Co-precipitation with Iron Hydroxide and X-ray Fluorescence Analysis of Trace Metals in Water

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Preconcentration of transition trace ions by coprecipitation on iron-hydroxide has been combined with energy-dispersive X-ray fluorescence for environmental water analysis. The optimized preconcentration procedure implies adding 2 mg of iron to a 200 ml water sample, adding dilute NaOH up to pH 9, filtering off on a Nuclepore membrane after a 1 h equilibration time, and analyzing. Quantitative recoveries could then be obtained for Ni, Cu, Zn and Pb, e.g. at the 10 μg/l level in waters of varying salinity while Mn was partially collected. (In fact, for a given problem the iron carrier amount can be adjusted to obtain a satisfactory compromise between high recovery and low detection limit). The precision is 7–8 % at the 10 μg/l level, and the detection limits are in the 0.5–1 μg/l range. Various environmental water samples are analysed by way of illustration.

KEY WORDS: X-ray fluorescence; energy-dispersive XRF; trace metals; iron hydroxide coprecipitation; preconcentration; water.

INTRODUCTION

In trace element analysis, sorption methods of preconcentration are of prime importance for their high efficiency and simplicity. A number of inorganic coprecipitants are known to have a high surface reactivity and thus an ability to efficiently collect microquantities from solution. Ferric hydroxide and hydrated ferric oxide have been studied extensively in this context, and their adsorption mechanism and characteristics are the subject of a huge literature, of which the most recent part has predominantly been published in the Soviet Union.

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Much of the earlier works on coprecipitation with ferric hydroxide were done as a sideline to gravimetric analysis. At the same time, ferric hydroxide has been used for the separation of carrier-free radio-tracers since the early days of radiochemistry. The role of ferric oxide and other hydrous metal oxides in the transport of heavy metals in environmental water and in controlling the transition metal levels in the ocean, has been recognized more recently. The sorption ability of hydrous metal oxides is also applied extensively in water and wastewater treatment.

As a preconcentration step prior to water analysis, iron hydroxide coprecipitation has been used in combination with e.g. colorimetry,[1] neutron activation analysis[2] and atomic absorption spectrometry.[3] Preconcentration by coprecipitation on iron hydroxide followed by filtration and direct multi-element analysis of the loaded filter seems particularly attractive in X-ray fluorescence(XRF), where the detection limit is often determined by the scatter background, proportional to the final target mass. Indeed, the high adsorption efficiency allows to use relatively small amounts of iron carrier, and the Paneth-Fajans-Hahn adsorption rule predicts that the abundant alkali and alkaline earth ions do not coprecipitate significantly since their hydroxides are quite soluble. Therefore a thin target can straightforwardly be obtained and the XRF-sensitivity will be favourable for a number of transition metals. Also, the Fe-signal can be used as an internal standard in the XRF-measurement.

Yet this preconcentration technique has seldomly been used in XRF. Only Bruninx et al.[4,5] reported on ferric hydroxide coprecipitation from 10^{-2} M KNO_3, for wavelength-dispersive XRF. Hubert and Chao[6] used ferric ions in combination with ammonium pyrrolidine-dithiocarbamate at an acid pH for target preparation in XRF.

In the present work we have studied the preconcentration of traces of Mn, Ni, Cu, Zn and Pb via ferric hydroxide coprecipitation for subsequent analysis by energy-dispersive XRF. Since this study was also motivated by an interest in trace metal scavenging during acid-iron waste dispersal in the marine environment[7] much stress was given to sea water as a matrix. The parameters of the preconcentration procedure have been optimized and the characteristics of the overall analysis procedure have been studied.

EXPERIMENTAL

Reagents

All the reagents were of A.R. grade. Deionised bidistilled water was used. Stock solutions with 1 g/l of individual metal ions were prepared by diluting Titrisol Merck ampoules. Further dilutions and mixing of these

metal solutions were performed freshly, just before experimentation, with 0.01 N HCl. A stock solution of iron (III) ($\simeq 8\,mg$/ml) was prepared by dissolving a specpure iron rod in dilute HNO_3 (1:4). This solution was further evaporated to dryness and then taken in HCl such that in the final solution it was maintained at 0.5 N. The iron concentration was once again checked by the o-phenanthroline method.[8]

Sea water collection

North Sea water, of 35‰ salinity and natural pH of 7.93, served as the matrix for much of the experimentation. It was collected at a distance of 10–15 km from shore and from 2–10 m depth, and brought to the laboratory on the day of collection. To remove the particulate and suspended material, the water was then filtered through a 0.4 μm pore-size Nucleopore polycarconate membrane of 47 mm diameter, using a Gelman 4200 magnetic filtration apparatus. After adjusting the pH to about 2.0 by concentrated HCl the samples were preserved in precleaned polythene bottles.

Procedure

For measurements at constant volume, 200 ml of the filtered and acidified sea water was taken. To this sample the desired amounts of metal spikes and the ferric solution were added. It was then stirred for about 10 minutes to enhance the equilibration between various ions. Ferric hydroxide was next obtained by appropriately adjusting the pH initially with 8 M NaOH and finally with 0.5 M NaOH. The final volume of the solution after precipitation was kept 202 ml in all such experiments. After precipitation, the solution was allowed to settle for one hour and then filtered through a 0.4 μm pore-size Nuclepore membrane under suction.

Next, the precipitate-loaded membrane containing the precipitate in a 9.6 cm^2 area, was stretched over a Teflon ring and was weighted by another such ring to prevent curling of the thin filter during drying. The precipitate was dried at room temperature for no more than 48 hours and then presented to X-ray unit.

Experimental blanks were prepared by treating the same volume of the matrix, with the same amount of Fe(III) and in the same way as the samples, except that no metal spike was added.

X-ray fluorescence measurements

The energy-dispersive XRF unit included a Kevex 0810 system: its instrumental and experimental details have been reported earlier from this laboratory.[9] The samples were counted for 3000–5000 sec in this unit

using the Mo secondary fluorescer and filter (40 kv, 40 mA). Excitation with Mo K X-rays was preferred because it allowed convenient measurements of Mn, Fe, Ni, Cu and Zn through their characteristic K-lines and Pb through L-lines. Together with each blank or sample, a Zr wire in a fixed position in front of the sample was measured to act as an external reference signal for X-ray tube intensity variations and dead-time losses.[10] The spectra were stored on magnetic tape and afterwards analyzed by a PDP 11/45 computer. The data reduction was based on a non-linear least-square peak fitting program, correcting for shifts in energy calibration and peak width.[11] The Fe-K_α signal served as an internal standard for X-ray measurements.

Calculation

From computerized data, the X-ray intensities were converted into amounts of the corresponding trace element via a series of commercially available thin film standards. A suitable X-ray absorption correction was applied, based on the scatter peaks in the spectrum.[12]

The Fe-mass per unit area of the loaded filter as determined by XRF, was generally lower than expected from colorimetric measurements, namely $68 \pm 3\%$ on the average for 48 observations. Obviously, the precipitate was not deposited homogeneously over the filter area, with some depletion occurring in the central area where the X-ray excitation-detection efficiency is highest. Since all results were related to the Fe-K_α internal reference signal, this load mass heterogeneity does not have any effect on the measured coprecipitation recoveries.

Wherever necessary the distribution ratio K_D was calculated as:

$$K_D = \frac{\text{amount of element in precipitate}}{\text{amount of element in solution}}$$

$$= \frac{\text{percent of element coprecipitated } (p)}{\text{percent of element remaining in solution}} \qquad (1)$$

$$= \frac{p}{100 - p}$$

Transformation of K_D into K_{D_v} taking into account the mass of Fe and the total volume of the solution, is as follows:

$$K_{D_v} = \frac{\text{amount of element per g Fe}}{\text{amount of element per ml solution}}$$

$$= K_D \times \frac{\text{volume of solution (ml)}}{\text{weight of Fe (g)}} \qquad (2)$$

Experiments that were performed at optimized volume and constant Fe concentration, thus yielded:

$$K_{D_v} = K_D \times \frac{202 \ (\text{ml})}{2 \times 10^{-3} \ (\text{g})}$$

or $\log K_{D_r} = \log K_D + 5.0043.$ (3)

RESULTS AND DISCUSSION

Under the optimized conditions a minimum of 5 replicate experiments were carried out for every parameter checking, and often up to 8–9. For other conditions the number of replicate experiments was usually 3.

pH-dependence

The effect of pH between pH 4.0 and 10.0, on the coprecipitation of 25 μg/l traces of Mn, Ni, Cu, Zn and Pb with 10 mg/l Fe(III) as hydroxide is shown in Fig. 1. Beyond pH 10.5 no experiment was possible due to clogging of the Nuclepore filter with heavy precipitation of alkaline earths.
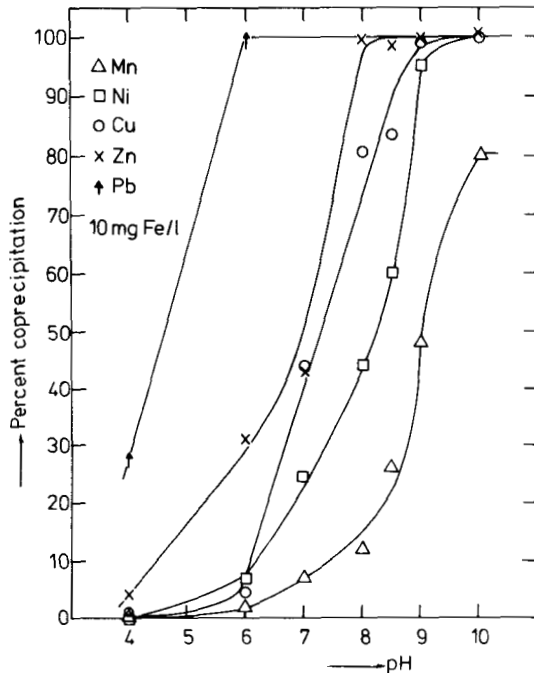

FIGURE 1 pH dependence of the co-precipitation of Mn, Ni, Cu, Zn, and Pb in sea water.

The properties of the sorbent surface as well as the characteristics of the trace elements present in the solution are both believed to contribute to the observed pH-dependence. Ferric hydroxide invariably develops a pH-dependent surface charge and amorphous ferric hydroxide, which is its typical form when precipitated freshly within a solution, has its isoelectric point at pH 7.2 in pure water.[13] Hence, generally it would be expected to carry down cationic species (by ion-exchange coprecipitation) above this value. But this iso-electric point of ferric hydroxide depends largely on the over-all composition and history of the solution[14] with a wide range of values between pH 6.0 and 8.5 having been reported.[15] In a solution of high ionic strength, such as sea water, very little is known regarding the zero point of charge of this collector.

While traces of Pb and Zn collect quantitatively beyond pH 6.0 and 8.0 respectively, Cu and Ni exhibit a nearly quantitative coprecipitation only at pH 9.0 and above. In the case of Mn, the collection yield is only about 50–55 % at pH 9.0. At the natural pH (8.0) of sea water, Zn and Pb are coprecipitated totally while Cu and Ni are collected up to about 80 % and Mn only about 11 % with an initial iron concentration of 10 mg/l.

The plot of log K_D versus pH shows two distinct parts for Cu and Ni: the increase of log K_D is slow up to pH 8.0 while a steep rise is observed between pH 8.0 and 9.0. For Mn the plot is linear all throughout. Both linearity[16] as well as non-linearity[17] have been mentioned in literature.

For none of the five trace elements studied, the distribution ratio or percent coprecipitation drops at pH 10.0 as was reported in 10^{-2} M KNO_3 medium.[16] The cause may be attributed to the difference in matrix with a heavy concentration of alkaline earths and its salinity. Alkaline earths, specifically magnesium, in its natural concentration level in natural sea water, have been reported[18] to effectively preconcentrate several trace elements at an alkaline range. Utilizing ^{65}Zn and 5 μg/l of Zn metal ion carrier, we have found that without any iron addition, 85 % of the zinc was included in the precipitate formed at pH 10.0. Hence, it may be suggested that, in the presence of iron as the coprecipitating substrate, the alkaline earths from the matrix may have a cumulative effect in not letting down the distribution ratio at pH 10.

As an optimum pH for the efficient collection of all the five trace elements, a pH of 9.0 was chosen for all further experiments.

Dependence on initial iron concentration

As can be seen from Fig. 2, the percent coprecipitation increases with increasing iron concentration for Mn, Ni and Cu, while the collection of Zn and Pb is quantitative (within the error on the XRF measurement) throughout the range studied.
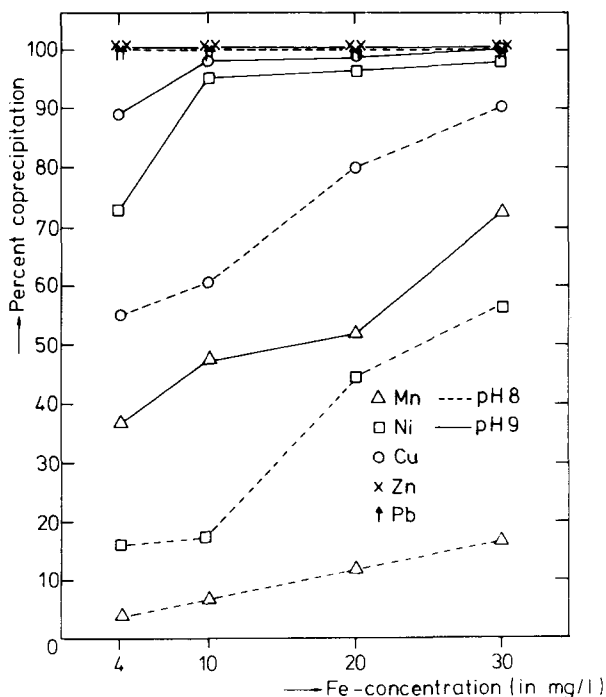
FIGURE 2 Influence on the coprecipitation of the initial iron-concentration (for $10–25\,\mu g/l$ metal spikes) at pH 8 and 9.

Plotting $\log K_D$ versus $\log$ (Fe concentration) yields linearly increasing curves for Mn, Ni and Cu (the recoveries of Zn and Pb were quantitative within the XRF-measurement uncertainty: hence no K_D-values could be calculated), as was also observed for e.g. radioactive tracers of Zn and Cd.[7,16] In fact, the $\log K_{D_v}$-values appear to be rather constant, independent of the iron concentration (with averages of 5.0 for Mn, 6.2 for Ni, 6.6 for Cu and >7 for Zn and Pb). This can be understood if an ion-exchange mechanism is the predominant interaction process, as suggested by Bruninx.[16] In that case, the reaction can be described by

$$n\mathrm{FeH} + \mathrm{M}^{2+} \rightleftharpoons \mathrm{Fe}_n\mathrm{M} + n\mathrm{H}^+$$
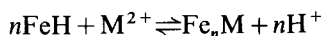
where FeH represents the iron-hydroxide. Applying the mass-action law would give

$$K = \frac{p.[\mathrm{H}^+]^n}{(100-p)[\mathrm{FeH}]} \tag{3}$$

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with p: percent metal coprecipitated and, considering the definition of K_D and K_{D_v} in eq. (1) and (2):

$$\log K_D = \log K + \log[\text{FeH}] + n\,p\text{H} \qquad (4)$$

$$\log K_{D_v} = \log K + n\,p\text{H} \qquad (5)$$

Hence, at constant pH, and as long as the concentration of unchanged iron-hydroxide nearly equals the total amount, $\log K_D$ is expected to increase with the iron-concentration and K_{D_v} is indeed expected to be constant.

In fact, this reasoning[16] also corresponds to assuming a homogeneous distribution of the microcomponent between the liquid solution and the carrier, as described by the well-known Berthelot-Nernst law. Also, when the concentration of the solute is small and only a small fraction of the carrier surface is occupied, the Freundlich isotherm, which is generally used to describe coprecipitation by surface adsorption, degenerates into the Berthelot–Nernst distribution.

Anyway, in practice, one could thus make a convenient compromise based on eq. (4) between a minimal amount of Fe, hence a high enrichment factor (expressed as the ratio of the original water sample weight to the target weight after the preconcentration step) and a low detection limit, on the one hand, and a high collection yield, hence an optimal precision and accuracy, on the other hand.

An iron-concentration of 2 mg/200 ml was preferred in all further experiments. Indeed, at pH 9, working at higher iron-concentrations implies only significant increases of the collection for Mn, but deteriorates the enrichment factor and leads in practice to brittle deposits that flake easily.

Also it can be noted from Fig. 2 that at very low iron-concentration in sea water of pH 8, Mn and Ni are not carried down significantly while Zn and Pb are accumulated appreciably.

Dependence on transition metal concentration

As can be seen from Fig. 3, all transition elements studied, except Mn, show a consistently high recovery within the concentration range 1 to 500 μg/l (concentrations above 100 μg/200 ml could not be studied by XRF because they caused non-adhesion or flaking of the iron-hydroxide precipitate on the Nuclepore filter). Bruninx[5, 16] has observed in most cases a decrease in $\log K_D$ value with increasing metal amount, perhaps as a result of the decreasing number of available sites of iron hydroxide for
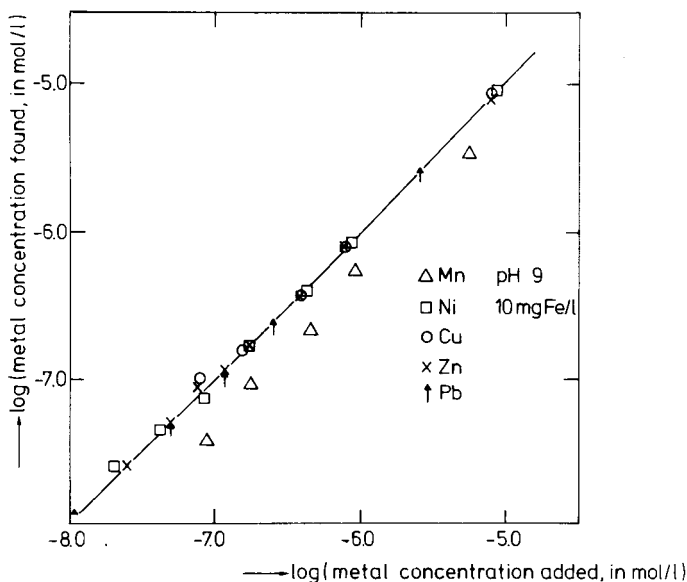
FIGURE 3 Dependence on the coprecipitation of the transition metal concentration.

binding trace ions, e.g. at pH 8.5, with 400 μg iron in a 40 ml 10^{-2} M KNO_3, when 100 μg metal spikes (e.g. Zn and Pb) were added. In the present XRF study, up to a metal ion concentration of 100 μg/200 ml, no such decrease was evident. By radio-tracer technique it was possible to examine higher metal concentrations employing a synthetic sea water medium.[7] The decreasing trend of logK_D was not obtained even though the metal:iron ratio was raised from as low as 1:400 up to 3:1 at a pH 8.0 or pH 9.0. Although the binding sites of iron hydroxide may be over-capacitated and ion-exchange coprecipitation may cease to carry down other metal ions, nevertheless, the possibility of individual precipitation due to matrix interaction and/or by simple metal hydrolysis under increased concentration cannot be ruled out. In this context, it may be mentioned that e.g. $Zn(OH)_2$ itself has been efficiently utilized[20] at alkaline pH as coprecipitant hydroxide collector for various trace elements. As a matter of fact, for 2 μg/200 ml spikes in a sea water matrix brought to pH 9, without any external iron addition, we found that Mn and Ni showed negligible precipitation between 0.7 and 2%, while Cu exhibited 11–15% precipitation; Zn: 20 to 28% and Pb: 33 to 38%, on the average. (Since the latter elements undergo a nearly quantitative collection in optimized conditions, it is not necessary to recalculate the observed recoveries to take this effect into account.)

In conclusion, it appears that, except for Mn, a satisfactory linearity exists between the transition metal level and the X-ray response, from a $100\,\mu g$ amount down to $1\,\mu g$, where statistic and blank problems become important.

Dependence on the sample volume

Based on eq. (4) and the findings of Bruninx,[16] one might expect that a steady decrease of the collection efficiency would occur with increasing volume and constant iron/metal ratio. This was indeed clearly observed at pH 8 for Mn, Ni and Cu, for $5\,\mu g$ transition metal spikes and 2 mg of Fe per 50 to 500 ml sea water sample: in every case the K_{D_v}-values appeared constant again. As can be seen in Table I, the collection efficiencies are so high at pH 9 that only for Mn, a clear trend can be noted (corresponding again to $\log K_{D_v} = 5.2 \pm 0.2$).

TABLE I

Influence of sample volume on the coprecipitation ($5\,\mu g$ metal spikes; 2 mg Fe; pH 9; 1 h equilibration)

	Percent coprecipitation $\pm$ standard deviation per measurement			
Sample volume:	50 ml	100 ml	200 ml	500 ml
Element:				
Mn	90 ± 5 (3)[a]	81 ± 4 (3)	48 ± 7 (9)	36 ± 8 (12)
Ni	96 ± 4 (3)	97 ± 2 (3)	99 ± 7 (7)	93 ± 7 (9)
Cu	101 ± 2 (3)	103 ± 2 (3)	95 ± 7 (7)	95 ± 7 (8)
Zn	106 ± 9 (3)	107 ± 5 (3)	103 ± 7 (8)	104 ± 16 (5)
Pb	99 ± 3 (3)	102 ± 6 (3)	100 ± 2 (5)	103 ± 7 (8)

[a]( ) = number of measurements.

In practice to keep at par with a fairly high enrichment factor as well as a reasonably rapid filtration time, a 200 ml volume seems optimum. At 500 ml, the preconcentration step is prolonged due to a 20–25 min filtration time.

Dependence on aging time

Iron hydroxide, once precipitated at pH 7.0, 8.0 and 9.0, was left in contact with the solution for varying lengths of time from 10 minutes to 30 days, to study the effect of aging on the percent recovery.

Fe (III) usually precipitates as an X-ray amorphous solid phase, with a surface reactivity for cations at an alkaline pH, the exact composition of

which is quite uncertain. The primary aggregate of ions in it may not necessarily be stable, hence in natural waters it may slowly transform to thermodynamically more stable forms[20] while recrystallisation and surface activity changes might influence the transition metal sorption.

Our experimental results did not show any dramatic effect beyond a 1 h equilibration time. Measurement of the surface area by the BET-method did not show any variation between a 2 h and 30 day age either.[7] A practical 1 h equilibration time was thus adopted.

Dependence on matrix composition

Parallel precipitation experiments were carried out on natural and synthetic sea water, on 3 % NaCl solutions and on bidistilled water samples. The XRF-results are presented in Table II. Both these data and similar results taken at pH 8, show that the strongly adsorbed ions, Zn^{2+} and Pb^{2+}, are not affected by the changing matrix. Mn^{2+}, and to a lesser extent Cu^{2+} and Ni^{2+}, appear to be collected significantly better in bidistilled water and NaCl solution than in sea water. Probably the metal

TABLE II

Influence of sample matrix on the coprecipitation (2–5 µg metal spikes; 200 ml sample; pH 9; 1 h equilibration)

	Percent coprecipitation[a] ± standard deviation per measurement			
Matrix:	Bidistilled water	3 % NaCl	North Sea water	Synthetic sea water
Initial Fe-amount: 0.8 mg Element:				
Mn	86 ± 9	93 ± 6	37 ± 6	
Ni	104 ± 7	100 ± 7	73 ± 4	
Cu	92 ± 6	95 ± 3	89 ± 9	
Zn	109 ± 7	106 ± 7	103 ± 13	
Pb	98 ± 5	91 ± 4	99 ± 10	
Initial Fe-amount: 2.5 mg Element:				
Mn	98 ± 7	93 ± 3	48 ± 7	50 ± 10
Ni	112 ± 3	108 ± 8	95 ± 7	110 ± 3
Cu	101 ± 8	98 ± 4	99 ± 7	103 ± 2
Zn	104 ± 9	103 ± 4	106 ± 2	109 ± 4
Pb	98 ± 4	102 ± 4	99 ± 4	10 ± 4

[a]Average result from 4 measurements.

speciation is a most important factor in this context. However, Table II proves that the possible inhibitory effect of a highly ionic complex matrix, seen for low Fe concentration levels, is overcome for an optimized Fe concentration.

For practical purposes one can assume that in a less complex matrix than sea water, the collection yields will be equal or more favourable than those reported above. For any highly different matrix a separate check should be made before applying the method.

Precision

The precision can be assessed from the standard deviations per measurement, given in Tables I and II, and, more explicitly, from Table III. It appears that, at the $10 \mu g/l$ level, the variation coefficient amounts to 7–8 % on the average. Since such a precision has earlier been found to be typical for XRF-analyses at these count rates,[12] it is obvious that the X-ray measurement and spectrum evaluation contribute more to the overall uncertainty than the proposed preconcentration step.

TABLE III
Precision under optimized conditions (2 mg Fe; 200 ml; pH 9; 1 h equilibration)

Element	Individual results, in $\mu g/l$ for subsequent analyses ($10 \mu g/l$ metal spike)	Average percent collection yield $\pm$ standard deviation per measurement
Mn	5.1; 5.9; 4.6; 5.9; 4.6; 5.5; 5.1; 5.3	52.5 ± 5.1
Ni	9.4; 9.3; 8.6; 10.6; 9.7; 8.5; 9.6; 10.5	95.3 ± 7.5
Cu	10.3; 9.4; 10.4; 8.6; 11.6; 10.5; 10.4	101.7 ± 9.4
Zn	10.3; 9.2; 11.1; 10.6; 9.1; 11.4	102.8 ± 9.1
Pb	10.4; 10.1; 9.9; 9.9; 10.8; 10.6; 9.8; 10.9	103.0 ± 4.3

Sensitivity

In the optimized conditions the preconcentration factor typically equals 50,000, or if one takes the filter backing weight into account, approximately 15,000. This is superior or comparable to most other preconcentration techniques.

The detection limits, calculated as three times the square root of the blank spectrum from scattered X-rays and impurity characteristic X-rays, were typically just below $1 \mu g/l$.

Applicability

To illustrate the applicability of XRF analyses combined with iron hydroxide coprecipitation, a number of analyses were carried out on sea water, river water, tap water, bottled drinking water and mine water, as shown in Table IV. The results for the Albert canal, a channel drawing water from the river Meuse and providing most of the drinking water supply of Antwerp, for tap and drinking water and for underground water from a mine in the French Cévennes area, were derived from 200 ml samples. In case of sea water, volumes of 500–1000 ml were used, instead of 200 ml, in order to reduce detection limits, at the expense of the filtration time, of course. It should be stressed that the sea water data cannot be considered as representative for North Sea water since no special precautions were taken to eliminate metal losses or contamination thoroughly.

TABLE IV
Illustrative analyses of filtered water samples

	Measured concentration, in μg/l, and stand. dev. per analysis				
Element	Near-shore North Sea water	River water	Mine water[a]	Laboratory tap water	Bottled mineral drinking water
Mn	$\leq$0.4	$\leq$0.6	110$\pm$20	$\leq$0.6	$\leq$0.6
Ni	2.0$\pm$0.3	6.1$\pm$0.2	50$\pm$5	3.4$\pm$0.2	$\leq$0.4
Cu	2.3$\pm$2.0	17$\pm$5	$\leq$6	47$\pm$2	7.6$\pm$1.9
Zn	11$\pm$2	12$\pm$1	8000$\pm$600	70$\pm$2	6.9$\pm$2.9
Pb	1.6$\pm$0.5	15$\pm$10	62$\pm$6	$\leq$0.8	$\leq$0.8

[a]Parallel NAA and SSMS on this sample yielded on the average: Mn: 120, Ni: 80, Cu: 2, Zn: 10900, Pb, 50 μg/l.

We believe that iron-hydroxide coprecipitation and XRF analysis can provide a straightforward and simpe, yet powerful technique for analysis of environmental water samples.

Acknowledgements

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