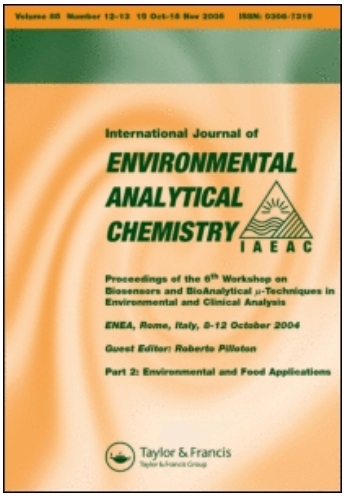

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J. Smits[a]; R. Van Grieken[a]
[a] Department of Chemistry, University of Antwerp (U.I.A.), Wilrijk, Belgium

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Chelating 2,2′-Diaminodiethylamine Cellulose Filters and X-ray Fluorescence for Preconcentration and Trace Analysis of Natural Waters†

J. SMITS and R. VAN GRIEKEN

Department of Chemistry, University of Antwerp (U.I.A.), B-2610 Wilrijk, Belgium

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The 2,2′-diaminodiethylamine (DEN) functional group can be expected to have ideal properties for the chelation of transition metals and their collection from aqueous solutions, independent of the alkali and alkaline earth ions concentration. Introducing DEN into cellulose filters allows straightforward preconcentration of trace cations by a simple filtration step, and the DEN-filter constitutes a suitable target for X-ray fluorescence (XRF) analysis. The linearity between the XRF-response on the loaded DEN-filter and the trace cation concentration in the solution appears excellent, up to a total filter capacity of *ca.* 3 μeq . cm^{-2}. The detection limits are around 0.5 μg . l^{-1} in most practical cases. Accuracy and precision are around 10%. The applicability of the proposed procedure is illustrated on a comparative basis by XRF-analysis of drinking water and surface water, after preconcentration by DEN-filtration and by alternative procedures.

KEY WORDS: Trace metals, water analysis, X-ray fluorescence, preconcentration, chelating filter, surface water, drinking water.

INTRODUCTION

Ion-collecting filters offer excellent perspectives for preconcentration in X-ray fluorescence (XRF): the trace metal collection is accomplished by a simple filtration step and the loaded filters can directly be presented to the X-ray analysis instrument as ideal thin targets with low atomic number

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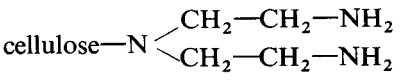
matrix. For direct preconcentrations from natural water samples, the strongly acid and basic ion exchange filters, that Campbell *et al.*[1] studied, cannot be applied directly since they require acid or base addition and also collect alkali and alkaline earth ions which are usually abundant in natural waters and occupy the limited ion-exchange filter capacity. Filters with chelating iminodiacetate[2] or 1-2-hydroxyphenylazo-2-naphthol[3] functional groups collect at a natural pH but still show a significant affinity towards alkali and alkaline earth ions, while thiocarbamate filters are unstable and should be prepared immediately before use.[4]

Theoretical considerations[5] show that chelating cellulose filters containing 2,2′-diaminodiethylamine (often called diethylenetriamine or DEN) as functional groups:



should be ideal for trace ion preconcentrations. Polyethyleneamines have already been used sporadically in resins, silicagel and glass beads for preconcentration from various aqueous solutions, including sea water.[6-8]

In the present work, the DEN-cellulose filters are studied for their characteristics in combination with energy-dispersive XRF and for their applicability.

EXPERIMENTAL

X-ray fluorescence set-up

The energy-dispersive XRF-unit included a high voltage generator and Kevex-0810 subsystem with W-anode X-ray tube, secondary targets of Ti, Ge, Mo, Ag, Sn and Nd, and a turnable 16-sample holder. The X-rays were registered by a 30-mm^2 Si(Li) detector with 170 eV FWHM at 5.9 keV, amplification and pulse pile-up rejection systems and a 4096-channel analyser and magnetic tape recording unit for off-line computer spectrum evaluation. For calibration a series of commercial thin-film standards was available.

DEN-filter synthesis

After a considerable effort to optimize the synthesis procedure,[9] the following synthesis prescription can be recommended. Preswell e.g. 10 dried Whatman-41 cellulose filters (5.5 cm diameter) during 30–60 minutes in 200 ml dry N,N-dimethylformamide (DMF, distilled with 10 ml benzene/100 ml DMF). After adding 6 ml $POCl_3$, heat the mixture to 90°C

during at least 15 minutes. Wash the filters successively with DMF, water, 5% NaOH, water, 5% CH_3COOH, and water. Substitute the Cl-functional groups (approx. 9 μeq Cl . cm^{-2}) by heating the filters, under appropriate stirring, in an excess of purified DEN at 130°C during at least 2 hours. In the final filters, the exchange capacity in filtration experiments is 3.6 μeq . cm^{-2} on the average, the lateral distribution of the functional groups is homogeneous within 10% and typical blank levels are 0.16 μg Fe . cm^{-2}, 0.02 μg Cu . cm^{-2} and 0.05 μg Zn . cm^{-2}.

Filtration unit

In earlier experiments the collection of suspended matter and dissolved trace ions was done in a Gelman N°42000 magnetic filtration unit, in which a Nuclepore 0.4 μm pore-size membrane and a DEN-cellulose filter were placed on top of each other. Photographic measurements of the ion distribution in the DEN-filters, after collection from radioactively labelled water samples, pointed to serious heterogeneities, partially matching the heterogeneities in the Nuclepore filter load, and to a poorly defined DEN-filter load area. Such heterogeneities would lead to XRF-inaccuracies since the excitation-detection efficiency of the X-ray set-up is not homogeneous in the target plane.[10] Ultimately, a home-made plexiglass filtration unit of straightforward cylindrical shape was used to yield a homogeneous flow over a well-defined filter area of 10.2 cm^2. Collection of suspended matter, if required, was accomplished previously in a separate filtration over a Nuclepore membrane.

Experimental procedure

Solutions of 100 ml, at natural pH, were filtered separately through a Nuclepore membrane and then, at a rate of less than 1 ml . min^{-1} . cm^{-2}, through a DEN-filter. After drying in a desiccator, the filters were suspended on a Teflon ring fitting into the XRF-unit sample holder and analysed for 3000 sec, e.g. using Mo secondary fluorescer excitation at 40 kV-40 mA tube conditions. The characteristic X-ray peak areas were calculated using a non-linear least-squares fitting computer program.[11-12]

RESULTS AND DISCUSSION

Characteristics of DEN-filters versus trace ion collection

In an earlier study[5] on the preconcentration of trace cations by DEN-filters, it was found that, provided the flow rate is below 1–2 ml . min^{-2} . cm^{-2} and the pH above 5–6, a collection efficiency of 90–100% can be achieved for Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+},

Cd^{2+}, Eu^{3+}, Hg^{2+}, Pb^{2+} and UO_2^{2+}, if the total transition metal load is below the 30–35 μeq chelating capacity of a 10-cm^2 DEN-filter. The recoveries are unaffected by alkali and alkaline earth ions, halides, bicarbonate, sulfate, phosphate and humic material up to unrealistic concentration levels. Only NH_4^+ and amino acids interfere at concentration levels above 20 meq.l^{-1}.

Of the anions, the following are collected nearly quantitatively in the optimal pH range of 3 to 6 at a flow rate below 0.7 ml.min^{-1}.cm^{-2}: vanadate, chromate, arsenate (but not arsenite), selenite and selenate, molybdate, stannate, tungstate.[13] However, at an ionic strength above 0.01 eq.l^{-1} the collection yields of anions are depressed. Therefore, the DEN-filters do not appear ideal for direct trace anion preconcentration from most natural waters.

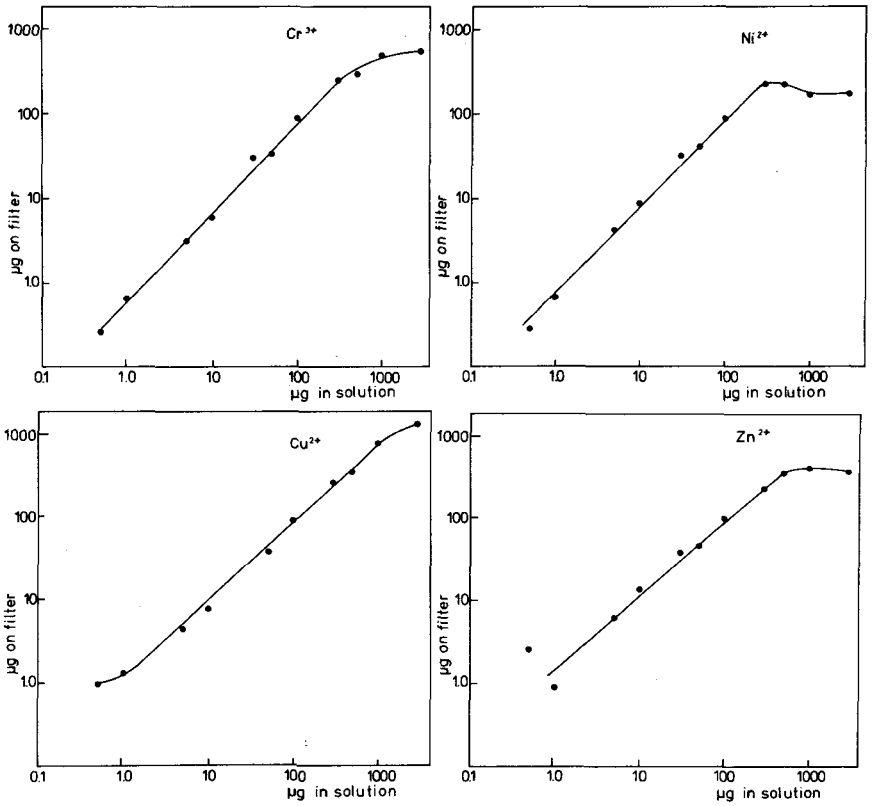


FIGURE 1A Proportionality between X-ray fluorescence response on the loaded DEN-filter and the trace metal ion concentration in the original solution, for Cr^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+}.

Linearity of X-ray response versus concentration

To determine the concentration range in which the X-ray response is linear, cation preconcentrations were carried out from 100 ml solutions containing 0.5 to 100 μg, and from 1-l solutions containing 300 to 5000 μg of simultaneously Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and UO_2^{2+}, together with 80 ppm Ca^{2+}, all as chlorides and nitrates. Some of the XRF-results are represented in Figs. 1A and 1B. Positive deviations from linearity at the lower concentration end are due to contamination or inaccurate blank corrections. At the high concentration end the deviations point to exceeding of the collection capacity of the filter. The deviation occurs at 300 to 500 μg of every ion, corresponding to a total of 2.0 to

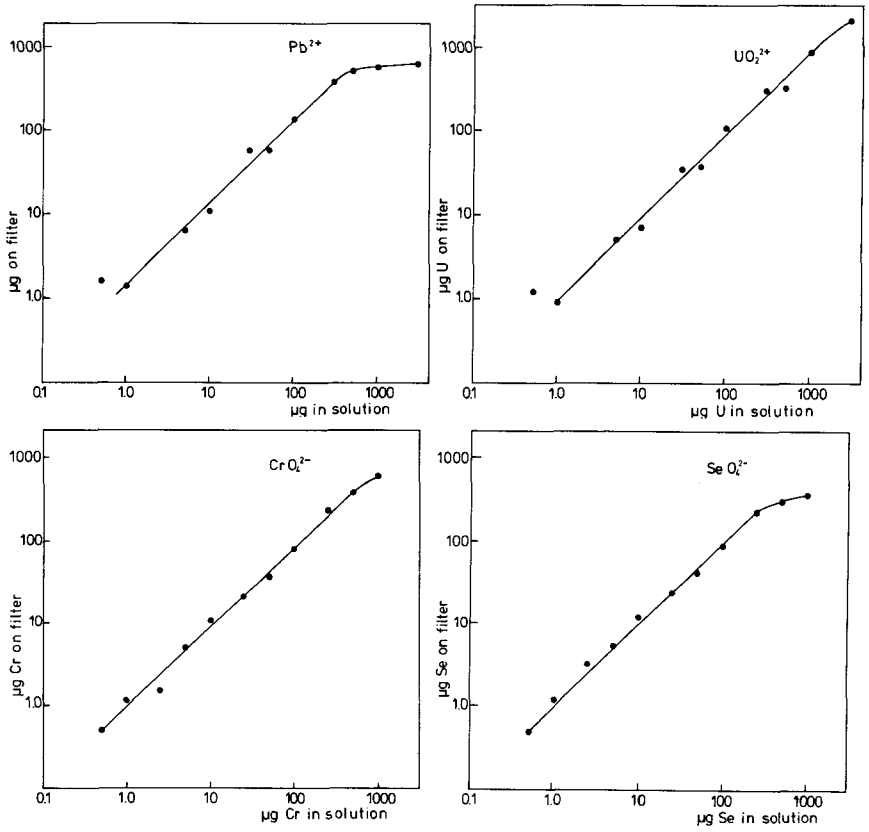


FIGURE 1B Proportionality between X-ray fluorescence response on the loaded DEN-filter and trace metal concentration in the original solution, for Pb^{2+}, UO_2^{2+}, CrO_4^{2-} and SeO_4^{2-}.

3.5 μeq.cm^{-2} binding capacity of the filter. The relative point at which such deviation from linearity occurs indicates the order of selectivity of the DEN-filter for the different ions, namely

$$Hg^{2+} > UO^{2+} > Cu^{2+} > Pb^{2+} > Cr^{3+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+} > Mn^{2+}.$$

For the solutions containing between 0.5 and 300 μg of each element, correlation coefficients (between added concentration and XRF-response) ranging from 0.9954 to 0.9989 were calculated in all cases. Clearly a satisfactory proportionality exists between the trace cation and XRF-signal.

Also, 100 to 250-ml solutions containing 0.5 to 1000 μg of V (as VO_3^-), Cr (as CrO_4^{2-}), As (as AsO_4^{3-}), Se (as SeO_4^{2-}), Mo (as MoO_4^{2-}), W (as WO_4^{2-}) and Br^- were preconcentrated at pH 4.5 at 0.5 ml.min^{-1}.cm^{-2} and the loaded DEN-filters were analysed. Some results are included in Fig. 1B. At the lower concentration end, no deviations were observed, obviously because laboratory contamination effects were negligible for those elements. At higher concentrations, a deviation occurred already at 0.06 μeq.cm^{-2} for Br^-, but at appr. 1.5 μeq.cm^{-2} for AsO_4^{3-} and SeO_4^{2-}, up to appr. 5.5 μeq.cm^{-2} for VO_3^- and WO_4^{2-}, and the results pointed to the following order of selectivity:

$$WO_4^{2-} > VO_3^- > MoO_4^{2-} > CrO_4^{2-} > SeO_4^{2-} > AsO_4^{3-} \gg Br^-.$$

For all the oxyanions, correlation coefficients between 0.9970 and 0.9997 were found.

X-ray absorption in the DEN-filter

The absorption coefficient μ (in cm^2.g^{-1}) of the DEN-filters (9.25 mg.cm^{-2}) was measured for different X-ray energies E by transmission experiments, and these measurements, with a correlation coefficient of 0.9981, led to the following relation:

$$\ln \mu = 7.55 - 2.42 \ln E$$

The absorption correction depends, of course, on the distribution of the fluorescent material within the filter. After filtration through a DEN-filter, the in-depth trace ion distribution is certainly not homogeneous, but depends on the total trace ion load, the concentration, the sample volume and the filtration rate. This situation is similar to the problem of filter penetration in XRF-analysis of atmospheric dust particles collected by drawing air through a filter.[14] Some information on the ion distribution

can be extracted from the ratio of front—and backside—XRF-measurements on the filters.[15] Numerous measurements, on typical loaded DEN-filters, showed that the average distribution was such that the absorption correction factor amounted to 1.20 for Cr, 1.15 for Mn, 1.10 for Fe, 1.09 for Ni, 1.08 for Cu, 1.05 for Zn (K_α-lines) and 1.03 for Pb (L_β-lines). In practice, however, the absorption correction factors for an assumed homogeneous distribution can be used since they appeared accurate to within 1–5%. Only for elements yielding X-rays below 4.5 keV, special care should be taken.

Detection limits

Table I lists some typical detection limits, defined as three times the square root of the background count rate (depending on scatter, proportional to the filter thickness, and on the characteristic peaks from blank filter impurities). These hypothetical detection limits assume no mutual interference of the elements; in practical cases the detection limits can be somewhat less favourable. In general, it may be stated that most elements can be measured down to $0.5\,\mu g.l^{-1}$ with the present preconcentration and analysis procedure.

TABLE I

Interference-free detection limits for some elements (collected as cations or anions) for 3000 sec XRF-measurement after preconcentration on a DEN-filter

	Detection limits, in $\mu g.l^{-1}$, for a 1-l water sample collected on a 10-cm^2 DEN-filter			
	Secondary fluorescer system			
Element	Ge	Mo	Ag	Sn
V	0.07	0.25	0.8	0.9
Cr	0.07	0.2	0.6	0.8
Mn	0.05	0.2	1.4	0.8
Fe	2.2	2.5	2.5	3.3
Cu		0.2	0.8	1.0
Zn		0.4	0.4	0.4
As		0.1	0.3	0.2
Se		0.05	0.1	0.1
La[a]		1.4	3.5	4.9
W[a]		0.35	0.3	0.5
Hg[a]		0.3	0.25	0.4
Pb[a]		0.2	0.4	0.2
U[a]		0.2	0.2	0.3

[a]Detection through L-lines. K-lines in other cases.

Accuracy and precision

Synthetic water samples containing 25 μg of Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Eu^{3+}, Pb^{2+} and U (as UO_2^{2+}) and 80 ppm Ca, were analysed in 16-fold by XRF. Table II lists the average apparent collection yields, calculated relative to commercially available thin-film standards, after X-ray absorption correction. Except for Ni^{2+}, the apparent positive and negative deviations from a 100% collection yield can all be attributed to uncertainties in the XRF-analysis and calibration procedure. Both the accuracy and precision of the overall procedure appear to be around 10%.

TABLE II

Average apparent collection yield and precision for 16 analyses of synthetic water samples preconcentrated onto DEN-filters

Ion	Apparent collection yield, in percent	Relative standard deviation per measurement in percent
Cr^{3+}	104	9
Fe^{3+}	104	10
Co^{2+}	97	10
Ni^{2+}	90	14
Cu^{2+}	100	11
Zn^{2+}	105	11
Eu^{3+}	105	9
Pb^{2+}	102	8
UO_2^{2+}	97	7

Applicability

In a comparative study of the trace cation preconcentration by eight different procedures,[16] the procedure using DEN-filters appeared to be among the most simple and suitable for in-line or *in-situ* use. They form ideal targets for XRF, and should, therefore, be indicated for routine XRF-analysis of drinking water and natural water samples.

This feature was first tested by a comparative trace metal analysis of a drinking water batch (pH 8) taken from the Antwerp drinking water supply, which has a rather high hardness. The suspended matter was immediately filtered off and analysed separately. The filtered water was analysed using Mo-excitation, by three techniques developed in this laboratory: filtration through a DEN-filter, cocrystallisation on 1-(2-pyridylazo)-2-naphthol (PAN)[17] and chelation by 8-hydroxyquinoline (oxine) followed by adsorption onto activated carbon.[18] The results are given in Table III: the data for the three preconcentration techniques are the average of 4, 5 and 7 analyses, respectively. Mn^{2+} is not quantitatively

TABLE III

Transition metal concentration in tap-water from drinking water supply, measured by XRF in combination with different preconcentration techniques

Element	Concentration (and stand. dev. per meas.), in $\mu g.l^{-1}$			
	Suspended, collected on 0.4 μm Nuclepore membrane	Dissolved, determined after preconcentration using		
		DEN-filters	PAN-cocrystallisation[17]	Oxine chelation and actived carbon adsorption[18]
Mn	0.4 (0.1)	—	0.4 (0.2)	0.9 (0.1)
Fe	2.8 (0.6)	2.5 (0.3)	3.4 (0.5)	4.5 (0.3)
Ni	<0.2	2.3 (0.1)	2.3 (0.2)	2.4 (0.1)
Cu	0.1 (0.02)	1.8 (0.1)	1.3 (0.1)	2.2 (0.1)
Zn	0.1 (0.04)	2.7 (0.5)	2.3 (0.2)	3.5 (0.2)
Pb	<0.2	<0.1	<0.1	—

collected by the DEN-filter at a pH below 9, due to the absence of a ligand field stabilisation energy in the complexation of Mn^{2+} by DEN. For the other elements, the results of DEN-filtration and PAN-cocrystallisation agree very well, on the average, in spite of the low concentration levels involved. The results from the activated carbon method appear slightly higher, probably because this procedure collects somewhat better the trace metals in colloids and strong complexes with humic material. The relative standard deviation per measurement, at a concentration level of $2.5\,\mu g.l^{-1}$, is at 10% for the DEN-filtration and PAN-cocrystallisation method, and at 5% for the activated carbon procedure. The DEN-procedure, simply consisting of a filtration only, can easily be applied for direct *in-situ* preconcentration at various points of a water distribution network by fixing a suitable filter holder onto the tap and having a 0.5–1-l volume run through at a rate of $100\,ml \cdot h^{-1} \cdot cm^{-2}$.

In a second applicability test, 10 samples were taken from rivers in the Belgian Ardennes region. Only the Meuse river was expected to be polluted by various industrial and domestic sources, and the small river Warche from tanneries. The samples were filtered off immediately on Nuclepore membranes, and preconcentration through DEN-filters was applied to 0.5-l filtered samples, and both PAN-cocrystallisation and precipitation with sodium diethyldithiocarbamate (DDTC)[19] were applied to 1-l aliquots. The concentrations, measured by Mo-excitation during 3000 sec, are listed in Table IV: they are the results of single determinations for the dissolved phase, and the average of three

TABLE IV

Concentration[a] in $\mu g\,l^{-1}$, for several rivers in the Belgian Ardennes

River and sampling point:	Lesse, Chamly				Lesse, Anseremme				Ourthe, Orthobertogne				Ourthe, Nisramont				Ourthe, Houffalize			
	Suspended	Dissolved			Suspended	Dissolved			Suspended	Dissolved			Suspended	Dissolved			Suspended	Dissolved		
Elements		I[a]	II[a]	III[a]		I	II	III		I	II	III		I	II	III		I	II	III
Cr	0.6	<0.2	<0.2	<0.3	1.1	<0.2	<0.2	<0.2	0.6	0.3	0.5	<0.2	0.9	<0.2	<0.2	<0.2	0.6	<0.2	<0.2	<0.2
Mn	6.6	—	1.4	4.5	13	—	1.4	4.5	17	—	4.3	4.6	32	—	0.2	5.3	21	—	0.3	3.2
Fe	86	24	36	25	300	7.3	5.8	12	190	75	69	70	200	21	14	22	140	15	14	19
Ni	<0.2	1.4	1.4	1.8	0.3	2.0	1.6	2.1	<0.5	1.7	2.4	1.9	0.1	1.9	1.4	1.7	0.3	2.1	1.5	2.0
Cu	0.2	2.2	1.5	1.7	2.8	4.7	2.9	4.5	<0.3	1.5	0.9	0.7	1.4	2.2	1.3	1.3	0.2	0.9	0.8	0.7
Zn	3.1	19	20	10	14	11	19	17	3.1	15	9.3	6.1	7.0	17	9.4	3.2	1.9	14	6.5	1.5
Pb	3.1	0.9	1.1	1.8	20	0.8	0.9	4.5	4.4	0.6	1.6	1.0	7.2	0.7	0.4	1.0	1.1	0.5	1.1	0.4
U	0.3	<0.3	—	—	<0.2	0.5	—	—	0.9	0.6	—	—	0.4	0.4	—	—	0.2	<0.3	—	—

River and sampling point:	Ourthe, Tilff				Salm, Trois-Points				Amblève, Rivage				Warche, Malmédy				Meuse, Liège			
	Suspended	Dissolved			Suspended	Dissolved			Suspended	Dissolved			Suspended	Dissolved			Suspended	Dissolved		
Element		I	II	III		I	II	III		I	II	III		I	II	III		I	II	III
Cr	8.2	1.5	0.8	0.3	0.5	0.4	0.3	<0.2	16	0.9	0.4	0.4	1700	15	8.2	5.7	8.6	0.8	0.6	0.4
Mn	12	—	0.8	3.1	29	—	1.3	9.0	21	—	0.4	2.7	21	—	77	80	23	—	54	57
Fe	170	32	10	32	170	21	20	24	300	12	11	15	550	23	16	29	810	8.0	7.3	11
Ni	0.1	10	3.2	3.1	0.1	1.9	1.9	4.1	0.3	2.5	1.7	2.3	1.3	1.9	2.3	3.5	0.9	5.5	3.8	5.1
Cu	1.2	4.4	2.5	2.7	0.3	1.5	1.3	1.2	2.3	2.2	1.8	2.2	10	0.2	0.7	1.3	5.0	5.1	3.2	6.7
Zn	13	94	60	43	3.7	18	20	10	14	18	15	12	36	3.9	10	4.1	130	86	56	99
Pb	6.6	0.5	0.5	1.1	1.7	0.4	0.5	0.7	11	0.7	1.4	1.2	15	0.4	0.4	1.4	33	0.9	1.7	0.7
U	0.2	1.3	—	—	0.2	<0.3	—	—	<0.3	0.8	—	—	0.5	1.2	—	—	<0.2	6.2	—	—

[a]I: Preconcentration by DEN-filtration.
II: Preconcentration by PAN-cocrystallisation.
III: Preconcentration by DDTC-precipitation.

measurements for the suspended material (the total suspended matter load varied between $3\,mg.l^{-1}$ to $80\,mg.l^{-1}$ for the Warche river). It appears that the Warche river is mainly characterised by extremely high suspended Cr-levels (and to a much lesser extent, dissolved Cr^{3+}-levels), high dissolved Mn^{2+} and suspended Cu. These features are still reflected at the sampling locations downstream from this site. The more industrialized sites show increased values for several elements, as can be expected. Considering the inaccuracies that are inherent to work at low concentration levels and the problems in representative collection of natural water, the results for the three preconcentration techniques in Table IV are generally in good agreement, with the DEN-results being close to the average measured dissolved concentrations. Preconcentration by DEN-filtration can thus advantageously be applied for simple multi-element preconcentration of natural and polluted surface water.

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