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Separation of Trace Elements from Natural Water and Waste Water*

By

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With 1 Figure

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Trace elements play an important role in the environment, in particular in the biosphere. Some trace elements are very toxic, e. g. As, Cd, Hg, Pb; others, e. g. Fe, Zn, Mo are essential for life and found in organisms in the form of bioinorganic complexes. For many elements the difference between essential and toxic concentrations is not great. Within the last few decades the concentrations of trace elements in the environment have changed appreciably as a result of especially traffic, households and industry. The determination of trace elements in natural waters, identification of their chemical form and their separation are therefore of great importance.

Chemical Forms of Trace Elements in Natural Waters

Trace elements may be present in natural waters (ground water, river water, lakes and sea-water) in the form of cationic and anionic species or neutral complexes, in colloidal form or in suspended matter. The suspended solids can either be filtered off or separated by centrifuging. For filtration, membrane filters of 0.45-μm pore size are mostly used. Particles passing such filters are considered to

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be constituents of the solution. All filtration devices have the disadvantages that the volume of sample is limited to some 100 ml because of choking of the filter pores. Greater volumes up to 10 or 100 litres can be handled in a flow centrifuge, and gram amounts of suspended matter can be obtained in this way. The method used for collecting the suspended matter does not seem to cause significant differences in the results obtained for the trace elements present[1].

After filtration or centrifugation the water still contains colloidal particles. The trace elements may be bound on these particles or present in true solution. Cationic and anionic species can be separated by treating the solution with small amounts of the appropriate ion-exchanger. Use of larger amounts of ion-exchangers may lead to appreciable adsorption of neutral species or colloids. Sorbents such as activated carbon, on the other hand, will preferentially bind colloidal particles or neutral complexes. Experiments with ion-exchangers and sorbents have therefore been carried out in order to discriminate between the chemical forms of the various trace elements in natural water.

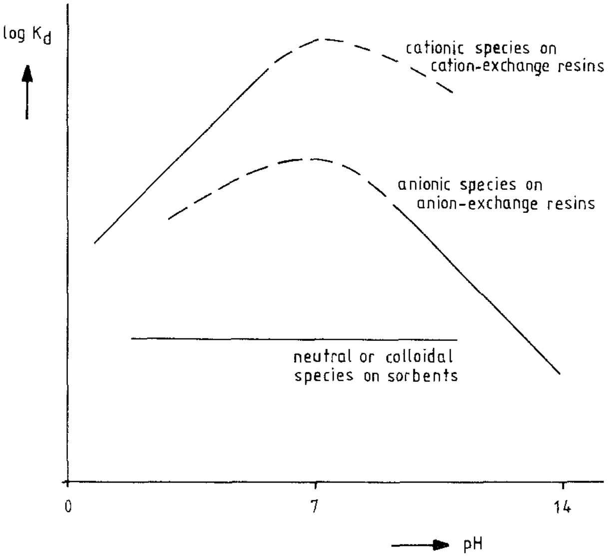

Fig. 1. Distribution coefficients for trace elements, as a function of pH

Investigation of the effect of pH on the distribution coefficients (K_d) of trace elements on sorbents or ion-exchange resins should also give information about the chemical form in which the trace elements are present. This is shown schematically in Fig. 1. To a first approximation the distribution coefficient does not depend on pH for neutral species. For cation exchange on a strongly acidic cation-exchange resin log K_d increases linearly with pH below pH 7 if the influence of other cations is neglected

$$\log K_d = \log K_1 + n \log [\bar{H}] + n \text{ pH} \qquad (1)$$

where K_1 is the exchange equilibrium constant, n the charge on the cation (M^{n+}) and $[\bar{H}]$ the concentration of the exchangeable protons in the resin. For small concentrations of M^{n+}, $[\bar{H}]$ can be assumed to be constant. Other cations which may be present in the solution or added in order to increase the pH will occupy some of the exchange sites and hence diminish $[\bar{H}]$ at above pH 7. If M^{n+} undergoes hydrolysis at higher pH-values, in the reaction sequence

$$M^{n+} \rightarrow M(OH)^{(n-1)+} \quad M(OH)_2^{(n-2)+} \ldots \quad \ldots M(OH)_n \qquad (2)$$

the curve for log K_d *vs* pH will change its slope and decrease as soon as neutral complexes or colloidal particles are formed. Anionic species will exhibit a similar behaviour, but the curves for log K_d *vs* pH will be mirror-images of those for cationic species, with respect to a reflection axis at pH 7. For anion-exchange on strongly basic anion-exchange resins, log K_d decreases linearly with pH above pH 7 if the influence of other anions is neglected;

$$\log K_d = \log K_2 + n \log [\overline{OH}] - n \log K_w - n \text{ pH} \qquad (3)$$

where K_2 is the exchange equilibrium constant, n the charge on the anions, $[\overline{OH}]$ the concentration of exchangeable hydroxyl ions in the resin, and K_w the ionic product of water.

Separation by Ion-Exchange

The concentration of some trace elements in Rhine water, as found by instrumental neutron-activation analysis, is given in Table I[1]. The concentrations of the more abundant elements calcium and sodium are also presented in this table. The water sample was taken near Gernsheim on 26 February 1979, in a 10-litre polyethylene bottle. The pH was 6.5 and the water temperature 7° C. Immediately after sampling the water was filtered through Millipore 0.45-μm membrane filters, then 80-ml samples of the filtered water were shaken for 1 hr with 0.2 g of cation-exchange resin (Dowex 50 W X 12), anion-exchange resin (Dowex 1 X 4), activated carbon (Degussa, Carbopuron 4 n) and Hyphan cellulose exchanger (Riedel de-Haen, Seelze) respectively. After filtration through an 8-μm membrane filter the solutions were adjusted to pH 1 by addition of 30% hydrochloric acid (Suprapur) in order to avoid losses of trace elements by adsorption on the walls of the vessels.

Table I. Concentration of Some Trace Elements in Rhine Water as Found by Instrumental Neutron-Activation Analysis (μg/l) (Ca: 64 mg/l, Na: 45 mg/l)

Ag	0.03	Hg	0.4
As	0.4	Sb	0.4
Co	0.3	Se	0.2
Cr	1.4	U	0.7
Fe	35.3	Zn	22.0

The results are presented in Table II. Calcium is bound on the cation-exchange resin and the cellulose exchanger, but not on the anion-exchange resin or the activated carbon. It can therefore be concluded that it is mainly present in cationic form. Similar results are obtained for manganese and copper, although these elements are partly retained on the anion-exchange resin, which indicates that some will be present as anionic species. From the relatively high amount of copper which is bound on activated carbon it can be concluded that this element is present in form of complexes, but that these complexes are not very stable, because copper is also bound on the cation-exchange resin. Because of the relatively high manganese content of the activated carbon used, the results for retention of manganese on it could not be evaluated. Iron is not bound on the cation-exchange resin, in agreement with the fact that because of hydrolysis cationic iron species are very improbable under these

Table II. Relative Amounts of Ca and the Trace Elements Fe, Mn, Cu Bound on the Cation-Exchange Resin Dowex 50, the Anion-Exchange Resin Dowex 1, the Cellulose Exchanger Hyphan and Activated Carbon

	Dowex 50 (%)	Dowex 1 (%)	Hyphan (%)	Activated carbon (%)
Ca	94 ± 2	0	98 ± 2	0
Fe	0	74 ± 4	64 ± 4	29 ± 4
Mn	84 ± 2	6 ± 2	99 ± 2	—
Cu	100 ± 5	10 ± 5	100 ± 5	85 ± 7

conditions. The fixation of a large proportion of the iron on the anion-exchange resin and the cellulose exchanger Hyphan indicates the presence of anionic complexes of iron.

For comparison, the experiments were repeated with solutions of the same elements in triply distilled water with and without the addition of small amounts of nitrilotriacetic acid (20 μg/l) as complexing agent. The results obtained confirmed the conclusions drawn about the chemical forms of the elements in Rhine water, especially for copper. In presence of nitrilotriacetic acid copper was not bound on the cation-exchange resin, but $90 \pm 5\%$ was bound on the Hyphan cellulose exchanger.

It should be mentioned that separation of trace elements from water is strongly disturbed by impurities in ion-exchange resins. These impurities form strong complexes with elements such as copper, and can prevent their fixation by ion-exchange if the complexes are neutral or of the wrong charge-sign for binding to the exchanger used. Careful washing of the exchangers is therefore necessary if they are to be used for separation of trace elements.

Separation by Complexation and Adsorption on Activated Carbon

Separation of trace elements from natural waters, in particular from sea-water, was investigated by adding various complexing agents and shaking the samples (at different pH values) with small amounts of activated carbon[2]. Dithizone and sodium diethyldithiocarbamate were found to be very suitable complexing agents because both form rather stable complexes with a great many trace elements. The most favourable pH was found to be 8.5 for dithizone and 5.5 for sodium diethyldithiocarbamate.

To separate as many trace elements as possible a two-step procedure was developed. After filtration, the solution (1 litre) is first adjusted to pH 8.5, then 2 ml of 0.02% dithizone solution in acetone and 2 ml of a suspension containing 30 mg of activated carbon (Degussa, Carbopuron 4 n) are added and the mixture is shaken for 15 min. The weakly red dithizone and its complexes are quickly adsorbed on the activated carbon. The solution is filtered through an 8-μm membrane filter, the pH is adjusted to 5.5 and 2 ml of 0.02% sodium diethyldithiocarbamate solution and 2 ml of the activated carbon suspension are added. The mixture is again shaken for 15 min, then the activated carbon is filtered off and combined with that used in the first step.

Table III shows the various results obtained. It can be seen that many trace elements are collected with 90—100% efficiency by this procedure. After collection, these elements can be determined by instrumental multielement analysis, e. g. by neutron-activation followed by γ-spectroscopy.

Table III. Separation of Trace Elements from Sea-Water:

I by activated carbon alone (pH 8.5)
II by activated carbon plus dithizone (pH 8.5)
III by activated carbon plus sodium diethyldithiocarbamate (pH 5.5)
IV by the combination of activated carbon plus dithizone (pH 8.5) plus sodium diethyldithiocarbamate (pH 5.5)

Element	I (%)	II (%)	III (%)	IV (%)
Ag	85 ± 14	85 ± 3	55 ± 15	93 ± 5
As	66 ± 12	67 ± 15	32 ± 19	78 ± 17
Au	100 ± 30	100 ± 10	100 ± 20	100 ± 10
Br	$(10 \pm 2) \times 10^{-4}$	$(4 \pm 1) \times 10^{-4}$	$(7 \pm 3) \times 10^{-4}$	$(10 \pm 2) \times 10^{-4}$
Ca	1.0 ± 0.5	2.0 ± 0.3	2 ± 1	3 ± 1
Cd	49 ± 13	95 ± 27	77 ± 27	98 ± 14
Ce	87 ± 21	82 ± 11	43 ± 16	90 ± 10
Co	40 ± 6	81 ± 8	76 ± 10	95 ± 8
Cr	91 ± 3	96 ± 3	36 ± 2	98 ± 3
Eu	100 ± 8	95 ± 6	76 ± 34	98 ± 7
Fe	74 ± 15	77 ± 8	70 ± 6	92 ± 6
Hg	97 ± 10	100 ± 10	100 ± 10	100 ± 8
K	$(8 \pm 1) \times 10^{-3}$	$(5 \pm 1) \times 10^{-3}$	$(10 \pm 2) \times 10^{-3}$	$(8 \pm 2) \times 10^{-3}$
La	100 ± 10	100 ± 10	91 ± 3	100 ± 7
Mo	50 ± 33	21 ± 9	100 ± 10	100 ± 8
Na	$(3 \pm 1) \times 10^{-5}$	$(3 \pm 1) \times 10^{-5}$	$(6 \pm 3) \times 10^{-5}$	$(4 \pm 1) \times 10^{-5}$
Sb	18 ± 5	40 ± 9	56 ± 20	74 ± 12
Sc	95 ± 10	100 ± 5	70 ± 5	100 ± 5
Se	77 ± 18	61 ± 17	40 ± 9	76 ± 12
U	100 ± 10	100 ± 20	78 ± 2	100 ± 7
Zn	96 ± 4	100 ± 10	100 ± 10	100 ± 6

Separation by Chelating Anchor Groups

Separation of trace elements with Hyphan cellulose exchanger has already been mentioned. Table II shows that relatively high yields are obtained for iron, which is not bound by a cation-exchange resin. The same trace elements can be separated very effectively from mineral waters[3]. If hydrolysis products of high molecular weight are present it is advisable to add acetate in order to form the acetato complexes, because these are bound much more easily than the hydrolysis products.

The following separation procedure[3] was applied. After filtration through a 0.45-μm Millipore filter the samples are adjusted to pH 6—8, if necessary, and passed through a separation column containing 2 g of Hyphan (capacity 0.5 mmole/g). The column is 5 cm long and 2 cm in diameter, and the flow-rate was 30 ml/min. The trace elements can be eluted with 50 ml of 1 *M* hydrochloric acid (except cobalt, which is bound too firmly). After elution the trace elements can be collected on 0.1 g of Hyphan, the eluate being neutralized with sodium hydroxide (Suprapur) and shaken with the Hyphan for 30 min. The enrichment factor is 2×10^4 with respect to the original solution.

Table IV. Trace Element Content in Mineral Waters and Sea-Water, Obtained by Separation with the Cellulose Exchanger Hyphan (μg/l; means and standard deviations for three samples of the same origin)

Element	„Kaiser Friedrich“ spring, Offenbach	„Staatlich Fachingen“ spring	„Emser Kränchen“ spring	Salt spring	Sea-water (North Sea)
Mn	—	310 ± 35	66 ± 6	232 ± 14	1.1 ± 0.2
Fe	11.3 ± 1.5	19.5 ± 2.5	12.7 ± 1.1	30 ± 7	1.5 ± 0.5
Ni	1.0 ± 0.1	2.0 ± 0.2	1.1 ± 0.3	1.0 ± 0.5	1.2 ± 0.2
Cu	2.1 ± 1.0	0.8 ± 0.2	68 ± 3	3.4 ± 1.5	2.7 ± 0.2
Zn	2.8 ± 0.1	6.6 ± 1.0	26 ± 15	10.8 ± 1.2	5.6 ± 0.2
Ta	4.9 ± 1.5	—	—	6.0 ± 3.5	—
Pb	2.7 ± 1.3	0.7 ± 0.1	0.9 ± 0.1	2.5 ± 0.5	1.7 ± 0.4
U	12.0 ± 0.6	—	—	1.1 ± 0.5	2.7 ± 0.2

Table IV shows the trace element content in some mineral waters, determined by this procedure. Energy-dispersive multielement X-ray fluorescence is very suitable for identification and determination of the trace elements.

Separation of Traces of Actinides by Co-precipitation with Barium Sulphate

Co-precipitation of actinides with barium sulphate is described in the literature[4-7]. The presence of alkali-metal ions is important, because anomalous mixed crystals are formed in which three barium ions are substituted by one actinide(IV) ion and two alkali-metal ions[8]. Potassium ions are most effective because their ionic radius (0.133 nm) is nearly identical with that of barium (0.134 nm).

The optimal conditions for the co-precipitation are to make the solution (30—100 ml) $1 M$ in sulphuric acid and 10^{-3}—$10^{-1} M$ in potassium sulphate, heat to the boiling point, add 2 ml of $10^{-2} M$ barium nitrate dropwise, cool for 1 hr, and filter off.

The co-precipitation yield is 99% for thorium, uranium(IV) and americium(IV). This has been proved for $\sim 10^{-6} M$ Th and U, and $\sim 10^{-10} M$ Am. At lower concentrations determination of the co-precipitation yield becomes more difficult. The actinides can be isolated by dissolution of the barium sulphate in a hot alkaline solution of EDTA or DTPA (diethylenetriaminepenta-acetic acid), followed by oxidation of the complexing agent.

Separation by Co-precipitation with Hydrous Ferric Oxide or Ferric Phosphate

Precipitation of hydrous ferric oxide or ferric phosphate is a common operation in water technology, but very little is known about the concomitant behaviour of trace elements. Therefore co-precipitation of the trace elements Ag, As, Cd, Cu, Pb and Zn by hydrous ferric oxide and ferric phosphate has been studied with simulated waste water solutions as substrate, under the conditions used in practice for waste-water handling, radioactive labelling and γ-spectroscopy being used for the determinations.

To 50-ml samples of $0.1 M$ sodium chloride containing 5 μg each of Ag, As (as arsenate), Cd, Cu, Pb and Zn, 9 mg of $FeCl_3 \cdot 6H_2O$ were added and the iron was precipitated by addition of 1.0—1.2 ml of $0.1 M$ sodium hydroxide (final pH 8.5). After stirring for 10 min and settling for 50 min the precipitate was filtered off. The activity in the solution was measured by γ-spectroscopy before and after precipitation. The same experiment was done in the presence of phosphate (at pH 6.5). Both precipitations were repeated in the presence of humic acid (25 mg/l) and $0.1 M$ sodium bicarbonate. The results are presented in Table V.

The highest co-precipitation yields are obtained with hydrous ferric oxide precipitation in presence of humic acid at pH 8.5 (column II). Co-precipitation of silver is low under all conditions used. The values for silver could only be reproduced if the experiments were done in absence of light in a dark room. With daylight working the co-precipitation values varied between 0 and 100%. Co-precipitation of arsenic is much higher with hydrous ferric oxide precipitation (columns I, II, III) than with ferric phosphate precipitation (columns IV, V, VI), which can be explained by the influence of the excess of phosphate on the co-precipitation of arsenate. Co-precipitation of cadmium is low if the hydrous ferric oxide is precipitated in absence of humic acid and bi-carbonate (column I). Copper, lead and zinc are co-precipitated with high yields under all conditions.

Table V. Separation of Trace Elements from Simulated Waste Water by Co-Precipitation
(means and standard deviations for three experiments)

I Hydrous ferric oxide precipitation in presence of 0.1 *M* NaCl (pH≈8.5)
II Hydrous ferric oxide precipitation in presence of 0.1 *M* NaCl and 25 mg of humic acid per litre (pH≈8.5)
III Hydrous ferric oxide precipitation in presence of 0.1 *M* NaCl/0.1 *M* $NaHCO_3$ (pH≈8.5)
IV Ferric phosphate precipitation in presence of 0.1 *M* NaCl (pH≈6.5)
V Ferric phosphate precipitation in presence of 0.1 *M* NaCl and 25 mg of humic acid per litre (pH≈6.5)
VI Ferric phosphate precipitation in presence of 0.1 *M* NaCl/0.1 *M* $NaHCO_3$ (pH≈6.5)

	I (%)	II (%)	III (%)	IV (%)	V (%)	VI (%)
Ag	43.1 ± 0.2	55.6 ± 0.5	38.0 ± 2.2	42.4 ± 0.9	40.4 ± 1.0	36.2 ± 1.2
As	97.5 ± 0.8	98.9 ± 0.2	87.8 ± 0.1	72.5 ± 1.2	34.9 ± 2.8	34.7 ± 0.4
Cd	36.6 ± 8.9	95.8 ± 0.7	97.0 ± 0.2	87.0 ± 0.6	90.6 ± 0.7	98.0 ± 0.1
Cu	97.3 ± 1.1	96.5 ± 0.2	94.6 ± 0.1	96.7 ± 0.8	90.0 ± 0.3	95.5 ± 0.1
Pb	98.1 ± 0.4	98.2 ± 0.2	93.9 ± 0.8	95.8 ± 0.3	95.6 ± 0.3	95.6 ± 0.6
Zn	80.6 ± 9.4	99.3 ± 0.1	97.5 ± 0.4	97.8 ± 0.5	98.2 ± 0.4	97.1 ± 0.6

Summary

Separation of Trace Elements from Natural Water and Waste Water

Methods of discrimination between different chemical forms of trace elements in natural waters and for their separation are discussed and results given for their application to Rhine water. Various methods of trace element separation are presented: separation from sea-water by adsorption on activated carbon in presence of complexing agents, separation from mineral waters by use of the chelating cellulose exchanger Hyphan, separation of actinide elements by co-precipitation with barium sulphate, co-precipitation from waste water with hydrous ferric oxide and with ferric phosphate.

Zusammenfassung

Trennung von Spurenelementen aus natürlichem Wasser und Abwässern

Methoden der Unterscheidung verschiedener chemischer Formen der Spurenelemente in natürlichen Wässern und ihre Trennung werden diskutiert und für Rheinwasser angewendet. Folgende Ergebnisse von Spurenelement-Trennungen werden beschrieben: Abtrennung aus Meerwasser durch Adsorption an Aktivkohle in Gegenwart von Komplexbildnern, Abtrennung aus Mineralwässern unter Verwendung des chelatbildenden Zelluloseaustauschers Hyphan, Abtrennung der Actinidenelemente M^{IV} durch Mitfällung mit Bariumsulfat, Mitfällung mit Eisenhydroxid und Eisenphosphat aus Abwasser.

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