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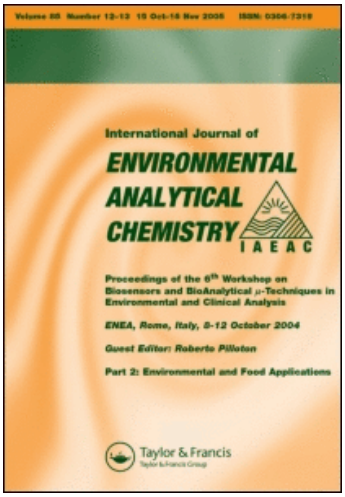

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Tessier, A. , Campbell, P. G. C. and Bisson, M.(1979) 'Evaluation of the APDC-MIBK Extraction Method for the Atomic Absorption Analysis of Trace Metals in River Water', International Journal of Environmental Analytical Chemistry, 7: 1, 41 — 54
To link to this Article: DOI: 10.1080/03067317908071477
URL: http://dx.doi.org/10.1080/03067317908071477

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Intern. J. Environ. Anal. Chem., 1979, Vol. 7, pp. 41–54
0306-7319/79/0701-0041 $04.50/0
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Printed in Great Britain

Evaluation of the APDC-MIBK Extraction Method for the Atomic Absorption Analysis of Trace Metals in River Water

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(*Received January 10, 1979*)

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The analytical performance of a chelation/extraction procedure for concentrating trace metals from natural water samples has been investigated. The metals (Cd, Co, Cu, Ni, Pb, Zn), chelated with ammonium pyrrolidine dithiocarbamate, were concentrated by solvent extraction in methyl isobutyl ketone at a sample pH of 4; the organic phase was analyzed by flame atomic absorption spectrophotometry. Sensitivity of the method tested was adequate for surface waters and precision proved to be good. The chelates were found to be stable in the organic phase for at least ten days. In the two rivers studied, the recovery of spiked metals proved to be independent of sampling stations but slightly dependent on sampling dates; this latter dependence suggests the existence of weak matrix effects. No significant interferences from linear alkyl sulphonate (1 mg/l) or from humic acid (3 mgC/l) were detected.

KEY WORDS: Trace metals, river water, chelation-extraction, APDC-MIBK.

INTRODUCTION

Responding to an increased awareness of the biological importance of trace metals in the environment, many governmental agencies have introduced surveillance programmes involving the routine screening of environmental samples for a range of trace metals. A great variety of techniques are currently available for these analyses, each with its particular advantages and disadvantages.[1,2] However, as has been demonstrated recently by the results of interlaboratory comparisons,[3] the application of these techniques to natural waters is deceptively simple. Sample contamination, analyte loss and diverse matrix effects can all

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adversely affect the reliability of methods developed for the analysis of synthetic mixtures. The selection of an analytical method should thus be based on an assessment of such analytical criteria as detection limit, sensitivity, specificity, accuracy and precision, as they pertain to natural water samples. The final choice will often be influenced by such practical matters as complexity of the method, availability of equipment and facilities, and economy.[1,4]

As the basic analytical technique employed in a trace metal monitoring programme designed to handle a large number of aqueous samples, conventional flame atomic absorption spectrophotometry presents as advantages a high selectivity and a fundamental simplicity. However, with many trace elements its mediocre sensitivity constitutes a serious disadvantage; for most natural waters a preliminary concentration step will be required. Concentration by evaporation, though conceptually simple, often proves laborious. Furthermore, as the concentration of dissolved solids rises, the danger of precipitation and co-precipitation increases, as does the potential for matrix interferences. Other techniques, such as co-precipitation, co-crystallization, ion exchange and solvent extraction have been reviewed critically by Riley *et al.*[5] Of these, addition of a non-selective chelator, followed by quantitative extraction of the metal complexes with a small volume of an appropriate water immiscible solvent appears the most promising; atomic absorption analysis then provides the required selectivity and several metal determinations can be made on a single extract. Concentration factors of 10 or greater are readily obtained and signal enhancement due to the use of an organic solvent of good burning characteristics also contributes to the desired increase in sensitivity;[6–9] furthermore, the extraction step is expected to reduce the bulk inorganic matrix.

Of the many chelator-solvent pairs that have been suggested in the literature, the combination of ammonium pyrrolidine dithiocarbamate (APDC) and methyl isobutyl ketone (MIBK) is perhaps the most widely used, being relatively non-selective[7,10] yet highly efficient.[9,11] We have used this pre-concentration technique, coupled with flame atomic absorption spectrophotometry, to analyze a variety of river water samples. In the present paper we report on the analytical performance of this procedure when applied to natural water samples, with particular reference to the effect of sample composition on trace metal recovery.

EXPERIMENTAL

Reagents and glassware

All stock solutions were prepared with filtered (0.22 μm) deionized water (Millipore Milli-Q3RO/Milli-Q2 system) and reagent grade chemicals or

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better. Methyl isobutyl ketone (Anachemia Ltd.) was distilled before used; the fraction boiling in the range 116–117°C/760 mm was collected and stored in an opaque bottle at 4°C until use. Aqueous 1% (v/v) solutions of ammonium pyrrolidine dithiocarbamate (Fisher Scientific Co.) were purified by two successive extractions with MIBK (20 ml per 100 ml solution). The aqueous APDC solution was freshly prepared before each series of analyses and stored in a polyethylene bottle at 4°C until use. The digestion mixture contained 1.5 g of potassium persulphate (J. T. Baker Co. Ltd., analyzed reagent) and 10 ml of ultra-pure sulphuric acid (BDH Chemicals, Aristar grade) per 100 ml of solution.[12]

The metal calibration standards for atomic absorption spectrophotometry were prepared from commercially available stock solutions (1000 μg/ml; Fisher Scientific Co.) by dilution with deionized water containing ultra-pure nitric acid (5 ml/l; BDH Chemicals, Aristar grade). As a precaution against losses by adsorption, the standard solutions were always freshly prepared.

Before use, all laboratory ware utilized for the analysis of trace metals was soaked in nitric acid (20% v/v) for 48 h, then in deionized water for 24 h and finally rinsed with deionized water. Similarly, membrane filters (Millipore HAWP, 0.45 μm or Nuclepore, 0.4 μm) were soaked for 2 h in a gently stirred solution of dilute nitric acid (3% v/v) and for 2 h in deionized water before use.

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Apparatus

Atomic absorption measurements were obtained with several different spectrophotometers (Varian Techtron Models AA-5 or AA-575; Perkin-Elmer Model 306) equipped with strip chart recorders. Deuterium background correction was used to compensate for nonspecific absorption. An air-acetylene flame was employed and optimal operating conditions (lamp current, air-fuel mixture, wavelength, slit opening, damping, etc.) were established for each element in preliminary trials and then maintained for subsequent analyses. A Radiometer (Model PHM 28) pH meter was used for pH measurements. Dissolved organic carbon was determined with a Beckman Total Organic Carbon Analyzer (Model 915A).

Samples

River water samples (1 l) were collected from 12 sampling stations maintained on the Yamaska and Saint-François Rivers (Québec, Canada) on four occasions during 1975 (February, April, August and November). A 500 ml portion of each sample was filtered through a 0.45 μm membrane

filter (Millipore HAWP) in the field within 6 h after collection of the sample. Both the filtered and unfiltered portions were then acidified with ultra-pure nitric acid (5 ml/l) and stored in polyethylene bottles at 4°C until analysis.

A large water sample (8 l) from the James Bay watershed on the Canadian Shield was filtered through a glass fiber filter (Whatman, GF/C, 1.2 μm nominal pore size) that had previously been combusted at 550°C for 8 h, and the filtrate was acidified with ultra-pure nitric acid (5 ml/l). This sample contained 12 mg organic carbon per liter, most of it being humic material (Dr. S. A. Visser, personal communication).

Aqueous solutions of linear alkyl sulphonate (LAS, U.S. Environmental Protection Agency, NERC, Cincinnati) and humic acid (Aldrich Chemical Co.) were also used for testing possible interferences by these compounds in the chelation/extraction procedure. The humic acid solution was prepared by dissolving the compound at pH 9.0 with gentle heating, and filtering through a polycarbonate membrane (Nuclepore, 0.4 μm nominal pore size), whereas the LAS solution was prepared by dilution of an EPA standard ampoule (5.55% active LAS). Standardization of each solution was based on its organic carbon content. Trace metals were added and after one day equilibration the solutions were acidified as usual (5 ml HNO_3/l) and analyzed.

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Analytical procedures

The chelation/extraction procedure involved five steps: (i) the sample (400 ml) was adjusted to pH 4.0 ± 0.1 with ammonium hydroxide, and placed in a 500 ml Pyrex volumetric flask; (ii) APDC reagent (10 ml of pre-purified 1% aqueous solution) was added; (iii) after vigorous shaking, the solution was allowed to stand for 1 h; (iv) MIBK (40 ml) was added and the flask was shaken with a mechanical shaker for 12 minutes; (v) once the two phases had separated, deionized water was carefully introduced into the flask *below* the solvent water interface (to prevent back extraction of the chelates into the aqueous phase[13]), by means of a pipette, thus raising the upper organic layer into the narrow neck of the flask. The volumetric flask was stored in the dark at 4°C until the upper layer was analyzed by flame atomic absorption spectrophotometry. Blanks were also run through the entire procedure, using acidified (5 ml HNO_3/l) deionized water in the place of the sample. Solvent saturated with water was aspirated to establish the baseline between sample readings.

This procedure was employed to concentrate trace metals in natural water samples, in LAS and humic acid solutions, and in aqueous standards; six metals were subsequently analyzed, four (Cd, Cu, Pb, Zn)

on a routine basis in the Yamaska and Saint-François river samples, and two (Co, Ni) less frequently.

Quantitation was achieved either by reference to a calibration plot, obtained with standards prepared in deionized water, or by a standard addition technique.[14] For the latter, two separate additions were performed, each one containing the complete range of metals to be analyzed; the spikes were chosen so as to increase the original trace metal concentrations by approximately 50 and 100%.

Samples to be digested (400 ml) were treated with the potassium persulphate reagent (8 ml) and boiled for 2 h in 800 ml Kjeldahl digestion flasks. After cooling to room temperature, the samples were diluted back to their original volume and analyzed according to the standard chelation/extraction procedure described above.

RESULTS AND DISCUSSION

Effect of pH on extraction efficiency

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Conflicting opinions exist in the recent literature concerning the optimum pH at which an efficient extraction can be performed simultaneously for many trace metals. Some authors[15–17] suggest low pH values near 2.8 while others[18,19] favor higher values of about 4. The influence of sample pH on the overall efficiency of the chelation/extraction procedure was determined at intervals of 0.5 pH units over the pH range 1.5–9. Subsamples of a trace metal stock solution containing 50 μg/l each of cadmium, cobalt, copper, molybdenum, nickel, lead and zinc were prepared, the pH was adjusted, and the chelation/extraction procedure was carried out. After the addition of APDC, the pH was measured again.

The results, expressed as relative absorbance (Figure 1), show that in the sample pH range 3–8 the extraction efficiency is virtually independent of pH for six of the seven metals studied; a slight decrease is observed at high pH values for Cu, Pb and Zn, whereas a marked reduction in extraction efficiency is noted at pH values <3 for all metals but Mn. Although little detailed information is available in the literature, several authors have noted a similar decline in moderately acidic solutions,[9,20] but often at somewhat lower pH values. Comparison with existing data is, however, difficult as analysts have employed varying amounts of APDC and MIBK, and some have added buffers (e.g., acetate, citrate). Furthermore, it is not always clear at which step the pH was measured; the sample pH is altered by addition of the chelating agent[9,21] and by extraction with MIBK.[21]

With regard to the apparent decrease in extraction efficiency at high pH values for Cu, Pb and Zn, similar results have been presented by Kinrade

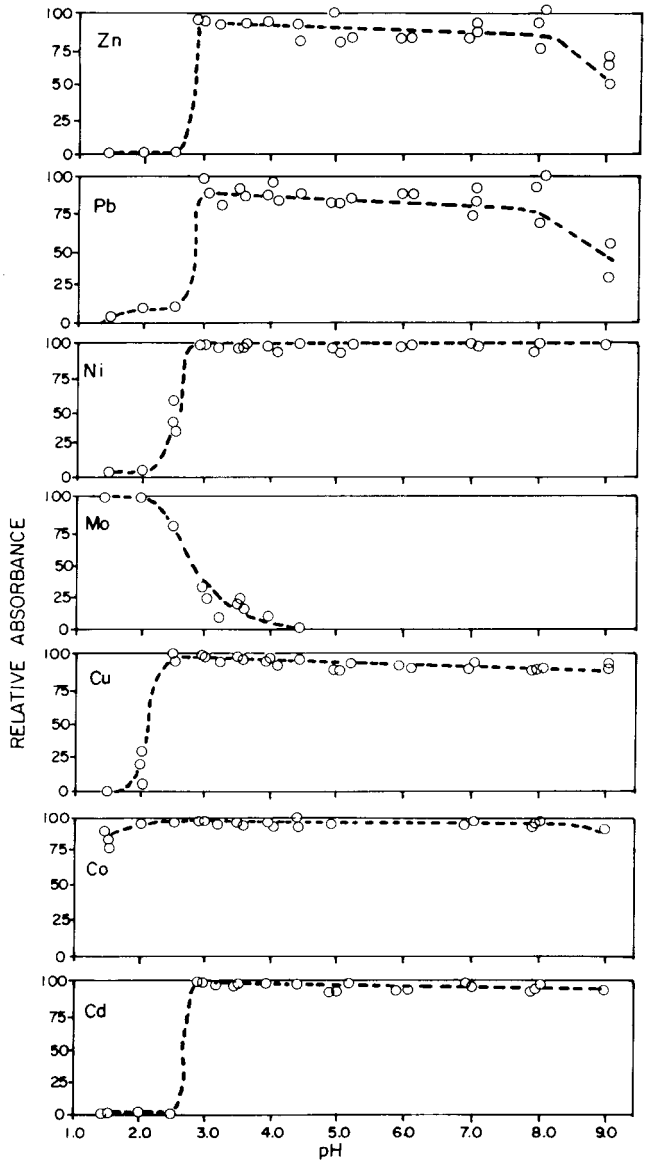

FIGURE 1 Efficiency of the APDC/MIBK method as a function of sample pH.

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and Van Loon[9] for a mixture of chelating agents (APDC + diethylammonium diethyldithiocarbamate) and by Koirtyohann and Wen[20] for APDC. According to these latter authors the extraction of Cu, Pb and Zn is complete or nearly so in a single extraction except at low pH (i.e. below pH 3) and extraction efficiency does not decrease as the pH is increased; they suggest that the small decrease in relative absorbance is associated with pH effects on nebulization and/or transport of the organic solvent to the flame. In the present study, no effort was made to elucidate whether the observed decrease was due to variation in extraction efficiency or simply to physical effects.

The simultaneous extraction of Cd, Co, Cu, Ni, Pb and Zn is clearly feasible in the pH range 3 to 8. In this work, an intermediate sample pH of 4 was subsequently chosen; this corresponds to an extraction pH of approximately 4.9, the shift in pH being due to the addition of APDC. In the case of molybdenum, however, the marked decrease in relative absorbance in the pH range 2–4 effectively precluded its analysis at a sample pH of 4.

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Sensitivity and precision

Plots of absorbance as a function of trace metal concentration in the initial aqueous sample showed a linear relationship in the following concentration ranges: copper, nickel and cobalt, 0–100 μg/l; lead, 0–30 μg/l; cadmium and zinc, 0–20 μg/l. The sensitivity of the overall procedure, defined as the metal concentration needed in the original sample to obtain a 1% absorption after chelation and extraction, is given in Table I. Comparison of these values with those obtained on the same instrument by direct aspiration of an aqueous sample shows a 17 to 36 fold increase in sensitivity. The detection limits, defined as the concentrations needed to obtain a signal equal to twice the baseline variation, are: cadmium, 0.2 μg/l; copper and zinc, 0.5 μg/l; nickel, 1.5 μg/l; cobalt, 2.0 μg/l; lead, 2.5 μg/l. Sensitivity and detection limit could be improved to a certain extent by increasing the sample to MIBK ratio;[11] for a given sample volume, a practical limitation is however imposed by the solubility of MIBK in water ($\simeq$2 ml/100 ml at room temperature) and by the number of analyses to be performed on a single extract. Further gains in sensitivity could also be achieved by using flameless atomic absorption to analyze the MIBK extracts directly[22–24] or after back extraction.[25–26]

Replicate analyses were performed on ten identical samples of both filtered and unfiltered river water. A known small amount of each metal was added to all aqueous samples to insure that there were sufficient quantities of all metals for analysis. The analytical results (Table I) show

that the precision of the overall analytical procedure is acceptable at the observed trace metal concentrations.

TABLE I

Sensitivity and precision of the chelation/extraction procedure as determined on natural water samples

Metal	Sensitivity[a] (μg/l)	Coefficient of variation[b] Filtered sample (%)	Coefficient of variation[b] Unfiltered sample (%)
Cadmium	0.6	6.7 (3.4)	2.5 (5.8)
Cobalt	2.9	3.3 (5.6)	2.4 (5.2)
Copper	2.1	2.7 (15.3)	5.1 (39.6)
Nickel	2.2	1.8 (48.1)	2.3 (45.5)
Lead	4.4	10.3 (5.9)	3.2 (49.1)
Zinc	0.7	3.4 (58.3)	1.6 (103)

[a]Sensitivity is defined as the concentration needed to produce a 1% absorption.
[b]The coefficient of variation was obtained from ten replicate analyses; the metal concentration (μg/l) is given in parentheses.

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Chelate stability

The metal-APDC complexes must remain stable in the MIBK solution during the time necessary to perform a minimum of extractions; furthermore, in the case where large numbers of water samples have to be treated, it might be advantageous to accumulate MIBK extracts before undertaking the trace metal concentration measurements, provided that the complexes do not decompose.

In order to check the stability of the APDC complexes, a portion of a standard trace metal stock solution, containing 25 μg/l each of cobalt, copper, nickel, lead and zinc and 5 μg/l of cadmium, was treated with APDC and extracted; the MIBK extract, as well as a second portion of stock solution, were stored in the dark at 4°C. After 10 days, a fresh stock solution as well as the 10 day old solution were both extracted and trace metal analyses were performed on all three MIBK extracts. The results given in Table II indicate that all the metal-APDC chelates tested were stable in MIBK solution for at least 10 days. Instances of instability over much shorter time periods have been reported for the APDC chelates of nickel, lead and zinc.[9,11] The greater stability noted in the present work can probably be attributed to the storage of the MIBK extracts at 4°C in the dark.[11] Chelate extracts obtained from natural water samples from the

Yamaska and Saint-François rivers were occasionally checked for stability; they too were found to be stable for periods of at least 8 days.

TABLE II

Stability of metal solutions and of metal-APDC complexes

Metal	Concentration[a] of metal ion as referred to the aqueous solution (μg/l)		
	Freshly prepared and extracted[b]	10 day old solution freshly extracted	10 day old extracts
Cd	5.0±0.1	5.0±0.1	4.9±0.1
Co	25.0±0.2	24.7±0.3	24.4±0.5
Cu	25.0±0.4	25.8±0.2	25.2±0.5
Ni	25.0±0.6	24.5±0.4	24.2±0.6
Pb	25.0±1.1	25.3±0.4	24.7±0.4
Zn	25.0±0.2	25.2±0.2	24.6±0.6

[a]Mean and standard deviation for three replicate determinations.
[b]Fixed as the reference value.

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Effect of changes in the sample matrix

Concentrations of cadmium, copper, lead and zinc were determined on 48 samples, both filtered and unfiltered, collected from the Yamaska and Saint-François rivers. The chelation/extraction atomic absorption procedure was employed and trace metal quantitation was achieved with the standard addition technique. The increase in absorbance attributable to metal addition can be used to assess the effects of matrix variations on trace metal recovery.[1] Mean values of the increases in absorbance for a given metal spike were compiled for each of the 12 sampling stations and for each of the four sampling dates; one-way analysis of variance[27] was applied to these data to test the equality of the several means. It should be noted that assumptions underlying the analysis of variance, particularly homoscedasticity, were found to be satisfied in all cases with the exception of zinc in filtered samples. Application of this statistical method did not indicate any significant difference (level of significance 5%) between the mean value at each station (mean of the four sampling dates), i.e. no significant spatial variability.

For cadmium, copper and lead, significant differences (level of significance 5%) were however observed between the mean values calculated for each sampling date (mean of the 12 stations); mean values for one particular campaign are significantly higher than those for the three other

TABLE III

Mean values and standard deviation for recovery of spiked metals in the Yamaska and Saint-François river samples relative to that from deionized water[a,b]

Campaign	Sample treatment[c]	Cd	Cu	Pb	Zn
1	NF	99±4	99±5	98±7	106±12
	F	100±4	96±6	99±19	104±14
2	NF	109±8	101±6	114±14	101±7
	F	112±5	102±4	119±18	106±11
3	NF	100±4	111±5	92±8	96±9
	F	102±2	104±5	90±13	101±5
4	NF	103±3	104±7	95±11	104±6
	F	106±6	101±8	91±10	108±2

[a]Recovery in deionized water is fixed arbitrarily as 100%; metal spikes were 10 μg/l for Cu, Pb, Zn and 2 μg/l for Cd.
[b]Mean values and standard deviation were calculated for 12 sampling stations.
[c]NF: unfiltered; F: filtered.

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sampling dates, which can be considered as equal (Table III). In an attempt to explain this apparent temporal variation, we investigated possible relationships between the values of the absorbance attributed to a given metal addition in each sample and the corresponding values of conductivity and soluble organic carbon; in neither case was a significant correlation found. The absence of correlation with these integrative parameters does not however rule out possible effects of specific compounds upon metal recovery. Further examination of Table III indicates that maximum errors of about 15% would have been incurred in determining the concentration of trace metal if a calibration curve had been used for quantitation instead of the standard addition technique. From a practical standpoint, in view of the numerous possibilities of error linked to each step from sampling to analysis, the use of a calibration curve prepared in a natural water matrix would seem to represent an acceptable compromise between analytical accuracy and laboratory capacity (i.e. number of samples analyzed). For more accurate results, however, use of a standard addition technique would be required.

Interference from organic compounds

The chelation/extraction procedure excludes most of the inorganic constituents and should thus minimize matrix effects attributable to the bulk inorganic solutes present in the original sample. Possible effects of organic

compounds present, which can either compete with APDC for binding the metals or be extracted into the organic phase, cannot however be dismissed so easily. Kinrade and Van Loon[9] mentioned that biodegradable detergents appeared to affect the recovery of metals; other authors have observed strong effects of synthetic surfactants,[20] especially LAS, and of humic[20] or fulvic[28] acids upon the recovery of added metals by an APDC/MIBK method. The possible effects of organic matter on the chelation/extraction procedure were thus investigated using either synthetic solutions of LAS and humic acid or a natural water sample (James Bay sample) known to have a high humic acid concentration. In comparison with the range of dissolved organic carbon concentrations commonly found in surface waters[29] (0.1–10 mg/l), the concentration chosen for humic acid (3 mg C/l) appears representative; the concentration of LAS chosen (1 mg/l) was however somewhat higher than those likely to be found in natural waters.[30] All the samples, as well as deionized water control samples, were spiked with known metal concentrations and divided into two portions; one of these was digested with the acid persulphate solution to destroy organic matter before being subjected to the chelation/extraction step, whereas the other was analyzed directly by the chelation/extraction procedure without prior digestion. Of the many available digestion procedures, the persulphate and sulphuric acid mixture has been found[12] to be the most satisfactory for releasing organically bound metals in natural water samples, especially for those containing high levels of organic matter. Furthermore, the procedure is not too time consuming, and the digestion mixture has already been employed[31] before the APDC/MIKB step without reported interference; components of other digestion mixtures are known to affect trace metal recovery[8,32,33].

Application of one-way analysis of variance to test the equality of the several means for each spike of metal (Table IV) revealed no significant differences (level of significance 5%) between the mean value for undigested deionized water and the other mean values, except for cobalt. Contrary to the observations of Pakalns and Farrar,[21] our results do *not* indicate a strong inhibitory effect of LAS or humic acid upon trace metal recovery. Careful examination of the experimental procedure employed by these authors does not reveal any significant difference from the one described here, except for the trace metal concentrations added which were much higher in their experiments; for a given concentration of LAS or humic acid they found greater inhibitory effects at *high* metal concentrations.

Reduction in Co recovery in digested samples is explained by the change in oxidation state of that metal (i.e. Co(II)→Co(III)) which affects both the stability of the cobalt-APDC complexes and the kinetics of their

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TABLE IV

Influence of organic matter in undigested or digested samples upon recovery of spiked metals

Metal	Concentration added in the water phase (μg/l)	Recovery (%)[a]							
		Deionized water		LAS (1 mg/l) solution		Humic acid (3 mg C/l) solution		James Bay sample (12 mg C/l)	
		Undigested[b]	Digested	Undigested	Digested	Undigested	Digested	Undigested	Digested
Cd	2	100±6	109±9					103±6	106±15
Cd	4	100±9	107±7					100±10	106±0
Cd	5	100±0.3	103±0.3	99±1	100±3	96±2	98±2		
Co	10	100±12	32±8					118±7	104±3
Co	20	100±3	31±7					98±7	97±3
Co	25	100±2	56±9	104±2	46±6	104±7	63±4		
Cu	10	100±8	105±4					107±4	109±4
Cu	20	100±3	102±3					99±2	109±4
Cu	25	100±1	97±7	99±4	104±1	86±10	108±1		
Ni	10	100±0	95±5					118±0	105±12
Ni	20	100±0	93±2					96±2	95±6
Ni	25	100±3	103±3	94±5	102±2	83±7	93±7		
Pb	10	100±26	91±13					91±8	108±0
Pb	20	100±4	96±6					87±6	102±10
Pb	25	100±5	112±2	110±3	111±1	111±7	112±0		
Zn	10	100±15	82±12					96±4	99±13
Zn	20	100±7	95±7					95±8	94±3
Zn	25	100±4	101±1	99±2	98±4	102±8	100±3		

[a]Mean and standard deviation for three replicate determinations.
[b]Arbitrarily fixed as the reference value (100).

formation. Organic matter in the James Bay sample apparently protected Co against oxidation, although decolourization of the sample by the digestion mixture was complete.

Comparison between digested and undigested samples indicates that APDC competes efficiently with other complexing agents (e.g. humic acids) for the trace metals and/or that the natural chelates are extracted into MIBK. Further examination of Table IV (columns 3 and 4) indicates that the inorganic products resulting from digestion with the persulphate-sulphuric acid mixture do not seriously affect subsequent metal recovery. Contrary to the observations of Midgett and Fishman,[33] removal of excess persulphate was found to be efficient, as checked by a benzidine test.[34] This digestion step could thus be used to treat samples high in soluble organic matter (e.g. wastewaters) as well as unfiltered samples. In the latter case, the results would provide an estimate of the concentration of all metals other than those held in resistant mineral particle lattices.

In conclusion, the APDC/MIBK extraction procedure has proved to be eminently satisfactory for concentrating cadmium, cobalt, copper, nickel, lead and zinc from river water samples prior to analysis by atomic absorption spectrophotometry. Overall analytical precision is good and the sensitivity of the method is acceptable for surface water samples. When refrigerated, the metal-APDC chelates are stable in the organic phase for at least ten days; accumulation of MIBK extracts before analysis is feasible, thus increasing the flexibility of the method as part of a trace metal monitoring programme.

Results of the experiments designed to evaluate the effects of sample composition on trace metal recovery suggest that such matrix effects are effectively minimized by the chelation/extraction procedure. In control experiments, with realistic concentrations of both trace metals and organic matter, neither linear alkyl sulphonate nor humic acid significantly influenced trace metal recovery. In the two rivers studied the recovery of spiked metals did vary slightly between sampling dates, presumably reflecting changes in the sample matrix, but the observed differences were relatively small ($\leq 15\%$).

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Acknowledgements

The authors acknowledge the financial support of the Quebec Department of Natural Resources, Water Quality Branch, and that of the National Research Council of Canada. The secretarial skill of F. Bordeleau was most appreciated as was the able technical assistance provided by M. Bordeleau, P. Boisvert and G. Trudel.

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