

# Radionuclide-Humic Acid Interactions Studied by Dialysis

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Dialysis has been used to study the interaction between radionuclides and humic acid. The technique gives information on 1) the complexing capacity of the humic acid samples, i.e. the concentration of complexing sites, and 2) the radionuclide - humic acid complexes by a) its stoichiometry (i.e. metal ion/ligand ratio), and b) interaction constants. The applicability of the technique is illustrated by studies on the interaction between a humic acid and  $^{134}\text{Cs}^+$ ,  $^{85}\text{Sr}^{2+}$ ,  $^{60}\text{Co}^{2+}$ , and  $^{154}\text{Eu}^{3+}$ .

In the course of time it has been unambiguously demonstrated that humic- and fulvic acids interact with metal cations by forming rather stable, and often soluble complexes(1,2). The increasing awareness of a possible pollution of the environment, e.g. in connection with the disposal of nuclear waste, emphasizes the need for additional knowledge about the interaction between relevant metal ions, e.g. radionuclides commonly present in nuclear waste, and humic substances. The possible presence of soluble and rather stable complexes may play an important role in determining the migration behavior of the metal ions under shallow land burial conditions. The influence of humic- and fulvic acids on the migration behavior of metal ions has been discussed previously (2-6).

A variety of techniques, including ion-exchange equilibrium (7), potentiometric titration(8,9), application of ion-selective electrodes(9,10), spectroscopic measurements(11), liquid-liquid partition(12), and gel filtration(13), have applied to studies on metal ion - soil organic matter interactions. The former of these was originally developed by Schubert (7) and later was successfully modified by Ardakani and Stevenson (14). Together with the application of ion-selective electrodes, the ion-exchange equilibrium technique is, for the time being, the more applied method. However, a general disadvantage

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using these techniques is the lack of immediate information about the complexing capacity of the ligand. In the past, the effective ligand concentration  $[A]$  has been expressed in terms of molar units (11, 15), amount of ligand material (16), and concentration of complexing sites (17, 18); the latter of these terms seems to be the more appropriate as it characterizes the humic acid samples more satisfactorily than an average molecular weight.

Recently, Weber and co-workers reported on the application of dialysis to the determination of the complexing capacity of fulvic acid for a series of metal cations (19, 20). In the present paper we report a further elaboration on the dialysis technique to allow simultaneous determination of complexing capacity for the humic acid sample, and interaction constants for the metal ion - humic acid complexes, as well as the stoichiometry of the latter. The technique furthermore opens up a possibility for an indirect determination of apparent ionization constants for the humic acids.

### Experimental

Samples (10 mL) of humic acid in the appropriate buffer ( $\mu = 0.05-0.1$ ), typically containing between 0.1 and 2.0 grams of humic acid per litre (determined by electronic absorption spectroscopy), were placed in regenerated cellulose dialysis bags. The closed bags were placed in 100 mL bottles, previously filled with 40 mL of the buffer containing varying concentrations ( $10^{-7} - 10^{-4} M$ ) of the metal ions  $Cs^+$ ,  $Sr^{2+}$ ,  $Co^{2+}$ , or  $Eu^{3+}$ , and trace amounts of  $^{134}Cs^+$ ,  $^{85}Sr^{2+}$ ,  $^{60}Co^{2+}$ , or  $^{154}Eu^{3+}$ , respectively.

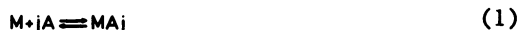
The present studies were carried out using commercially available humic acid, obtained as the corresponding sodium salt (EGA H1,675-2) and dissolved in a phosphate buffer ( $pH = 6.99$ ), and an acetate buffer ( $pH = 4.47$ ), respectively. The humic acid solutions were dialyzed against pure buffer solution prior to their use in the complex formation experiments in order to remove any low molecular fractions that could pass through the dialysis membrane.

The closed bottles were agitated gently for approximately 48 hours, the temperature being kept at  $25.0 \pm 0.1^\circ C$  by a Heto 02 PT 923 thermostat. After equilibration, samples mL of the solutions outside the dialysis bag were withdrawn, and the contents of metal ions,  $[M]_O$ , were determined by  $\gamma$  counting (Kontron MR 252 Automatic Gamma Counting System) and comparison with standard solutions. The relatively high ionic strength of the buffer solutions ( $\mu = 0.05-0.1$ ) ensures an equal distribution of low molecular species that pass the dialysis membrane, i.e.  $[M]_O$  measured in the solution outside the dialysis bag equals that inside the bag. Blind-tests, i.e. using dialysis bags containing pure buffer solution, revealed that equilibrium was in general obtained after 25 - 30 hours. Furthermore the blind-tests afforded information on the possible sorption of metal ions on the dialysis bags as function of metal ion concentration:  $Z([M]_O)$ .

Dialyses are normally carried out with four different humic acid concentrations, each of which is combined with seven different metal ion concentrations (up to  $2 \times 10^{-5}$  mol/L). For the determination of the complexing capacity a further series of three metal ion concentrations (up to ca.  $10^{-4}$  mol/L) was added in the case of the lowest humic acid concentration, in order to occupy all sites available.

### Theory

Metal ions, M, react with humate anions, A, to form complexes of the general type  $MA_j$ , taking only mononuclear species into account.



$$I = \frac{[MA_j]}{[M][A]^j} = \frac{[M]_c}{[M]_f [A]^j} \quad (2)$$

The latter relation being valid since  $[MA_j] = [M]_c$ .

Since the metal ions interact with the humate anions to form the complexes the dissociation of the humic acid should be taken into account:



$$\frac{[HA]}{[A]} = \frac{[H]}{K_A} \quad (4)$$

As  $[A]$  in the present context is the concentration of humate anions, which may possibly participate in the complex formation  $K_A$  has to be regarded as an apparent ionization constant, not of necessity equal to that obtained by acid-base titration.

The total concentration of complexing sites available is given by the expression (5), the number of ligands being occupied in the complex formation being equal to  $j[MA_j] = j[M]_c$ .

$$[A]_t = [HA] + [A] + j[M]_c = \left( \frac{[H]}{K_A} + 1 \right) [A] + j[M]_c \quad (5)$$

It is important to note that  $[A]_t$  cannot be regarded as a universal constant for a given humic acid sample, as it may be dependent of the nature of the participating metal ions, M (12).

The total amount of metal ions,  $M_t$ , can be expressed as a sum of the amounts of metal ions in the dialysis bag, in the solution outside the latter, and the amount possibly sorbed on the bag (cf. Fig. 1).

$$M_t = V_i ([M]_c + [M]_0) + V_o [M]_0 + Z([M]_0) \quad (6)$$

A rearrangement of the relation (5) gives the following expression of the actual free ligand concentration  $[A]$ .

$$[A] = ([A]_t - j[M]_c) / \left(1 + \frac{[H]}{K_A}\right) \quad (7)$$

Combining the equations (2) and (7) affords the expression (8) for the so-called pH dependent Metal ion - Humic acid Interaction constant  $\beta$ .

$$\frac{[M]_c}{[M]_f ([A]_t - j[M]_c)^j} = \frac{1}{\left(1 + \frac{[H]}{K_A}\right)^j} = \beta \quad (8)$$

where  $[M]_c$  is given by

$$[M]_c = \frac{M_t - Z([M]_0)}{V_i} - \left(1 + \frac{V_0}{V_i}\right) [M]_0 \quad (9)$$

It shall be remembered that part of the metal ions, which are not engaged by the humic acid complexation, may interact with the buffer solution, containing a certain concentration of 'buffer-ligands',  $[L]$ , i.e.  $[M]_f < [M]_0$ . The metal ion - buffer-ligand interaction is given by the following set of equations.



$$[ML_i] / ([M]_f [L]^i) = \beta_{ML_i} = \prod_{j=1}^i K_{ML_j} \quad (11)$$

Since  $[M]_0 = [M]_f + \sum [ML_i]$  we obtain the rather simple relation, (12), between  $[M]_f$  and  $[M]_0$ .

$$[M]_f = [M]_0 / \left(1 + \sum_{i=1}^n \beta_{ML_i} [L]^i\right) = [M]_0 / Q \quad (12)$$

In cases where  $[M]_c \ll [A]_t$  eqn's (8) and (9) can be simplified as follows, incorporating (12)

$$\beta [M]_f [A]_t^j = \frac{\beta [M]_0 [A]_t^j}{Q} = \frac{M_t - Z([M]_0)}{V_i} - \left(1 + \frac{V_0}{V_i}\right) [M]_0 \quad (13)$$

which easily is rearranged into the expression (14):

$$[M]_0 = \frac{M_t - Z([M]_0)}{V_i} \left( \frac{\beta}{Q} [A]_t^j + \left(1 + \frac{V_0}{V_i}\right) \right)^{-1} \quad (14)$$

It is seen that for fixed values of  $\beta$  and  $Q$  (i.e. fixed pH),

$V_o$ , and  $V_i$  plots of  $[M]_o$  vs.  $(M_t - Z([M]_o))/V_i$  will result in straight lines, the slope being dependent of  $[A]_t$  only, i.e. the amount of humic acid. It is noted that an increasing amount of humic acid causes a decrease in the slope  $\alpha$  (cf. Fig. 2).

$$\alpha^{-1} = \frac{\beta}{Q}[A]_t^j + \left(1 + \frac{V_o}{V_i}\right) \quad (15)$$

Introducing the term  $y = \alpha^{-1} - (1 + V_o/V_i)$  we have

$$y = \beta[A]_t^j/Q \quad (16)$$

which gives

$$\log y = \log \beta + j \log [A]_t - \log Q \quad (17)$$

By means of the complexing capacity,  $w$  (eq/g),  $[A]_t$  is expressed in terms of the amount (in g/L) of humic acid, or sodium humate,  $(HA)_w$ , present in the solution.

$$[A]_t = w(HA)_w \quad (18)$$

Accordingly (17) can be rearranged into

$$\log y = (\log \beta + j \log w - \log Q) + j \log (HA)_w \quad (19)$$

A plot of  $\log y$  as function of  $\log (HA)_w$  represents a straight line, the slope being equal to  $j$ , the number of ligands pr. metal ion (cf. Fig. 3). The intercept,  $\log \beta + j \log w - \log Q$ , may in principle be used for the calculation of  $\beta$ , if  $w$  is known, since  $\log \beta = (\log \beta + j \log w - \log Q) - j \log w + \log Q$ . However, since determinations of intercepts in general may be rather defective, it seems more reasonable to use the dialysis results directly, calculating  $\beta$  according to eqn. (8). In general up to 20-30 individual sets of  $[A]_t$  and  $[M]_c/[M]_f$  will be available for this purpose vide supra). Determination of the complexing capacity is carried out by increasing the metal ion concentration to a level, where all sites available in the humic acid, under the actual pH-condition, will be occupied. For convenience a solutions with low humic acid concentration,  $(HA)_w$  (0.1 - 0.2 g/L) are used for this purpose. A plot of  $[M]_f$  ( $\equiv [M]_o/Q$ ) as a function of  $[M]_c$  will feature a vertical asymptote at  $[M]_c = [M]_{c,max}$  (cf. Fig. 4), the complexing capacity,  $w$ , being determined by

$$[A]_t = j[M]_{c,max} = w(HA)_w \quad (20)$$

which gives

$$w = j[M]_{c,max}/(HA)_w \quad (21)$$

The total concentration of complexing sites (in eq/L) is extracted from eqn. (20), since  $w$  and  $(HA)_w$  are both known. Finally  $\beta$  can, as mentioned, be calculated by eqn. (8).

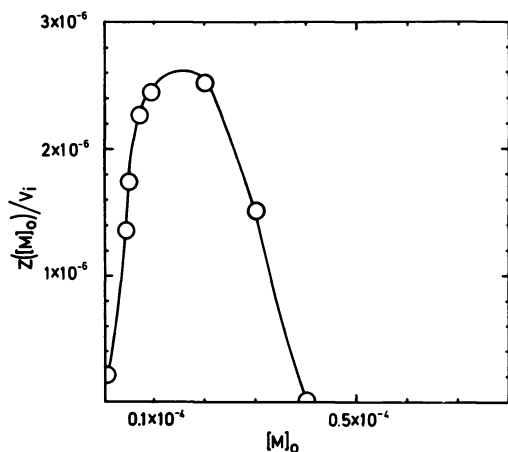


FIGURE 1. Sorption of europium ions on dialysis bags as function of europium concentration.

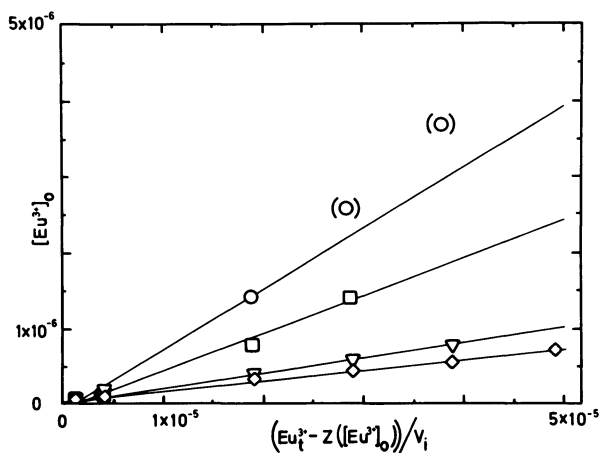


FIGURE 2. Variation in europium concentration outside the dialysis bag as function of the total amount of europium.

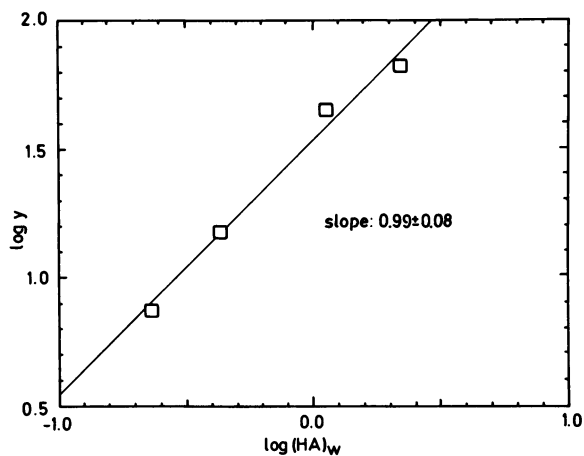


FIGURE 3. Determination of the number of ligands pr. europium ion ( $j$ ) in Eu-HA complexes.

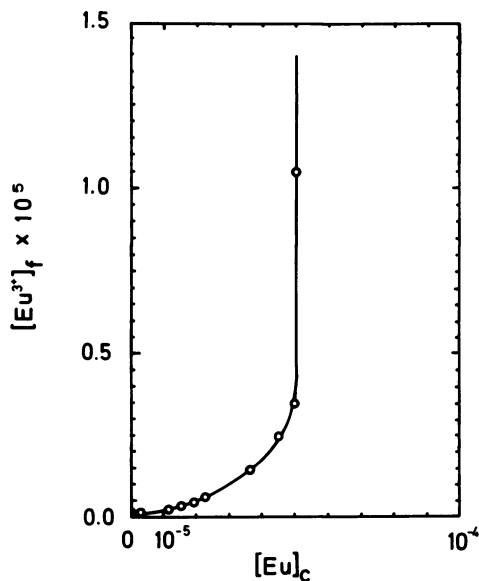


FIGURE 4. Free europium ion concentration as function of the concentration of complexed europium.

## Results and Discussion

Based on previously reported results, it is expected that  $\text{Eu}^{3+}$  ions will interact strongly with the humate anions, leading to complexes exhibiting rather high stability constants. Bertha and Choppin(18) reported simultaneous formation of 1:1 and 1:2 complexes, the corresponding stability constants being  $\log \beta^1 = 7.8$  and  $\log \beta^2 = 10.7$ , respectively ( $\text{pH} = 4.50$ ). A somewhat lower stability constant for a 1:1  $\text{Eu}^{3+}$  - fulvic acid complex was found ( $\log \beta^1 = 6.90$ )(18) in close agreement with results reported by Marinsky et al. ( $\log \beta^1 = 6.36$ )(21). On the other hand it is expected that  $\text{Co}^{2+}$  ions and humate anions will lead to considerably less stable complexes. Chimielewska (17) reported on Co-HA complexes in the pH-range 4.7 -5.8, the corresponding variation in  $\log \beta$  ranged from 4.65 to 5.49 and 5.65 to 6.29, respectively, for two different humic acid samples. The corresponding variations in the number of ligands per metal ion,  $j$ , were 1.08-1.3 and 1.4-1.59, respectively. Adhikari et al. (22) reported on a 1:1 Co-HA complex, the stability constant being  $\log \beta = 3.01$  ( $\text{pH} = 4$ ,  $T = 30^\circ\text{C}$ ). Additionally some results on Co-FA complexes are available (11, 15). In the cases of strontium and cesium no reports on the actual interaction with humate anions in solution have appeared. However, it has been reported that both types of ions sorb onto solid humic acid (24, 25).

An introductory series of experiments on the possible sorption of the metal ions on the dialysis bags revealed that only europium, to any significant extent, sorbed to the cellulose bags. Figure 1 depicts the sorption of  $\text{Eu}^{3+}$  by displaying the correction term  $Z([\text{Eu}^{3+}]_o)$  as function of  $[\text{Eu}^{3+}]_o$ .

In Figure 2 the relation between  $[M]_o$  and  $(M_f - Z([M]_o))/V_i$  is visualized for the humic acid interaction with  $\text{Eu}^{3+}$  ions in an acetate buffer ( $\text{pH} = 4.47$ ,  $\mu = 0.05$ ,  $T = 25.0^\circ\text{C}$ ). It should be remembered that the relation given in eqn. (14) is valid for  $[M]_c \ll [A]_t$  only. In cases where the latter condition is not satisfied, strong deviations from the straight lines are observed, as indicated in Figure 2 by the points in parentheses. The slopes of the lines were determined by a least square procedure to be  $8.04 \times 10^{-2}$ ,  $5.00 \times 10^{-2}$ ,  $2.03 \times 10^{-2}$ , and  $1.40 \times 10^{-2}$ , for  $(\text{HA})_w$  equal to 0.23, 0.43, 1.13, and 2.21 g/L, respectively. The corresponding  $\log y$ -values (cf. eqn. (17)) are 0.871 1.18, 1.65, and 1.82, respectively.

In Figure 3 the plot of  $\log y$  as a function of  $\log (\text{HA})_w$  is shown, the slope being determined to be  $j = 0.99 \pm 0.08$ .

In order to calculate  $[\text{Eu}^{3+}]_f$  (eqn. (12)) three different europium - acetate complexes have to be considered:  $\text{EuAc}^{2+}$ ,  $\text{EuAc}_2^+$ , and  $\text{EuAc}_3$ , the corresponding stability constants being  $10^{1.79}$ ,  $10^{3.11}$  and  $10^{4.24}$ , respectively, (26) corresponding to a correction factor  $Q = 8.48$ .

In Figure 4 the dependence of  $[\text{Eu}^{3+}]_f$  as function of  $[\text{Eu}]_c$  is depicted, the plot featuring the vertical asymptote at  $[\text{Eu}]_c = 5.1 \times 10^{-5}$  mol/L. Since the corresponding amount of sodium humate



is 0.23 g/L, the complexing capacity can be calculated, according to eqn. (21), to be  $(2.20 \pm 0.18) \times 10^{-4}$  eq/g.

Based on four different ligand concentrations  $[A]_t$ ,  $5.06 \times 10^{-5}$ ,  $9.46 \times 10^{-5}$ ,  $2.49 \times 10^{-4}$ , and  $4.86 \times 10^{-4}$  eq/L and seven different concentrations of europium ions, ranging from  $2.66 \times 10^{-7}$  to  $2.01 \times 10^{-5}$  mol/L, corresponding to 28 mutually connected sets of data, the overall Eu-HA interaction constant at pH = 4.47,  $\log \beta$ , is calculated (eqn. (8)) to be  $5.86 \pm 0.15$ .

The results obtained for the differential radionuclides are summarized in Table I.

TABLE I. Interaction Between  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Eu}^{3+}$  and Humic acid in Different Buffer Systems (Ph: phosphate buffer, Ac: acetate buffer)

M	pH	$\mu$	Q	$w \times 10^4$ (eq/g) <sup>a</sup>	j	$\log \beta$
Cs	7.00(Ph)	0.1	1.0 <sup>b</sup>	-	-	<1.2
Cs	4.49(Ac)	0.05	1.0 <sup>b</sup>	-	-	<1.2
Sr	6.99(Ph)	0.1	1.56	$2.16 \pm 0.40$	$0.82 \pm 0.15$	$3.32 \pm 0.23$
Sr	4.49(Ac)	0.05	1.13	$0.34 \pm 0.02$	$0.71 \pm 0.04$	$3.12 \pm 0.04$
Co	7.01(Ph)	0.1	6.49	$1.36 \pm 0.23$	$1.06 \pm 0.18$	$5.68 \pm 0.16$
Co	4.49(Ac)	0.05	1.97	$0.51 \pm 0.01$	$1.00 \pm 0.01$	$4.53 \pm 0.14$
Eu	4.47(Ac)	0.05	8.48	$2.20 \pm 0.18$	$0.99 \pm 0.08$	$6.15 \pm 0.15$

<sup>a</sup> complexing capacity of sodium humate

<sup>b</sup> assumed values; no data on Cs-Ph and Cs-Ac interactions available

For rather weak complexes, e.g. Cs-HA, we are not able to derive interaction constants properly by the dialysis technique. Decreases in  $[M]_0$  by less than 1%, relative to  $[M]_t$ , will be insignificant. Thus, it is seen that (cf. eqn.'s 8 and 13,  $[M]_c \ll [A]_t$ )  $\log \beta < -(1.30 + j \log [A]_t)$ , since  $[M]_f > 0.99[M]_t$  and (cf. eqn. 14)  $[M]_c < 0.01[M]_t(1 + V_0/V_1)$ .

In the case of cesium no significant variations in  $[M]_0$  were observed for  $(\text{HA})_w$  at least up to 1 g/L, neither in the acetate nor in the phosphate buffer system. Assuming the existence of 1:1 complexes only and taking the original sodium content in the sodium humate (27) as a measure for sites available for cesium complexation, we find  $\log \beta < 1.2$ .

In the case of europium a direct comparison between the above given data and those reported previously (18) is possible, since both studies are carried out at pH=4.5 although the ionic strength in the present study is 0.05 only, whereas Choppin used 0.1 (18).

The most striking difference between the two sets of data is the apparent discrepancy in the type of complexes found. We find

the 1:1 complex ( $j=0.99$ ) is formed only, in complete agreement with the results of Ardakani and Stevenson (14), who argued that  $j$  should be an integer. In contrast to this Choppin (18) reported that formation of both 1:1 and a 1:2 complexes, since  $j=1.6$  was found corresponding to a 2:3 ratio between the two types of complexes. However, the study by Choppin was carried out using trace amounts of metal ions only, in contrast to the present study as well as that by Stevenson, which is suggested to account for the apparent discrepancy. This may well be due to a presence of a small number of sites, exhibiting very high affinities towards europium ions, which will influence the results in the case of ultra-low metal ions concentrations only, as used by Choppin (18).

Secondly, it is noted that the present study reveals a Eu-HA interaction constant which is ca. 1.5 orders of magnitude lower than that reported for the 1:1 complex by Choppin (18). However, the origin of the humic acid may in this case play a crucial role. As indicated above, the studies on Co-HA interactions strongly suggest that interaction constants may vary up to several orders of magnitude for different samples of humic acid. Hence, the here reported Eu-HA interaction constant is simply to be regarded as a reflection of a relatively low complexing ability of the humic acid used. Similar indications have been obtained in parallel studies (28). Analogously the here derived Co-HA interaction constants are relatively low, although the same order of magnitude compared to those reported by Chimielewska (17).

In contrast to the Co-HA system, where the expected decrease in  $\log \beta$  with decreasing pH is observed, the Sr-HA interaction constant appears to be only slightly pH-dependent. However, small effects due to differences in ionic strength have to be taken into account.

Also the composition of the Sr-HA complexes apparently differs somewhat from those of Co-HA and Eu-HA, as the latter two types exhibit pure 1:1 character, whereas a tendency to a metal-deficient complex is found in the strontium case.

The different behavior of strontium and cobalt ions is not surprising. The former is an ordinary second-row element with strong tendencies to salt formation, whereas the latter is a transition metal with partly filled 3d-orbitals, which significantly will be involved in the complex formation.

Also the possible presence of mixed complexes, as  $M(OH)-A$ ,  $M(Ph)-A$ , and  $M(Ac)-A$ , may play a role, as may differences in hydration energies for the two types of ions (cf. ref. 29).

A deeper insight in the actual nature of the radionuclide - humic acid complexes requires further investigations, which, however, are outside the scope of the present work.

Finally, the complexing capacities,  $w$ , should be mentioned. Not surprisingly it is found that  $w$  decreases with decreasing pH in agreement with previously reported results (cf. ref.'s 19 and 20, as well as ref.'s cited therein). Additionally a pronounced dependence of the metal ion is seen. It is obvious that the complexing

capacity, towards europium ions is significantly higher than for cobalt- and strontium ions, the two latter capacities being nearly identical, which strongly suggests that the ionic charge may play an important role in this context. However, differences in complexing capacities have also been explained in terms of aggregation (19, 20).

The present paper has demonstrated the versatility of the dialysis technique in studies of interactions between metal ions and humic acid samples. The method allows facile determination of interaction constants, as well as of complexing capacities of the humic acid samples. It is noteworthy that the method described here, without modifications, can be applied to other areas of complex chemistry involving macromolecular ligands.

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### Symbols

$[HA]$	: concentration of undissociated humic acid
$[A]$	: concentration of humate anions, which may act as ligands (eq/L)
$[A]_t$	: total humate-ligand concentration (eq/L)
$(HA)_w$	: total humic acid (or sodium humate) concentration (g/L)
$w$	: complexing capacity of humic acid (or sodium humate) (eq/g)
$[L]$	: concentration of 'buffer-ligand' (mol/L)
$M_t$	: total amount of metal ions (mol)
$[M]_t$	: total metal ion concentration ( $\Sigma M_t / (V_1 + V_0)$ ) (mol/L)
$[M]_c$	: concentration of metal ions complexed by humate anions (mol/L)
$[M]_f$	: concentration of free (i.e. uncomplexed) metal ions (mol/L)
$[M]_o$	: concentration of metal outside the dialysis bag (mol/L)
$[MA]_j$	: concentration of metal - humate complex (mol/L)
$[ML]_n$	: concentration of metal - buffer-ligand complex (mol/L)
$\mu$	: ionic strength of the buffer solutions
$j$	: number of humate-ligands pr. metal atom in complex
$\beta$	: metal - humate interaction constant
$I$	: pH-independent metal - humate interaction constant
$K_A$	: overall humic acid ionization constant
$\beta_{ML_1}$	: stability constants for the metal - buffer complex
$Q$	: $[M]_o$ to $[M]_f$ conversion factor
$Z([M]_o)$	: correction of $M_t$ due to metal ions sorbed on the dialysis bags
$V_1$	: volume inside the dialysis bags (present study: 10 mL)
$V_0$	: volume outside the dialysis bags (present study: 40 mL)

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