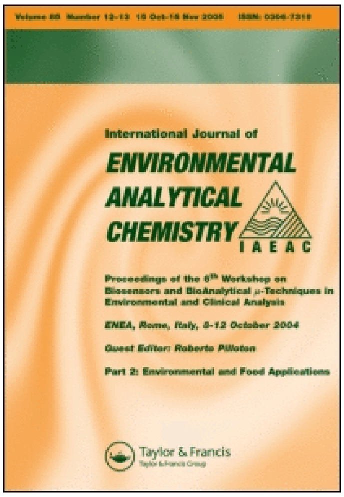

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Critical Comparison of Preconcentration Methods for Trace Ion Determination by Energy and Wavelength Dispersive X-Ray Spectrometry†

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In recent years, considerable progress has been made in the field of metal ion preconcentration from environmental water samples. The methods most widely used include ion-exchange, precipitation (and coprecipitation), adsorption and chelation with immobilized and non-immobilized reagents. As the mechanisms underlying the various methods are different, it is expected that these methods perform differently with respect to the enrichment factor, sensitivity and recovery of trace metal ions. In this investigation, the preconcentration of 10 cations, Ag, As, Co, Cr, Cu, Fe, Hg, Mn, Pb and Zn was studied. The methods of preconcentration include (1) cation-exchange resin-loaded filter paper, (2) precipitation with sodium diethyldithiocarbamate, (3) precipitation with ammoniumpyrrolidinedithiocarbamate, (4) chelation with oxine with subsequent adsorption on activated carbon and (5) chelation with diethyldithiocarbamate immobilized on controlled pore glass. Among the factors compared are the detection limits, sensitivity, precision, linearity and dependence of the recovery on the concentration of metal ions.

KEY WORDS: Preconcentration, X-ray spectrometry, trace ions.

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INTRODUCTION

X-ray fluorescence spectrometry for water analysis at environmentally relevant levels of trace ions requires a preconcentration step to insure adequate detection limits.[1] The good spectral resolution of XRF instruments has lead to the development of unselective preconcentration procedures most of which yield thin samples for better sensitivity and reduced interelement effects. Other advantages of preconcentration are (a) easier handling because of reduced sample mass, (b) elimination of interferences from varying matrix components, (c) less danger of systematic errors due to adsorption and contamination, and (d) the sample can be stored easily for later reinvestigation.

In spite of numerous efforts to develop suitable methods for preconcentration, literature data are of limited value in the selection of the most appropriate technique for a number of reasons: the experimental conditions vary over a wide range, interference studies are rather limited, two or more researchers may report different optimal parameters, very few real samples are run, detection limits are frequently extrapolated and sensitivities are obtained on different instruments. Many of these drawbacks are eliminated if one laboratory evaluates different methods.

The methods studied and reported in this paper are all taken from the literature and are applied as published with the exception of very obvious modifications where necessary. They are based on different chemical principles such as ion-exchange reactions, chelation, adsorption and precipitation. In most instances the preconcentration procedure includes a filtration step. One method utilizes cation exchange resin-loaded filter paper in the sodium form where the sodium is displaced by the trace ions in the water sample.[2,3] Diethyldithiocarbamate as the sodium salt (NaDDTC) and ammoniumpyrrolidinedithiocarbamate (APDC) are used[4,5] as precipitating reagents because of the low aqueous solubility of their metal chelates. Collection of the resulting precipitate on membrane filters yields samples that can be measured favorably by XRF. The dithiocarbamate functional group can also be immobilized on controlled pore glass beads (CPG) used in column form as a sampling and preconcentration tool.[6,7] After homogenization the glass is a suitable matrix for XRF determinations. A mixed mechanism of chelation and adsorption is the basis of a preconcentration method developed by Van Grieken and co-workers.[8,9] At suitable pH values, metal oxinates are formed and in a second step adsorbed on activated carbon. The activated carbon is filtered and the metal ions determined by XRF. The trace ions studied included Cr^{+++}, Mn^{++}, Fe^{++}, Co^{++}, Cu^{++}, Zn^{++}, Hg^{++}, Pb^{++},

As^{+++} and Ag^{+}, and were chosen to represent a reasonable compromise between ions of environmental importance and ions that are expected to cause chemical problems in the preconcentration step or in X-ray spectrometry.

The objectives of this study were manifold. First, fundamental figures-of-merit (e.g. detection limits, linear dynamic range, sensitivity and precision) of the preconcentration methods had to be determined under ideal one-element-at-a-time conditions within a single laboratory to eliminate any inconsistencies that are introduced by various laboratory environments. A second stage of this work was to determine to what extent concomitant ions exhibit an influence in the preconcentration step and/or XRF determinations. The levels of potential interferents were chosen to exhibit a realistic picture of the situations likely to occur in the analysis of natural water samples. The last stage of the present study consists of a test of the preconcentration methods using environmental water samples. In so doing, the ranges of concomitant elements chosen in the interference studies could be checked for any unexpected problems that have not been experienced. The experiments have been designed to yield a maximum of valid information without loss of statistical inference. For an accurate determination of the decision and detection limits, good estimates of the variability of the blank and the precision of the method at low concentrations are necessary. The single element calibration curves were established with 16 samples, five of which were blanks and five containing 1 μg of the trace element. Duplicates were run at 20, 50 and 100 μg to establish the linear dynamic range and to determine the relative standard deviation in the working range of the calibration function. Even though the decision and detection limits are frequently proportional to each other, large relative errors in the preconcentration of very minute amounts of the analyte and/or low recoveries can give very divergent estimates for decision and detection limits.[10,11,12] Volumes of 100 mL were used for the calibration, which corresponds to original concentrations of 10 ppb to 1 ppm of trace element in the water samples.

Occasionally interferences have been observed in preconcentration procedures. These may be due to salinity, high alkaline earth content, organics with complexing properties and other metal ions in similar or higher concentrations than the analyte elements. Since energy dispersive X-ray fluorescence spectrometry was one analytical finish, the effect of adjacent elements in the periodic table (e.g. Cu and Zn) that give overlapping K_α-K_β lines was of interest. A two level factorial design[13] was used for simplicity: as a lower level, a zero concentration was chosen (i.e. the absence of the potential interferent) whereas the higher level was determined to reflect realistically an environmental situation. This design was preferred over the more frequently used one-factor-at-a-time experiments because of economy and better representation of real samples containing several concomitant species.[14]

EXPERIMENTAL

Apparatus

A Philips model PW-1410 X-ray fluorescence spectrometer was used for all wavelength dispersive measurements. In all cases a LiF-200 analyzing crystal was used with gas flow and/or scintillation detector. A Mo, W or Cr X-ray tube was operated at suitable kV and mA settings. The counting times varied but did not exceed 200 s for the lowest concentrations and the blank. All spectrometer operations were under control of a NOVA 1220 computer.[15]

The energy dispersive X-ray fluorescence analyses were performed on a United Scientific (Nuclear Semiconductor Division) Spectrace 440 spectrometer. It is equipped with an automatic 20 position sample changer and a filter wheel with 5 source filters. It is interfaced to a NS 880 analyzer from Tracor Northern. A low wattage Ag X-ray tube (Watkins–Johnson) was operated in pulsed mode unless otherwise stated. The voltage was set to 30 kV for all elements except Hg^{++} where it was set to 40 kV, the current was adjusted depending upon the sample preparation technique to give a maximum system deadtime of 50%. A 0.025 mm Ag filter was used to lower the background caused by backscattered tube radiation. The system is controlled by a Digital Equipment Corporation PDP 11/05 computer using the special purpose language FLEXTRAN that is supplied by the vendor. The counting time was 1000 s for the blank and 1 μg samples and for the real water samples. All the other data were collected in 100–200 s counting time. All controlled pore glass samples were counted for 1000 s.

Reagents

The stock solutions were prepared from reagent grade chemicals and $CrCl_3 . 6H_2O$, $MnCl_2 . 4H_2O$, $FeSO_4 . 7H_2O$, $CoCl_2 . 6H_2O$, $CuCl_2 . 2H_2O$, $Zn(NO_3)_2 . 6H_2O$, $CdCl_2 . 2\frac{1}{2}H_2O$, As_2O_3, $HgCl_2$, $Pb(NO_3)_2$ and $AgNO_3$ were used. The $Ca(NO_3)_2$ and NaCl was supplied by Baker or Mallinckrodt in reagent grade quality. Sodium diethyldithiocarbamate (NaDDTC) and ammoniumpyrrolidinedithiocarbamate (APCD) were prepared by dissolution in deionized water in 0.1 and 1.0 wt/wt % respectively. Before use, these solutions were filtered through a Whatman 41 filter and made up fresh daily. The activated carbon was purified according to a published procedure.[16] The oxine (8-quinolinol, Baker) was dissolved in acetone (8 mg/mL) and kept for not more than a week at 4°C. The ion-exchange resin-loaded filter papers (SA-2, Reeve-Angel) were washed with three 40 mL portions of saturated NaCl solution and afterwards with 5 mL deionized water. This converted the ion-exchanger to the Na^+ form and removed at the same time major portions of the Ca and Fe contamination of the commercially available product. Controlled pore glass particles (Electro-Nucleonics, CPG-10, 200–400 mesh) were used as substrate for the immobilization of N-β-aminoethyl-γ-aminopropyltrimethoxysilane (Dow Corning Z-6020).

Preconcentration procedures

The wetted ion-exchange resin-loaded filter paper (25 mm diameter) was placed in a Millipore filtration apparatus. Up to 5 of these filtration apparatus could be used in parallel the vacuum being generated by a vacuum pump and connected to the flasks via a liquid nitrogen filled cold-trap. The water sample was adjusted to pH 3 ± 0.05 and filtered through the ion-exchange disk at a filtration rate of 40 ± 10 mL/min. The filtration step was repeated five or seven times after it was established that once or twice was insufficient. The disks were dried, sandwiched between two pieces of mylar and mounted on a sample cup (Chemplex).

The diethyldithiocarbamates were formed by adding 5 ml of the 0.1 % solution of the diethyldithiocarbamate sodium salt to a sample that has been adjusted to pH 4 with 2 mL of phosphate buffer. The solution was filtered through a Gelman filter (Metricel, GA-6, 0.45 μm) after standing for about 15 min. The ammoniumpyrrolidinedithiocarbamates (APDC) were prepared similarly, but they were stirred for 2–3 minutes before aging at least 20 min.[5]

The formation of the oxinates was accomplished by adjusting the pH value of the water samples to 8 ± 0.1 with NH_4Cl/NH_4OH buffer and adding a predetermined amount of oxine solution according to the recommendations given by van Grieken and co-workers[8,9] which takes into account the amount of oxine needed to complex Ca^{++} and Mg^{++}, and trace ions plus an excess of 5 ppm of reagent. Activated carbon (100 mg) was weighed in small cups and added to the sample solution contained in a glass bottle (as per Van Grieken). The bottle was then rotated for an hour to adsorb the oxinates on the carbon surface. Afterwards the carbon was filtered onto a Gelman filter and mounted moist on a Chemplex cup. The lower support of the filter was a mylar foil with small holes cut as drying of the sample was done in vacuum after mounting. This procedure was adopted because it was virtually impossible to handle the dry activated carbon. The controlled pore glass (CPG) with N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane was prepared according to a previously published procedure[1,6] and the capacity was determined by batch equilibration with Cu^{++} to be 0.5 mmol/g. From this the bisdithiocarbamate was formed by reacting 20 mL CS_2, 25 mL 0.25 M NaOH, 25 ml 2-propanol and 20 g CPG for 20 min at room temperature. The slightly yellow product was filtered and washed with 50 mL portions of 2-propanol and deionized water until the aqueous filtrate was clear. After air drying, the product was refrigerated and kept for 10 days at the longest. 200 mg of these glass beads were packed into a 50 mm long PTFE tubing and connected water tight with PTFE fittings (Fluoroware). The ends were covered with polypropylene frits. Preconcentration was achieved by pressure forcing the water sample adjusted to pH 8 with NH_4Cl/NH_4OH buffer through the column preconditioned by wetting with the same buffer. The pressure was supplied by compressed nitrogen and 20 psi were sufficient to achieve flowrates of approximately 30–40 mL per minute. The vessels were rinsed with deionized water and this washing solution was forced through the column as well. The columns can be opened immediately and the glass beads are dried in a vacuum desiccator. Afterwards, they are physically homogenized and sandwiched between two mylar foils. This preparation procedure is an improvement over the previously employed pelletization because of lower backscatter and it does not lead to greater random errors than the preconcentration step itself.

Interference studies

The preconcentration of all ten elements was tested at a concentration of 200 $\mu g\,L^{-1}$ in the presence of a five-fold excess of Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}. The effect of NaCl (0.5%) upon the preconcentration was studied as well as Ca^{2+} at a level of 100 mg/L. These studies were run as factorial designs using complete confounding of second and higher order effects[14,17]. This procedure requires that the random errors are independent of the concomitant species and that only primary effects are dominant. It can be shown, however, that moderate deviations from the first necessary condition does not alter the results severely other than overestimating the confidence level of the statistical testing procedure. The second condition, the dominance of primary effects is usually true of chemical experiments, but it should be kept in mind that all interpretations are given in the light of possible second order effects as shown in Table I. The error estimate of this procedure was derived indirectly by running an experimental unit with 16 separate measurements

TABLE I

Primary and two-factor effect confounding

Factor	Confounded with the following two-factor interactions						
Dummy	Pb/Cr	Cu/Mn	Ca/Co	Zn/Cd	—	—	—
Pb	—	Cu/Cr	Ca/Cd	Co/Zn	—	—	NaCl/Fe
Cu	—	Pb/Fe	—	—	—	—	NaCl/Cd
Ca	—	Pb/Cd	—	Zn/Cr	—	NaCl/Fe	—
Co	—	Pb/Zn	—	—	—	—	—
Zn	—	Pb/Co	—	Ca/Cr	—	NaCl/Mn	—
Dummy	—		Cu/Zn	—	Co/Fe	Mn/Cd	—
Dummy	—	Pb/Mn	Cu/Cr	—	Co/NaCl	—	—
NaCl	—	—	Cu/Cd	Ca/Fe	—	Zn/Mn	—
Mn	—	—	—	—	Zn/NaCl	—	Cr/Fe
Cd	—	Pb/Ca	Cu/NaCl	Co/Cr	—	—	—
Dummy	—	—	Cu/Co	Ca/Mn	Zn/Fe	—	NaCl/Cr
Cr	—		Ca/Zn	Co/Cd	—	—	Mn/Fe
Fe		Pb/Cu	Ca/NaCl			Mn/Cr	—
Dummy		Pb/NaCl	Cu/Ca	Co/Mn	—	—	Cd/Fe

for only ten potential interferents. The five additional degrees-of-freedom were carried along without assigning them a specific effect (i.e. as "dummy" parameters.) The results of these were taken as an error estimate.[14]

Environmental water samples

Sampling was performed at several locations throughout the state of Colorado to give a cross section of waste water, lake water, river water and tap water. At each sampling site, a 4 L sample was filtered through a 0.45 μm Metricel filter and acidified afterwards to pH 1 with HNO_3. Duplicate analyses were made on each sample with all five methods.

Data acquisition

The wavelength dispersive X-ray data were obtained by measuring the peak position and the background at each side of the peak. Net counts were used to construct calibration curves. The interference studies for Ag were done on the K- and L-lines and the incoherent scatter was recorded as well. The calibration curves for the energy dispersive X-ray fluorescence analysis were constructed using K_α or L_α integrals obtained by the method of Covell[18] without other treatment of the spectra. The interference experiments and environmental water samples were evaluated by digital filtering[19] and fitting to standard spectra obtained from the calibration standards.

RESULTS AND DISCUSSION

For routine analysis of environmental water samples a simple and rugged method of preconcentration is of utmost importance. To apply X-ray fluorescence to the determination of trace elements in environmental samples, a reliable, multielement preconcentration has to be achieved for a wide variety of environmental water types. The ability to have μg/L detection limits is desired. Initial studies were conducted for the ion-exchange method and the two precipitation methods to establish the optimal working pH. For the ion-exchange method, a pH value of 3 was found to be a good compromise for the trace ions investigated and a tolerance of ± 0.2 pH-units seemed to be acceptable.[20] The dithiocarbamates gave the best overall recovery at a pH of 4 ± 0.2. The other two methods have been investigated in this respect and previous reports[6,7,9] indicate pH values of 7 ± 0.2 and 8 ± 0.2 have been found to give good recovery for the immobilized dithiocarbamate and the oxinates adsorbed on activated carbon, respectively.

Recovery data have been reported in literature for all five methods and for the majority of elements the recovery was found satisfactory under the conditions reported. Two factors were identified as having the greatest influence upon recovery in a real analytical situation: the concentration of the analyte ion and the abundance of concomitant ions. In the absence of other concomitant ions, the relative recovery at 200 ppb was taken as a reference and ratioed to the relative recovery at 10 ppb. Table II gives selected recovery data for preconcentration from 100 mL solution. Dashes are shown where either no recovery is achieved, or the 10 ppb signal was below the detection limit. The errors given are composed mainly of the error of the background estimation and the error in estimating the signal at 10 ppb. The recovery of the ion-exchange paper seems to decrease at higher concentrations, whereas the precipitation methods work better at higher concentrations. Only the combined chelation and adsorption as done in the activated charcoal procedure appears to be independent of concentration in the range studied. No data are given for the immobilized dithiocarbamates as the thicker samples and higher average atomic number of the matrix yield lower sensitivities and 10 ppb of ions from 100 mL (1 μg) gives no detectable signal.

Calibration and detection limits

To construct the calibration curves, the spacing of the samples in the range of 0–100 μg was performed to give reliable estimates of the blank and 1 μg level and to establish the linear range. The six values between 20 and 100 μg could be used to estimate the precision of the methods. These data are given in Table III. The precision is worst for Hg, followed by Fe and Zn, both presumably because of the enhanced risk of laboratory contamination. Of the five methods, the activated carbon/oxinate precedure seem to be the one with the most limited capacity (linear dynamic range). Mercury is the one element for which a sufficient dynamic range is difficult to achieve. Figure 1 shows the "effective sensitivity" for all elements and methods. This term represents the slope of the calibration function and comprises the X-ray spectroscopic sensitivity which depends on the geometry of the sample and the enrichment factor, and the recovery of the individual element. This explains why the sensitivity is not a smooth function of the atomic number of the element. Another feature of the chosen subdivision of the calibration range was the fact that fairly reliable estimates of the blank and its standard deviation and the precision at low concentrations could be obtained. This and the fact that the calibration points are centered at fairly low concentrations made a good estimate of the decision and detection limits possible. The decision limits

TABLE II

Recovery at 10 ppb relative to recovery at 200 ppb [%]

	Cr	Mn	Fe	Co	Cu	Zn	As	Hg	Pb
Ion-exchange paper	—	121±9†	—	132±15	98±34	—	—	—	91±19
Sodium diethyldithiocarbamate	—	—	51±12	67±16	115±22	30±28	—	61±12	21±9
Ammonium Pyrrolidinedithiocarbamates	—	—	72±41	82±14	84±20	—	81±15	46±12	—
Activated carbon and oxinates	—	94±27	—	109±28	—	—	—	123±22	110±18
Controlled pore glass	—	—	—	—	—	—	—	—	—

†One standard deviation.

Table III

Relative standard deviation in absence and presence of concomitant ions [%]

	Cr	Mn	Fe	Co	Cu	Zn	As	Hg	Pb	Ag
Ion-exchange paper	$10^b/3^c$	8/1	7/3	15/1	$3/4^a$	18/4	-	$15/23^a$	5/2	—/4
Sodiumdiethyldithiocarbamate	—	—	10/4	6/2	3/2	6/8	—/12	20/3	13/4	—/4
Ammonium Pyrrolidinedithiocarbamate	/9	·	9/4	4/2	3/1	8/4	4/2	$8/4^a$	6/4	—/1
Activated carbon and oxinates	$8/7^a$	6/10	11/4	$8/3^b$	$3/3^b$	10/2	—/20	$17/4^b$	7/4	—/4
Controlled pore glass	23/	11/12	/23	—/7	9/19	—/7	—/26	16/6	5/12	—/7

[a] Linear dynamic range limited to 50 μg.

[b] R.S.D. in absence of concomitant ions.

[c] R.S.D. in presence of concomitant ions.

[d] stands for "not calculated".

have been calculated according to Currie's suggestion[10] and they are shown in Table IV. They lie generally between 0.1 and 10 μg. The only case where they are considerably higher is found for the chromium determination with the wavelength dispersive X-ray system. This appears to be a problem of excitation. Here, an additional comment on the inconsistencies of wavelength and energy dispersive decision limits is in order. The decision limit which is solely influenced by the reproducibility of the blank sample (and by the sensitivity) comprises errors from the sample preparation and from the instrument repeatability. Depending on which of the two is the limiting error, the decision limit may be better for one instrument using one method and for the other instrument if another method of preconcentration is employed. Similar reasoning applies for the detection limits. For this calculation, Currie's formula,[10] or, where the signals for the 1 μg sample were below the decision limit, Hubeaux's[11] definition had to be used to arrive at realistic detection limits. It is particularly important in trace analysis to abandon the "theoretical" detection limits, as it was found that counting statistics are rarely the

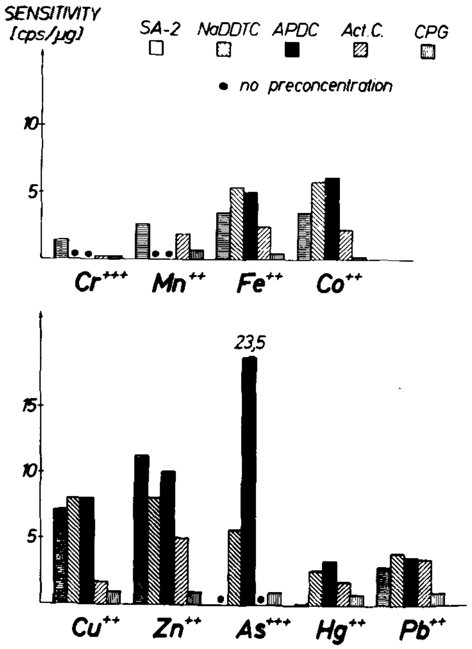

FIGURE 1 Sensitivities found for different preconcentration procedures for energy dispersive x-ray spectrometry.

TABLE IV

Decision limits and detection limits for energy dispersive and wavelength dispersive X-ray spectrometry [in μg]

	Cr	Mn	Fe	Co	Cu	Zn	Hg	As	Pb	Ag
Ion-exchange paper	$2^c/10^{a,d}$ $15^e/20^{b,e}$	0.2/0.7 0.4/1.0	1/2 $5^e/15^e$	0.2/— 0.4/—	1/0.5 3/1.0	3/— 16^e/—	9/2 13/4	— —	0.2/0.6 0.5/1.2	—/3 —/6
Sodiumdiethyldithiocarbamate	—	—	0.2/0.4 $0.4/8.0^e$	0.1/0.2 0.4/0.5	0.1/2 $0.5/4^e$	0.4/— 0.8/—	0.2/0.3 0.4/0.9	— —	0.1/2 $0.2/20^e$	—/2 —/3
Ammonium Pyrrolidinedithiocarbamate		—	0.7/0.6 $1./0/2.0^e$	0.3/0.2 0.4/0.3	0.2/1 $0.4/8^e$	0.6/— 13^e/—	0.1/0.2 0.3/0.3	0.1/— 0.5/—	0.2/0.4 $9^e/13^e$	—/3 —/4
Activated carbon and oxinates	2/16 $6^e/40^e$	0.4/0.2 0.7/0.4	1/1 $15^e/6^e$	0.4/2 0.6/—	0.4/2 $2/6^e$	1/— 15/—	0.3/0.1 0.5/0.5	— —	0.1/0.2 0.5/0.9	—/2 —/3
Controlled pore glass	8/70 $40^e/100^e$	0.9/1.0 $9^e/30^e$	— —	—	0.8/8 $20^e/17^e$	4/23 $26^e/30^e$	0.8/1 $23^e/15^e$	— —	0.4/1.4 2.0/	—/ /

[a] Decision limits.
[b] Detection limits.
[c] For energy dispersive XRF (top line).
[d] For wavelength dispersive XRF (lower line).
[e] Calculated according to Hubeaux *et al.* (11).
[f] Stands for "not calculated".

limiting factor, at trace levels the major part of random and systematic errors stems from sample preparation.[12] This is the reason why theoretical calculations on the basis of counting statistics[21] give only an insight into the quality of X-ray instruments and have no meaning in the sense of performance characteristics of the analytical method. Detection limits that are calculated from the calibration curve give intrinsically higher values and their estimation can only be improved by more data points close to the decision limit. In practice this can only be achieved by a two step procedure where the decision limit is established in a separate run. This was not done in this instance. On the other hand, the data from energy dispersive X-ray fluorescence spectrometry will be less favorable if large amounts of ions giving spectral overlap are present (e.g. FeK_β and Co K_α).

Interference studies

Spectral and chemical interferences were studied using a previously described[13,17] and tested[14] scheme of factorial "experimentation". The "two-level" design can only estimate "linear" effects. The very nature of this study did not permit estimation of spectral and chemical interferences separately, but rather gave an overall estimate of the bias. Generally, all the analyses were run on the energy dispersive X-ray spectrometer using a digital filter[19] for the removal of the background and a multiple least squares analysis with standard library spectra[22] to deal with the problem of overlapping peaks. The library spectra have been obtained from the one-element samples made up for the calibration procedure; blank samples were subtracted where necessary.

Silver was measured only on the wavelength dispersive system because the energy dispersive system was equipped with a Ag tube. For better precision and less background, the L-lines of Ag were used. The relatively low energy of the L_α line, however, can cause a particularly critical dependence of the signal on sample mass. On the other hand, it is known that concomitant elements may give rise to coprecipitation and lead to an unknown mass. Other effects which result in enhancement or depression of the Ag signal can occur as well. All of these effects are summed up in this experiment and only observed jointly. Table V shows an example of this aspect: the relative error as calculated from the "dummy" variables is smallest for measurement of the L-intensities, but interferences are observed from Cr, Fe, Co and Zn in the case of the ammoniumpyrrolidinedithiocarbamate (APCD) precipitation. These can be explained as X-ray absorption effects that are not offset by a high recovery. Only for chromium an increase in recovery appears to be the overriding influence.

TABLE V

Interferences in the determination of Ag

	Ammoniumpyrrolidine dithiocarbamate			Activated carbon and oxinates		
	L_{net}	$L_{compton}$	K_{net}	L_{net}	$L_{compton}$	K_{net}
Cr	+	+	0	0	+	0
Mn	0	0	0	0	+	0
Fe	–	0	0	0	0	0
Co	–	0	0	+	+	0
Zn	–	0	–	0	0	0
Cd	0	+	0	0	0	0
Pb	0	+	0	0	0	0
RSD [%]	1.0	1.3	3.0	2.0	2.0	4.0

+ Enhancement effect.
– Depression effect.
0 No significant influence.

Frequently, signal ratioing to the Compton scatter intensity can be used to correct for the varying sample weight.[23] This, in fact, corrected for the negative influences of Fe, Co and Zn, but additional positive effects from Cd and Pb became apparent. It can be argued that these are coprecipitation effects that were hidden in the absorption phenomena and appeared after correction of the data. If the Ag K-lines are measured, only the Zn effect upon the Ag signal rises above the significance level of 95%. The preconcentration of Ag using the activated carbon/oxinate procedure does not appear to suffer from absorption effects to a similar extent as the precipitation method, or if so, is offset by an enhanced recovery in presence of concomitant elements. The Compton correction again brings forth positive influences by suppressing absorption effects; these are masked by the random error when the K_α line is measured. All of these interdependencies need to be kept in mind when interpreting the interference data.

Table VI shows the results of the interference experiments for the ion-exchange impregnated filter method. Generally, concomitant ions cause a negative influence upon the recovery of trace ions. The only notable exception being Hg^{2+} whose retention is strongly enhanced by NaCl, Zn^{2+} and Cd^{2+}. The strong competing influence of Ca^{2+} for the exchange sites is apparent for all cations with the exception of Hg^{2+}. As^{3+} does not exchange with the sodium cations on the exchange resin. Zeros in Table VI and all following indicate "not tried" whereas, dashes represent no significant effect was observed.

TABLE VI

Interferences in the ion-exchange impregnated filter method

		Elements									
		Cr	Mn	Fe	Co	Cu	Zn[c]	As	Pb	Hg	Ag[K]
Interferents	NaCl	—	—	—	+2	−8	—	0	−40	+98	—
	Ca	−27	−62	−10	−30	−70	−24	0	−64	—	−9
	Cr	0	+5[a]	—	−2	—	—	0	—	—	—
	Mn	—	0	−7[a]	—	—	—	0	—	—	—
	Fe	—	—	0	—	—	—	0	−12	—	−14
	Co	—	—	—	0	—	—	0	—	—	—
	Cu	—	—	—	—	0	−33[a]	0	—		—
	Zn	—	+3	—	+3	—	0	0	−12	+52	−12
	Cd	—	—	—	—	—	—	0	—	+50	—
	Pb	—	−4	—	—	—	—	0	—	—	—
Percentage of overall expected mean		81	b	72	78	58	98	b	67	280	b

[a] Cases of K_α/K_β peak overlap.
[b] Not calculated.
[c] Data taken with X-ray tube in DC mode.

Other influences can be seen for the K_α/K_β overlaps, e.g. the influence of Cr^{3+} on Mn^{2+}, of Mn^{2+} on Fe^{2+} and of Cu^{2+} on Zn^{2+}. To test this assumption, the samples were also measured on the wavelength dispersive system. The results proved that the interferences were a result of the deconvolution procedure, rather than of a fundamental chemical or X-ray spectroscopic nature. The other influences, though significant, do not lend themselves to straightforward interpretation. The last row in Table VI was calculated for the overall mean of the interference experiments and normalized to the results from the calibration procedure to give a useful estimate of nonspecific effects of the "matrix" constituents, even in those cases where none of the individual effects approaches the significance level. These data confirm the suspicion that ionic matrix constituents of any type tend to decrease the recovery of an ion-exchange procedure. Mercury, however, gave a three times higher recovery in presence of other matrix constituents.

The interferences of the precipitation method employing sodium diethyldithiocarbamate (DDTC) are given in Table VII. Chromium and manganese were not included in this study because both cations did not give measurable precipitates with sodium diethyldithiocarbamate. Zinc and arsenic were the two ions where the biggest interferences were observed. While the NaCl and Pb^{2+} influence upon the Zn signal is not easily understood, Fe^{2+} and Cu^{2+} act as coprecipitants for As^{3+}. This can also

TABLE VII

Interferences in the sodium diethyldithiocarbamate precipitation method

		Elements									
		Cr	Mn	Fe	Co	Cu	Zn[b]	As	Pb	Hg	Ag[K]
Interferents	NaCl	0	0		—		+18	—	—	—	—
	Ca	0	0	—	—	—	—		—	—	—
	Cr	0	0	—	—	—	—	—	—	—	—
	Mn	0	0	—	−3.6	—	—	—	—	—	—
	Fe	0	0	0	—	—	—	+76	—	−8	—
	Co	0	0	—	0	—	—	—	—		—
	Cu	0	0	—	—	0	—	+44	−9	—	—
	Zn	0	0	—	+3.5	—	0	—	—	—	—
	Cr	0	0	—	—	−5	—	—	—	—	—
	Pb	0	0	—	—	—	−22		0	—	—
Percentage of overall expected mean		[a]	[a]	97	105	97	95	141	106	104	[a]

[a] Not calculated.

[b] Data taken with X-ray tube in DC mode.

be concluded from the higher overall recovery (141 %) of zinc in the presence of concomitant species. The recovery of all the other elements is within the experimental error the same as was observed from the calibration functions.

In Table VIII, the results of precipitation with ammoniumpyrrolidinedithiocarbamate is reported with respect to interfering elements. The recovery of Cu^{2+} seems to be lowered by most other ions by 1–7 % relative to the recovery in solutions containing only Cu^{2+}. The biggest influences are observed for Cr^{3+} and Zn^{2+}. It is interesting that the presence of other ions enhances the formation of the Cr-complex so that measurable quantities are recovered. Some of the effects (Fe^{2+} on Co^{2+}, Cu^{2+} on Zn^{2+} and Pb^{2+} on As^{3+}) are again a result of the deconvolution procedure that is used to take account of the spectral overlap.

The interferences found for the activated carbon procedure are summarized in Table IX. Systematic errors must be expected for the deconvolution procedure for Mn, Fe and Zn. The recovery of Cr^{3+} and Co^{2+} is greatly enhanced, and Fe^{2+} and Cr^{3+} cause a significant increase in the intensity of As^{3+}. As the As^{3+} cannot be preconcentrated from pure solutions, the percentage interference values are given for the mean of the interference study; thus the percentage-of-expected-mean value is missing.

Significant interferences have also been observed for the column-CPG method involving controlled pore glass beads as shown in Table X. These effects are particularly hard to interpret. Especially, NaCl and Ca^{2+} in

TABLE VIII

Interferences in the ammoniumpyrrolidinedithiocarbamate precipitation method

		Elements									
		Cr	Mn	Fe	Co	Cu	Zn[c]	As	Pb	Hg	Ag[netL]
Interferents	NaCl	—	0	—	—	−2	—	—	—	—	—
	Ca	—	0	—	—	−3.4	—	—	—	—	—
	Cr	0	0	—	—	−3.5	—	—	—	—	+2.6
	Mn	—	0	—	−3	—	—	—	—	—	—
	Fe	+32	0	0	−3.5[a]	−4	+10	−7	—	—	−2.4
	Co	—	0	—	0	−5.5	—	—	—	—	−3.6
	Cu	−20	0	—	—	0	−24[a]	−5	—	—	—
	Zn	—	0	—	—	−3.7	0		—	−2.8	—
	Cd	−18	0	—	−3	−6.9	—	—	—	—	—
	Pb	—	0	—	+3.7	−1.3	—	—	0	—	—
Percentage of overall expected mean		[b]	[b]	100	104	74	100	72	100	98	95

[a] Cases of K_α/K_β peak overlap.

[b] Not calculated.

[c] Data taken with X-ray tube in DC mode.

TABLE IX

Interferences in the activated carbon/oxinates adsorption method

		Elements									
		Cr	Mn	Fe	Co	Cu	Zn[c]	As	Pb	Hg	Ag[K]
Interferents	NaCl	—	—	—	—	—	—	—	—	—	—
	Ca	−14	—	-	—	—	—	—	—	—	—
	Cr	0	−61[a]		—	—	+5	+85	—	—	—
	Mn	—	0	−14[a]	—	—	—	−64	—	—	—
	Fe	+40	—	0	—	—	—	+110	—	—	
	Co	—	—	—	0	—	—	—	−6.6	—	—
	Cu	—	—	—	—	0	−21[a]	—	−7	—	—
	Zn	—	—	—	—	—	0	—	—	—	—
	Cd	—	—	—	—	—	—	—	—	—	—
	Pb	—	—	—	—	—	—	—	0	—	—
Percentage of overall expected mean		180	101	102	150	100	99	[b]	99	107	89

[a] Cases of K_α/K_β peak overlap.

[b] Not calculated.

[c] Data taken with X-ray tube in DC mode.

TABLE X

Interferences in the dithiocarbamate controlled pore glass column method

		Elements									
		Cr	Mn	Fe	Co	Cu	Zn[c]	As	Pb	Hg	Ag[K]
Interferents	NaCl	0	—	—	+34	-	—	—	+31	—	—
	Ca	0	—	+63	+28	—	—	—	+26	—	—
	Cr	0	+35[a]	—	−29	—	—	—	—	+20	—
	Mn	0	0	—	—	—	−15	—	—	—	—
	Fe	0	—	0	+40[a]	—	+15	+129	—	−12	—
	Co	0	—	—	—	—	−25	—	—	—	—
	Cu	0	−29	−65	—	0	−28[a]	—	—		—
	Zn	0	—	−50			—	—	—	—	—
	Cd	0	—	—	−16	—	—	—	—	−12	—
	Pb	0	−31	—	−14	—	—	—	0	—	—
Percentage of overall expected mean		[b]	65	[b]	[b]	93	[b]	[b]	87	120	[b]

[a] Cases of K_α K_β peak overlap.

[b] Not calculated.

[c] Data taken with X-ray tube in DC mode.

these concentrations seem to enhance the recovery of certain ions (Fe, Co, Pb). Cu^{2+} and Ag^{+} are the only ions not influenced in their preconcentration by other concomitant elements. Apart from the systematic effects it seems to be a worthwhile comparison to study the relative standard deviations in presence of these interferents. As stated above, the error estimates of the interference studies ("presence of interferents") were made from the dummy parameters with five degrees of freedom. In spite of the fact that the error estimates obtained in this manner may not be very precise an interesting observation can be made from the second entry in each row in Table III. On the whole, the relative errors in the presence of interferents seems to be equal to or smaller than for the pure solutions. It is important to realize that the random error introduced by spectrum deconvolution procedures using the energy dispersive system is far less critical than the bias that has to be expected[24] from multiple least squares procedures. Future work will have to identify more definitively the source of this deconvolution error.

Tables XI through XV show some results for the water samples collected as described earlier. All of these data were collected by the energy dispersive X-ray spectrometric analysis of the respective preconcentrated samples. Although these data are insufficient to draw final detailed conclusions from, certain trends can be noticed. Samples with a suffix *F* were filtered at the sampling site before acid preservation. Those without the suffix were acidified without filtration. Sample E was collected from a glacier lake at 4000 m altitude. There was a high organic content in this water. As a result, the dithiocarbamates could not be filtered. This is a general problem of these methods under detailed investigation in our laboratory. The ion-exchange impregnated filter paper tends to give consistently lower results than the other methods. This is attributed to saturation of the resin exchange capacity by Fe and Ca in the water. The sodium diethyldithiocarbamate method tends also to give lower results than the ammonium pyrrolidinedithiocarbamate (APDC). The APDC, activated carbon adsorption of oxinates and CPG methods appear to give the most internally consistent results. The CPG method tends to give the highest values except for Fe. This is not fully understood at this time, but may be a result of oxidation state of the iron in various waters as well as binding of the iron by organics. Note that in sample E where high organics are known to be present, the activated carbon adsorption of oxinates gives the highest result for iron. Presumably, humic complexes are also adsorbed by the activated carbon.[8,9] Most samples were collected in more or less pristine mountain areas. However, samples D and G were collected from a stream below a mining area, but several miles apart. Note the similar, high zinc values for these two samples.

Although the results in Tables XI through XV show that these methods

TABLE XI

Results from environmental water samples by ion-exchange impregnated filter paper [μg/L]

Element	Cr	Mn	Fe	Co	Cu	Zn	As	Hg	Ni	Pb
Sample										
AF	2.4	6.9	139	1.1	6.8	43	ND	23[a]	1.3	8.6
A	4.5	8.3	736	ND	7.2	40	ND	ND	ND	6.3
BF	3.6	ND	45	ND	5.8	38	ND	ND	1.8	5.6
B	3.6	5.4	144	ND	7.0	46	ND	21[a]	1.5	6.8
CF	5.0	ND	58	1.4	6.0	39	ND	18[a]	1.2	9.8
C	2.7	7.0	724	2.1	7.1	46	ND	27	0.7[a]	8.1
DF	2.0	19	70	ND	5.5	46	ND	ND	1.9	7.1
D	2.7	53	249	ND	11	69	ND	ND	1.8	11
EF	5.5	ND	281	ND	2.8	19	ND	3.0[a]	1.5[a]	11[a]
E	1.3	ND	396	ND	3.5	31	ND	ND	ND	15[a]
GF	4.8	27	78	1.3	7.5	54	ND	ND	2.2	11
G	4.6	27	155	N.D	7.2	52	ND	ND	1.3	11

ND Not detectable.

[a] Not run in duplicate.

TABLE XII

Results from environmental water samples by NaDDTC [μg/L]

Element	Cr	Mn	Fe	Co	Cu	Zn	As	Hg	Ni	Pb
Sample										
AF	NR	NR	229	4.5	13	34	ND	7.9[a]	8.5	8.2
A	NR	NR	>1000	6.1	23	35	ND	5.0[a]	7.3	9.1
BF	NR	NR	69	1.5	10	39	ND	4.9	7.0	7.7
B	NR	NR	324	3.2	13	37	ND	6.7	5.9	7.4
CF	NR	NR	68	1.3[a]	11	39	ND	3.2[a]	4.8	6.7
C	NR	NR	901	3.7[a]	11	37	ND	3.2[a]	3.6	11
DF	NR	NR	94	2.2	14	71	ND	4.9	6.6	8.8
D	NR	NR	413	2.1[a]	21	72	8.8[a]	3.6	4.3	12
EF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
E	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
GF	NR	NR	63	2.3	17	63	7.9[a]	7.6	8.7	ND
G	NR	NR	153	2.2	14	38	5.1	4.2[a]	3.9	8.0[a]

NR No recovery.
ND Not detectable.
NF Not a filterable precipitate.
[a] Not run in duplicate.

TABLE XIII

Results from environmental water samples by APDC [μg/L]

Element	Cr	Mn	Fe	Co	Cu	Zn	As	Hg	Ni	Pb
Sample										
AF	NR	NR	282	4.1	11	45	ND	11	11	9.2
A	NR	NR	>1000	4.4[a]	24	51	ND	3.1[a]	6.6	21[a]
BF	NR	NR	74	ND	18	45	ND	ND	9.5	15
B	NR	NR	278	2.9[a]	9.1	64	ND	6.8[a]	5.4	15
CF	NR	NR	63	ND	7.2	40	ND	ND	5.3	8.1
C	NR	NR	883	ND	8.7	59	ND	ND	3.0	8.8
DF	NR	NR	101	2.0	13	135	ND	3.0[a]	7.6	12
D	NR	NR	456	ND	19	157	ND	3.3[a]	3.7	6.5
EF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
E	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
GF	NR	NR	67	26	30	83	ND	3.8[a]	9.4	12
G	NR	NR	280	3.2	18	84	ND	4.7[a]	6.2	9.4

NR No recovery.
ND Not detectable.
NF Not a filterable precipitate.
[a] Not run in duplicate.

TABLE XIV

Results from environmental water samples by AC/oximes [μg/L]

Element	Cr	Mn	Fe	Co	Cu	Zn	As	Hg	Ni	Pb
Sample										
AF	26	197	320	4.5	20	97	ND	4.7	15	29
A	37[a]	244	>1000	ND	34	83	ND	6.2	12	23
BF	18[a]	189	245	ND	25	102	ND	6.7[a]	9.6	30
B	20	293	441	ND	18	86	ND	9.9	9.0	20
CF	26[a]	48.1	132	ND	22	66	ND	7.2	9.5	23
C	36	102	>1000	ND	18	88	180[a]	4.6	6.3	26
DF	21	661	183	2.1[a]	19	169	ND	ND	13	17
D	20[a]	730	521	ND	22	184	268	5.3[a]	6.5	21
EF	21	117	>1000	ND	16	68	509	5.2[a]	5.7	26
E	ND	162	>1000	ND	16	68	536[a]	4.5	5.3	34
GF	32[a]	633	189	3.8[a]	23	183	ND	5.7	19	29
G	32	662	436	3.7[a]	27	164	143	5.8[a]	9.5	23

ND Not detectable.

[a] Not run in duplicate.

TABLE XV

Results from environmental water samples by C.P.G. [μg/L]

Element	Cr	Mn	Fe	Co	Cu	Zn	As	Hg	Ni	Pb
Sample										
AF	9.6	77	249	12.2	59	47	ND	39	17	32
A	15	93	607	5.6	49	67	ND	35	21	ND
BF	6.5	71	366	6.7	30	76	ND	37	50	ND
B	7.9	111	533	9.3	48	71	ND	40	16	17[a]
CF	10	ND	154	0.5[a]	37	58	ND	34	15	8.4[a]
C	7.7	22	347	6.3[a]	61	64	ND	36	16	4.9[a]
DF	11	331	92	0.6	51	147	ND	40	19	ND
D	8.3	350	265	7.8[a]	51	158	ND	35	14	11
EF	9.1	22	318	5.3[a]	61	52	ND	45	19	20[a]
E	3.8	37	315	2.8[a]	41	30	24.6	41	9.6	ND
GF	10	272	77	8.7	37	174	ND	34	30	19
G	6.4	297	193	4.9	61	99	ND	38	31	15

ND Not detectable.

[a] Not run in duplicate.

have potential for screening trace elements at levels down to a few μg/L, much more research will be needed to fully test their reliability and to select those methods which can give the most reliable results. The various chemical complications in real samples strain the accuracy and precision which may be achieved. Yet, one of these or similar procedures, may provide a rapid, economical and perhaps automated method of screening of natural and industrial waste water.

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