linearly related to concentration. The effects of frequency, diffraction angle, and phase shift were examined and conditions for linearity of signal with concentration were determined. The detection limit for tri-anisylamine in acetonitrile was 2×10^{-8} M, with the selectivity inherent to a spectroelectrochemical method. Finally, a small amplitude ac potential was superimposed on a dc ramp, resulting in an output similar to that from ac voltammetry, but detected optically. The detection limits of the new method are compared to those for alternative spectroelectrochemical techniques.

Electroanalytical techniques based on amperometry and voltammetry can be extraordinarily sensitive, as evidenced by the picomole detection limits for amperometric detectors in liquid chromatography (1, 2) or the 10^{-8} – 10^{-10} M levels measurable by anodic stripping voltammetry (3) and pulse polarographic methods (4). Electroanalytical techniques can be miniaturized for use in vivo (5, 6) and are relatively fast and inexpensive. When a spectroscopic probe is combined with electrochemistry, a more selective analytical determination may be made. An analyte is detected on the basis of both its spectroscopic properties and its electroactivity, and potential interfering Faradaic or non-Faradaic processes can

usually be rejected because they are invisible to the spectroscopic probe. For example, transmission or reflection spectroelectrochemistry can be used to monitor electrogenerated absorbers, and the optical response is generally insensitive to processes which might interfere with conventional amperometric methods, such as charging current, surface Faradaic reactions, and any Faradaic processes which do not involve an absorber (7–10). The result is a more specific analytical probe for events associated with charge transfer.

In the majority of spectroelectrochemical techniques (7), the optical path length is determined by the diffusion layer thickness and is therefore quite short, usually less than 0.1 mm. Absorbances are generally less than 0.01, and sensitivity and detection limits are several orders of magnitude poorer than amperometric methods. Spectroelectrochemical techniques have been very useful for kinetic and thermodynamic studies, but their application to analysis has been inhibited by poor sensitivity. Several approaches have been used to improve sensitivity, some of which are based on parallel geometry (11, 12), where the optical beam passes parallel to the electrode surface rather than normal to it. Thin-layer cells have been constructed with path lengths of ca. 1 cm (13, 14), with one design (15) employing fiber optics to couple the cell to a commercial spectrophotometer. We have reported a different approach based on parallel geometry, in which optical diffraction is employed to limit the optical measurement to a region within a few micrometers of the electrode surface (16, 17). In effect, the electrode is used to fill or empty the region sampled by the spectroscopic beam on a time scale of 100 ms or less. Although the sampled region can be filled rapidly, it may have a path length which is much longer than the diffusion layer, resulting in significant sensitivity improvement over normal incidence reflection or transmission techniques. The most important advantage of the diffraction method in the present context is the ability to repeatedly fill and empty the sampled region of the solution electrochemically, thereby modulating the concentration of absorber. In effect, the op-

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