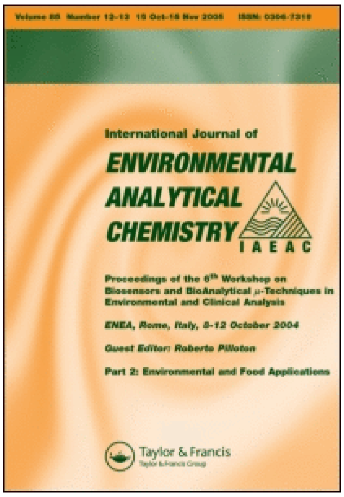

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Ammonium Pyrrolidinedithiocarbamate-Methyl Isobutyl ketone-Graphite Furnace Atomic Absorption System for Some Trace Metals in Drinking Water

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A critical study of the solution conditions and other parameters affecting the reliability of the ammonium pyrrolidinedithiocarbamate–methyl isobutyl ketone (APDC-MIBK) extraction system for Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, and Pb was made.

The following parameters were investigated in detail: pH of the aqueous phase prior to extraction, amount of APDC added to the solution following pH adjustment, the length of time needed for complete extraction and the time-stability of the chelate in the organic phase. Except for Ag and Cr which were quantitatively extracted only in a very narrow pH range (1.0–2.0 and 1.8–3.0, respectively), and Cd and Pb which were stable in the extracted MIBK phase only for 2–3 hrs, the solution conditions for quantitative extraction were not critical for the other metals. Simultaneous extraction of all the metals except Cd and Pb was also investigated. Good recoveries (100 ± 10%) were obtained for a number of spiked raw, treated and distributed drinking water samples covering a wide range of hardness. It is concluded that the APDC-MIBK-GFAA procedure is reliable and precise under proper solution conditions. The method is now routinely used in our laboratory for the determination of a number of the above metals in various Canadian drinking water supplies.

KEY WORDS: Trace metals, solvent extraction, APDC-MIBK, graphite furnace atomic absorption spectrometry, drinking water analysis.

INTRODUCTION

The determination of a number of metals in drinking water supplies has become an important area of pollution studies in recent years. However, many of these metals occur in drinking water at such low concentrations that they cannot be detected directly even by graphite furnace atomic absorption spectrometry (GFAAS), one of the most sensitive of analytical techniques. Indeed, a recent national survey of some Canadian water supplies showed that the majority of the 600 samples analyzed contained Cd, Cr, and Pb at or below the detection limit of GFAAS.[1] Furthermore, trace metal determination at sub-ng/mL level may be subject to matrix interference from the major constituents of drinking waters. Solvent extraction of trace metals from water samples is an effective way to concentrate metals to levels well above the GFAAS detection limits and enhancement factors as high as 100 can be easily obtained. In addition, this technique eliminates matrix effects, provides matrix normalization (i.e., making the matrix of all the samples the same as that of the standard), is simple, fast, easy to manipulate, and probably amenable to automated in-line analysis.

Ammonium pyrrolidinedithiocarbamate forms complexes with a number of metals simultaneously, and the complexes can then be easily extracted into organic solvents such as methyl isobutyl ketone (MIBK).[2-4] The APDC-MIBK system has been used for the simultaneous extraction and determination of some trace elements in sea water samples.[5,6] It was therefore decided to apply this system to the determination of trace elements in potable water. Few comprehensive studies have been published on the APDC-MIBK solvent extraction/atomic absorption procedure, and those that have been done[7,8] deal with only some aspects of the overall problems involved.

In this paper, a detailed study of the APDC-MIBK-GFAA system is made to determine: (i) the effect of pH on extraction efficiency; (ii) the time-stability of the metal chelates following the extraction at different pH; (iii) the optimum APDC concentration; and (iv) the minimum time required for quantitative extraction at metal concentrations normally encountered in fresh waters. Based on these studies, the feasibility of developing a simple and rapid APDC-MIBK-GFAA procedure for the single or simultaneous extraction and determination of Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, and Pb in raw, treated and distributed drinking waters is explored.

EXPERIMENTAL SECTION

Apparatus

The concentrations of the metals were determined using a Perkin–Elmer Model 603 atomic absorption spectrophotometer equipped with a HGA-2100 graphite furnace and a deuterium arc background corrector. Single element hollow cathode lamps were used as narrow line sources for all the elements except Cd and Pb which were determined by electrodeless discharge lamps to enhance sensitivity. Nitrogen purge gas was used for all the elements except Cr for which argon was used. Cd and Pb were determined in the gas interrupt mode.

An Orion Model 901 microprocessor ionalyzer equipped with a sleeve type Ag/AgCl single junction reference electrode and a low sodium-ion error glass electrode (Orion Models 90-01 and 91-01, respectively) was used for the measurement of pH. The time-stability of the aqueous solutions of APDC, and the solubility of MIBK in water and ammonium citrate solutions were determined with a Unicam Model SP1800 double-beam spectrophotometer using a pair of matched 1-cm Hellma quartz cells.

Nalgene (conventional polyethylene), 1000-mL screw-cap bottles were used as containers for water samples. All extraction studies were done in 125-mL Pyrex glass separatory funnels fitted with Teflon stopcocks and polyethylene stoppers.

Reagents and solutions

High-purity water was obtained by dustilling doubly deionized water in a Corning all-glass distillation system and was used throughout the present study.

Appropriate standard solutions of metals in 0.1% HNO_3 (Baker Ultrex) were prepared by serial dilution of the 1000 mg/L stock solutions (Fisher Scientific). A 500 mL multielement standard solution comprising 10 mg/L each of Co, Cr, Cu, and Fe; 50 mg/L Ni; and 2 mg/L each of Ag and Mn were prepared in 1% HNO_3 and stored in the dark in a 500 mL Nalgene polyethylene bottle. Solutions of lower concentrations were prepared daily as required by appropriate dilution of the multielement stock solution.

A 20% (w/v) solution of ammonium citrate buffer was prepared by dissolving 200 g of ammonium citrate, dibasic (ACS grade, Fisher Scientific) in 500 mL water and adjusting the pH to 7.2 with conc. NH_4OH. The solution was made up to one litre with water, and extracted for 3 min with 5 mL of a 1% solution of purified APDC and 25 mL MIBK. This operation was repeated until the aqueous layer was virtually free of any trace metal impurities as determined by GFAAS. The aqueous phase was stored in a one litre pre-cleaned polyethylene bottle.

A 2% (w/v) solution of APDC was prepared by dissolving 20 g of the compound (Baker analysed) in 1 L water and extracting for 3 min with 50 mL MIBK. The ketone layer was discarded and the extraction was repeated until the organic phase became colourless. The aqueous phase, when stored in a pre-cleaned polyethylene bottle at room temperature was stable for at least 1 month.

ACS Grade methyl isobutyl ketone (or 4-methyl-2-pentanone) supplied by Fisher Scientific was used without further purification.

ANALYTICAL PROCEDURE

Prior to use, all the containers were cleaned as described in a previous paper.[9]

a) Time stability of APDC solutions. Initially, spectra of a 1×10^{-3} M ($\simeq 0.01\%$, pH = 6.46) and a 1×10^{-4} M solution (pH = 6.72) of APDC were obtained in the region of 200–300 nm using water as the reference. Subsequent measurements were made during a one month period by recording absorbance values at 300 nm and 290 nm for the 10^{-3} M and 10^{-4} M solutions, respectively.

b) Solubility of MIBK in water and ammonium citrate. 0.5, 1.0, 2.0 and 5.0 mL MIBK were pipetted into 25 mL volumetric flasks and made up to the mark with water. The absorbance of the aqueous phase was measured at 256 nm with water as reference after vigorous shaking of each volumetric flask for 2 min.

The procedure for determining the solubility of MIBK in ammonium citrate solutions was basically the same as above. Measurements were done using 1.0, 2.0, 3.0, 4.0, 6.0 and 10.0% ammonium citrate at 304 nm with the corresponding ammonium citrate solution as the reference.

c) Effect of pH on the extraction of metals with APDC-MIBK. Citrate buffer (5 mL) was added to 20 mL of a standard metal solution (0.2 to 50 ng/mL depending on the GFAA detection limit of the metal in question). The pH was adjusted between 1–8 using 1 M HNO_3 or 1 M NaOH. (At pH values above 2.5, the addition of APDC changes the pH by 1–2 units and therefore the addition of a buffer was necessary to maintain the pH. At pH values below 2.5, the use of a buffer is not mandatory because the addition of APDC alters the pH only by 0.1–0.2 units). The solutions were then transferred to 125 mL separatory funnels, 5 mL of 2% APDC was added and the complex was extracted.

The metal concentration was determined by injecting 20 μL of the MIBK phase into the graphite furnace using an "Eppendorf" pipette fitted with disposable polypropylene tips. Decontamination of the tips from traces of metals was achieved by soaking them overnight in 1% HNO_3 (Baker Ultrex). The optimum "dry", "char", and "atomize" programme of HGA-2100 developed in this laboratory (Table I) was followed and the peak absorbance was noted. The results of duplicate determinations were then averaged to obtain plots of extraction vs. pH for each metal. Tests for completeness of extractions were made by multiple extractions of the

TABLE I

Optimized instrumental parameters for trace metals in the MIBK phase using graphite furnace atomic absorption spectrometry

			Ash		Atom	
Element	Line (nm)	Slit (nm)	Temp (°C)[a]	Time (s)	Temp (°C)[a]	Time (s)
Ag	328.1	0.7	300	10	2400	8
Cd	228.8	0.7	by-pass		1600	7
Co	240.7	0.2	500	10	2600	10
Cr	357.9	0.7	500	10	2600	10
Cu	324.8	0.7	600	10	2500	7
Fe	248.3	0.2	600	10	2600	8
Mn	279.5	0.2	500	10	2600	7
Ni	232.0	0.2	500	10	2600	9
Pb	283.3	0.7	400	10	2200	7

[a] Temperatures represent the meter settings on the control panel of the HGA temperature programmer. A drying temperature of 100 C for 30s was used for all metals except Cd which was dried at 100 C for 50s.

same aqueous phase and monitoring the trace metal content of each organic phase.

The effect of standing time on the stability of the metal chelates in the extracted MIBK phase at each pH value was also investigated. The organic layer was transferred into dry Pyrex centrifuge tubes immediately after extraction and the trace metal content was monitored with time. In these studies, the "aged" samples were compared to freshly extracted samples.

The procedure to ascertain the optimum extraction time and APDC concentration was the same as in (c) except that the separatory funnels were shaken for different time intervals (15–900 s) in the former case, and different amounts of APDC (2–10%) were added in the latter case.

d) Calibration and precision. The range of linear relationship between concentration and absorbance was determined by preparing a series of aqueous metal standards and extracting them under optimum solution conditions and aqueous to organic phase volume ratios (i.e. ^{v}aqueous/^{v}organic) of 1, 5, and 10. The calibration was done in triplicate for each element by extracting it singly, and also simultaneously along with the other metals.

The precision of the method was tested at concentrations of metals corresponding to 5, and 10 times the detection limit of each element. The extraction was done singly by preparing 20 solutions, each containing the same concentration of metal.

e) Effect of foreign ions. Optimum solution conditions were used for all elements. The studies were done at levels corresponding to 5, and 10 times the detection limit for each metal. The initial concentration of each foreign ion was significantly higher than usually found in fresh waters, and was progressively lowered until the response corresponded to 100% metal recovery. The foreign ions tested are listed later.

f) Analysis of water samples. Twenty samples of raw, treated and distributed water ranging in hardness (expressed as mg $CaCO_3/L$) from 1 to 554 were selected from a recent national drinking water survey.[1] The applicability of the extraction method was verified using the method of standard addition. As a further check, some selected samples from a second national survey which were found to contain trace elements at levels above the detection limit of the direct heated graphite atomization method were analyzed using the extraction procedure.

i) Determination of Cd and Pb. Samples of raw, treated and distributed water (25 mL) were transferred to 125 mL separatory funnels. Ammonium citrate buffer was added (10 mL), the pH was adjusted to 4–6, followed by the addition of 5 mL of 2%APDC and 5 mL of MIBK. The solution was then extracted for two minutes prior to the determination of cadmium by heated graphite atomization. In the case of lead analysis, 5 mL of 0.05% APDC was added prior to extraction. Recovery studies were done by spiking the samples with different amounts of the metals.

ii) Determination of Ag, Co, Cr, Cu, Fe, Mn and Ni. The method used was the same as above except for the pH which was adjusted to 2.0–2.5. Also, no buffer was added. Recovery studies were made by extracting the metals singly, and also simultaneously after multielement addition.

Many of the raw water samples tested contained appreciable amounts of Fe and Mn. In these cases, recovery studies were made by completely removing the metals from the samples by repeated extraction and then spiking the metal-free samples with concentrations of Fe and Mn corresponding to 5 and 10 times the detection limit of each metal.

RESULTS AND DISCUSSION

a) The stability of APDC solutions. The complexation efficiency of APDC is considerably influenced by its hydrolytic stability. The decomposition of APDC in aqueous medium is pH-dependent and proceeds by the mechanism[10] shown in Figure 1. From the apparent rate constant data given in the literature,[11] the halflife ($t_{\frac{1}{2}}$) values for APDC were calculated to be: 32 min, 59 min, 2 hr, 20 hr, 9 d, 90 d and 170 d at pH values ≤ 2, 3, 4, 5, 6, 7 and 7.3, respectively. In the present case, the APDC solutions corresponding to 10^{-1} M (1%; pH, 7.55), 10^{-3} M (pH, 6.46), and 10^{-4} M

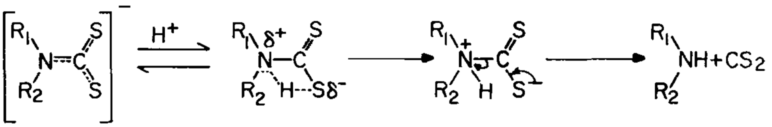

FIGURE 1 Mechanism of decomposition for dithiocarbamates.

(pH, 6.72) were found to be stable for at least one month, consistent with the above data. In contrast, calculations based on the apparent rate constant data[11] for the decomposition of the diethyldithiocarbamate, one of the most commonly used ligands gave ($t_{\frac{1}{2}}$) values of 7 s, 30 s, 5 min and 51 min at pH values $\leqq 2, 4, 5$, and 6, respectively. Thus, APDC is more stable than sodium (or ammonium) diethyldithiocarbamate, especially at pH $\leqq 4$, and is the ligand of choice in this work.

b) Solubility of MIBK in high-purity water and ammonium citrate. The solubility of MIBK in water, and in 1.0, 2.0, 3.0, 4.0, 6.0 and 10.0% ammonium citrate was found to be 2.6, 2.4, 2.0, 1.7, 1.5, 1.3, 1.2 and 0.5%, respectively, at 25°C. These values are comparable to those reported by Everson and Parker.[12] The data show the need either to extract standards and samples at the same aqueous to organic phase volume ratio or to pre-equilibrate the MIBK with water (or the appropriate concentration of citrate buffer) if loss of precision and accuracy of the analysis are to be avoided.

c) Effect of pH on extraction efficiency. The relationship between the pH of the aqueous solution prior to the addition of APDC and % extraction is shown in Figure 2. Complete transfer from aqueous to the organic phase occurs for most metals in a single extraction over a wide pH range: 1–2 for Ag: 2–8 for Cd; 1–6 for Fe; and 3.5–8 for Pb. Although not shown in Figure 2, Co, Cu and Ni are quantitatively extracted in the pH range 1–8. These results for Cd, Co, Cu, Fe and Ni at the ng/mL level using GFAAS are in agreement with those reported at the μg/mL level using flame AA.[6-8,13,14] Thus, it appears that extraction efficiency is virtually independent of the initial aqueous concentration of the above metal ions provided the solubility of the metal chelate is not exceeded in the organic phase.

The results for Cr, Mn and Pb differ somewhat from those reported in the literature. Gilbert and Clay,[15] and Midgett and Fishman[16] showed that Cr is extracted quantitatively in the pH range 1.5–2.5 and 2.8–3.5, respectively, from an unbuffered medium. In the present study quantitative extraction was attained at pH values 1.8–2.0 and 1.8–3.0 on buffering with citrate and acetate, respectively. Similarly, Lakeman[2] reported poor extraction of Mn at pH $\leqq 4$, but the present study shows that Mn is

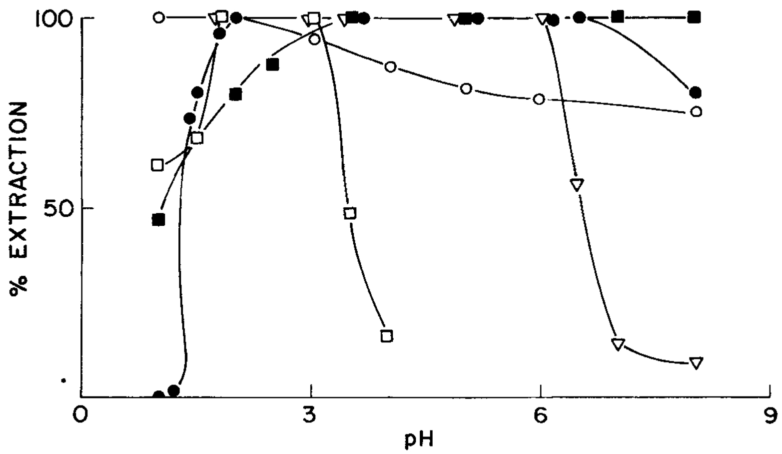

FIGURE 2 Effect of pH on the extraction of some trace metals using the APDC-MIBK procedure (^{v}aqueous/^{v}organic = 5): ○ Ag, 4 ng/mL; □ Cr, 20 ng/mL; ▽ Fe, 20 ng/mL; ● Mn, 6 ng/mL; ■ Pb, 8 ng/mL.

quantitatively extracted in the pH range 1.8–2.0 and 1.8–6.5 in the presence of citrate and acetate buffer, respectively. Olsen *et al.*[17] also found 100% extraction of Mn at a pH of 3.5 in the presence of phthalate buffer. Note that the citrate buffer interferes with the extraction of both Cr and Mn probably by forming a more stable citrate complex which is not extractable into MIBK. Therefore, an acetate buffer is recommended for the extraction of Cr and Mn above pH 2.0. Everson and Parker[18] reported quantitative extraction of Pb in the pH range 1–8 as opposed to 3.5–8.0 in the present case. This discrepancy may be due to differences in the concentrations used in both studies (5 ng/mL compared to 1000 ng/mL used by Everson and Parker).[18]

d) The time stability of the metal chelates. The time stability of each metal chelate in the extracted MIBK phase and the corresponding pH range is shown in Table II. The order of stability may be given as: Cd $\simeq \mathrm{Pb} < \mathrm{Mn} \simeq \mathrm{Ni} \simeq \mathrm{Ag} < \mathrm{Fe} < \mathrm{Cu} < \mathrm{Cr} \simeq \mathrm{Co}$. Thus, Cd and Pb were stable only for 2 hr and 3 hr, respectively, in the pH range 4–8; almost 85% Pb and 50% Cd were lost in 20 hr. Below pH 4, the chelates were stable only for ≤ 1 hr; nearly 84% Cd and 87% Pb were lost in 3 hr and 7 hr, respectively. Although silver pyrrolidinedithiocarbamate was stable only for one day in the pH range 3–6, no loss occurred at least up to 20 days in the pH range 1–2. Mansell[19] found the Mn chelate to be stable only for 1 hr at a pH of 3.5; however, the present study shows that the complex remained stable for 1 day in the pH range 1–6, and disappeared

TABLE II

Optimum solution conditions for the quantitative extraction of some metal-APDC chelates from aqueous solution into MIBK

Element	pH range	{APDC}/{Metal}[a]	Extraction[b] time (s)	Chelate[c] stability (hr)
Ag(I)	1.0–2.0	$\geqq 5 \times 10^2$	$\geqq 15$	216 (1–2); 24 (3–8)
Cd(II)	2.0–8.0	$\geqq 5 \times 10^3$	$\geqq 5$	2 (4–8); 0.5 (2–3)
Co(II)	1.0–8.0	$\geqq 1 \times 10^5$	$\geqq 5$	960 (1–5); 78 (6–8)
Cr(VI)	1.8–3.0	$\geqq 2 \times 10^5$	$\geqq 180$	300 (1.8–3.0)
Cu(II)	1.0–8.0	$\geqq 1 \times 10^2$	$\geqq 5$	168 (2–8); 48 (1)
Fe(III)	1.0–6.0	$\geqq 1 \times 10^5$	$\geqq 120$	96 (1–5); 24 (6)
Mn(II)	2.0–6.0	$\geqq 3 \times 10^5$	$\geqq 120$	24 (1.8–6.5); 10 (7–8)
Ni(II)	1.0–8.0	$\geqq 1 \times 10^3$	$\geqq 60$	48(2–4); 20 (5–8); 3 (1)
Pb(II)	3.5–8.0	2.5×10^2–2.5×10^4	$\geqq 5$	3 (4–8); 0.5 (3.5)

[a] Brackets denote concentration in weight/volume.

[b] Extraction time represents the time required for shaking the separatory funnels manually.

[c] Chelate stability represents the period during which the absorbance values for the metal remain more or less the same as those obtained immediately after extraction. The numbers within the bracket represent the range of pH values.

completely only after 3 days. Cu and Ni were quantitatively extracted in the pH range 1–8 (Figure 2), but at pH 1, the chelates were stable only for 2 days and 3 hr, respectively; beyond pH 1, however, the stability extended up to 1 week and 20 hr, respectively. Although Fe was completely extracted at pH 6, the complex remained stable only for 1 day at this pH and nearly 50% loss occurred in 4 days; but, at pH 1–5, the complex was stable up to 4 days. The complexes of Co and Cr were stable at least for one month in the pH range 1–5 and 1–3, respectively. These data clearly show that errors can result when measurements are not made within the time interval of stability at the corresponding pH range.

This instability may be attributed to the decomposition of the chelates resulting in the loss of metals by adsorption onto the walls of the centrifuge tube. This was confirmed by draining the tube, rinsing with acetone, soaking overnight in 5 mL of 1% HNO_3 and determining the metals in the nitric acid solution. The amount lost was almost quantitatively recovered. The metal chelates might decompose more rapidly if the MIBK phase were left in contact with the aqueous phase. This may be one of the reasons why Mansell[19] found the Mn chelate to be stable only for about one hour. Jenne and Ball,[20] Roberts,[21] and Olsen *et al.*[17] could stabilize the Mn complex for 3 days, 1 week, and 2 weeks using 20% acetone, 2.5% APDC in 95% ethanol, and a 1:1 acetone-HCl mixture, respectively.

e) Length of time needed for completeness of extraction. Extraction

TABLE III

Extraction time versus extraction efficiency for Cr, Fe, Mn and Ni using APDC-MIBK

	% extraction efficiency			
Time (s)	Cr	Fe	Mn	Ni
5	56	30	90	71
10	—	56	92	80
15	61	74	—	84
30	68	84	—	90
45	—	88	—	—
60	76	92	96	100
120	89	100	100	100
180–900	100	100	100	100

was complete in 5 s of shaking time for Cd, Co, Cu, Pb, and in 15 s for Ag. But, as shown in Table III, 1 min is taken for Mn and Ni, 2 min for Fe, and 3 min for Cr. These data were obtained for each metal at one optimum pH value at which the chelate is highly stable. However, Table III clearly shows that complete extraction can be obtained for all the elements over the entire pH range if a 3-min extraction time is used. It is obvious from these results that the chelates are formed instantly in the aqueous phase and concurrently extracted into MIBK.

f) Effect of APDC on extraction. Figure 3 shows the plot of % extraction as a function of the logarithm of APDC to metal concentration ratio. Quantitative extraction of Ag, Cd, Co, Cr, Cu, Fe, Mn and Ni occurs when the initial {APDC}/{Metal} ratio is greater than or equal to 5×10^2, 5×10^3, 1×10^5, 2×10^5, 1×10^2, 1×10^5, 3×10^5 and 1×10^3, respectively. In general, an initial concentration of 2% APDC will be sufficient to quantitatively extract these metals simultaneously from most natural waters. However, in the case of Pb, there is an upper (2.5×10^4), and a lower (1.25×10^2) limit. The upper limit is probably caused by the formation of a non-extractable species of Pb; however, more studies are needed to elucidate the reasons for this rather unusual behaviour. Because of this constraint, it may not be possible to extract Pb simultaneously with the other metals.

The solution conditions required for the quantitative extraction of the metals of interest in this study are shown in Table II. Note that all the metals listed excepting Cd and Pb can be simultaneously extracted in the pH range 2–3 at {APDC}/{Metal} ratio $\geq 3 \times 10^5$ with an extraction time

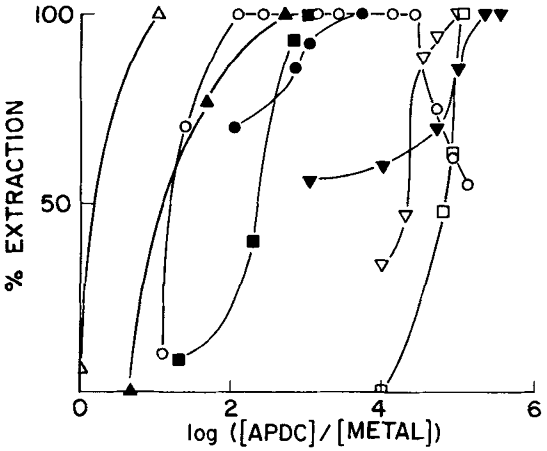

FIGURE 3 Effect of APDC on the extraction of some trace metals using the APDC-MIBK procedure: ▲ Ag, 4 ng/mL; ● Cd, 0.2 ng/mL; ▽ Co, 20 ng/mL; ▼ Cr, 20 ng/mL; △ Cu, 20 ng/mL; □ Fe, 20 ng/mL; ■ Ni, 50 ng/mL; ○ Pb, 8 ng/mL.

of 3 min. If Ag and Cr are excluded, the pH range for simultaneous extraction becomes 2–6. Cd may also be extracted simultaneously with the other metals as long as it is determined within 2 hr following extraction. Obviously, Pb cannot be included in this scheme. It is clear that routine simultaneous extraction of most metals can easily be obtained except for Ag, Cd, Cr and Pb which are more prone to solution conditions. The short term stability of 2 hr for Cd and 3 hr for Pb call for rapid measurement, and the narrow pH range for Ag and Cr necessitate careful pH adjustment.

g) Calibration and precision. The linear working range, detection limit (2 × std. deviation of blank), sensitivity (mass of metal for 0.0044 Absorbance units), and enhancement ratio (signal enhancement in the MIBK phase relative to the aqueous phase) for the various metals in the extracted MIBK phase are given in Table IV. The values for these parameters in the organic phase remain unchanged at ^{v}aqueous/^{v}organic 1, 5 and 10 and for the single or simultaneous extraction of the metals. No signal enhancement is observed for Co, Cr, Cu, Fe and Pb, while enhancement occurs for Ag, Cd, Mn, and Ni. In the case of Ag, the increase in sensitivity in the MIBK phase is nearly twice that in the aqueous phase. The detection limit quoted in Table I is for the MIBK phase. In the aqueous phase, its value will depend upon ^{v}aqueous/^{v}organic; thus, at ^{v}aqueous/^{v}organic = 10, the detection limit in ng/mL would be: 0.02, 0.008, 0.24, 0.2, 0.2, 0.2, 0.07, 1.4 and 0.1 for Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb, respectively.

TABLE IV

Analytical parameters for metals in the MIBK phase using graphite furnace atomic absorption spectrometry

Element	Sensitivity[a] (1×10^{-12}g)	Detection[b] limit (ng/mL)	Linear working range (ng/mL)	Enhancement[c] ratio	Precision[d] 5×	10×
Ag	6.6	0.10	0–12	1.9	6	3
Cd	4.6	0.05	0–1	1.6	7	2
Co	55.0	2.0	0–100	1.2	2	1
Cr	29.0	2.0	0–60	1.0	2	1
Cu	13.9	2.0	0–40	1.0	2	1
Fe	31.4	2.0	0–80	1.0	3	2
Mn	8.0	0.5	0–20	1.4	6	3
Ni	135.4	10.0	0–400	1.4	1	1
Pb	14.1	1.0	0–10	1.0	6	3

[a] Mass for 0.0044 absorbance with purge gas flow in the normal mode (50 mL/min) excepting Cd and Pb for which the interrupt mode was used. Nitrogen was the purge gas for all elements excepting Cr for which argon was used.

[b] Detection limit (= 2 × std. deviation of blank) refers to the organic phase. Its value in the aqueous phase would depend on the ratio of the aqueous phase volume to the organic phase volume.

[c] Enhancement ratio refers to the signal enhancement in the MIBK phase relative to the aqueous phase under the same operating conditions.

[d] Percent coefficient of variation (95% confidence level) at 5×, and 10× detection limit. Each value represents the average of 20 determinations in the MIBK phase.

Table IV also gives the precision obtained in the MIBK phase at 5, and 10 times the detection limit of each metal. The values given, expressed as % coefficient of variation at the 95% confidence level, are the average of 20 determinations. Considering the levels of trace elements involved, the range of the precision values (1%–7%) is acceptable.

h) Effect of foreign ions. As shown in Table V, extraction at 5, and 10 times the detection limit of each of the metals showed no interference from: HCO_3^-, SO_4^{-2}, PO_4^{-3}, NO_2^-, NO_3^-, F^-, Cl^-, Br^- and I^- at levels up to 200 mg/L; CN^-, EDTA, and humic acid as the sodium salt at levels up to 25 mg/L; Ca^{+2}, Mg^{+2}, Na^+, and K^+ at levels up to 300 mg/L, and many other metals at the levels indicated. However, interference was observed in the extraction of Ag, Cr, and Mn (Table VI). Only 1 mg/L Fe, 0.06 mg/L Cd, and 0.125 mg/L Cu could be tolerated for Ag. In the case of Cr, no interference was found up to 2.5 mg/L Fe and 0.5 mg/L each of the several metals listed in Table V. More than 0.25 mg/L Fe interfered seriously with the extraction of Mn. However, the concentrations of these interferents found in almost all drinking waters are appreciably lower than the concentrations used in this study, and therefore the effects of these ions may be considered insignficant.

TABLE V

Effect of foreign ions on the extraction of Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, and Pb with APDC-MIBK

Interferent	Concentration (mg/L)[a]
$HCO_3^-, SO_4^{-2}, PO_4^{-3}, NO_2^-, NO_3^-, F^-, Cl^-, Br^-, I^-$	200
CN^-, EDTA, Humic acid	25
$Na^+, K^+, Ca^{+2}, Mg^{+2}$	300
Fe and Mn (for all metals except Ag, Cr, Mn)	10
Ag, Al, As, Cd, Co, Cr, Hg, Ni, Pb, Se, Zn (for all metals except Ag, Cr, Mn)	2

[a] The values given correspond to the concentration of the interferents at least up to which no interference occurs in the extraction procedure. The concentrations given for SO_4^{-2}, PO_4^{-3}, NO_2^- and NO_3^- correspond to S, P, N and N, respectively.

TABLE VI

Interferences in the APDC-MIBK extraction of Ag, Cr and Mn

Interferent	Interferent concentration (ng/mL)	% interference		
		Ag	Cr	Mn
Cd	250	−50[a], −35[b]	0	0
	125	−25, −15	0	0
	60	0	0	0
Cu	1,000	+100, +70	0	0
	250	+45, +15	0	0
	125	0	0	0
Fe	5,000	+25, −39	17[a], 8[b]	+630[a], +215[b]
	2,500	+24, −35	0	+340, +70
	1,000	0	0	+240, +20
	500	0	0	+113, +8
	250	0	0	0 0

[a,b] The numbers represent the degree of interference at 5 ×[a] and 10 ×[b] detection limit of each of the elements of interest, respectively.

See Table I for detection limits.

TABLE VII

Percent recovery of metals in spiked samples of raw, treated and distributed drinking water using APDC-MIBK-GFAA

Concentration of spike (ng/mL)	% Recovery								
	Ag	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb
0.2	—	96 ± 7[a]	—	—	—	—	—	—	—
0.4	100 ± 3	101 ± 4	—	—	—	—	94 ± 6	—	—
0.6	104 ± 2	98 ± 3	—	—	—	—	—	—	—
0.8	—	95 ± 4	—	—	—	—	103 ± 5	—	—
2.0	103 ± 3	—	—	92 ± 6	97 ± 4	—	93 ± 4	—	104 ± 5
4.0	100 ± 4	—	94 ± 5	96 ± 3	105 ± 2	98 ± 3	97 ± 3	—	—
6.0	98 ± 3	—	—	—	101 ± 3	—	—	—	95 ± 5
8.0	—	—	96 ± 3	97 ± 2	105 ± 2	—	—	—	98 ± 6
10.0	—	—	—	97 ± 4	104 ± 4	96 ± 1	98 ± 2	—	101 ± 5
20.0	—	—	97 ± 2	91 ± 6	95 ± 2	93 ± 2	—	101 ± 1	—
40.0	—	—	97 ± 4	—	—	102 ± 4	—	104 ± 1	—
50.0	—	—	—	—	—	98 ± 1	—	—	—
80.0	—	—	—	—	—	—	—	102 ± 4	—
100.0	—	—	95 ± 5	—	—	—	—	101 ± 5	—
200.0	—	—	—	—	—	—	—	104 ± 2	—

[a] Values given represent the average of the triplicate analyses each of 20 raw, treated and distributed drinking water samples ranging in hardness from 1 to 554 mg $CaCO_3$/L. The values are more or less the same for single as well as simultaneous extractions. The measure of precision is the standard deviation.

i) Application of the APDC-MIBK-GFAA method to the analysis of drinking water samples. The method of standard addition was used to test the reliability of the APDC-MIBK-GFAA system; 20 samples each of raw, treated and distributed water samples ranging in hardness from 1 to 554 mg $CaCO_3$/L were analyzed. A summary of the % recovery of each metal in the various samples is shown in Table VII. The average percentage recovery is within 100 ± 10% for all the metals by single as well as simultaneous extractions. Similar recoveries were also obtained on the pre-extracted samples using single or simultaneous extraction.

In Table VIII, the APDC-MIBK-GFAA procedure is compared with the direct method for the determination of Cd, Cu and Pb in ten selected drinking water samples. The good agreement between the two methods shows that the extraction procedure can be reliable and precise, if applied under proper solution conditions. The slightly higher values by the extraction method for the majority of samples probably indicates that the direct method may still be subject to some matrix effects.

TABLE VIII

Comparison of the APDC-MIBK-GFAA procedure for the determination of Cd, Cu and Pb in selected drinking water samples with the direct method

Sample no.	Cadmium (ng/mL)		Copper (ng/mL)		Lead (ng/mL)	
	Direct[a]	This work	Direct[b]	This work	Direct[c]	This work
1	0.02	0.03	5.0	4.3	3.6	3.9
2	0.26	0.29	8.0	7.4	81.3	83.1
3	0.10	0.14	7.0	6.7	18.2	17.9
4	0.54	0.51	1.0	1.3	8.1	8.6
5	0.43	0.50	213.0	220.0	2.8	3.0
6	1.02	1.10	1.0	1.5	23.0	22.6
7	5.70	5.92	11.0	10.0	5.7	5.9
8	3.78	3.85	7.0	7.3	36.0	36.4
9	1.48	1.40	9.0	8.6	12.0	11.7
10	2.08	2.13	4.0	4.4	45.5	46.2

[a] 20 μL of sample directly injected into the graphite furnace and atomized at 1400°C for 7s (see Ref. 1).
[b] Direct aspiration of sample into an air-acetylene flame (see Ref. 1).
[c] Direct determination in the presence of lanthanum nitrate by the procedure of Thompson *et al.*[22]

CONCLUSION

The APDC-MIBK-GFAA procedure outlined in this paper can be used for the reliable determination of Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, and Pb either by individual extraction of each of these metals or by simultaneous extraction of all the metals except Cd and Pb. The procedure has already been applied to the determination of Cd, Cr, and Pb in 600 drinking water samples as part of a national survey to be published shortly.

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