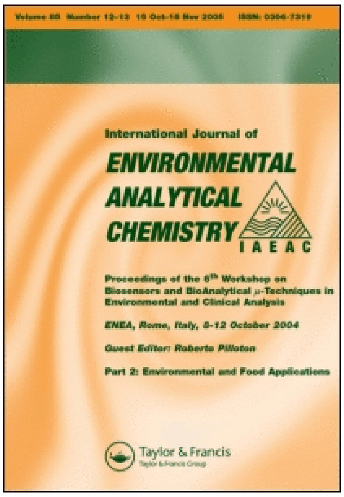

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Bruno M. Vanderborght[a]; Rene E. Van Grieken[a]
[a] University of Antwerp (U.I.A.), Wilruk, Belgium

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Trace Metal Analysis of Water Containing Humic Substances by X-ray Fluorescence

BRUNO M. VANDERBORGHT and RENÉ E. VAN GRIEKEN
University of Antwerp (U.I.A.), B-2610 Wilrijk, Belgium

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Chelation by oxine followed by adsorption on activated carbon results in the efficient collection of many trace metal ions, independent of the trace metal concentration and of high alkali and alkaline earth ion abundances. Preconcentration factors around 10000 are often achieved. When this preconcentration procedure is combined with energy-dispersive X-ray fluorescence, accurate and precise analysis can be carried out, as was proven in several experiments. The technique can also be applied for the determination of divalent ions in natural waters containing up to 10 ppm of humic substances. Trivalent ions can quantitatively be collected from natural water provided sufficient activated carbon is added. Omitting the oxine chelation prior to the activated carbon adsorption step still results in collection of a sometimes important fraction of the trace metal ions from natural waters. This is related to organically bound or colloidal forms of the trace metals.

KEY WORDS: X-ray fluorescence; trace metals; activated carbon; oxine chelates; humic substances; water.

INTRODUCTION

In recent years much evidence has been produced on the important role of interactions between metal ions and organic molecules in natural waters. It has been shown that the naturally occurring humic and fulvic acids exhibit strong chelating properties for metal ions, and they deeply affect the solubilisation, transport processes and biological interactions of heavy metals.

Surprisingly little attention has hitherto been devoted to the effect of these chelating agents when accepted analysis procedures are being applied to natural water samples. In natural waters a large fraction of the heavy metals can be present in strong organic complexes, which are difficult or slow to dissociate, or strongly adsorbed onto organic or inorganic colloids. On the other hand analysis procedures are mostly developed for metal ions in a free form, and their applicability is demonstrated on synthetic solutions. In natural waters the heavy metals might thus behave unexpectedly, e.g. during the chemical preconcentration step which often precedes analysis procedures for ppb-concentration levels, and the recovery of the metals in samples to be analyzed might bear no relation to the recovery of the metals in the test solutions.

A striking example of such a case has recently been provided for the well-known trace metal collections from sea-water onto Chelex-100 resin columns[1] in which standard additions with ionic radiotracers showed quantitative recoveries, while a large fraction of the metals in real seawater simply passed through the column.[2] Also liquid-liquid extraction with APDC has appeared to be inadequate.[2]

A preconcentration step consisting of adsorption of trace metals on activated carbon, after the addition of oxine (8-hydroxyquinoline) as a chelating agent for the free metal ions, was expected not to suffer from similar drawbacks. Indeed, this procedure efficiently collects metal ions as oxinates,[3,4] and activated carbon is known to be a good adsorber both for humic substances[5] and thus probably also for metal-humic acid complexes, and for colloids.[6] This procedure was developed and investigated in combination with energy-dispersive X-ray fluorescence analysis, a technique that offers multi-element capabilities, high speed and low cost, and exhibits optimal sensitivity and reliability for thin homogeneous samples.

Preconcentration involving adsorption on activated carbon has recently drawn the attention of several other authors, e.g. refs. 6–9.

APPARATUS AND X-RAY FLUORESCENCE MEASUREMENTS

The X-ray fluorescence analysis unit was a Kevex 0810 system, including a 60 kV-4 kW water cooled Röntgen tube with W-anode and an interchangeable secondary target. The characteristic X-rays were measured, after collimation, by a 30 mm^2 Si(Li) detector with 170 eV resolution at 5.9 keV. The voltage pulses, proportional to the X-ray energy, were led through an amplifier, into an analog-to-digital converter and pulse height analyser (4096 channels). The X-ray spectra were stored on magnetic tape and afterwards analysed by a PDP 11/45 computer. Using Mo as a secondary target with the Röntgen tube always operating at 40 kV-40 mA, it was possible to determine elements with $Z < 50$ through their K_α radiation and those with $Z > 50$ through their L_α- and L_β-emission. The data reduction was based on an iterative least squares peak fitting program, correcting for shifts in energy calibration and peak width.[10] For the purpose of calibration in X-ray fluorescence, a series of thin film standards, purchased from Micromatter Co., Seattle, U.S.A., was used.

Gamma spectrometry for tracer experiments was performed on a 63 cm^3 coaxial Ge(Li) detector Philips APY 45 A/N, connected to a 4096 channel analyzer. Atomic absorption spectrometry was carried out on a Perkin Elmer 503 Flameless Atomic Absorption Spectrometer with Massman oven. Spectrophotometric measurements for derminations of oxine and humic material were performed with a Beckman Cecil 202 double beam UV-spectrometer. All chemical manipulations were carried out in a laminar flow clean air bench. Oxine was obtained from UCB (No. 1508), the AC was a Baker Analysed Reagent (No. 1991) purified according to ref. 11, and the humic material was purchased from Fluka (No. 53680).

ANALYSIS PROCEDURE

In earlier work[3,4] we studied the adsorption isotherms for oxine ($\overline{\mathrm{Ox}}$) and metal oxinates ($\overline{\mathrm{MOx}_2}$) on activated carbon (AC), the time dependence of the adsorption, the effect of pH on the oxine adsorption, the influence on the trace metal recovery yield of alkali and alkaline earth concentrations and of excess free oxine remaining in solution after the formation of the metal-oxine complexes.

From the conclusions reached the following optimal enrichment procedure can be recommended:

1) to a water sample of e.g. 1 liter in a glass erlenmeyer brought to a pH value near 8, add oxine (as a saturated solution in acetone) up to a final concentration Q, in ppm, given by: ($S, C_{\mathrm{Mg}}, C_{\mathrm{Ca}}$ are explained below; the coefficients were obtained in ref. 3)

$$Q = S + (0.35 \times C_{\mathrm{Mg}} + 0.20 \times C_{\mathrm{Ca}}) + 5 \tag{1}$$

2) only if a significant amount of metal oxinate precipitate forms (e.g. in Mg-rich waters): filter off the precipitate on a Nuclepore 0.4 μm pore-size membrane filter
3) add a quantity of activated carbon sufficient to adsorb all metal oxinates in solution, assuming a capacity of typically 0.5 mmol $\overline{\mathrm{MOx}_2}$ per gram AC. It might be safe to use a 5 to 10 fold excess of AC to assure quantitative recovery, but even then 50–150 mg activated carbon per liter is usually sufficient.
4) shake for about 1 hour
5) filter off the AC on a 0.4 μm pore size Nuclepore membrane filter.
6) analyse the loaded filter from step (5) or both filters resulting from steps (2) and (5) by X-ray fluorescence as described above.

The first term in Eq. (1), S, is the oxine concentration necessary to complex the transition metals in the solution, usually to $M^{II}\overline{Ox}_2$ or $M^{III}\overline{Ox}_3$. (A rough estimation of S is usually feasible when the water type is known.)

An oxine quantity corresponding to S plus "0.35 × analytical concentration of Mg, in ppm" and "0.20 × analytical concentration of Ca, in ppm" plus a 5 ppm oxine excess (the last term in Eq. (1)), suffices to fully chelate most transition metals, while the alkali ions remain essentially uncomplexed and the alkaline earth ions are partially in the mono-chelate form only and practically not in the $M^{II}\overline{Ox}_2$ form (the mean ligand numbers for Mg^{2+} and Ca^{2+} are 0.66 and 0.06 respectively).[3] This can be calculated from known stability constants.[12] In this way a "selective complexation" of the heavy metals is accomplished with respect to the usually abundant alkali and alkaline earth ions, hence the minimum oxine quantity is used and the maximum enrichment factor will eventually be obtained.

Of course, only if optimal sensitivities are required, eq. (1) should be applied, and a minimum weight of oxine and AC should be added. In other cases (or in combination with analysis techniques where a minimum sample weight is not preferable), a safe excess of oxine and AC can be used.

Earlier[3,4] we have added oxine in solid form to the water sample and heated to 60°C to dissolve the oxine. However adding the oxine as a solution in acetone (solubility ca. 100 mg oxine per ml acetone) avoids the necessity of heating the sample and greatly reduces the analysis time.[8] The acetone (typically 100 μl per 1 liter water sample) does not interfere with the metal-oxinate adsorption since the adsorption selectivity is much in favour of the latter. This selectivity is partly due to the very low solubility of metal oxinates in water resulting in a favourable energy change on adsorption. The π-orbitals of the oxine ligands also result in a larger adsorption energy than in the case of acetone adsorption.

The correction for X-ray absorption effects is very simple in this case, when the sample to be analysed (activated carbon) is collected on a surface filter (Nuclepore membrane) without any appreciable penetration into the filter.[13] The absorption coefficients μ (in $cm^2 g^{-1}$) were obtained by transmission measurements through Nuclepore filters, AC, and occasionally, alkaline earth oxinates. In the case of AC one finds experimentally: $\log \mu = 3.3 - 2.4 \log E$, where E (in keV) is the X-ray energy of the element of interest.

RESULTS AND DISCUSSION

Experiments on synthetic water samples

The adsorption capacity of AC for oxine remains essentially constant in the pH 2 to 10 range.[3] Since the protonation of oxine varies strongly with pH, the adsorption must occur mainly through π-orbital overlap with the AC surface. Therefore one can expect an analogous insensitivity of the adsorption of metal oxinates to pH variations between pH 2 and 10. In this range the adsorption of metals on AC will thus only depend on the formation of stable oxinates. For many metals Fig. 1 shows the pH range in which quantitative precipitation of metal oxinates occurs. Since most oxinates are highly unsoluble, one may assume that in the same pH ranges stable oxinate complexes are formed and that quantitative metal adsorption on AC is hence to be expected. This was confirmed by the following experiment. Six 300 ml solutions were prepared containing approximately 15 ppb of Mn^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Ag^{+} and Eu^{3+} simultaneously. To each solution 250 μl of a radioactive solution containing ^{54}Mn, ^{65}Zn, ^{60}Co, ^{109}Cd, ^{110m}Ag and $^{152-154}Eu$ tracers were added. The pH of the solutions was adjusted between 4 and 9 in six steps. Subsequently 100 μl oxine solution was added so that the final oxine concentration was 20 ppm. Finally 30 mg AC was added to all solutions. After 1 hour of shaking the AC was filtered off and the metal recovery was measured by Ge(Li) γ-ray spectrometry on the AC loaded filrer and on the remaining solution. Results of this experiment are shown in Table I. There is a good agreement with the data in Figure 1. Hence one might extrapolate that near natural pH level some 40 metal ions can efficiently be adsorbed on AC. The proposed preconcentration procedure clearly has a truly multielement character.

TABLE I

Collection of metal oxinates as a function of pH.

	Percent recovery					
pH	Mn^{2+}	Co^{2+}	Zn^{2+}	Cd^{2+}	Ag^{+}	Eu^{3+}
4.2	0	98	19	13	64	69
5.0	2	98	75	23	80	105
5.5	35	99	96	88	70	108
6.2	87	97	96	100	76	91
7.0	94	98	95	101	69	96
8.1	110	100	98	105	76	87
9.1	108	99	97	105	72	99

Unlike many other preconcentration procedures, adsorption of metal oxinates is not prone to interference by high concentrations of alkali and alkaline earth ions. Indeed, experiments on solutions containing up to

1000 ppm Ca^{2+}, 20 ppm Mg^{2+} and 10% Na^{+} did not show any effect.[3] Also addition of NH_4^+ concentrations up to 1% did not influence the recovery of 20 ppb Mn, Co, Ni, Cu, Zn and Pb by the proposed procedure. High salinity water samples might thus favourably be analysed by this technique.

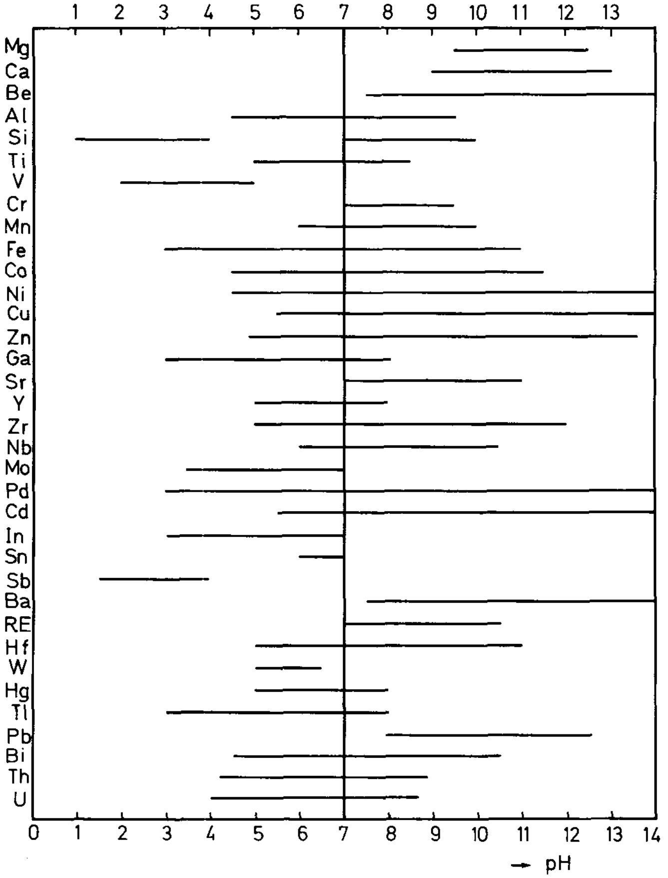

FIGURE 1 pH ranges for which elements can quantitatively be precipitated with oxine (data taken from I. M. Kolthoff, E. B. Sandell, E. J. Mehan and S. Bruchenstein: "Quantitative Chemical Analysis," McMillan Co., London, 1969).

In Figure 2 the analysis results for dilutions of a multi-element solution are plotted versus the added concentrations. Minimum amounts of oxine and a constant amount of activated carbon were used. At the lower concentration end some deviations appear to occur for Cu^{2+}, Zn^{2+} and Pb^{2+}, probably due to an inaccurate blank correction. Excluding those few values,

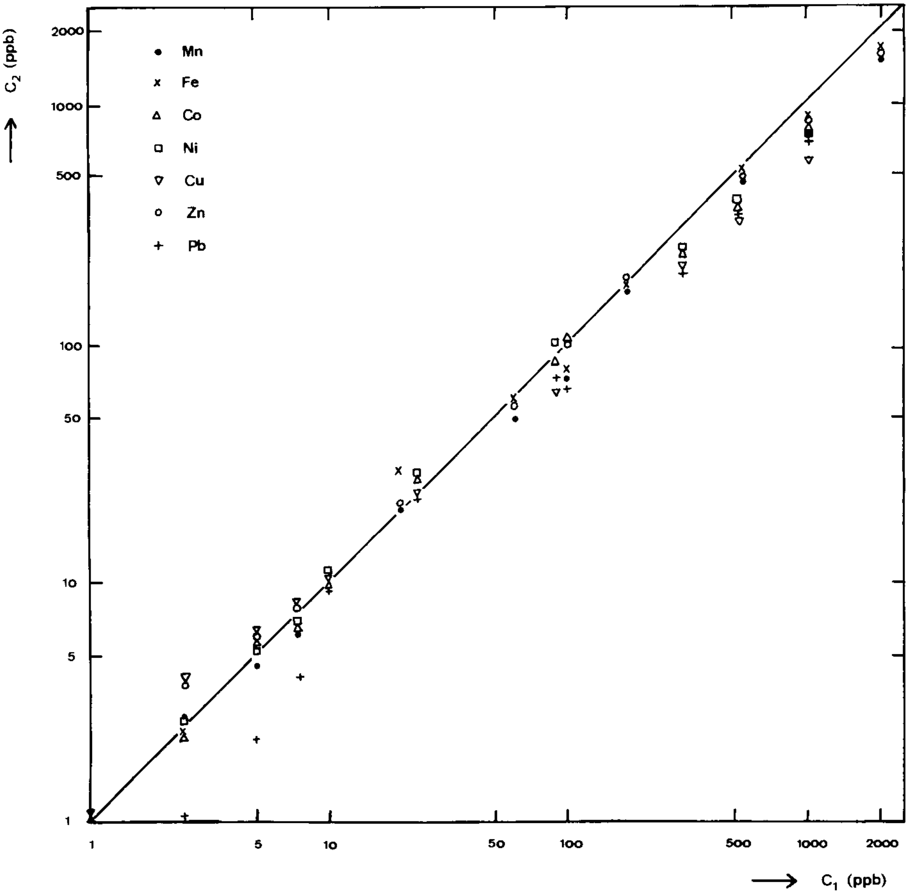

FIGURE 2 Proportionality between added and measured concentrations of various ions.

one finds correlation coefficients of 0.9991 for Mn^{2+}, 0.9995 for Fe^{3+}, 0.9985 for Co^{2+}, 0.9981 for Ni^{2+}, 0.9985 for Cu^{2+}, 0.9995 for Zn^{2+} and 0.9993 for Pb^{2+}.

The recovery at high concentrations can be increased at the expense of a lower enrichment factor, by using more activated carbon. Table II proves that also in the presence of 10 ppm Na^+ and Mg^{2+} and of varying amounts of Ca^{2+}, the recovery of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} is essentially independent of the trace ion concentration between 10 and 600 ppb.

The overall reliability of the proposed method was tested on intercomparison sample W3, distributed by the International Atomic Energy Agency as an acidified concentrate to simulate, after dilution, "a fresh

TABLE II

Percent recovery for increasing concentrations of transition elements in the presence of Na^+, Mg^{2+} and Ca^{2+}

Initial concentration in ppb	Percent recovery							Concentration, in ppm		
	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Na	Mg	Ca
10			87	104	84		87	10	10	10
10			84	100	95		88	10	10	500
20	110	120				115		10	10	10
20	100	115				100		10	10	500
30			83	100	70		73	10	10	30
60	83	95				87		10	10	30
100			88	94	76		71	10	10	90
180	96	89				93		10	10	90
300			94	108	75		70	10	10	300
600	92	92				89		10	10	300
Average recovery and % stand. dev.	96±10%	102±14%	87±5%	101±5%	80±10%	97±11%	87±9%			

water sample", as far as inorganic composition is concerned. The sample had previously been analysed by many laboratories in an intercomparison run.[14] Table III compares the present results to both the concentrations given by the organizers and those found, on the average, by the participating laboratories. For the present analyses the pH of 500 ml of the IAEA sample was adjusted with concentrated NaOH and 25 mg oxine was dissolved in it. No visible precipitate of metal oxinates appeared and 80 mg AC was added. After a 90 min shaking the AC was filtered off on a Nuclepore membrane filter and, after drying, measured by XRF. The agreement of the data appears to be very satisfactory except for Cr. that might be incompletely collected, and for Zn, which might be due to some contamination.

TABLE III

Comparison of measured and given values for IAEA's synthetic intercomparison water samples, W-3.

	Concentration in ppb		
Element	This work	Average found by other laboratories	Given value
V	8.9	8.4	8.0
Cr	5.9	11.0	12.0
Mn	10.3	10.8	12.0
Fe	50.0	49.6	32.0
Co†	5.9	11.9	12.1
Ni	11.2	10.7	12.0
Cu	12.2	12.5	12.0
Zn	19.1	13.6	12.0
As	12.5	15.6	16.0
Pb	27.8	30.3	16.0
Hg	1.7	1.6	1.0

†Important interference of Fe K_β on Co-determination.

Experiments on natural water samples

The analysis procedure was applied to water samples from the Albertkanaal, a channel which draws water from the river Meuse and provides the drinking water supply for the city of Antwerp, and to laboratory tap water, which is extra pressurized drinking water. In these experiments, after removing the particulate matter on a Nuclepore 0.4 μm membrane, 50 mg oxine was dissolved in 500 ml water, the metal oxinate precipitate was filtered off, 100 mg AC was added, resulting in a preconcentration factor 5000, and finally the AC was also filtered off. Table IV shows separately the metal quantities, expressed as ppb, collected by precipitation and coprecipitation as oxinates and those collected by the subsequent adsorption on AC. It appears that a single oxine precipitation–coprecipitation step, as recommended by several investigators,[15] is insufficient for quantitative collection of all trace metal ions: indeed an additional fraction between 16% and 100% of the total is recovered from the remaining solution in the subsequent adsorption step. Obviously, either oxinate precipitation–coprecipitation is not effective enough as a trace ion collector at these low concentration levels, or an important fraction of the trace metals occurs in an organic form which is not recovered in the precipitation–coprecipitation process. The high Fe and Zn concentrations, seen in Table IV for the tap water are due to colloidal hydroxyde formation during storage in the metal container which provides the higher pressure necessary for some of the laboratory work.

TABLE IV

Fraction of the trace elements collected on the metal oxinate precipitate and on the AC for river and tap water.

	River water			Tap water		
Element	Collected by (co-) precipitation with oxine, in ppb	Collected by subsequent adsorption on AC		Collected by (co-) precipitation with oxine, in ppb	Collected by subsequent adsorption on AC	
		in ppb	in % of total		in ppb	in % of total
Ti	0.52	0.87	62	2.2	1.0	31
V	—	3.8	100	—	1.1	100
Mn	1.6	3.4	68	3.6	5.7	61
Fe	15.4	10.8	41	212.0	97.0	31
Ni	5.6	2.5	31	0.4	3.0	88
Cu	9.8	1.8	16	7.2	3.2	31
Zn	9.2	2.2	19	125.0	46.0	27
Pb	0.7	1.0	59	0.6	1.0	62

For the same tap and river water samples and an additional batch from the same river, Table V compares the total results as obtained above with the data found when the oxine addition step was omitted, hence when adsorption on AC was applied to the original water sample. The fraction collected without oxine addition appears to be quite similar for both water types and above 50% for Ti, Mn, Fe and Cu. The Pb-concentration is close to the detection limit. It is well known that free metal ions are very poorly adsorbed on AC.[5] An effective metal recovery by AC adsorption alone thus points to an important fraction of the metal being in organic or colloidal form. It has been reported in the litereature[16] that natural waters contain 35 to 96% with an average of about 70% of the Cu content in a non-ionic form, which agrees with our data.

The substances which, in natural waters, bind metal ions into organic complexes or onto organic particles, or link them to clay particles, are mainly humic substances. The role of humic substances in aquatic chemistry has received considerable attention recently. Several experiments were carried out with pure humic material in order to check its influence on the proposed analysis procedure.

TABLE V

Comparison of ion recovery by activated carbon without and after prior oxine addition.

	River water					Tap water		
	Sample 1		Sample 2		Average percent collected without oxine			
Element	Without oxine addition (in ppb)	After oxine addition (in ppb)	Without oxine addition (in ppb)	After oxine addition (in ppb)		Without oxine addition (in ppb)	After oxine addition (in ppb)	Percent collected without oxine
Ti	1.9	1.4	1.2	1.7	100	2.0	3.1	65
V	0.2	3.8	<0.6	2.5	<14	<0.2	1.1	<18
Mn	4.1	5.0	2.7	3.8	76	7.0	9.3	75
Fe	22.5	26.0	39.0	56.0	78	266	309	86
Ni	4.3	8.1	8.3	18.0	49	1.1	3.3	33
Cu	10.5	11.6	3.5	5.3	78	9.0	10.3	87
Zn	6.0	11.3	19.0	49.0	46	85.0	171	50

To 300 ml solutions containing 10 to 15 ppb of Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Eu^{3+} in doubly distilled water spiked with radioactive ^{54}Mn, ^{60}Co, ^{65}Zn, ^{109}Cd and $^{152-154}Eu$, aliquots of the humic material were added in concentrations of approximately 1, 2, 5, 10 and 15 ppm. The solutions left to equilibrate for 2 weeks were then analysed by chelation to oxine, adsorption on 30 mg AC and Ge(Li) spectrometry. Figure 3 shows that for bivalent metal ions, the recoveries are high and not critically dependent on the humic material concentrations. The somewhat lower collection efficiency for Cd^{2+} is consistent with the lower stability of the Cd-oxine complex. The presence of about 2 ppm humic material, typical for many water types, does not induce any significant error on the analysis result. The recovery of trivalent ions, however, is strongly influenced by humic material in this case where a limited amount of AC was added. This fact bears to the particularly strong binding of trivalent metals to the structure of humic substances.[17]

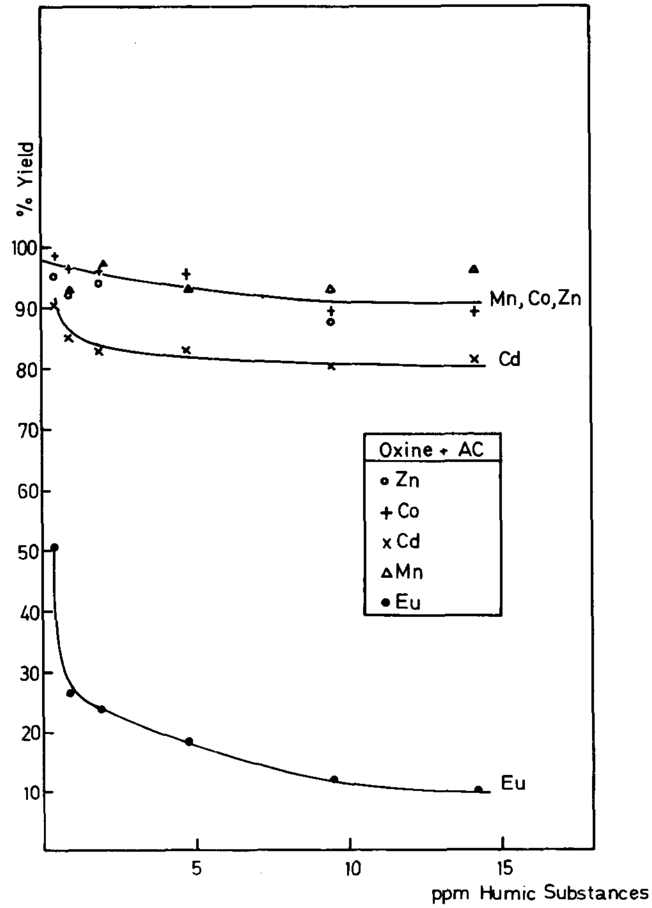

FIGURE 3 Influence of humic acid on metal ion recoveries for the proposed procedure of chelation by oxine followed by adsorption on activated carbon.

To study the adsorption of humic material on AC in more detail, an adsorption isotherm was recorded at room temperature. It is shown in

Figure 4 and gives the relation between the adsorption capacity of the AC as a function of the equilibrium concentration of humic material in solution. The isotherm is of the Langmuir type but has an importantly lower maximum capacity than the adsorption isotherms of oxine and metal oxinates on AC.[3] The humic substances are large macromolecules and cannot penetrate into the micropores of the AC, so that a much smaller surface is available for adsorption. For quantitative adsorption of humic material from solution, a large amount of AC is necessary (see below).

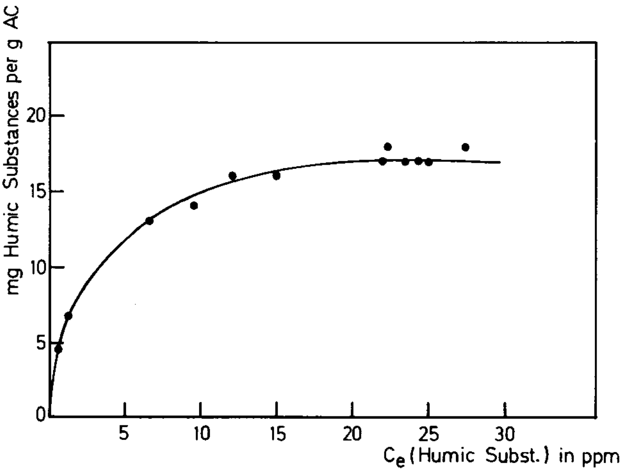

FIGURE 4 Adsorption isotherm of humic material on activated carbon.

Finally, the experiments that yielded Figure 3 were repeated but now without the addition of oxine: the equilibrated solutions of the humic material and trace metal ions with radioactive spikes were adsorbed directly on 30 mg AC, filtered off and measured by Ge(Li) spectrometry. The results are plotted in Figure 5. The metal recovery first increases with increasing humic concentration, but above an about 2 ppm humic substance concentration, decreases again, except for Eu where the recovery decreases monotonically with increasing humic material concentration. Since trivalent Eu ions are strongly chelated by humic material, complexation is almost quantitative even at low humic material concentration. In the given conditions the maximum capacity of AC for humic substance adsorption is exceeded (cf. Figure 4) and the percent recovery of humic-substance and thus of Eu that is chelated to humic substance, decreases with increasing concentration. For the less stable bivalent metal-humic complexes, the maximum in the curves of Figure 5 is a compromise between increasing complexation of the metals by humic material and decreasing percent recovery of the humic substances with increasing concentration. In the absence of organic compounds less than 40% of the free metal ions is adsorbed on the AC. Since metals are chelated in the presence of humic material or oxine and since the selectivity for organic adsorption over metal ion adsorption is striking, the fraction of metal ion adsorption in the presence of organic compounds is negligible, and the 30% to 50% metal recovery in the presence of 10 ppm humic material (Figure 5) is entirely due to adsorption of metal humates.

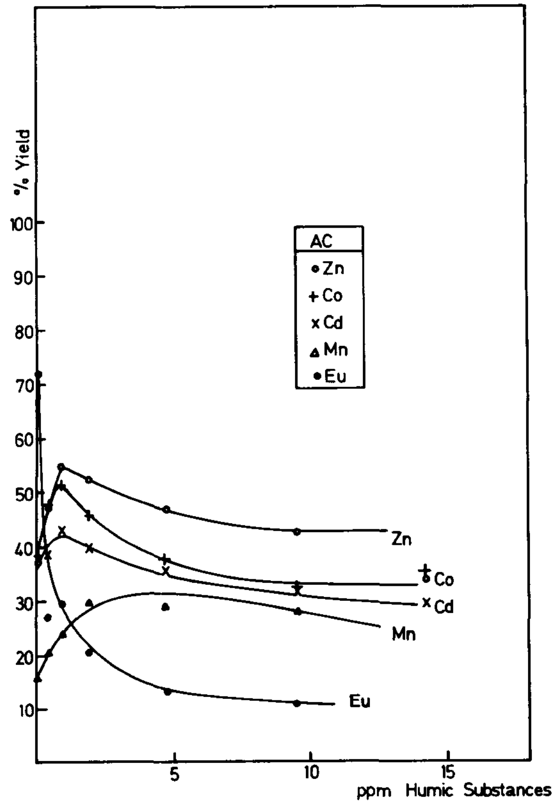

FIGURE 5 Influence of humic acid on the recoveries of metal ions when single adsorption on activated carbon (without prior oxine addition) is applied.

This conclusion implies that metal humates can be quantitatively recovered by adsorption on AC when enough AC is added, so that the capacity is not exceeded. The results in Figure 3 could thus be altered to complete recovery for all the elements by adequate adaptation of the AC quantity. To prove this important point experiments were carried out in which solutions containing 15 ppb Mn^{2+}, Zn^{2+} and Eu^{3+}, radioactive tracers of ^{54}Mn, ^{65}Zn, $^{152-154}Eu$ and 3 ppm humic material were left to equilibrate and then analysed by the proposed procedure, using a constant oxine addition but varying amounts of AC far exceeding the usual amount of 10 mg AC/100 ml. The results represented in Figure 6 clearly show that

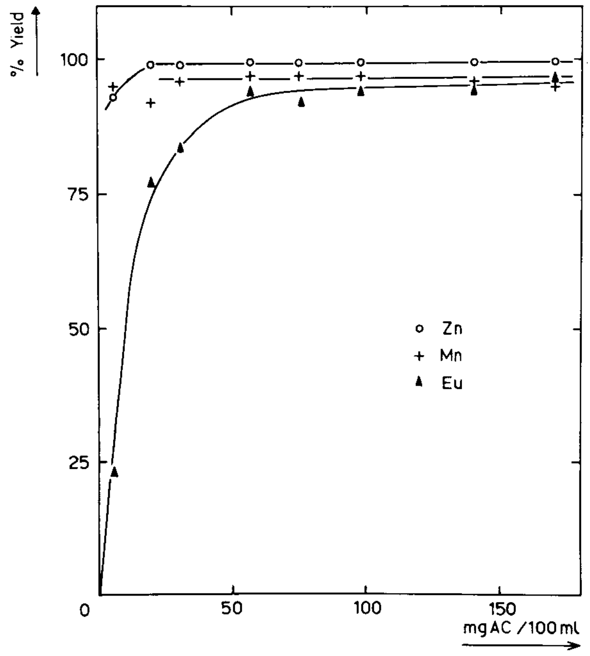

FIGURE 6 Influence of the activated carbon amount on the recovery of trivalent and divalent ions, for solutions containing 3 ppm humic material.

for typical natural waters, increased AC additions will lead to quantitative recoveries even of trivalent ions, at the expense of a lower preconcentration factor, of course.

For Zn, the data in Table V compare well to the collection yield values, in Figure 5, for a 2 ppm humic material concentration (typical for the water samples used for the experiments in Table V). For Mn, however, the experimental values in Table V are significantly higher and this must be related to the collection of colloidal, non-humic Mn in the natural waters.

For the purpose of comparison, tap water samples were analysed by X-ray fluorescence, using both this technique and co-crystallisation on 1-(2-pyridylazo)-2-naphtol[18] for pre-concentration. The results, assuming quantitative recoveries in both cases, are listed in Table VI. The experiments using AC yield a somewhat higher result, probably due to a more complete collection of the naturally occurring metal-humic material complexes on AC.

TABLE VI

Comparison of results for tap water with values obtained after another preconcentration step.

Element	Concentration in solution, in ppb Measured by the present technique	 Measured by XRF after co-crystallisation on PAN[18]	Concentration in suspension, in ppb, measured by XRF on filter[19]
Mn	0.87 (6%)†	0.42 (20%)	0.5
Fe	4.5 (7%)	3.3 (8%)	2.8
Ni	2.4 (4%)	2.2 (4%)	—
Cu	2.2 (4%)	1.4 (5%)	0.2
Zn	3.5 (5%)	2.4 (4%)	0.2

†( ): percent variation coefficient.

The experiments carried out in multiplicity point to a very satisfactory reproducibility with an overall variation coefficient being close to 5%.

If one defines the preconcentration factor as the ratio of the original to the final sample weight, values between 1000 and 10000 are calculated.[4] In X-ray fluorescence analysis detection limits are usually defined as three times the square root of the background. Taking into account the—assumedly constant—blank impurities of the oxine, AC and Nuclepore filter, and the X-ray scatter by the filter and precipitate contributing to the background, and assuming a 2000 sec counting time, one calculates theoretical detection limits for 1 liter samples corresponding to values around 0.1 to 1 ppb for most transition elements.

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