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Determination of Trace Amounts of Copper in Natural Water Samples by Flame Atomic Absorption Spectrometry Coupled with Flow Injection On-Line Solid Phase Extraction on Ambersorb 563 Adsorption Resin

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Ambersorb 563 adsorption resin was used for on-line separation/preconcentration and determination of copper by flow injection flame atomic absorption spectrometry. Copper was quantitatively recovered from the model solutions on mini column at the appropriate pH without adding chelating reagent. The elution step was performed with a stream of 0.25 mol L^{-1} HNO_3 at 5.0 mL min^{-1}, which introduced copper directly into the nebuliser of the flame atomic absorption spectrometer. The proposed method was successfully applied to the determination of copper in natural water samples. The detection limit (3σ) was 1.0 μg L^{-1} for preconcentration at the flow rate 5.0 mL min^{-1}. The recoveries of spike additions to water samples exceeded 95%.

Oznaczano ślady miedzi w naturalnych próbkach wody w przepływie metodą AAS i z użyciem (on-line) żywicy Ambersorb 563, która służyła do wstępnego zatężania Cu. Do roztworu nie dodawano chelatów. Do wymywania miedzi stosowano roztwór HNO_3 o stężeniu 0,25 mol L^{-1}. Szybkość przepływu tego roztworu, wprowadzanego bezpośrednio do nebulizatora spektrometru, ustalono na 5,0 mL min^{-1}. Granice wykrywalności oszacowano na 1,0 μL^{-1}. Odzysk miedzi dodanej do próbek wody był lepszy niż 95%.

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Preconcentration techniques including coprecipitation, cloud point extraction, membrane filtration, solvent extraction, solid phase extraction are a necessity for the sensitive atomic absorption spectrometric determination of heavy metal ions at low concentrations in high salt content samples. The use of on-line flow injection techniques for this purpose is very popular [1–3]. Flow injection analysis and solid phase extraction combination has been successfully applied to the determination of trace heavy metal ions using several types of solid phase materials including activated carbon, PTFE, Amberlite XAD resins, C18, activated alumina, cellulose, chelating resins as column packing material [4–11]. In this combination, retention and elution of the analytes are two important steps. In the first step analyte ions are adsorbed on solid sorbents. In the second step, the analytes are desorbed by using a suitable elu-ting agent. Some literature surveys about on-line separation and preconcentration in flow injection analysis of trace metal ions was reported by various researchers [12–14].

Ambersorb adsorption resins (Ambersorb 347, Ambersorb 348, Ambersorb 572, Ambersorb 575 *etc.*) are synthetic carbonaceous adsorbents. They have good adsorption properties: large surface area, porosity, durability, uniform pore distribution. They have been used for the separation, preconcentration and isolation of organic substances from various media especially natural waters [15–17]. Ambersorb 563 is also a member of Ambersorb resin family. Its surface area and size are 600 m^2 g^{-1} and 20–60 mesh, respectively. Like other members of this family Ambersorb 563 is a partially pyrolyzed sulfonated styrene/divinylbenzene polymer.

To our knowledge, the use of Ambersorb resins for preconcentration and separation of trace heavy metal ions is still very limited. Kenduzler and Turker [18] have been using Ambersorb 572 for preconcentration and separation of iron prior to its flame atomic absorption spectrometric determination. Narin *et al.* have proposed a procedure for speciation of Cr(VI) and Cr(III) in natural water samples on Ambersorb 563 resin [19].

Various studies on the on-line solid phase extraction of copper have been already performed. Ferreira *et al.* [20] used calmagite as a complexing agent for copper with the on-line sorption of the complexes in an Amberlite XAD–2 resin column. In another study, 1,10-phenanthroline was used for the on-line preconcentration/separation of copper and other metal ions [21]. De Peña and co-workers have proposed an on-line precon-centration procedure for copper traces involving synthetic zeolites as a solid phase material [22]. An on-line solid phase extraction system using PTFE packed column for the flame atomic absorption spectrometric determination of copper in water samples has been established by Anthemidis *et al.* [23]. The determination of copper in seawater by flame atomic absorption spectrometry (FAAS) was performed after on-line separation preconcentration on Muromac A–1 chelating resin mini column [24].

The aim of the present study was to establish an on-line separation/preconcentration system for the determination of the trace copper in natural water samples on microcolumn packed with Ambersorb 563 adsorption resin. For this purpose, various analytical parameters including pH, flow rates of sample and eluent, effect of matrix ions were studied and discussed.

EXPERIMENTAL

Reagents

All solutions were prepared with distilled deionized water. Copper(II) standard solution was prepared from 1000 mg L^{-1} solution of copper(II) nitrate and diluted as required with distilled water.

Ambersorb 563 Resin was purchased from Supelco, Bellefonte, US. In order to remove organic and inorganic contaminants, Ambersorb 563 was washed consecutively with methanol, water, 1 mol L^{-1} HNO_3 in acetone, water, 1 mol L^{-1} NaOH and water. A bead size of resin 20–60 mesh was selected for the preconcentration procedure. Smaller resin particles could have improved retention capacity, but the flow rates of sample solution and eluent solution ought to have been reduced, with subsequent increase in preconcentration time.

Phosphate buffer solution was prepared by mixing an appropriate volumes of 1 mol L^{-1} phosphoric acid and 1 mol L^{-1} sodium dihydrogen-phosphate solutions up to pH 2. Acetate buffer solutions were prepared by mixing the appropriate volumes of 1 mol L^{-1} acetic acid and 1 mol L^{-1} ammonium acetate solutions up to pH 4 and 6. Ammonium chloride buffer solutions were prepared by mixing the appropriate amounts of 0.1 mol L^{-1} ammonia and 0.1 mol L^{-1} ammonium chloride solutions till pH 8–10 was reached.

Apparatus

A Perkin–Elmer Model 3110 atomic absorption spectrometer, equipped with a copper hollow cathode lamp operating at 15 mA, was used throughout this work. The wavelength and spectral band pass were set at 324.8 nm and 0.7 nm, respectively. The nebulizer uptake rate was adjusted to give the optimum response for conventional sample introduction, and was finally fixed at 6.0 mL min^{-1}. An acetylene flow rate of 2.5 L min^{-1} was used with an airflow rate of 8.0 L min^{-1}. A model Nel pH 900 digital pH meter (Nel Electronic, Turkey) equipped with a combined glass-calomel electrode was used for the pH measurements.

The flow system comprised a four-channel variable speed perilstatic pump (Ismatec MCP–Standard, Switzerland), a home made PVC column (0.4 mm I.D., 4.0 cm long) and 2 two-way valve. The other parts of the system connected with Tygon tubings (1.3 mm I.D.) from Ismatec, (Switzerland) were employed to propel the sample, reagent and eluent. The flow injection system used is shown in Figure 1.

The PVC mini column was dry-packed with 250 mg of Ambersorb 563. A small amount of glass wool was placed at both ends of the column to prevent loss of the resin. The resin bed was approximately 3.6 cm long. To clean the resin, the column was successively washed with a blank solution. After each elution, it was ready for re-use without further pretreatment.

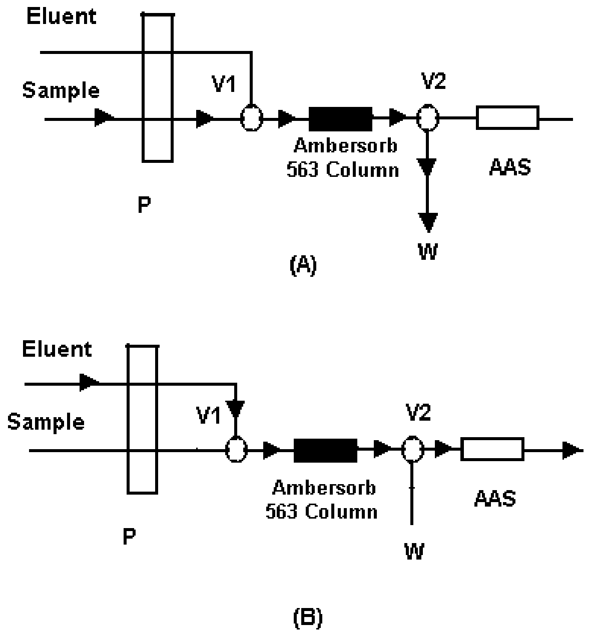

Figure 1. Schematic diagram of flow injection system used for the optimization of loading (A) and elution (B) conditions; V1: Valve 1, V2: Valve 2, W: Waste, P: Pump

Preconcentration system

The complete cycle of separation and enrichment of the copper at pH 9 without any chelating agent on Ambersorb 563 resin column, consisting of two steps: loading-Step 1 and elution-Step 2. These steps are described below.

In the Step 1 (Fig. 1 part A), V1 (valve 1) was switched on the flow direction of the mini column and V2 (valve 2) was switched on flow direction of waste. The sample solution that contains copper ions at pH 9 passed through the Ambersorb 563 column at 5.0 mL min^{-1} flow rate. In this step copper(II) ions were adsorbed on the Ambersorb 563 column. In the Step 2 (Figure 1 part B), the position of the V1 was changed to flowing direction of the eluent solution. Also the direction of the V2 was changed to flowing direction of the nebulizer of flame atomic absorption spectrometer. The adsorbed copper ions on the Ambersorb 563 mini column were eluted with 0.25 mol L^{-1} HNO$_3$ (5.0 mL min^{-1}) into the nebulizer. Finally the absorbance signals for copper were recorded.

RESULTS AND DISCUSSION

Effects of pH

In order to evaluate the pH effect on copper(II) recovery, the pH of the sample solution containing 0.25 µg mL^{-1} copper(II) was varied by adding buffer solutions.

The results are presented in Figure 2. Copper was quantitatively recovered in the pH range of 8.0–9.5. The recovery values for copper were quantitative at pH 8–10 when the pH of the aqueous solution was adjusted with ammonia and sodium hydroxide. The further studies were performed at pH 9 by using ammonium chloride buffer solution. The volume of the buffer added (2.0–10.0 mL) had no effect.

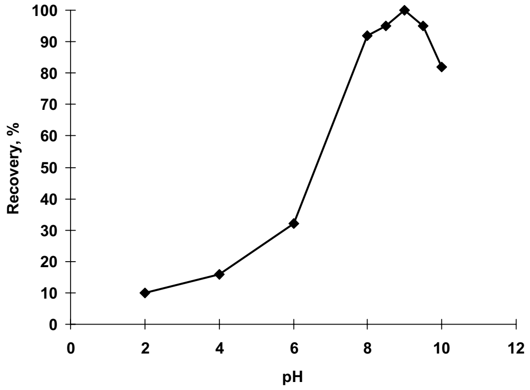

Figure 2. Effect of pH on the enrichment of copper(II) (n = 3)

Eluent type and volume

In order to achieve quantitative recovery values on the flow injection system presented for copper ions, various solutions including HNO_3 at the concentration range of 0.1–1.0 mol L^{-1} and HCl at 0.5 and 1.0 mol L^{-1} were tested for the elution of copper ions from the column. Quantitative recoveries were obtaining for all examined eluting solutions. The volume of the eluent solution was also examined by using 0.25 mol L^{-1} HNO_3 at 5.0 mL min^{-1} flow rate. The recovery of copper ions was not quantitative for eluent volumes smaller than 400 µL. For larger volumes, copper ions were quantitatively recovered. Therefore, the volume of 500 µL of 0.25 mol L^{-1} HNO_3 as eluent was used in the following experiments.

The stability and potential regeneration of the Ambersorb 563 column were also examined. The Ambersorb 563 column can be reused after regeneration with 1.0 mL of 1 mol L^{-1} HNO_3 and 10 mL of distilled water, respectively, and relatively stable up to 200 runs.

Flow rates

As the retention of copper ions on Ambersorb 563 depends on the flow rate of the sample solution, its effect was examined under the optimum conditions by passing 10 mL of the sample solution through the column. The effect of the sample and eluent loading rate on the preconcentration/separation of copper ions was investigated in the range of 1.0–8.5 mL min^{-1}. It was found that the recovery values for copper ions were quantitative within the entire range examined for both: th esample and the eluent solutions. Thus, a flow rate of 5.0 mL min^{-1} was employed as the sample and eluent flow rate.

Matrix effects

The influences of the various matrix ions on the on-line preconcentration of copper ions on Ambersorb 563 were also investigated. Tolerable amounts of foreign ions that gave less than a 5% error on the copper determination from 0.25 µg mL^{-1} copper ions solutions were evaluated. The recoveries were not affected up to 10 g L^{-1} of Na^+, 1 g L^{-1} of K^+, 1 g L^{-1} of Ca^{2+}, 2.5 g L^{-1} of Mg^{2+}, 15 g L^{-1} of Cl^- and 1 g L^{-1} of SO_4^{2-}. These amounts of foreign ions were not retained on the resin, prior to their easy elution from the column. The recoveries of sodium, potassium, magnesium and calcium ions were determined using flame photometer and/or FAAS and found to be less than 0.2%.

Analytical performance of the on-line preconcentration system

Calibration graph for the on-line preconcentration and elution for copper (0.0–5.0 µg mL^{-1}) was prepared under optimized conditions and found to be linear, according to the following equation:

$$A = 0.0006C \pm 0.0013 \qquad r = 0.9999\ (n = 15)$$

where A denotes absorbance and C is copper ions concentration in µg mL^{-1}. The average values of triple parallel determinations of each solution were taken to statistical calculations.

The analytical performance of the flow injection atomic absorption spectrometry system for the enrichment of copper(II) was examined. The enrichment factor for copper was 50. The detection limit for copper based on three times the standard deviations of the blank was 1.0 mg L^{-1} (n = 10). The relative standard deviation of copper determinations was 1.4%.

Determination of copper in water samples

The recovery analysis of the seawater samples from the Mediterranean Sea (Antalya, Turkey) spiked with various amounts of copper(II) such as 1.25, 2.5 and 5.0 µg was performed using the flow injection on-line separation/preconcentration system coupled to the flame atomic absorption spectrometry. The results given in Table 1 demonstrate that the presence of alkaline and alkaline earth metals in the samples had no significant effect on the recovery of copper ions.

Table 1. Analysis of seawater sample spiked with copper(II) (sample volume = 20 mL, n = 3)

Added, µg	Found, µg	Recovery, %
0	0.40 ± 0.01	–
1.25	1.64 ± 0.01	100 ± 1
2.5	2.80 ± 0.10	96 ± 4
5.0	5.30 ± 0.10	98 ± 2

The presented on-line preconcentration method preceded the GFAAS determination of copper in other water samples of various origin. The results found by flow injection FAAS and GFAAS are in good agrement, as shown in Table 2.

Table 2. Copper levels in various water samples (N = 4)

Sample	Concentration, µg L^{-1}	
	Present Work	GFAAS
Tap Water	3.46 ± 0.02	3.24
River Water (Zamanti)	3.11 ± 0.12	4.12
River Water (Karasu)	2.16 ± 0.17	2.02
Seawater I	3.59 ± 0.31	N.D.
Seawater II	3.79 ± 0.31	N.D.

N.D.: not determined.

Comparison with other preconcentration methods

Comparative data from recent papers on solid phase extraction of copper coupled with FAAS are summarized in Table 3. The preconcentration/separation method for copper presented in this study is the most promising since the preconcentration factor is 50. The detection limit of the system is superior to the other preconcentration/separation techniques for copper [25,27,29]. The matrix effects are reasonably suppressed. The elution can be easily performed with diluted nitric acid. The relative standard deviation for the copper determination is lower in comparison with some other methods [20,25,30]. The presented method also involves simpler apparatus and much lower equipment and running costs.

Table 3. Comparative data from recent papers on solid phase extraction coupled with the FAAS determination of copper

Analyte	Complexing media	Adsorbent	Eluent	Preconcentration factor	Detection limit, µg L^{-1}	Relative standard deviation, %	References
Cu	Calmagite	Amberlite XAD–2	1 mol L^{-1} HCl	32	0.15	2.7–6.0	20
Cu, Cd, Zn, Co	Ditihione	PTFE	MIBK	69.3	1.40	2.10	25
Cu	1,10-phenanthroline	RP-C18	Ethanol	32	0.3	3	26
Cu, Fe, Ni, Cd, Co, Zn	Pyrocatechol	Amberlite XAD–2	2 mol L^{-1} HCl	100	3.76	3.9	27
Cu, Cd	DDTC	C-18	Methanol	114	0.2	1.4	28
Cu	Cupferron	Benzophenone	Ethanol	–	5.5	4	29
Cu, Cr, Co, Fe, Pb	Calmagite	Cellulose nitrate	HCl	250	0.06	<10	30
Cu	Ammonia/ ammonium chloride buffer	Ambersorb 563	0.25 mol L^{-1} HNO_3	50	1.0	1.4	Present Work

CONCLUSION

A simple on-line preconcentration system for the flame atomic absorption spectrometric determination of copper(II) has been tested. The method permits fast and precise analysis of copper(II) content in water samples to be performed without any contamination. Not only water samples but also geological and biological samples and similar media can be investigated with the presented on-line method as well.

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