

TRACE METALS DETERMINATION IN WATER

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ABSTRACT

Trace metals in water were preconcentrated with solvent extraction. Then the extracts were reextracted to water in the medium of concentrated nitric acid. The recoveries of the trace metals at concentration of $0.25\mu\text{g/mL}$ were found to be 90%-96%. The concentration of Cu, Cd, Zn and Pb were determined in river of Büyük Menderes, Sakarya and Kızılırmak. At the same time river water were evaporated to dryness and were determined the trace metals concentration.

1. INTRODUCTION

Atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and atomic fluorescence spectroscopy (AFS) are some of the major techniques used in the determination of trace metals in natural water and other media. The medium is known to have no effect on the metal determination using these techniques.¹ However the solutions need to be preconcentrated prior to the analysis performed on natural waters, plants and vegetables since the amount of metals present in these media is quite low.² There are various techniques developed for the preconcentration of solutions. Among these short column chromatography is based upon the adsorption of metal ions on various gels.^{3,4}

Another widely used method for the preconcentration is the adsorption of the ions on activated carbon. This can be done by either passing the solution, containing metal ions, through a layer of activated carbon placed evenly onto a filter paper or shaking the solution with activated carbon and filtering the resulting mixture through a filter paper.^{5,6}

However the most widely used method among the preconcentration techniques is the liquid-liquid extraction. This method is based upon using one organic and one inorganic phase completely immiscible in each other and extracting the complexed metal ions into the organic phase from the solution.⁷⁻⁹ The most generally used

complexing agents are chlorides, bromides diethyldithiocarbamate, hydroquinone, pyrogallol, phenantrolin and the organic phases generally employed are aldehydes, ketones, ethers, halogenated hydrocarbons and aromatic solvents. The metal present in the extract can either be directly determined in flame AAS or reextracted in water and determined in much simpler media such as water.

In this study regained percentage of the trace metals extracted into water phase from the organic phase were determined. The same method was also employed in the determination of trace element in waters of Kızılırmak, Sakarya and Büyük Menderes rivers preconcentrated by vaporisation.

MATERIAL AND METHOD

The equipment and the material used in the trace metal determinations are as follows:

Perkin-Elmer AAS 400, Orion pH meter, 1 mg/L stock solutions of Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} prepared from analytical grade reagents, 1% NH_3 and HNO_3 solutions, 5% ammonium pyrolydinedithiocarbamate (APDC) solution and methylisobutyl ketone (MIBK).

The Recovery of Trace Metals

The pH of solutions containing 0.25 $\mu\text{g}/\text{mL}$ Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} were made 1, 3, 5, 7 and 9 and before they were taken into a separation funnel with a capacity of 250 mL, 2 mL solution of APDC was added to 100 mL of this solution and the funnel was slightly shaken. Then solutions were treated with 7 mL MIBK in order to extract the resulting metal complexes and the funnel was vigorously shaken for 30 seconds. It was then kept on bench for 15 minutes in order to allow ample time for the formation of the phases. The aqueous phase at the bottom was discarded and the organic phase was taken into a 50 mL beaker. The solution was evaporated up to dryness and then 5 mL of concentrated HNO_3 was added. It was then evaporated in the ventilation hood. This procedure was repeated by the readdition of 5 mL of HNO_3 after the solution became an oily like residue. The final residue was dissolved in 5 mL of 6.5% HNO_3 . The recovery percentage was calculated by analysing first the standart solutions containing 0.25 $\mu\text{g}/\text{mL}$ Cu^{2+} , Zn^{2+} , Pb^{2+} , and Cd^{2+} and secondly the Cu^{2+} , Zn^{2+} , Pb^{2+} , and Cd^{2+} solutions extracted into water using an AAS absorbance of which had been adjusted to zero by distilled water, (Fig 1).

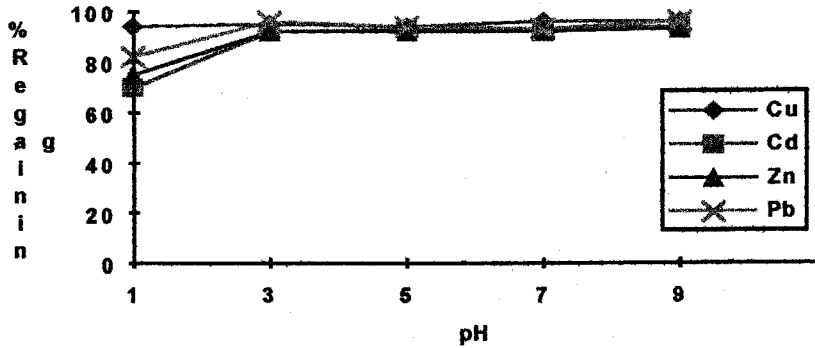


Fig 1. The percentage of recovered trace metals versus pH.

Recovery of the Trace Metals with Other Ions

The selective recovery of the trace elements in the presence of other abundantly present metals and ions in natural water were carried out individually and together at a pH of 4 by adjusting Ca^{2+} to 60 $\mu\text{g/mL}$ (with $\text{Ca}(\text{NO}_3)_2$), Mg^{2+} to 30 $\mu\text{g/mL}$ (with $\text{Mg}(\text{NO}_3)_2$), SO_4^{2-} to 150 $\mu\text{g/mL}$ (with H_2SO_4) and Cl^- to 10 $\mu\text{g/mL}$ (with HCl) in a 100 mL solution containing 0.25 $\mu\text{g/mL}$ Cu^{2+} , Zn^{2+} , Pb^{2+} , and Cd^{2+} . The mixture was taken into a separating funnel with a capacity of 250 ml, 2ml solution of 5% APDC was added to it and was shaken vigorously for 30 minutes. The aqueous phase was discarded and organic phase was taken into a 50 ml beaker and the above procedure was repeated. The recovery percentages were calculated and tabulated in Table 1.

Table 1. The percent recovery of the trace metals, only standards and with other ions (average of five results close)

Metal	Standard (0.25 $\mu\text{g/mL}$)	Ca^{2+} (60 $\mu\text{g/mL}$)	Mg^{2+} (30 $\mu\text{g/mL}$)	SO_4^{2-} (150 $\mu\text{g/mL}$)	Cl^- (50 $\mu\text{g/mL}$)	Mix of the ions
Cu	95 \pm 2	95 \pm 2	95 \pm 2	95 \pm 2	95 \pm 4	95 \pm 3
Pb	95 \pm 3	95 \pm 2	95 \pm 3	95 \pm 3	90 \pm 3	95 \pm 3
Zn	90 \pm 2	90 \pm 3	90 \pm 4	90 \pm 2	96 \pm 3	90 \pm 3
Cd	96 \pm 2	96 \pm 4	96 \pm 2	96 \pm 3		96 \pm 3

The Determination of Trace Metals in River Waters:

A. 200 ml river water (from Kızılırmak, Sakarya and Büyük Menderes) was filtered from a blue band filter paper, the pH was adjusted to 4 and the concentrations of Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} were determined as before. The results are given in Table 2.

Table 2. Concentration of the trace metals in river water ($\mu\text{g/L}$)

Metal	Büyük Menderes		Sakarya		Kızılırmak	
	Reextracted	Evaporated	Reextracted	Evaporated	Reextracted	Evaporated
Cu	3.2 \pm 0.2	3.8 \pm 0.4	6.5 \pm 0.4	6.4 \pm 0.9	4.2 \pm 0	4.4 \pm 0.5
Cd	1.2 \pm 0.3	1.8 \pm 0.2	2.4 \pm 0.3	3.2 \pm 0.2	3.6 \pm 0.2	3.2 \pm 0.3
Zn	6.6 \pm 0.2	6.8 \pm 0.3	10.4 \pm 0.4	10.6 \pm 0.2	14.0 \pm 0.4	14.8 \pm 0.3
Pb	6.2 \pm 0.2	5.8 \pm 0.3	6.4 \pm 0.4	5.9 \pm 0.3	4.3 \pm 0.3	4.8 \pm 0.4

B. 200 mL river water filtered from blue band filter paper and added with 1mL concentrated HNO_3 was evaporated to dryness in water bath. The residue was dissolved in 5mL 6.5% HNO_3 and Cu^{2+} , Zn^{2+} , Pb^{2+} , and Cd^{2+} ions were determined. The result are given in Table 2.

RESULTS AND DISCUSSION:

The Effect of pH on Recovery Percentages:

In a series of studies to determine the pH at which the highest recovery percentage was obtained Cu^{2+} , Zn^{2+} , Pb^{2+} , and Cd^{2+} were observed to be extracted to organic phase and reextracted into water in a pH range of 3 - 9 Figure 1. That was why all the studies were carried out at a pH of 4. The purpose of reextraction of the trace metals into aqueous phase enables one to carry out the determinations in aqueous phase rather than in organic phase. The organic solvents are highly inflammable and the analysis have to be completed rapidly since their vapour pressures are quite high. The problems encountered in AAS, sometimes forces people to search other avenues. The aqueous phase eliminates many of these problems. The introduction of organic compounds into the flame prevents its instability and obviates some of the problems in the nebuliser such as clogging and explosion.

The Effects of Abundantly Present Metals Upon the Recovery of Trace Elements

In order to investigate the effect of abundantly present metals, the major metals in river waters were determined with flame photometry (Ca^{2+} , Mg^{2+}), titrimetry (Cl^-) and colorimetry (SO_4^{2-}) without concentrating the water. The mean values of these ions were added to 100 mL trace elements solution and the trace elements were determined seperately and together. The recovery efficiencies of trace metals were found to be independent from these ions,(Table 2).

The Trace Element Analysis in River Water

Since the major ions present in water were found not to effect the trace metal analysis Cu^{2+} , Zn^{2+} , Pb^{2+} , and Cd^{2+} were analysed in 200 mL river water. The analysis of water obtained from Kızılırmak, Sakarya (near Ankara) and upper parts

of Büyük Menderes waters (May 1999) after being filtered from blue band filter paper, were extracted in MIBK and reextracted into water,(Table2) The metal concentrations were found to be low with regard to environmental pollution. The samples were taken from middle Kızılırmak, Sakarya, and upper Büyük Menderes rivers. The higher metal concentrations observed in Sakarya and Kızılırmak rivers compared with Büyük Menderes clearly indicate the higher extent of environmental pollution in these regions.

Since the metal concentrations found by the evaporation of river water were similiar, the reextraction of trace metals into water from MIBK is a quite time effective technique.

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