



Quality assessment of drinking water with HCPTA

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A SIMPLE AND rapid extraction method for copper lead and cadmium with a new reagent 4-(4-chlorophenyl)-2-phenyl-5-thiazoleacetic acid (HCPTA) in n-butyl acetate has been developed. The determination of metal ions was carried out with flame atomic absorption spectrophotometry subsequent to their preconcentration using this extraction method. Physicochemical parameters of extraction method have been optimized with respect to pH, extractant concentration, equilibration time and additional cations and anions. The quantitative extraction was observed at pH 8.2 within 10 minutes. The stoichiometric composition of the extracted complexes was determined to be $[M(\text{CPTA})_2]$, where M = metal ion. The extraction constants ($\log K_{\text{ex}}$) of copper, lead and cadmium were found to be -10.39 ± 0.12 , -9.7 ± 0.11 and -10.44 ± 0.11 respectively. The developed procedure was applied the determination of these metals in samples of drinking water from Rawalpindi/Islamabad area and the results have been compared with the permissible levels of WHO.

Introduction

The determination of trace elements particularly the heavy metals in natural water has received increasing attention in pollution studies. The monitoring of the concentration levels of essential and toxic elements in these samples helps to assess the degree of environmental pollution. However, most of the elements found in natural waters are present at ultratrace levels and can only be reliably determined by a sensitive analytical technique. Among the different analytical techniques generally used for the determination of trace metals in drinking water the atomic absorption spectrophotometry (AAS) is particularly useful because of its reduced susceptibility to interference. But with the normal flame AAS technique, the sensitivities attainable for natural water samples are such that direct analyses are impractical because of the matrix interferences and strong light scattering effects etc.

To overcome the above mentioned problems various preconcentration methods such as co-precipitation and co-crystallization (Gomiscek, 1978), chelate solvent extraction (Sturgeon, 1980), ion exchange resins (Guedes, 1979), and electrolysis (Batley, 1977) etc. are generally applied to the analysis of trace metals. The solvent extraction is of great value in preconcentration of trace metals as it is simple, rapid, easy to manipulate and eliminates matrix effects. The solvent extraction technique has an added advantage of sensitivity enhancement when an organic solvent is used to estimate the extracted metals using AAS.

This is due to improved nebulizing efficiency as a result of rapid transport of the metallic species into the flame.

Several chelating extractants like ammonium pyrrolidinedithiocarbamate (APDC), dimethylglyoxime (DMG) oxine, dithizone, sodium diethyldithiocarbamate (NaDDC), HTTA etc., (Sekine, 1977) are generally used for the extraction of metals prior to their quantification by a suitable technique. The APDC is one of the most widely used reagents but has certain disadvantages of relative instability and slow rate of formation of metal complexes.

In the present work an attempt has been made to overcome these difficulties by choosing the reagent 4-(4-chlorophenyl)-2-phenyl-5-thiazoleacetic acid (HCPTA) as chelating extractant. The complexes of copper, lead and cadmium with HCPTA were preconcentrated by solvent extraction technique from the samples of drinking water prior to their determination with AAS.

Experimental reagents

Stock solutions of copper lead and cadmium (1000 mg L^{-1}) were prepared by dissolving one gram of Specpure metal (Johnson Matthey Chemicals Limited) in minimum amount of nitric acid. The resultant solution was diluted to one litre with water. Fresh working standard solutions were prepared by appropriate dilutions as required, immediately before use. All the reagents used were of Analar grade except 4-(4-chlorophenyl)-2-phenyl-5-thiazoleacetic acid (HCPTA) from Wyeth Laboratories Ltd., which was used as such. A 4 per cent (W/V) solution of HCPTA was prepared in n-butyl acetate and was further diluted with n-butyl acetate as required. Buffer solutions of pH 1 to 10 having ionic strength of 0.1 M were prepared by mixing appropriate volumes of solutions of KCl and HCl (pH 1-3), CH_3COONa and CH_3COOH (pH 4-6), NH_4Cl and NH_4OH (pH 6-7.5) and H_3BO_3 , NaCl and NaOH (pH 8-10).

Extraction procedure

Metal solution of 5 mg mL^{-1} was prepared by appropriate dilution of the stock solution with buffer solutions of the desired pH in a 35 ml glass vial with a screwed polyethylene cap. Five milliliters of this buffer solution was equilibrated for ten minutes with an equal volume of HCPTA solution in n-butyl acetate using a wrist action Griffin & George shaker. The contents were centrifuged for three minutes for phase separation. The concentration of the metal in the separated organic phase was determined by atomic absorption spectrophotometry using an air-acetylene flame and

the optimized instrumental parameters against similarly prepared standard solutions. A blank solution without the metal was also prepared and treated under identical conditions. The signal evaluation was made by subtracting the absorbance of blank from the absorbance of sample. All experiments were conducted at an ambient temperature of 23 ± 1.0 °C.

Determination of metals in drinking water

About 100 ml of water sample was quantitatively transferred into a separating funnel along with 100 mg of each of NaF and NaSCN. A few drops of cresol red indicator were added and the pH was adjusted to 8.4 by the drop wise addition of 1.0 M NaOH by observation of the colour change from yellow to violet. Then 10 ml of 4 per cent HCPTA solution was added to the funnel and the contents were shaken vigorously for 10 minutes. After phase separation the organic layer was assayed for its metal contents by atomic absorption spectrophotometry. A blank was also prepared and treated similarly.

Results and discussion

The extraction of copper lead and cadmium with HCPTA and their subsequent determination with flame atomic absorption spectrophotometric technique has been investigated in detail. Various physicochemical parameters of the extraction method have been optimized. The criterion for the optimization was the selection of conditions where maximum extraction was occurred.

The effect of pH on the extraction of metals with 1.0 per cent HCPTA solution from aqueous at pH 1-10 solutions indicates that no HCPTA-metal chelate is formed below pH 6.0 and quantitative extraction was observed at pH 8.2 and above. A pH of 8.4 was therefore selected for the subsequent studies. The extraction was found to be completed within 10 minutes and no adverse effect was observed on prolonged shaking.

The optimum reagent concentrations were found to be 0.1 per cent for copper and lead, and 0.2 per cent for cadmium. However, a concentration of 4 per cent HCPTA solution was used for the analysis of real water samples, in order to compensate the reagent depletion by other extractable potentially occurring in the medium.

The stoichiometric compositions of the extracted complexes were determined by the method of slope analysis using the following equation.

$$\log D = \log K_{\text{ex}} + n\text{pH} + n \log [\text{HCPTA}]_0 \quad (\text{i})$$

where D is the distribution ratio, K_{ex} is the extraction constant of the complex and $[\text{HCPTA}]_0$ is the molar concentration of the reagent in organic phase. The plots of logarithm of the distribution coefficient of metals versus logarithm of the ligand concentration at pH 8.4 were straight lines. The slopes of these plots were found to be 2.06 ± 0.09 , 1.93 ± 0.06 and 2.14 ± 0.10 for Cu, Pb and Cd respectively, indicating that the number of chelating ligand attached to the metal ion is equivalent to the charge of the

central metal ion with the liberation of two protons during complexation. The stoichiometric composition of the complex is, therefore, established to be $[\text{M}(\text{CPTA})_2]$, where M = metal ion. From the intercepts of these plots the extraction constants ($\log K_{\text{ex}}$) were computed by using equation (i) and were found to be -10.3 ± 0.12 , -9.7 ± 0.11 and -10.44 ± 0.11 for Cu, Pb, and Cd respectively.

The effect of various masking agents (F^- , Br^- , ClO_4^- , HCO_3^- , CH_3COO^- , SO_4^{2-} , SCN^- , $\text{C}_2\text{O}_4^{2-}$, citrate, ascorbate, EDTA and cyanide) on the extraction of these metals was checked under the optimized extraction conditions. The data show that oxalate, citrate, ascorbate, cyanide and EDTA masked the extraction of copper completely. The extraction of lead is masked by ascorbate and EDTA, whereas that of cadmium by EDTA only. This is probably due to the formation of more stable metal complexes of these ions as compared to the CPTA. Therefore, these ions should be absent before the extraction of the metals of interest with HCPTA. The effect of other cations (Li^+ , K^+ , Cs^+ , Mg^{+2} , Ca^{+2} , V^{+5} , Mn^{+2} , Fe^{+3} , Co^{+2} , Zn^{+2} , Pd^{+2} , Pt^{+4} , Hg^{+2} , Al^{+3}) on the extraction of the metals of interest was also studied and the data revealed that upto 10 mg L^{-1} of the cations, no depression in the absorption signal of these metals was observed. Similar results were obtained when the concentration of cations were increased upto 100 mg L^{-1} , except for Mn, Fe, Pd and Al which depressed the absorption signal of copper by 8, 13, 13, and 72 per cent, respectively. Similarly the extraction of lead was decreased in presence of V (35 per cent), Fe (72 per cent), Pd (38 per cent), Hg (20 per cent) and Al (29 per cent), whereas that of cadmium by Pd (24 per cent) and Al (13 per cent). The decrease in the extraction is probably due to the hydrolysis of these cations under the experimental conditions and the adsorption of metal ions on these precipitates.

For the quantitative estimation of the metals using AAS, known amount of metals were extracted in n-butyl acetate under the optimized extraction conditions. These organic extracts were then aspirated into an air-acetylene flame to optimize the instrumental conditions for the direct measurement of the metals in the organic solvent. The criterion for the optimization of the instrument was the selection of instrumental parameters which produces maximum and reproducible absorption signal with low background. Seven drinking water samples from Rawalpindi/Islamabad are were subjected to the determination of Cu, Pb and Cd employing the developed procedure. It was observed that when the ratio of the organic to aqueous phase was less than 0.5, a third phase was formed due to the precipitation of Ca and Fe. This precipitation was inhibited by the addition of NaF and NaSCN to the aqueous phase before extraction. The determined metal concentrations in the water samples are presented in table 1 along with the recommended concentrations of WHO. The determined concentrations of Cu, Pb and Cd were ranged from 2.8-10.2 (average 5.36), 7.5-86.0 (average 36.6) and 1.4-4.8 (average 2.9) mg L^{-1} respectively. The sample AA* was not included in these calculations. It was collected after keeping it in contact with

Table 1. Determined concentration of metals (mg L^{-1}) in drinking water

in the pipes for 72 hours, in order to see any effect on the concentration levels of the metals of interest. It was found that the concentration of lead was increased significantly indicating the contribution of lead from the household plumbing. The determined average concentrations of the metals of interest are within the recommended values of WHO.

Conclusions

The HCPTA is a good reagent for the quantitative extraction of metals. The extraction procedure adopted is simple, rapid, accurate and reliable. The other cations have little effect on the extraction of metals with this reagent. The application of the procedure to the determination of metals in water samples has been found satisfactory.

References

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