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The Determination of Interactions of Cobalt (II) with Organic Compounds in Seawater using Cathodic Stripping Voltammetry

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ABSTRACT

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A method is presented to determine the Co-complexing capacity of seawater using cathodic stripping voltammetry (CSV) with adsorptive collection of Co (II) complexes with either nioxime or dimethylglyoxime (DMG). The method takes advantage of ligand competition for Co^{2+} exerted by the ligand added for CSV and natural complexing material in the seawater. Conditional stability constants for complexation of Co with nioxime and DMG in seawater of salinities between 1 and 35 were calibrated by ligand competition with EDTA. The 'detection window' of the method is determined by the Co-complexing ability of the added ligand, as expressed by the α-coefficient (= product of the conditional stability constant, K'_{CoL}, and the ligand concentration, C_L) of the natural complexing ligand, L. With DMG as the added ligand, the detection window lies between $10^{5.2}$ and $10^{7.2}$ at a salinity of 35. The range of the detection window is shifted by varying the DMG concentration or by using nioxime for complexation of Co^{2+}. DMG was used to determine the Co-complexing capacity in samples originating from the estuary of the Scheldt River and the Irish Sea. A variable fraction of 45-100% (average 73%) of dissolved Co was found to occur very strongly complexed. The ligand concentration was less than the Co concentration in most of the samples. Values for log K'_{CoL} were very high, and fell within in a narrow range of 15.6-17.5. The estuarine data suggest that the organically complexed Co behaves conservatively.

INTRODUCTION

The speciation of trace metals in natural waters, especially as a result of complexation by organic material, has important implications for the geochemical cycling, biological activity and environmental toxic effects of trace

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metals. There are several methods by which the interactions of trace metals with organic ligands can be studied, such as liquid chromatography, ion exchange, anodic and cathodic stripping voltammetry, potentiometry, response by organisms, fluorescence quenching, and extraction. Among these the electrochemical methods are excellently suitable because of their high sensitivity and simplicity. Using anodic stripping voltammetry (ASV), such metal–organic interactions have been determined for Cu, Zn, Cd and Pb (e.g. Chau et al., 1974; Duinker and Kramer, 1977; Imber et al., 1984; Plavšić et al., 1982). Disadvantages of ASV relate to the fact that the degree of complex dissociation during the plating step is an unknown quantity, and that the sensitivity is insufficient to determine the free (uncomplexed) metal concentration in unpolluted seawater (e.g. free Cu, Huizenga and Kester, 1983).

In cathodic stripping voltammetry (CSV) the preconcentration step consists of the adsorptive collection on a hanging mercury electrode (HMDE) of the complex of the metal ion with a chelator which is added to the solution. Competition between the added chelator and the natural organic complexing ligands for the metal ions in seawater forms the basis for a method for determining the organic interactions of several metals, such as Cu (van den Berg, 1984), Zn (van den Berg, 1985) and Ni (van den Berg and Nimmo, 1987). The advantages of this technique are that the ligand competition is accurately known from the stability of the complex with the added chelator; once equilibrium has been attained between metal ions and ligands in the sample, this equilibrium is not altered in any way by the measuring step; and finally, the sensitivity of CSV is very high, with typical limits of detection of 0.01–0.1 nM. Together with the wide applicability of CSV, this creates the possibility of studying the speciation of a variety of metal ions in natural waters.

The strong organic complexation of Ni in seawater (van den Berg and Nimmo, 1987) suggests that perhaps by analogy Co is complexed similarly. Indeed, preliminary measurements of the labile Co concentration in seawater of oceanic origin have indicated an increase upon photo-oxidation of the sample (Donat and Bruland, 1988). We therefore developed a procedure to determine the interaction of Co(II) with organic compounds in seawater using CSV. Two chelating agents, dimethylglyoxime (DMG) and cyclohexane-1,2-dione dioxime (nioxime), are compared, and their conditional stability constants are calibrated for Co^{2+}-complexation in seawater of salinities between 1 and 35. The organic speciation of Co is then determined in samples originating from estuarine and coastal waters.

THEORY

The following two equations form the basis of a linear relationship between the Co ion concentration, $[Co^{2+}]$, and $[CoL]$, which is the concentration of Co^{2+} complexed by the organic ligand L

$$C_L = [L'] + [CoL] \qquad (1)$$

and

$$K'_{CoL} = [CoL]/([Co^{2+}][L']) \qquad (2)$$

where C_L is the total ligand concentration, which is equal to the Co-complexing capacity and includes the concentration of L initially complexed by Co; $[L']$ is the concentration of L not complexed by Co, which includes 'free' L as well as L complexed by H and the major ions Ca, Mg, and Na; and K'_{CoL} is the conditional stability constant for the formation of CoL. Substitution in eqn. (2) for $[L']$ using eqn. (1) and rearrangement yields the following relationship (van den Berg and Kramer, 1979; Ruzic, 1982; van den Berg, 1982)

$$[Co^{2+}]/[CoL] = [Co^{2+}]/C_L + (K'_{CoL}C_L)^{-1} \qquad (3)$$

According to this equation a plot of $[Co^{2+}]/[CoL]$ as a function of $[Co^{2+}]$ (a van den Berg/Ruzic plot; Kramer, 1986; Apte et al., 1988) is linear, and values for the ligand concentration and conditional stability constant can be obtained from the Y-axis intercept and the slope using a simple linear least-squares regression. However, such a plot is curved if more than one complex is formed (in the presence of more than one complexing site or ligand), necessitating the use of either an interative calculating procedure or a non-linear least-squares regression (van den Berg, 1982, 1984). Nevertheless, complexing titrations of natural waters often generate linear plots (like all samples in the present work), because the titration only covers a limited range of metal concentrations and because the detectable ligands are to some extent restricted by the 'detection window' (discussed below).

Data for a calculation of the complexing capacity are obtained from a titration of the sample with stepwise increments of Co. The labile Co concentration, $[Co_{labile}]$, at each level of Co is measured using CSV, whereas concentrations of $[CoL]$ are calculated from a mass balance of the Co concentration

$$[CoL] = C_{Co} - [Co_{labile}] \qquad (4)$$

where the total dissolved Co concentration, C_{Co}, includes the non-labile fraction which is released by photo-oxidation of the sample.

The mass balance of the Co concentration in the presence of DMG is given by

$$C_{Co} = [Co'] + [Co(DMG)_2] + [CoL] \qquad (5)$$

where $[Co']$ is the inorganic Co concentration.

The labile Co concentration is that which equilibrates with the added ligand (DMG), and is measured by CSV. Thus the labile Co concentration is defined by

$$[Co_{labile}] = [Co'] + [Co(DMG)_2] \qquad (6)$$

The CSV peak current, i_p, is directly related to the labile Co concentration via the sensitivity, S (=peak current/Co concentration (nA/nM))

$$i_p = S[Co_{labile}] \qquad (7)$$

which is calibrated by standard Co additions to the sample. The definition of the labile Co concentration (eqn. (6)) includes [Co′], because a small constant fraction of the added Co ends up as Co′, the rest being complexed by DMG. The concentration of Co^{2+} is directly related to the labile Co concentration

$$[Co^{2+}] = [Co_{labile}]/\alpha' \qquad (8)$$

where α' is the overall α-coefficient (Ringbom and Still, 1972) of Co^{2+} (excluding complexation by L)

$$\alpha' = (\alpha'_{Co'} + \alpha_{CoDMG})$$

where $\alpha_{Co'}$ is the α-coefficient for inorganic complexation of Co^{2+} ($\log \alpha_{Co'} \approx 0.24$ in seawater of pH 8 (Turner et al., 1981)), and α_{CoDMG} the α-coefficient for complexation of Co^{2+} by DMG

$$\alpha_{CoDMG} = \beta'_{CoDMG_2}[DMG']^2 \qquad (9)$$

[DMG′] being the concentration of DMG not complexed by Co (approximately [DMG′] = the total DMG concentration, C_{DMG}) and β'_{CoDMG_2} the conditional stability constant for the formation of $Co(DMG)_2$ in seawater

$$\beta'_{CoDMG_2} = [CoDMG_2]/([Co^{2+}][DMG']^2) \qquad (10)$$

It is assumed that the 2:1 complex of DMG with Co^{2+} is predominant at the DMG concentration used in the experiments, analogous with the complexation of Ni^{2+} (van den Berg and Nimmo, 1987) (the value for α_{CoDMG} is not affected if this assumption is incorrect as it is calibrated in the same conditions as used in the experiments).

In practice the following relationship (obtained by substitution for $[Co^{2+}]$ in eqn. (3) using eqn. (8)) is more convenient to use for the van den Berg/Ruzic plot than eqn. (3), because the labile, rather than the free, Co^{2+} concentration is measured directly

$$[Co_{labile}]/[CoL] = [Co_{labile}]/C_L + \alpha'/(C_L K'_{CoL}) \qquad (11)$$

The values for $[Co_{labile}]$ in eqn. (11) are obtained directly from the CSV peak current because $[Co_{labile}] = i_p/S$ (eqn. (7)), and concentrations of [CoL] from eqn. (4). S is calibrated by standard additions of Co to one of the samples in which the Co-complexing capacity was previously saturated by a Co increment greater than the complexing capacity (in practice the kinetics of complex formation of L are very slow in seawater because of the competition by the major cations (van den Berg, 1984; van den Berg and Nimmo, 1987), and no significant equilibration of Co^{2+} with L′ is expected to take place during the short period of a few minutes between a standard addition and the CSV measurement even if the ligand is not fully saturated with Co^{2+}; repeat measurements showed that the peak height of a standard Co addition was indeed constant). Comparison of S with the slope of a plot of i_p as a function of the Co concentration (see Fig. 3a) provides a means of estimating whether the end of the titration has been reached, as these should then be equal.

Values for C_L and K'_{CoL} are calculated by linear least-squares regression from 1/slope and $\alpha'/(\text{Y-intercept} \times C_L)$ of a plot of $[Co_{labile}]/[CoL]$ as a function of $[Co_{labile}]$.

Calibration of β'_{CoDMG_2} and $\beta'_{CoNioxime_2}$

Values for β'_{CoDMG_2} and $\beta'_{CoNioxime_2}$ (the conditional stability constant for complexation of Co^{2+} by nioxime) are calibrated in UV-irradiated seawater by ligand competition with a chelating ligand (EDTA), of which the stability constants for complexation of Co and the major ions are known (Martell and Smith, 1974). This procedure is similar to that carried out previously for Zn complexation by APDC (ammonium pyrrolidinedi thiocarbamate) (van den Berg, 1985) and Ni complexation by DMG (van den Berg and Nimmo, 1987).

The peak current, i_p, is directly proportional to the concentration of the adsorbing complex, $CoDMG_2$, via a proportionality factor, S_1

$$i_p = S_1 [CoDMG_2] \tag{12}$$

In the absence of EDTA and in UV-irradiated seawater eqn. (5) reduces to

$$C_{Co} = [Co']_0 + [CoDMG_2]_0$$

where the subscript 0 indicates the absence of EDTA. Substitution of the concentration terms by the products of the α-coefficients with $[Co^{2+}]$ and rearrangement gives

$$[Co^{2+}]_0 = C_{Co}/(\alpha_{Co'} + \alpha_{CoDMG}) \tag{13}$$

Substitution in eqn. (10) for $[Co^{2+}]$ using eqn. (13) and for β'_{CoDMG_2} using eqn. (9) with rearrangement gives

$$[CoDMG_2]_0 = \alpha_{CoDMG} C_{Co}/(\alpha_{Co'} + \alpha_{CoDMG}) \tag{14}$$

In the presence of added EDTA the mass balance (eqn. (5)) is given by

$$C_{Co} = [Co'] + [Co(DMG)_2] + [CoEDTA]$$

where $\alpha_{CoEDTA} = K'_{CoEDTA}[EDTA']$ (= the product of the conditional stability constant of CoEDTA and the concentration of EDTA not complexed by Co^{2+}). The concentration of $[CoDMG_2]$ is diminished by competition for Co^{2+} by EDTA

$$[CoDMG_2] = \alpha_{CoDMG} C_{Co} / (\alpha_{Co'} + \alpha_{CoDMG} + \alpha_{EDTA}) \qquad (15)$$

The ratio, X, of the peak current in the presence, over that in the absence of EDTA is given by

$$X = i_p / i_{p,0} = S_1 [CoDMG_2] / (S_1 [CoDMG_2]_0)$$

which after cancellation of S_1 and substitution using eqns. (14) and (15) converts to

$$X = (\alpha_{Co'} + \alpha_{CoDMG}) / (\alpha_{Co'} + \alpha_{CoDMG} + \alpha_{EDTA}) \qquad (16)$$

Values for α_{CoDMG} can be calculated by fitting X to eqn. (16) as a function of the EDTA′ concentration using a non-linear least-squares computer program. The concentration of EDTA′ (required for α_{EDTA}) is computed from

$$[EDTA'] = C_{EDTA} - (1 - X) C_{Co} \qquad (17)$$

Approximately, $[EDTA'] = C_{EDTA}$ as $C_{Co} \ll C_{EDTA}$.

Alternatively, values for α_{CoDMG} can be calculated (and then averaged) from single values for X using a rearranged version of eqn. (16)

$$\alpha_{CoDMG} = [(\alpha_{Co'} + \alpha_{CoEDTA}) X - \alpha_{Co'}] / (1 - X) \qquad (18)$$

From this a value for β'_{CoDMG_2} can be calculated using eqn. (9).

Equations (16) and (18) are more rigorous than analogous equations derived previously for Zn-APDC complexation (van den Berg, 1985) as inorganic complexation of the metal ($\alpha_{Co'}$ here, and α_{Zn} in the previous paper) is not neglected. In eqn. (16) $\alpha_{Co'}$ is indeed very small compared with α_{CoDMG}, and its elimination would be justified (though unnecessary), but this should not be done with α_{Zn} as α_{ZnAPDC} is of similar magnitude to α_{Zn}.

The equations for nioxime are equivalent to those for DMG.

EXPERIMENTAL

Instrumental, chemicals and sampling

A PAR polarograph with a PAR 303A static mercury drop electrode and a PAR 305 magnetic stirrer was used for the voltammetric measurements. The drop size was 2.9 mm^2. The reference electrode was Ag/AgCl, saturated KCl.

Stock solutions of DMG and nioxime (0.1 M) were prepared in HPLC-grade methanol (BDH). Stock aqueous pH buffer solutions contained 1 M boric acid/0.5 M NaOH (pH 8.5), 1 M HEPES/0.5 M NH_4OH (pH 7.8), and 2 M triethanolamine (TEA)/1.6 M NH_4Cl (pH 8.7). A solution of 0.5 M $NaBH_4$

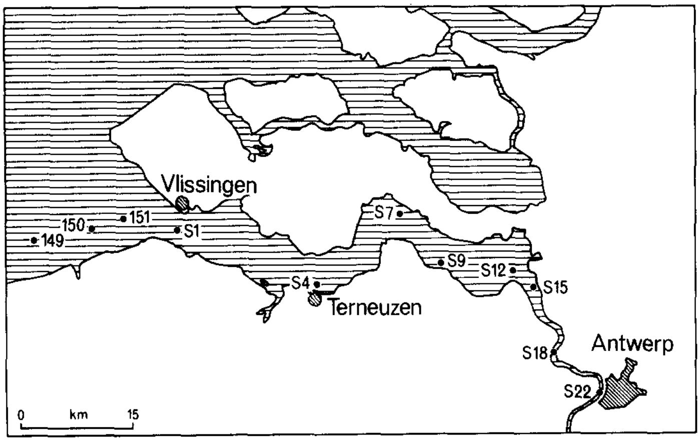


Fig. 1. Map showing the locations of the sampling stations on the Scheldt Estuary.

was prepared in 0.2 M NH_4OH. The buffer solutions were equilibrated with 0.1 mM MnO_2, and then filtered to remove contaminating metal ions (van den Berg, 1984). The EDTA stock solution was 0.1 M and the pH was neutralised by adding NaOH. Standard solutions of Co were prepared by dilution of an atomic absorption standard solution (BDH). The pH measurements were calibrated on the NBS pH scale.

Samples were collected on the estuary of the River Scheldt. The sample bottles had been soaked previously with 1 M HCl rinsed with Milli-Q water, and rinsed with the sample prior to filling. All samples were air-pressure filtered (0.45 μm) and stored in the refrigerator until analysis. The sample stations in the Scheldt Estuary are indicated in Fig. 1. Seawater from the Menai Straits was collected by pumping near the marine institute in Menai Bridge and a sample from the Indian Ocean was collected at a depth of 2000 m. Water from the latter sample was used for the calibration of the conditional stability constants of DMG and nioxime with Co. The complexing capacity titrations were carried out at room temperature ($\approx 25°C$) in a 'clean room' supplied with filtered air.

Procedure to determine the Co-complexing capacity

Aliquots of seawater (10 ml) were pipetted into Teflon polarographic cells, and 0.5 ml of the TEA buffer and 50 μl of the DMG solution were added. Co was added so that the Co concentration varied between 0.1 and 2.5 nM in 10–15 increments. The solutions were covered with a watch glass and were allowed to equilibrate overnight. Then the labile Co concentration was determined using an adsorption potential of -0.9 V and a stirred adsorption period of 120 s, followed by a quiescence period of 10 s. The pulse rate was 10 s^{-1} and the scan rate was 20 mV s^{-1}. The sensitivity of the CSV measurement was calibrated by means of standard additions of Co to several of the aliquots and was used to corroborate the value obtained from a tangent along a plot of the peak height versus the Co concentration in the equilibrated aliquots.

The initial Co concentration in the sample was measured after 3 h of UV-irradiation of 30 ml of an acidified sample (pH 2.5) using a 1 kW high-pressure mercury lamp. Co(III), which forms during the irradiation step and which is not electroactive, was reduced by addition of 20 μl of the $NaBH_4$ solution after the irradiation.

Determination of values for β'_{CoDMG2} and $\beta' Co_{Nioxime2}$ at various salinities

Seawater originating from the Indian Ocean and having a salinity of 35 was UV-irradiated for 3 h. This water was diluted with UV-irradiated distilled water to obtain lower salinities of 20, 10 and 1. For β'_{CoDMG_2}, quantities (10 ml) of this seawater containing 1×10^{-4} M DMG, 0.1 M TEA buffer and approximately 50 nM Co were equilibrated overnight with EDTA at concentrations between 0.1 and 6 mM in 8 increments. The labile Co concentrations were then determined by CSV directly. The same procedure was followed for $\beta'_{CoNioxime_2}$ with 5×10^{-6} M nioxime and 0.03 M HEPES buffer.

RESULTS AND DISCUSSION

Comparison of different CSV procedures to determine the labile Co concentration

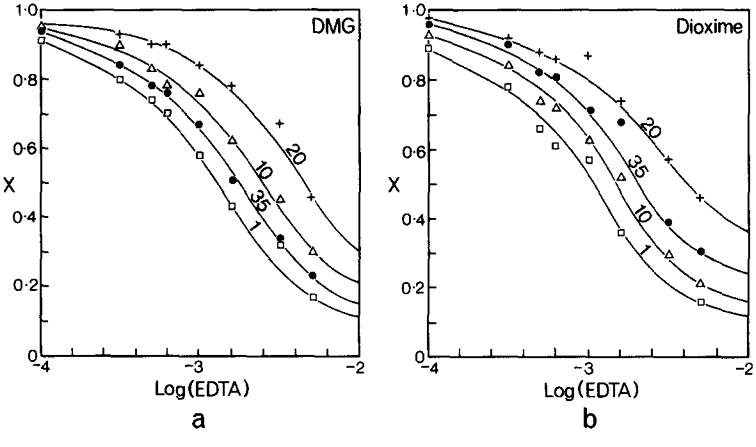
Two variants of the CSV method have been proposed to determine Co in seawater. The original method uses DMG and a solution pH of 9.2 (Pihlar et al., 1981); one variant uses TEA as pH buffer (pH 8.7) and a higher DMG concentration of 2 mM (Zhang et al., 1988), the other variant uses nioxime as the added chelator and uses HEPES to buffer the pH, as this was found to further enhance the sensitivity (Donat and Bruland, 1988). The sensitivities of these procedures were compared by determining Co in UV-irradiated seawater. It was found that the two variants had very similar sensitivity, both producing a better-defined Co peak than the original procedure. Both variants were therefore employed to attempt to study Co speciation in seawater.

The sensitivity for Co increases with the DMG concentration until approximately 3 mM DMG, after which it remains constant (Zhang et al., 1988). This suggests that the 2:1 (DMG:Co) complex adsorbs, as adsorption of the 1:1 complex would cause the sensitivity to peak at a lower level of DMG, followed by a decrease at higher concentrations when the 1:1 complex is superseded in solution by the 2:1 variety. The information available for the nioxime complex (Donat and Bruland, 1988) suggests a similar mechanism.

Calibration of the conditional stability constants, β'_{CoDMG_2} and $\beta'_{CoNioxime_2}$

The conditional stability constants for complexation of Co^{2+} by DMG and nioxime in seawater cannot be calculated from literature data as no information is available about competition by the major ions. The conditional stability constants were therefore calibrated in separate experiments by equilibration with EDTA. The effect of additions of EDTA on the peak height for Co in seawater of various salinities is shown in Fig. 2. The values for K'_{CoEDTA} (from Martell and Smith, 1974) were corrected for the pH and major ion competition using free ionic Ca^{2+} and Mg^{2+} concentrations calculated from an ion pairing model after Dickson and Whitfield (1981) (Table 1). The values for β'_{CoDMG_2} and $\beta'_{CoNioxime_2}$ were calculated using eqns. (18) and (9) and are shown in Table 1.

The stabilities of the Co complexes of DMG and nioxime in seawater are both very high, higher than that of the EDTA complex. The DMG complex with Co is weaker than that with Ni ($\log \beta'_{NiDMG_2} = 17.2$ at salinity = 32 (van den Berg and Nimmo, 1987)) which is in line with expectation, as the EDTA complex of Co is also weaker than that of Ni. The complexes of Co with DMG are weaker than those with nioxime. DMG was selected for the present study of organic Co complexation in seawater, as it was thought that such complexed Co would dissociate fully (and would therefore be undetectable) in the presence of nioxime.



a b

Fig. 2. The determination of (a) β'_{CoDMG_2} and (b) $\beta'_{CoNioxime_2}$ by ligand competition with EDTA. The salinity is indicated on the plots. (a) $C_{DMG} = 1 \times 10^{-4}$ M; (b) $C_{Nioxime} = 5 \times 10^{-6}$ M.

TABLE 1

Values for the conditional stability constants for complexation of Co^{2+} by EDTA (from Martell and Smith, 1974) and by DMG and nioxime in seawater

Salinity (‰)	log K'_{CoEDTA}	log β'_{CoDMG_2}	log $\beta'_{CoNioxime_2}$
35	7.62	12.85 ± 0.10	15.62 ± 0.08
20	7.85	13.28 ± 0.07	16.09 ± 0.20
10	8.15	13.01 ± 0.05	15.92 ± 0.22
1	9.14	12.72 ± 0.16	16.75 ± 0.13

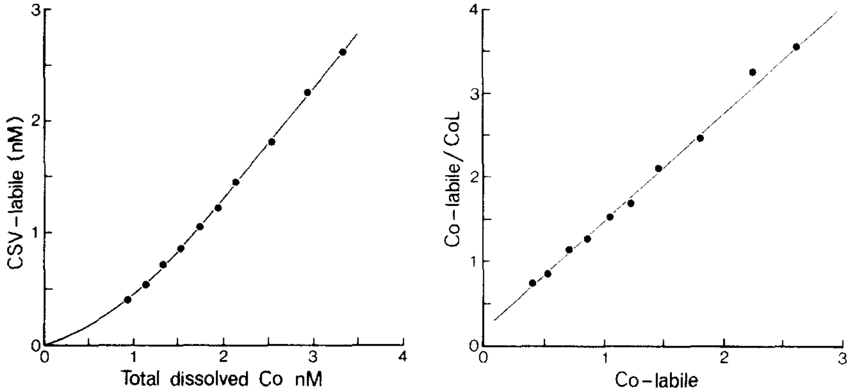


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Fig. 3. Complexing capacity titrations: plots of (a) the CSV-labile Co concentrations as a function of the total dissolved Co concentration and (b) of $[Co_{labile}]/[CoL]$ as a function of $[Co_{labile}]$ for station S4 of the Scheldt Estuary.

Complexing capacity titrations

The CSV-peak height was found to increase linearly with the Co concentration in most samples, as the ligands in these samples were almost fully saturated by the Co initially present in the sample. A plot of the labile Co concentration as a function of the total Co concentration in a sample originating from the Scheldt Estuary is shown in Fig. 3a. A small amount of curvature was apparent only for the first few data points. The van den Berg–Ruzic plot was straight (Fig. 3b), indicating that only one competing complexing ligand was predominant in the present conditions, as was the case in all other samples tested.

The organic complexation of Co in seawater

The results of the complexing capacity titrations with Co are summarised in Table 2. It can be seen that all samples were found to contain organic com-

TABLE 2

The concentrations of dissolved Co and the Co-complexing capacity (C_L), values for log K'_{CoL} and the fraction (%) of Co which is complexed by organic material in samples from estuarine and coastal origin. The standard deviations are the 1σ confidence limits calculated from the linear least-squares regression

Sample	Salinity	C_{Co} (nM)	C_L (nM)	log K'_{CoL}	Organic Co (%)
Scheldt Estuary					
S149	30.06	0.65	0.56±0.01	16.6±0.1	86
S150	29.82	0.63	0.29±0.02	16.3±0.2	46
S151	29.03	0.69	0.53±0.06	15.8±0.1	77
S1	25.01	0.87	0.47±0.01	16.3±0.1	54
S4	24.02	0.94	0.76±0.01	16.3±0.1	81
S7	19.92	1.03	1.13±0.04	15.7±0.1	100
S9	18.96	1.16	0.84±0.02	16.1±0.1	72
S12	13.78	1.08	0.84±0.06	16.0±0.1	78
S15	10.24	1.36	0.78±0.04	16.3±0.1	57
S18	7.74	1.42	0.95±0.05	16.5±0.1	67
S22	3.97	1.04	0.55±0.02	17.5±0.2	53
Menai Straits					
	32	0.35	0.40±0.04	15.6±0.1	100

plexing ligands capable of binding Co. In most samples the ligands were fully saturated with Co, as the Co concentration was slightly greater than the available ligand concentration.

The stability of the CoL complexes is very great as can be seen from the conditional stability constants (log values), which were found to lie within a relatively narrow band between 15.7 and 17.5 at all salinities (Fig. 4) on average about 8 orders of magnitude greater than the equivalent value for EDTA, which is usually considered a strong chelating agent. Comparative values for complexes of Ni^{2+} of the type NiL are a little higher at log $K'_{NiL}=17.3$–18.7 (van den Berg and Nimmo, 1987). Although the sample with the lowest salinity has the highest value for log K'_{CoL}, there are not enough data, especially at low salinities, to establish whether the stability of the complexes decreases systematically with increasing salinity as a result of competition by Ca^{2+} and Mg^{2+}.

One can only speculate at present about the nature of ligands which form complexes of such great stability in the marine environment. Possibilities include the formation of complexes of Co^{2+} with porphyrins or their derivatives, or with metallothioneins. Metalloporphyrins have been shown to occur in sediments (Palmer and Baker, 1978) and metallothioneins are known to be produced by molluscs for instance (Viarengo et al., 1988).

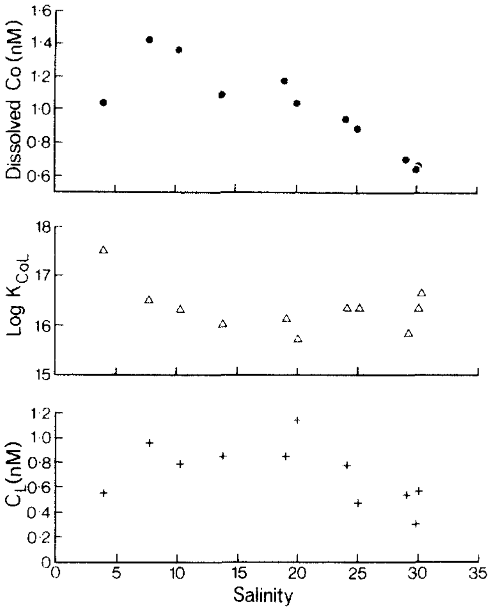

Fig. 4. Plots of the Co concentration, the ligand concentration, and the conditional stability constants (log values) as a function of the salinity of the Scheldt Estuary.

The organic speciation of Co in the seawater samples was calculated using the determined ligand concentrations and conditional stability constants, and is shown in Table 2. It can be seen that a variable fraction of the total dissolved Co concentration (between 46 and 100%) occurred in very stable organic complexes.

The dissolved Co concentration, the ligand concentration and the log K'_{CoL} values determined in the Scheldt Estuary have been plotted as a function of the salinity in Fig. 4. The dissolved Co concentration is high, presumably as a result of pollution in the upper reaches of the estuary. After a strong increase at salinity = 7 the Co concentration is gradually diluted with seawater. The bulge-shape of the Co concentration is quite typical for transition metals in estuarine waters (e.g. Ackroyd et al., 1986; Newton and van den Berg, 1987).

The distribution of the Co-complexing ligands generally follows the same pattern as that for Co. This is illustrated by a plot of the ligand concentration as a function of the Co concentration in Fig. 5. The covariation of the Co and the ligand concentrations throughout the estuary is perhaps not surprising considering the great stability of the complexes and the high fractions of Co and ligands which occur as complexes. A similar covariation with complexing

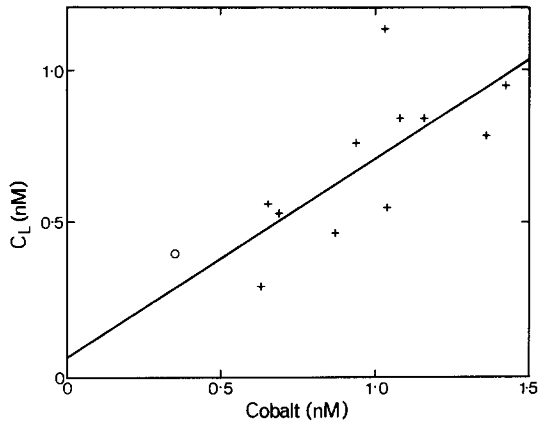

Fig. 5. The ligand concentration as a function of the Co concentration in the Scheldt Estuary. The sample indicated by a 'O' originated from the Menai Straits.

ligands has been observed previously for Cu and Zn in the same estuary (van den Berg et al., 1987).

The analytical detection window for K'_{CoL}

The ligand concentrations determined in samples from the Scheldt Estuary using CSV for Cu, Zn (van den Berg et al., 1987) and Co differ greatly, those for Cu and Zn being around 100 times higher than for Co. Although different metal ions perhaps occupy different complexation sites, and although the complexation capacity for each metal ion was determined in the presence of the other competing metal ions, some of the difference is likely caused by the different detection window of each ligand used for the CSV determination. The window of detection is of importance as it is likely that a great variety of complexing ligands is present in natural waters. The detection window therefore determines which ligand, or group of ligands, is detected (van den Berg et al., 1990).

The detection window is framed by α_{CoDMG} and its width is determined by the reproducibility of the CSV analysis. In the presence of 5×10^{-4}M DMG in seawater log α_{CoDMG} lies between 6.2 (at salinity = 35) and 7.6 (at salinity = 1). Complexing ligands with a value for α_{CoL} 10× greater than that for α_{CoDMG} would be largely ($\approx$90%) non-labile, whereas those with a value 10× smaller would be almost fully ($\approx$90%) labile. This stability region is therefore taken as the detection window, as it is unlikely that fractions much less than 10% of the dissolved Co concentration can be detected accurately. Thus the detection window (in terms of α-coefficients) of the present experiments is situated at

$5.2 < \log$ window < 7.2 at salinity $= 35$, whereas it is $6.6 < \log$ window < 8.6 at salinity $= 1$. The implication of this is, that ligands with stability constants of $14.2 < \log K'_{\mathrm{CoL}} < 16.2$ at salinity $= 35$, and of $15.6 < \log K'_{\mathrm{CoL}} < 17.6$ at salinity $= 1$ can be determined accurately at a ligand concentration of 1 nM. Weaker or stronger complexing ligands can be determined by either decreasing or increasing the DMG concentration, or by using a different ligand for the CSV analysis. The concentrations of ligands stronger than the indicated window would still be determined accurately from the slope of the plot of $[\mathrm{Co}_{\mathrm{labile}}]/[\mathrm{CoL}]$ versus $[\mathrm{Co}_{\mathrm{labile}}]$ using labile Co concentrations obtained at elevated C_{Co}, but the value for K'_{CoL} would not be accurate because of the apparent small magnitude of the Y-axis intercept compared with the noise of the data.

To determine whether the α-coefficients of the complexing ligands detected in this study correspond to the detection window, values for $\log \alpha_{\mathrm{CoL}}$ were calculated for all the samples, and were plotted against $\log \alpha_{\mathrm{CoDMG}}$ (which varied as a function of the salinity) in Fig. 6. The detection window is indicated by dashed lines, and a linear least-squares regression of the data by a solid line. It can be seen that almost all data are situated within the detection window, although at the high side of it, and two points appear just above it. Also, the values for $\log \alpha_{\mathrm{CoL}}$ appear to vary in a non-linear fashion with $\log \alpha_{\mathrm{DMG}}$. This skewered distribution suggests that the complexing ligand (or site) detected does not reflect an average value for a group of ligands, but instead appears to represent a particular complexing ligand (or site), which behaves in a conservative fashion (at salinities > 7) in the estuary.

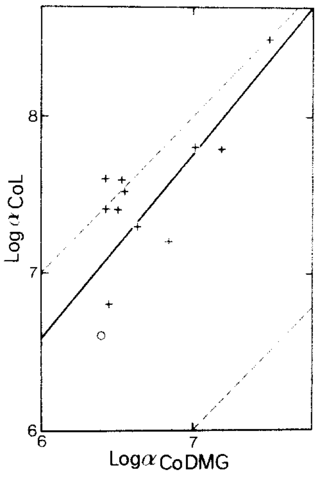

Fig. 6. Values for $\log \alpha_{\mathrm{CoL}}$ as a function of $\log \alpha_{\mathrm{CoDMG}}$. The detection window is situated between the dotted lines, whereas the solid line represents a linear least-squares regression through the data. The sample indicated by a 'O' originated from the Menai Straits.

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