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Determination of cadmium(II), copper(II), manganese(II) and nickel(II) species in Antarctic seawater with complexing resins

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Abstract

The strong species of cadmium(II), copper(II), manganese(II) and nickel(II) in an Antarctic seawater sample are investigated by a method based on the sorption of metal ions on complexing resins. The resins compete with the ligands present in the sample to combine with the metal ions. Two resins with different adsorbing strengths were used. Very stable metal complexes were investigated with the strong sorbent Chelex 100 and weaker species with the less strong resin, Amberlite CG-50. Strong species were detected for three of the considered metal ions, but not for Mn(II). Cu(II) is completely linked to species with a side reaction coefficient as high as log $\alpha_{M(I)}=11.6$ at pH = 7.3. The ligand concentration was found to be similar to that of the metal ion, and the conditional stability constant was around 10^{20} M^{-1}. In the considered sample, only a fraction of the metal ions Cd(II) and Ni(II) is bound to the strong ligands, with side reaction coefficients equal to log $\alpha_{M(I)}=5.5$ and 6.5 at pH = 7.3 for Cd(II) and Ni(II), respectively. These findings were confirmed by the test with the weaker sorbent Amberlite CG-50. It can be calculated from the sorption equilibria that neither Mn(II) nor Ni(II) is adsorbed on Amberlite CG-50 under the considered conditions and, in fact, only a negligible fraction of Mn(II) and Ni(II) was adsorbed. A noticeable fraction of Cd(II) was adsorbed on Amberlite CG-50, meaning that cadmium(II) is partially linked to weak ligands, possibly chloride, while no copper(II) was adsorbed on this resin, confirming that copper(II) is only combined in strong species. These results are similar, but not identical, to those obtained for other seawater samples examined in previous investigations.

Keywords: Natural ligands in seawater; Speciation of metal ions; Resin titration; Seawater

1. Introduction

Geochemical cycling, the distribution in the environment and the bioavailability of trace metal ions depend on their chemical speciation. It is widely believed that metals combine with inorganic and organic ligands at relatively high concentrations and with weak complexing properties. However, stronger ligands at trace concentrations have been found in various natural waters by using voltammetric methods based on ligand competition (van den Berg and Donat, 1992; Achterberg and van den Berg, 1994; Shank et al., 2004; Sander et al., 2005). Side reaction coefficients of copper(II) were estimated as high as 10^7 at pH 7–8. Copper(II) complexes

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with a higher side reaction coefficient have been detected in some high and low salinity waters (Pesavento et al., 2001a,b, 2002, 2004) through a different ligand competition method based on the sorption of metal ions on complexing resins (Pesavento and Biesuz, 1995). In this method, the competitive ligand is the solid sorbent. For instance, strongly sorbing resins, such as those containing iminodiacetic groups, make it possible to evaluate side reaction coefficients as high as 10^{10}–10^{12} in the case of copper(II) at a pH close to neutral. These ligands are at nM level, but, since their complexation constant is very high, they are important in the complexation of metal ions even at these concentration levels.

The accuracy of the method was tested by examining synthetic solutions (Pesavento and Biesuz, 1995; Pesavento et al., 2000, 2004) containing a known concentration of identified ligands. The stability constants of the complexes were found to agree with those in the literature. The method was applied to sea and fresh waters (Pesavento et al., 1999, 2001a,b, 2002) for several metal ions and with different sorbing resins. In some cases, extremely stable complexes were determined, with reaction coefficients much higher than those found in previous speciation investigations based on different methods, including CLE–CSV (competitive ligand equilibration–cathodic stripping voltammetry).

The Resin Titration (R. T.) method is based on the sorption of a free metal ion on a complexing resin, without any addition of metal. Recently a CLE–CSV method has been developed on the same principle as R. T., but with a soluble competing ligand. (Nuester and van den Berg, 2005). In CLE–CSV methods, the metal ion is usually added to the solution to titrate the excess ligands that are not complexed by the metal ion originally present.

The interesting feature of the R. T. method is that many metal ions can be investigated simultaneously. This paper examines copper(II), cadmium(II), nickel(II) and manganese(II) in an Antarctic seawater sample to detect very strong metal complexes in such a remote area. This can help identify the origin of the ligands.

Two different resins are used: the strongly sorbing resin Chelex 100, containing iminodiacetic groups, to investigate the stronger complexes; and the carboxylic resin Amberlite CG-50 to characterize the weaker species. The two resins have well differentiated detection windows (van den Berg and Donat, 1992; Shank et al., 2004), particularly for copper(II) (Pesavento et al., 1999, 2002). The detection windows of Chelex 100 and Amberlite CG-50 for the four metal ions are reported in Fig. 1. It shows that Amberlite CG-50 does not adsorb Mn(II) and Ni(II), even if they are free ($\alpha_{M(I)}=1$), since the alkaline earth metal ions compete for the complexing sites of the resin. On the contrary, Chelex 100 can sorb all the metal ions considered here.

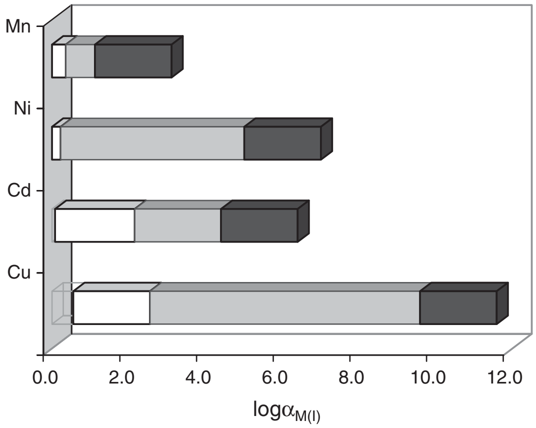

Fig. 1. Detection windows of Cu(II), Cd(II), Ni(II) and Mn(II) at $V=300$ mL, pH=7.3 and $w=0.150$ g for Chelex 100 (black) and at pH=6.95 and $w=0.100$ g for Amberlite CG-50 (white) calculated with K^* values reported in Table 1. Grey bars represent the side reaction coefficients of the complexes completely dissociated by Chelex 100, but not adsorbed at all on Amberlite CG-50.

2. The model for resin titration

A list of the symbols is reported at the end of this paper.

The resin titration (R. T.) method is based on sorption of the metal ions on a resin at different V/w, V being the volume of the solution phase, in mL, and w the amount of water in the resin phase, in g. The amount of water in the resin phase is constant and equal to the grams of dry resin multiplied by 2.5, if the pH is higher than 4 for Chelex 100 and higher than 6 for Amberlite CG-50. w depends on the acidity at those pH for which the resins are partially deprotonated (Pesavento et al., 1993, 1994). The resin titration curve is obtained by plotting the concentration of the metal ion adsorbed on the resin (c, nM) as a function of V/w. Examples are reported in Figs. 2 and 3.

The concentration of adsorbed metal ions depends on the species stability in solution phase and on the sorbing properties of the complexing resin. The stability of the species in solution is measured by the side reaction coefficient of the metal, $\alpha_{M(I)}$, the ratio of total to free metal ion in solution (Ringbom and Still, 1972). The sorbing properties of the resins are measured by the partition coefficient K^* (Pesavento and Biesuz, 1995; Pesavento et al., 2002), which is the ratio of the metal ion concentration in the resin phase to free metal ion

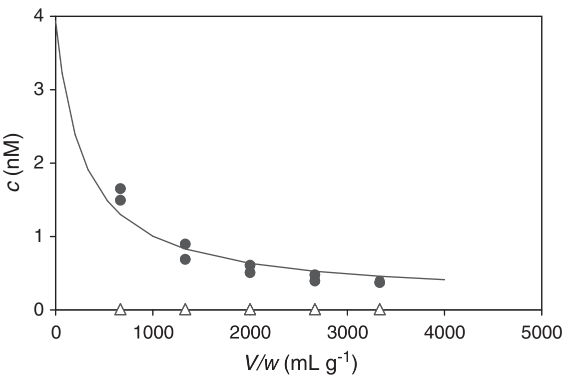

Fig. 2. R. T. curves of copper(II) in the Antarctic seawater sample. △: Amberlite CG-50 (0.100(2) g, pH range 4.40–6.87); ●: Chelex 100 (0.150(2) g, pH range 4.21–7.30).

concentration in solution. K^* can be calculated at each particular set of experimental conditions as described in previous papers (Pesavento and Biesuz, 1995; Pesavento et al., 2002).

The concentration of metal ions adsorbed at each point of the titration (V/w) is modelled by the following relationship:

$$c = c_w + \frac{c_{tot,res} - c_w}{1 + \frac{\alpha_{M(I)} \cdot V}{K^* \cdot w}} \qquad (1)$$

$c_{tot,\ res}$ is the total concentration of the metal ion that is adsorbed on the resin when $\alpha_{M(I)}V/K^*w$ is negligible with respect to 1, i.e. at low V/w; c_w is the concentration of the adsorbed metal ion when the second term to the right in Eq. (1) is negligible, at high V/w. Thus c_w is evaluated directly from the titration curve when a constant concentration of metal ion is adsorbed.

$c_{tot,\ res}$ is evaluated from Eq. (1) assuming $\alpha_{M(I)}/K^*$ constant. If the acidity varies, the validity of this assumption must be evaluated in each particular condition. Since K^* is known, from the value of $c_{tot,\ res}$, the side reaction coefficients are evaluated at each acidity level, and the constancy of the ratio $\alpha_{M(I)}/K^*$ checked.

The concentration of metal ions in equilibrium with the resin is given by the difference $c_{tot,\ res} - c_w$. This concentration can be estimated through a complexation model widely used in speciation studies (van den Berg and Donat, 1992; Achterberg and van den Berg, 1994; Laglera and van den Berg, 2003; Shank et al., 2004). According to this model a 1 to 1 complex MI is formed by the metal M with the ligand I in solution:

$$\mathrm{M} + \mathrm{I} \rightleftarrows \mathrm{MI} \quad K_{M(I)} = \frac{[\mathrm{MI}]}{[\mathrm{M}]c'_I} \qquad (2)$$

where $K_{M(I)}$ is the conditional equilibrium coefficient and c'_I is the total concentration of the free ligand. The linearization method, independently proposed by Ružić (1982) and by van den Berg (1982), is here modified to take into account the peculiarities of the resin titration method. The concentration of free metal ions in the solution phase is evaluated from the concentration of metal adsorbed on the resin according to the relationship (Pesavento et al., 2001a,b):

$$[\mathrm{M}] = cV/K^*w \qquad (3)$$

Considering that the independent variable in R. T. is V/w and that the titration points can be at different acidities, in the presence of ligands at total concentration c_I, the modified Ružić–van den Berg relation becomes:

$$\frac{cV}{(c_{tot,res} - c)K^*[\mathrm{H}]^n w} = \frac{1}{\frac{K_{M(I)t}}{\beta_{an}} c_I} + \frac{cV}{c_I K^* [\mathrm{H}]^n w} \qquad (4)$$

$K_{M(I)t}$ is the complexation constant, independent of the acidity, in relation with the conditional stability constant, $K_{M(I)}$, by:

$$K_{M(I)t} = \frac{K_{M(I)} c'_I}{[\mathrm{I}]} \approx K_{M(I)} \beta_{an} [\mathrm{H}]^n \qquad (5)$$

The above relationship is true in the simplifying hypothesis that the side reaction coefficient of the deprotonated ligand I is much higher than one.

The parameters c_I and $K_{M(I)t}/\beta_{an}$ can be evaluated from the straight line obtained by plotting $cV/(c_{tot,\ res} - c)$

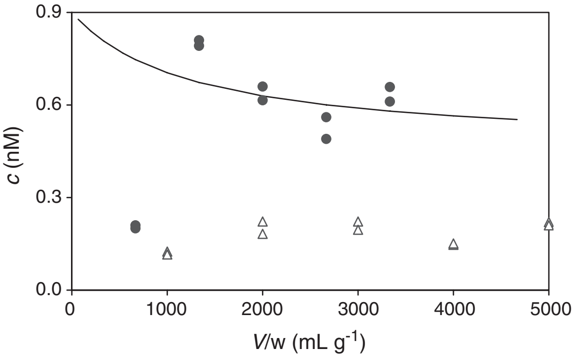

Fig. 3. R. T. curves of cadmium(II) in the Antarctic seawater sample. △: Amberlite CG-50 (0.100(2) g, pH range 4.40–6.87); ●: Chelex 100(0.150(2) g, pH range 4.21–7.30).

$K^*[\mathrm{H}]^n w$ vs. $\dfrac{cV}{K^*[\mathrm{H}]^n w}$. The constant $K_{\mathrm{M(I)t}}/\beta_{an}$ corresponds to the equilibrium constant of the reaction:

$$\mathrm{M} + \mathrm{H}_n\mathrm{I} \rightleftarrows \mathrm{MI} + n\mathrm{H} \tag{6}$$

The detection window of the specific titration is (Pesavento et al., 1999, 2001a,b):

$$\frac{0.1K^*w}{V} < \alpha_{\mathrm{M(I)}} < \frac{10K^*w}{V} \tag{7}$$

These limiting values are reported for Chelex 100 and Amberlite CG-50 at a particular set of conditions in Fig. 1. For instance, if Chelex 100 is used, copper(II) species with $\alpha_{\mathrm{M(I)}}$ higher than $10^{11.6}$ are not detected at all. Those with $\alpha_{\mathrm{M(I)}}$ lower than $10^{9.6}$ are detected, but their side reaction coefficient cannot be evaluated, since a quantitative sorption occurs, independently of V/w. In this case, only the limit value can be estimated. With Amberlite CG-50, which is a weaker resin, the Cu(II) species with $\alpha_{\mathrm{M(I)}}$ higher than $10^{2.6}$ are not sorbed, while those with $\alpha_{\mathrm{M(I)}}$ lower than $10^{0.6}$ are completely sorbed.

3. Materials and methods

3.1. Sample

The sample investigated was obtained by mixing two Antarctic seawaters obtained from the Antarctic Environmental Specimen Bank, with sample codes SW/13S/SS5860/13/Y1_250A and SW/13S/SS5860/11/Y5_250. Information about the two samples is reported on the BCAA web site (http://www.bcaa.unige.it). The samples, preserved at −30° in polyethylene bottles, were thawed and mixed to obtain a volume sufficiently high to perform the resin titration here proposed.

3.2. Reagents

Amberlite CG-50 [CAS 9042-11-9] (weakly acid resin, 100–200 mesh) was obtained from Sigma-Aldrich and Chelex 100 [CAS 68954-42-7] (Na-form, 50–100 mesh) from Bio-Rad Laboratories, Richmond CA. The capacity of the two resins (mmoles of active groups per g of dry resin) and the amount of water adsorbed under different conditions were determined as previously described (Pesavento et al., 1994; Pesavento and Biesuz, 1995).

Both resins were cleaned according to the procedure described by Pesavento et al. (1999, 2001a,b). This treatment is required to eliminate trace level heavy metal ions possibly present in the resins. The resins were used in H^+ form. Metal ion standard solutions were obtained from Merck (Titrisol Standard Solutions). Other reagents were Suprapure Merck.

3.3. Instrumentation and apparatus

A Varian Model 400 Atomic Absorption Spectrometer (AAS-ETA), with Zeeman Effect background correction and Model 96 autosampling, was used to determine metal ions in the stripping solutions (Pesavento et al., 1999, 2001a,b). The standard addition method was used for the quantification, with a multiple linear regression in the case of Mn(II) (Grotti et al., 1999). The detection limits in the stripping solutions ($\mathrm{HNO_3}$ 0.4 M) were 0.3 nM for Cd(II); 3.1 nM for Cu (II); 8.5 nM for Ni(II); 0.5 nM for Mn(II). Considering that the preconcentration was always higher than 20, the limits are adequate to the concentration levels of the original seawater.

The H^+ concentration was measured potentiometrically by a combined glass electrode (Amel Mod. 411/CGC/12, saturated KCl filling solution) standardized in NaCl 0.58 M, as reported in Pesavento et al. (1999, 2001a,b).

All manipulations were carried out in a laminar vertical flow hood, using polythene gloves.

3.4. Other materials

Containers, micropipettes, tips and other laboratory materials were made of polyethylene or polystyrene. Tissue filters were used for the separation of the resins. The filtration apparatus was made of polycarbonate (Sartorius, Model SM 165.10).

All the devices were cleaned as previously described (Pesavento et al., 1999, 2001a,b). The metal concentrations adsorbed by the resin in R. T. procedure were evaluated by subtracting the concentration of the blank obtained by treating the resin with 0.1 M $\mathrm{HNO_3}$.

3.5. Procedure for the resin titration (R. T.)

The resin titrations were carried out separately for the two resins Chelex 100 and Amberlite CG-50. The same amount of resin (0.150(2) g of Chelex 100 and 0.100 (2) g of Amberlite CG-50) was contacted with different aliquots of sample with volumes ranging from 100 to 500 mL. Large volumes were used to obtain a high preconcentration. The subsamples were equilibrated with the resins for 24 h, on a shaking plate. This long equilibration time is required when metal species with slow dissociation rates are present. Species that do not dissociate within 24 h are considered inert.

The acidity of each aliquot was measured following equilibration.

The resins were separated, washed with 100 mL of Milli-Q and dried at 40 °C, placed in a 10 mL containers and contacted with 2 mL of the stripping solution, 1 M HNO_3 for 1 h to desorb the metal ions. The solutions were then diluted to 5 mL with Milli-Q water. The concentrations of Cd(II), Cu(II), Mn(II), Ni(II) were determined in each eluate by AAS-ETA, in order to simultaneously titrate the four metal ions and concentrations were referred to the original volumes. Each titration was repeated twice.

4. Results and discussion

An Antarctic seawater sample obtained as reported in the experimental section above was examined by the resin titration method (R. T.) using Chelex 100 to investigate the presence of strong metal complexes with ligands at low concentration, similar to those found in other seawater samples (Pesavento et al., 1999, 2001a,b). A titration with a resin having a much lower detection window, such as Amberlite CG-50 (see Fig. 1), was also carried out for comparison, even if predictably Mn(II) and Ni(II) are not adsorbed under the considered conditions.

The titrations with the two resins were carried out independently. The four metal ions, Cd(II), Cu(II), Mn(II) and Ni(II) were examined.

The concentrations of metal ions adsorbed from different sample volumes (V), in duplicate experiments, with each subsample treated with the same amount of resin, are reported in Tables 1 and 2, together with the final pH after equilibration. A satisfactory agreement between the two replicates is observed, the relative standard deviation being respectively 3.7%, 12.4%, 0.3% and 3.1% for Cd(II), Cu(II), Mn(II) and Ni(II) in the case of Chelex 100.

Table 2
Resin titrations of Antarctic seawater with Amberlite CG-50 (0.100 (2) g of dry resin)

V (mL)	pH	$c_{Cd(II)}$ (nM)	α_{Cd}	$c_{Cu(II)}$ (nM)	α_{Cu}	$c_{Mn(II)}$ (nM)	α_{Mn}	$c_{Ni(II)}$ (nM)	α_{Ni}
100	4.40	0.12	<4	<lod$^{(a)}$	>3.6 10^2	<lod	–	<lod	–
100	4.50	0.12	<4	<lod	>3.6 10^2	0.09	–	0.36	–
200	5.64	0.18	<4	<lod	>3.6 10^2	0.06	–	0.75	–
200	5.87	0.22	<4	<lod	>3.6 10^2	0.06	–	0.76	–
300	6.71	0.22	<4	<lod	>3.6 10^2	0.04	–	0.63	–
300	6.53	0.20	<4	<lod	>3.6 10^2	0.03	–	0.44	–
400	6.77	0.15	<4	<lod	>3.6 10^2	<lod	–	<lod	–
400	6.90	0.15	<4	<lod	>3.6 10^2	0.01	–	0.28	–
500	6.66	0.22	<4	<lod	>3.6 10^2	0.03	–	0.52	–
500	6.87	0.22	<4	<lod	>3.6 10^2	<lod	–	0.34	–

$^{(a)}$Concentration in the eluate below the detection limit (lod).

As an example, the resin titration curves obtained for copper(II) and cadmium(II) are reported in Figs. 2 and 3. Copper(II) was not adsorbed at all on Amberlite CG-50, which indicates that weak complexes with $\alpha_{M(I)} < 3.6\ 10^2$ at pH = 6.95, are not present in the considered sample. The limit value corresponds to the upper $\alpha_{M(I)}$ limit for Amberlite CG-50. These weak complexes were present in other seawaters (Pesavento et al., 1999, 2001a,b, 2004). The fraction of cadmium (II) adsorbed on Amberlite CG-50 is a significant part of the total.

The continuous curves in Figs. 2 and 3 were calculated according to Eq. (1) with the experimental parameters. The results of R. T. with Chelex 100 and Amberlite CG-50 are summarized in Table 3. In the first row, $c_{tot,\ Che}$ values for each metal ion are reported, which is considered the total dissolved metal. The present method cannot detect species with $\alpha_{M(I)} > 10K^*_{Che}\ w/V$, but a test carried out on the certified seawater CASS 3 (Pesavento et al., 1999) showed that $c_{tot,\ Che}$ corresponds

Table 1
Resin titrations of Antarctic seawater with Chelex 100 (0.150(2) g of dry resin)

V (mL)	pH	$c_{Cd(II)}$ (nM)	α_{Cd}	$c_{Cu(II)}$ (nM)	α_{Cu}	$c_{Mn(II)}$ (nM)	α_{Mn}	$c_{Ni(II)}$ (nM)	α_{Ni}
100	4.27	0.20	–	1.65	3.85 10^5	0.40	<9	7.32	2.28 10^1
100	4.21	0.20	–	1.49	3.48 10^5	0.63	<9	7.66	1.29 10^1
200	6.90	0.80	3.13 10^4	0.69	9.71 10^{10}	0.63	<9	5.81	4.74 10^5
200	6.55	0.79	8.73 10^3	0.90	1.61 10^{10}	0.51	<9	5.70	1.31 10^5
300	6.97	0.66	1.40 10^5	0.50	1.34 10^{11}	0.51	<9	4.87	8.96 10^5
300	6.90	0.62	1.98 10^5	0.61	7.81 10^{10}	0.42	<9	4.94	–
400	7.07	0.47	–	0.48	1.57 10^{11}	0.42	<9	3.40	–
400	7.25	0.56	–	0.39	3.85 10^{11}	0.44	<9	3.25	–
500	7.30	0.66	2.47 10^5	0.37	3.94 10^{11}	0.44	<9	4.40	2.58 10^6
500	7.28	0.61	4.49 10^5	0.40	3.24 10^{11}	0.40	<9	4.07	3.96 10^6

Table 3
Results obtained for the Antarctic seawater sample by resin titration with Chelex 100 and Amberlite CG-50

	Cu(II)	Cd(II)	Ni(II)	Mn(II)
$c_{\mathrm{tot,\ Che}}$ (nM)	4(1)	0.9(3)	9(1)	0.5(1)
$c_{\mathrm{w,\ Che}}$ (nM)	0.16(5)	0.5(1)	3.4(5)	0.5(1)
c_{I} modified Ružić (nM)[(a)]	3.9(2)	0.3(1)	5.3(9)	–
log $K_{\mathrm{M(I)}}$[(b)]	~ 19.6	~ 14.4	~ 14.1	–
$c_{\mathrm{tot,\ Amb}}$ (nM)	<lod	0.20(3)	0.4(2)	0.04(0)
c_{int} (nM)[(c)]	0.16(5)	0.3(1)	–	–

The standard deviation is reported in brackets and refers to the last significant number.

[(a)] Obtained by modified Ružić procedure (see Eq. (5)).

[(b)] Approx values evaluated from $\alpha_{\mathrm{M(I)}}$ and c_{I}.

[(c)] $c_{\mathrm{int}} = c_{\mathrm{w,\ Che}} - c_{\mathrm{tot,\ Amb}}$.

to the certified total concentration, while this it is not using Amberlite CG-50 (Pesavento et al., 2001a,b).

The concentration of Cd(II) and Mn(II) is considerably different in the Antarctic seawater sample and in a sample from the Ligurian Sea previously examined by R. T. with the same resins (Pesavento et al., 1999, 2001a,b). In the Ligurian Sea sample, Mn(II) concentration was two orders of magnitude higher, while that of Cd(II) was five times lower. The concentration of Cd(II) in the Antarctic sea sample was consistent with the findings of other authors (Scarponi et al., 1997). In the same area, at the beginning of the summer season, Cd (II) was at the same concentration in the water column with a mean value of 0.7(1) nM.

Only manganese(II) is adsorbed on Chelex 100, so that other species, including Mn(IV), are not detected. Not only is the Mn(II) concentration lower in the Antarctic seawater sample, but the stability of the complexes is lower too, as seen from the fact that Mn(II) is completely adsorbed on Chelex 100, while it was in equilibrium in the case of the Ligurian Sea water.

The values of $c_{\mathrm{tot,\ res}}$, reported in Table 3, were obtained considering only those points for which $\alpha_{\mathrm{M(I)}}/K^*$ was constant. If $c_{\mathrm{tot,\ res}}$ is known, the value $\alpha_{\mathrm{M(I)}}/K^*$ at each titration point is calculated from Eq. (1) and then $c_{\mathrm{tot,\ res}}$ can be recalculated considering only the points for which $\alpha_{\mathrm{M(I)}}/K^*$ is actually constant. Tables 1 and 2 show the values of $\alpha_{\mathrm{M(I)}}$ obtained from Eq. (1) and Table 4 the values of K^*. Only in the case of cadmium(II) with Chelex 100, the points at pH around 4.3 have $\alpha_{\mathrm{M(I)}}/K^*$ significantly higher than that of the other titration points. This is clearly seen from the titration curve reported in Fig. 3, in which the first point is outside the curve.

The concentration of weakly complexed species, c_{w}, is obtained from the highest volumes, for which the concentration of adsorbed metal is independent of V/w, as seen in Fig. 3 for cadmium(II). This shows that some metal is completely adsorbed on Chelex 100 being combined in weak species with $\alpha_{\mathrm{M(I)}}$ lower than $0.1K^*_{\mathrm{Che}}\ w/V$. In the case of cadmium(II), the presence of weaker species is confirmed by the Amberlite CG-50 titration, which is also reported in Fig. 3. This figure shows that only a part of Cd(II), linked to weak complexes, completely dissociated in the presence of Chelex 100, is adsorbed on Amberlite CG-50. Copper (II) is not adsorbed at all on Amberlite CG-50, confirming that it is completely linked to strong ligands in the sample considered here.

K^* was evaluated according to the procedure previously described (Pesavento et al., 1999, 2001a,b). The algorithm used for this purpose is in MS-Excel format (Pesavento et al., 2001a,b A) and can be requested from the authors. In marine water at neutral pH, the counter ions in the resin phase are alkaline earth metals. They have a significant influence on K^* as previously discussed (Pesavento et al., 2001a,b A). For convenience, the K^* values of relevance to the present investigation are reported in Table 4.

When V/w increases, the solution acidity increases, due to the exchange of H^+ present in the resin with alkaline and alkaline earth metal ions in the sample. In seawater, where a high concentration of these cations is present, a high fraction of counter ions in the resin phase is constituted by alkaline and alkaline earth metals (Pesavento and Biesuz, 1995). Resins were here employed in H^+ form to reduce manipulation after the cleaning procedure. The acidity difference between the replicates is due to small variations of the resin mass contacted with the subsamples. In the present investigation, no buffer was added in order to avoid contamination.

The concentration of the ligands responsible for the formation of species in equilibrium with Chelex 100 can be evaluated by the modified Ružić–van den Berg equation (Eq. (4)). In principle, the equilibrium coefficient in Eq. (4), $K_{\mathrm{M(I)t}}/\beta_{an}$, can be estimated, but in the titrations here considered the ordinate at the origin was affected by a significant error that prevented an accurate evaluation of $K_{\mathrm{M(I)t}}/\beta_{an}$. On the other hand, the concentration of the ligand I, c_{I}, obtained by Eq. (4), is reported in Table 3. No result is given for Mn(II) since it was quantitatively adsorbed by Chelex 100. The concentration of the ligand I, evaluated with the modified Ružić–van den Berg equation, is not significantly different to that of the species in equilibrium with the resin ($c_{\mathrm{tot,\ Che}} - c_{\mathrm{w,\ Che}}$). The copper(II) ligands are at concentration similar to that of the metal ion, while the

Table 4
K^{*} values for Chelex 100 and Amberlite CG-50 calculated according to Pesavento et al. (1999, 2002)

pH	Chelex 100				pH	Amberlite CG-50			
	$K^{*}_{\mathrm{Cd(II)}}$	$K^{*}_{\mathrm{Cu(II)}}$	$K^{*}_{\mathrm{Ni(II)}}$	$K^{*}_{\mathrm{Mn(II)}}$		$K^{*}_{\mathrm{Cd(II)}}$	$K^{*}_{\mathrm{Cu(II)}}$	$K^{*}_{\mathrm{Ni(II)}}$	$K^{*}_{\mathrm{Mn(II)}}$
4.27	$1.69\ 10^{3}$	$1.68\ 10^{8}$	$5.00\ 10^{4}$	$8.05\ 10^{1}$	4.40	$2.39\ 10^{2}$	$1.62\ 10^{3}$	$1.06\ 10^{1}$	$9.31\ 10^{0}$
4.21	$1.47\ 10^{3}$	$1.27\ 10^{8}$	$4.29\ 10^{4}$	$7.97\ 10^{1}$	4.50	$3.22\ 10^{2}$	$2.36\ 10^{3}$	$1.42\ 10^{1}$	$1.30\ 10^{1}$
6.90	$1.14\ 10^{8}$	$2.12\ 10^{8}$	$5.60\ 10^{8}$	$7.03\ 10^{4}$	5.64	$3.53\ 10^{3}$	$3.74\ 10^{4}$	$1.14\ 10^{2}$	$1.48\ 10^{2}$
6.55	$2.81\ 10^{7}$	$5.24\ 10^{12}$	$1.42\ 10^{8}$	$1.74\ 10^{4}$	5.87	$4.75\ 10^{3}$	$4.53\ 10^{4}$	$1.29\ 10^{2}$	$1.70\ 10^{2}$
6.97	$1.47\ 10^{8}$	$2.74\ 10^{13}$	$7.22\ 10^{8}$	$9.09\ 10^{4}$	6.71	$1.85\ 10^{4}$	$8.26\ 10^{4}$	$1.50\ 10^{2}$	$2.04\ 10^{2}$
6.90	$1.14\ 10^{8}$	$2.12\ 10^{13}$	$5.60\ 10^{8}$	$7.03\ 10^{4}$	6.53	$1.32\ 10^{4}$	$7.04\ 10^{4}$	$1.48\ 10^{2}$	$2.01\ 10^{2}$
7.07	$2.09\ 10^{8}$	$3.89\ 10^{13}$	$1.02\ 10^{9}$	$1.29\ 10^{5}$	6.77	$2.08\ 10^{4}$	$8.77\ 10^{4}$	$1.50\ 10^{2}$	$2.05\ 10^{2}$
7.25	$3.70\ 10^{8}$	$6.88\ 10^{13}$	$1.79\ 10^{9}$	$2.28\ 10^{5}$	6.90	$2.70\ 10^{4}$	$1.01\ 10^{5}$	$1.51\ 10^{2}$	$2.06\ 10^{2}$
7.30	$4.26\ 10^{8}$	$7.94\ 10^{13}$	$2.07\ 10^{9}$	$2.63\ 10^{5}$	6.66	$1.68\ 10^{4}$	$7.87\ 10^{4}$	$1.49\ 10^{2}$	$2.03\ 10^{2}$
7.28	$4.03\ 10^{8}$	$7.51\ 10^{13}$	$1.96\ 10^{9}$	$2.49\ 10^{5}$	6.87	$2.54\ 10^{4}$	$9.79\ 10^{4}$	$1.51\ 10^{2}$	$2.06\ 10^{2}$

The pH is that after equilibration with the resin. Concentrations of the major constituents of the sample: $c_{\mathrm{Na}}+c_{\mathrm{K}}=0.46$ M, $c_{\mathrm{Ca}}+c_{\mathrm{Mg}}==6.4\ 10^{-2}$M ($I=0.58$ M).

strong ligands of cadmium and nickel are at a considerably lower concentration than that of the metal ion. It was assumed that the number of protons (n) released by the ligand I when complexing the metal ion is equal to 2. However, similar values of c_{I} were obtained also for $n=1$. The value $n=2$ was assumed because the slope obtained by plotting log $\alpha_{\mathrm{M(I)}}$ vs. pH is very close to this value (see Fig. 4).

Table 3 reports the approximate value of the conditional constants at pH=7.3, obtained from $\alpha_{\mathrm{M(I)}}$ and c_{I}. Complexes with a similar stability constant were detected also in different seawaters (Pesavento et al., 1999, 2001a,b). The nature of the ligands responsible for the strong complexation is unknown. For comparison it can be observed that the conditional stability constants at pH=7 of Cu(II), Ni(II) and Cd(II) with EDTA are respectively about log $K'_{\mathrm{f}}=16$, 16 and 14.

van den Berg and Donat (1992) proposed procedures with detection windows log $\alpha_{\mathrm{M(I)}}$ from 2.60 to 6.36, depending on the nature and concentration of the competing ligand, and a similar detection window was reported in a very recent paper (Nuester and van den Berg, 2005). Of course, this detection window does not allow the detection of copper(II) species with log $\alpha_{\mathrm{M(I)}}=11.3$, like those identified by R. T. with Chelex 100.

Weaker metal species of Cd(II) and Ni(II), which were here found by titration with Chelex 100, can be those detectable by other speciation methods, in particular by CLE–CSV with soluble competitive ligand.

The concentrations of metal ions adsorbed on Amberlite CG-50 are reported in Table 3. Only a negligible concentration of nickel(II) and manganese(II) was adsorbed on Amberlite CG-50, because of its weak sorbing properties (see Fig. 1, for the corresponding detection windows). In the case of copper(II) the sorption on Amberlite CG-50 is near zero, although this resin is strongly sorbing for copper(II): this proves that copper (II) is completely combined in strong species in the original sample. Only in the case of cadmium(II) some metal (22% of the total) was sorbed on Amberlite CG-50. The titration plot (see Fig. 3) is parallel to the abscissa, indicating that these cadmium(II) species are completely dissociated by the weak resin Amberlite CG-50. Only a higher limit for $\alpha_{\mathrm{M(I)}}$ can be evaluated, $\alpha_{\mathrm{M(I)}}<4$, as reported in Table 3. Considering that the reaction coefficient of the Cd(II)–Cl^{-} complexes is around 8 (Bixler and Larson, 1974), the identified complexes are probably the Cd^{2+}–Cl^{-} complexes. The weak species detected by Chelex 100 titration are at a concentration higher than that of the metal ions adsorbed on Amberlite CG-50, as can be seen from the titration curve in Fig. 3. This indicates that species of intermediate strength are also present. The difference $c_{\mathrm{int}}=c_{\mathrm{w,\ Che}}-c_{\mathrm{tot,\ Amb}}$ is reported in the last row of Table 3. In the case of Cd(II), c_{int}

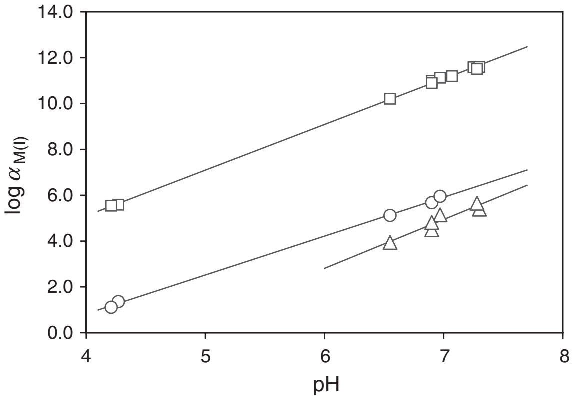

Fig. 4. Log $\alpha_{\mathrm{M(I)}}$ values of each subsamples of the Antarctic seawater reported in function of the pH, obtained from R. T. with Chelex 100: (△) cadmium(II); (□) copper(II); (○)nickel(II).

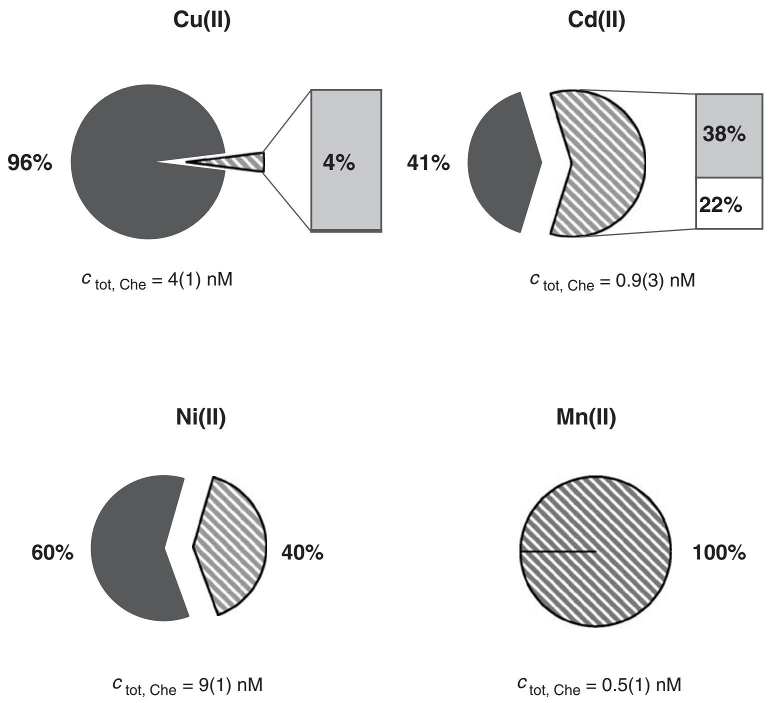

Fig. 5. Distribution of the species of Cd(II), Cu(II), Mn(II) and Ni(II) in the Antarctic seawater. Cake: fractions detected by R. T. with Chelex 100. Bar: fractions detected with Amberlite CG-50. ■ Fraction in equilibrium with Chelex 100 (strong complexes), ▨ fraction quantitatively adsorbed on Chelex 100, ■ fraction quantitatively adsorbed on Chelex 100, but not adsorbed on Amberlite CG-50 (intermediate complexes), ☐ fraction adsorbed on Amberlite CG-50 (weak complexes).

represents an important fraction of metal ion and corresponds to species with $0.1K^*_{\text{Che}}\ w/V<\alpha_{\text{M(I)}}<10K^*_{\text{Amb}}\ w/V$. Since Ni(II) and Mn(II) are only faintly adsorbed on Amberlite CG-50, at the considered conditions, the species of intermediate stability cannot be detected.

The distribution of the metal ions identified in the Antarctic sample is summarized in Fig. 5.

5. Conclusions

The resin titration method employing two different sorbing resins was used to study the speciation of Cu(II), Cd(II), Ni (II) and Mn(II) in an Antarctic seawater sample. The same resins were previously used for the characterization of Ligurian Sea water samples (Pesavento et al., 2001a,b). The method made possible the identification of different metal fractions in the Antarctic seawater.

Strong metal complexes partially adsorbed on Chelex 100, with side reaction coefficients ranging between the limits indicated by Eq. (7) (reported in Fig. 1), were identified for Cd(II), Cu(II) and Ni(II), but not for Mn(II). The experimental values of $\alpha_{\text{M(I)}}$ were high, for example equal to $10^{11.6}$, at pH = 7.3, in the case of copper(II). The strong species constitute only a fraction of the metal in the case of cadmium(II) and nickel(II), but the total metal in the case of copper(II). Using the same procedure, similar complexes were also found in the Ligurian Sea water, with similar reaction coefficients, but at different concentrations. The conditional stability constant of Cu(II) complexes is even higher than that found in the Ligurian Sea at similar pH.

The complexes at intermediate strength, with reaction coefficients ranging between the limits $0.1K^*_{\text{Che}}\ w/V<\alpha_{\text{M(I)}}<10K^*_{\text{Amb}}\ w/V$, constitute a large fraction of the total metal ion only in the case of cadmium(II). Species of intermediate strength were detected in the Ligurian Sea sample.

The very weak complexes, with $\alpha_{\text{M(I)}}<10K^*_{\text{Amb}}\ w/V$, were detected only in the case of cadmium and were found to have $\alpha_{\text{M(I)}}<4$.

The proposed classification assumes a precise, non-operational meaning, when a thermodynamic parameter, the side reaction coefficient of the species, or at least its limiting value, is evaluated by the R. T. procedure.

Of particular interest is the presence of strong complexes of Cu(II), also in the Antarctic seawater here examined. The strong species can be detected thanks to the fact that the detection window of the R. T. method is very high. In contrast with what was found in the case of other seawaters (Pesavento et al., 2001a,b), all the dissolved copper(II) is here linked to strong ligands. The presence of strong Cu(II) ligands in many other seawaters has been demonstrated (van den Berg and Donat, 1992), but their stability constants were much lower than those evaluated here through R. T. with Chelex 100.

The occurrence of weaker metal species in the Antarctic seawater is proved by the fact that often a fraction of the metal is quantitatively adsorbed by Chelex 100, and sometimes it is also at least partially adsorbed on Amberlite CG-50, as it was found in the case of cadmium(II).

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Appendix A

List of symbols

[H]	proton concentration in the solution phase, (M);
[M]	free metal ion in solution, (M);
c	metal concentration adsorbed on the resin, (M);
c_I	concentration of the strong ligand in solution in all the protonated forms, (M);
c'_I	total concentration of the free ligand in solution in all protonated forms, (M);
$c_{tot,\ res}$	maximum concentration of metal ion sorbable on the resin, (M);
c_w	concentration of metal ion quantitatively sorbed, (M);
K^*	partition coefficient: ratio of the concentration of the metal in the resin phase to that of the free metal in solution
$K_{M(I)}$	conditional complexation constant of the reaction: $M+I \rightleftharpoons MI$
$K_{M(I)t}$	complexation constant of reaction: $M+I \rightleftharpoons MI$
n	number of proton released in the reaction $M+H_nI \leftrightarrows MI+nH$
V	volume of the solution phase (mL)
w	mass of water in the resin phase (g)
$\alpha_{M(I)}$	Side reaction coefficient of the metal in the solution phase: ratio of the concentration of metal species in solution to the concentration of the free metal ion in solution: $\alpha_{M(I)}=\frac{[M]+\sum[MI]_i}{[M]}$
β_{an}	n-protonation constant of I in solution phase

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