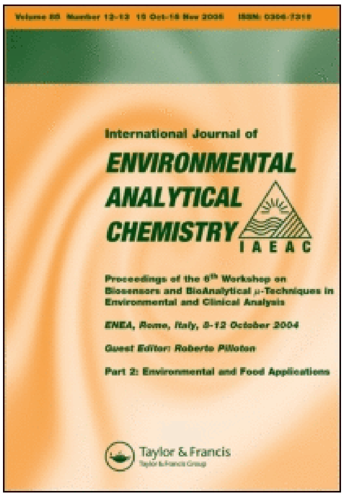

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APPLICATION OF A POLYETHYLENEIMINE—AGAROSE CHELATING ADSORBENT TO THE SAMPLING, PRECONCENTRATION AND FLAME AAS DETERMINATION OF COPPER IN TAP WATER

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A simple, inexpensive and rapid method has been developed for the determination of copper in tap water. The analyte is sampled with preconcentration on a recently synthesised polyethyleneimine—agarose chelating adsorbent and determined by flame atomic absorption spectrometry. The effects of sample flow rate, sample pH, adsorbent volume, eluent flow rate and sample matrix on the recovery of copper were investigated. It was found that a volume of only 0.05 ml of the adsorbent packed in a column (i.d. 5.7 mm) efficiently accumulated copper at flow rates up to 15 ml/min. A device for on-site sampling of tap water was constructed from a 60 ml syringe with the adsorbent packed in the conical outlet of the syringe. It was tested by 22 households and resulted in a mean recovery of 99 ± 10% for copper concentrations ranging between 8 and 650 μg/l.

KEY WORDS: Polyethyleneimine—Agarose adsorbent, sampling, preconcentration, copper analysis, tap water, flame atomic absorption spectrometry.

INTRODUCTION

Copper is one of the most frequently determined metals in potable water[1-11] because the local distribution system of pipes and tanks adds substantial amounts of the element to the water delivered from the water works. Hence it is essential in monitoring programs to sample the water at the tap. Moreover, the time the water has been allowed to flush before sampling can profoundly effect the copper concentration. Water that has been standing in the piping system often shows several times higher metal concentrations than water which has been running, for instance, for 10 minutes. Problems of a technical or esthetical nature may occur for copper concentrations exceeding 0.2 mg/l, while health effects, especially for bottle-fed children, appear for concentrations above 2 mg/l[12].

Several different instrumental techniques for metal determination have been used during recent years to directly quantify copper in tap water[1-4]. Flame atomic absorption spectrometry (FAAS) can sometimes be used directly[4], but generally requires a preconcentration step. A number of preconcentration techniques have been employed[5-11]. Columns containing chelating ion-exchangers or other adsorbents have been most widely used[7-11]. Disturbances from the matrix may sometimes be reduced or eliminated by the preconcentration step. FAAS is the preferred instrumental finish as it is widely available, less subject to disturbances than most other techniques and readily incorporated in a flow analysis system.

The aim of the present work has been to develop a simple procedure for the determination of copper in tap water for monitoring purposes. It should permit the sampling to be carried out by an untrained member of the household. The sample should also be in a form that allows it to be sent by ordinary mail to the laboratory for the copper determination. Adsorption of the copper on a solid would fulfil these requirements provided that a fairly selective high capacity adsorbent can be found. A small sampling column can then be used, which exhibits a moderate resistance to flow in order to make the sampling convenient for the user. The kinetics of the uptake must be rapid so that variations in the flow rate only marginally affect the efficiency of the column. A preconcentration factor of about 10 would be sufficient for a FAAS finish considering the concentration level previously given for the appearance of disturbances from the presence of copper. Since the analytical system is intended for monitoring purposes a fair accuracy, say of 10%, would be acceptable.

The preparation and properties of a chelating polyethyleneimine(PEI) metal adsorbent was recently reported[13]. The support is a crosslinked agarose gel with the trade name Novarose™. It is an efficient scavenger of transition metals, but does not accumulate alkali and alkaline earth metals. The large capacity of the adsorbent for copper (500 μmol/ml packed bed) and the fast kinetics of adsorption should make this adsorbent excellent for the preconcentration of this metal. It is not commercially available but is easily prepared by mixing PEI with Novarose in a carbonate buffer. The resulting hydrophilic material is stable with no change in performance after several hundred enrichments and its applicability for monitoring copper in tap water is evaluated here.

EXPERIMENTAL

Apparatus and analyses

Most studies of the preconcentration procedures were carried out with the TraceCon computer controlled flow analysis equipment (Knapp Logistics, Graz, Austria).

Copper concentrations in test solutions at the mg/l level were determined by FAAS, Perkin-Elmer 2380, using the 234.7 nm wavelength and a 0.7 nm spectral slit width. At the μg/l level, copper was measured by graphite furnace atomic absorption spectrometer (GFAAS), Perkin-Elmer 5000 (equipped with a HGA-400 graphite furnace and an AS-40 autosampler), using the platform technique. A sample volume of 20 μl without matrix modifier was injected, dried, charred at 1000°C and atomized at 2300°C. Direct analysis of tap water samples was carried out either by FAAS or by inductively coupled plasma atomic emission spectrometry (ICP-AES). The operational conditions for the ICP-AES (Spectro-flame, Spectro, Kleve, Germany) were; rf power 1.15 kW, fixed torch; flow rates, coolant 14 l/min, auxiliary 1 l/min and nebulizer 0.5 l/min; aspiration rate 2 ml/min, Meinhard nebulizer. Non acidic test samples were acidified with 100 μl of concentrated hydrochloric acid per 10 ml of sample before measurement. Evaluation was made from calibration curves obtained with matrix-matched standards.

pH was determined with a Radiometer PHM 84 (Radiometer, Copenhagen, Denmark) after calibration with certified buffers.

Reagents

The PEI-Novarose chelating adsorbent was prepared from polyethyleneimine (BASF AG, Ludwigshafen) with a molecular weight of 50 kD and Novarose (Inovata AB, Stockholm) with an exclusion limit of about 200 kD.

A copper(II) stock solution of about 1000 mg/l was prepared by dissolving the required amount of copper nitrate in de-ionized water. The solution was standardised by FAAS using AAS standards. The test solutions were prepared by dilution of this solution or a 1000 mg/l AAS standard.

Acetate buffers (pH 5.5) were prepared from ammonium acetate and acetic acid.

A synthetic tap water (STW) stock solution was made by dissolving analytical grade sodium carbonate, sodium chloride, and sodium sulfate in Milli-Q water to yield 370, 50 and 40 mmol/l of carbonate, chloride and sulphate, respectively. These concentrations are a hundred times larger than the average values for Swedish lake waters. No effort was made to include the major cations since they are not taken up by the PEI-Novarose adsorbent. The stock solution was diluted a 100 times and used as sample medium. Test solutions of copper(II) in STW were prepared by addition of the appropriate amount of a 100 mg/l copper stock solution. Adjustments of pH were made by addition of 1 M hydrochloric acid.

Enrichment

Columns (i.d. 5.7 mm) were packed using the previously described method[13] and the adsorbent was confined between two 25 μm frits (Omnifit, UK) and attached to the TraceCon apparatus. Usually a 0.1 ml column and a flow rate of the sample through the column of 5–6 ml/min were employed. The volumetric flow rate through the column could only be deliberately altered by changing the diameter of the tubing. It was calibrated after changing the tubings or columns and at the beginning of each set of experiments. Flow rates higher than about 9 ml/min could not be achieved because of the back pressure of the system, which also made it difficult to reach the same flow rate for different columns. Higher flow rates were investigated with manual enrichment using a 60 ml plastic syringe (BS 5081 A81 Sherword Medical, UK), for the injection of the sample and eluent. The column was connected to the syringe by a piece of rubber tubing.

The copper(II) solution was pumped through the column and the effluent was collected in either 10 or 20 ml portions for analysis. After the enrichment step the column was washed with 2 ml of 10 mM acetate buffer, pH 5.5, and then eluted by about 4 ml of 1 M hydrochloric acid. The eluted column was reconditioned with 15 ml of 0.1 M acetate buffer, pH 5.5.

In the experiments with direct aspiration of the adsorbent suspension into the flame, a column with only a bottom frit was used. After preconcentration, the column was disconnected from the TraceCon and the adsorbent pushed out and transferred to a graduated test tube by manual injection of a few ml of 1 M hydrochloric acid. The mixture was then diluted to volume with the same acid and directly aspirated into the flame, while it was homogenized by mechanical stirring.

Preconcentration and analysis of tap water

For the on-site copper preconcentration of tap water, the following procedure was used. The conical outlet of the 60 ml polypropylene syringe was used to accommodate the adsorbent column between two frits. The diameter of the frits was around 6.0 mm. About 0.05 ml of the adsorbent was used for the column. After packing, the 2 mm long column was washed with 5 ml of 1 M hydrochloric acid and conditioned by 10 ml of 0.1 M acetate buffer.

The following instructions were given for the sampling. The tap water should be left flushing for 10 minutes before sampling. Then the syringe should be filled with water up to the 50 ml mark, the plunger inserted and pushed down at a speed equivalent to less than 15 ml/min. This is conveniently accomplished by putting one hand on the plunger, while the syringe is held in a vertical position by the other hand which rests, for instance, on the faucet. The weight of the hand is sufficient to create a sample flow of about 12 to 15 ml/min.

On return to the laboratory, the enriched column was washed by a few ml of Milli-Q water, eluted by 4 ml of 1 M hydrochloric acid and analysed by FAAS.

RESULTS AND DISCUSSION

Effect of adsorbent volume, flow rate and sample concentration

The effect of adsorbent volume, flow rate and sample concentration on the uptake and recovery of copper was studied with standard solutions of copper(II) in 10 mM acetate buffer, pH 5.5. The efficiency of the adsorption was determined by measurement of the copper concentration in the effluent from a 40 ml sample by GFAAS after acidification by 100 μl of concentrated hydrochloric acid per 10 ml of effluent. The results are presented in Table 1 and demonstrate the very efficient uptake of copper by the PEI-Novarose adsorbent. Higher flow rates than about 9 ml/min could not be studied with the TraceCon apparatus due to the back pressure. The data indicate, however, that quantitative removal of Cu(II) would be obtained at even higher flow rates.

In one experiment 200 ml of a 20 μg/l copper solution were pumped through a 0.25 ml column at 5 ml/min. The concentration in the effluent was still < 0.1 μg/l at the end of the experiment. If necessary, copper can hence be enriched from large volumes.

Table 1 Copper concentrations (μg/l) in effluents after passage of 40 ml of test solution. Influence of copper concentration, flow rate and adsorbent volume.

Adsorbent volume (ml)	*Flow rate (ml/min)*	*Sample (μg/l)*	*Retained Cu (%)*
0.50	7.9	20	99.9
0.50	7.9	100	99.5
0.50	7.9	500	99.8
0.25	6.7	20	100
0.25	6.7	100	99.9
0.25	6.7	500	100
0.25	9.1	20	98.0
0.25	9.1	100	99.7
0.25	9.1	500	100
0.10	8.2	20	99.1
0.10	8.2	100	99.8
0.10	8.2	500	99.7

The performance of the adsorbent was also investigated by elution-recovery measurements. Solutions of copper(II) in 10 mM acetate ranging from 0 to 500 µg/l were enriched on a 0.1 ml column at a flow rate of 7.3 ml/min. The copper accumulated from 40 ml of the test sample was eluted by 4 ml of 1 M hydrochloric acid at 2.7 ml/min and analysed. The absorbances as a function of the initial copper concentration are shown in Figure 1. Fitting a straight line to the data yielded a correlation coefficient of 0.9998 and an intercept of 1.6×10^{-3} absorbance unit, which indicates that the recovery is independent of concentration and that there is no blank from the adsorbent. Comparison with the corresponding calibration curve for standards in 1 M hydrochloric acid yielded an average recovery of 98.2 ± 3.1%.

The experiments with standard solutions of Cu(II) thus show that a small column and a high flow rate can be used during preconcentration. These are optimal conditions for field sampling. Further the desorption of Cu(II) from the column proceeds smoothly. However, these properties have to be confirmed for real samples.

Preconcentration from synthetic tap water (STW)

The speciation of copper(II) in tap water will be different from that in acetate buffers due to differences in pH and anionic composition. Such differences most likely effect the uptake of the element by adsorbents. The copper-binding capacity of the PEI-Novarose adsorbent increases slightly with pH in acetate buffers and it does not adsorb the major cations of tap water[13]. The adsorbent is also an anion exchanger and used in its acetate form in the present work. Thc acetate ions will be partly replaced by the anions in the tap water during the preconcentration which might affect the subsequent determination of

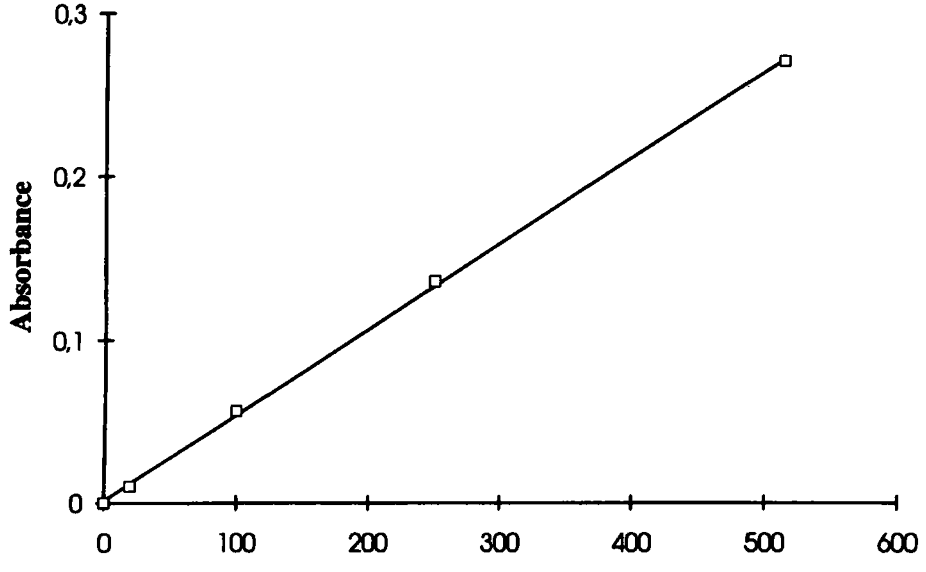

Figure 1 Absorbance of eluates as a function of sample concentration for the preconcentration of Cu(II) in 10 mM acetate buffer, pH 5.5. Column, 0.1 ml; sample volume, 40 ml; sample flow, 7.3 ml/min; eluent, 1 M HCl; eluent flow, 2.7 ml/min.

copper. The STW was used to study the tentative effect of pH and anionic composition on the recovery and quantification of copper in tap water.

The sensitivity of the FAAS determination of copper was compared for eluates from solutions of STW (pH 8.0), 10 mM acetate buffer (pH 5.5), and acetate buffered STW (pH 5.5). Portions of 10 ml of these solutions were passed through a 0.1 ml column, then eluted and spiked with copper(II). No significant change in the sensitivity between Cu(II) standards in 1 M hydrochloric acid and in the eluates was observed. A systematic study of the effect of hydrochloric acid and acetate concentrations on the sensitivity of copper determination by FAAS was also performed and no matrix effect was observed for mixtures of hydrochloric acid and acetate at concentrations up to 1 M and 0.03 M, respectively. Hence the calibration curve from standards in 1 M hydrochloric acid can be used.

The recovery of copper was compared for solutions of 0.5 mg/l of copper(II) in the three media mentioned above. Enrichment of 40 ml samples resulted in a recovery of 99–100% for the buffered samples. The recovery of the copper from the STW medium, pH 8.0, on the other hand, was only 89%. The low result for the STW, pH 8.0, medium could be an effect of slower adsorption kinetics of carbonate or hydroxide complexes in comparison with Cu^{2+}. This hypothesis was tested by measuring the recovery at different flow rates during the enrichment. Copper(II) solutions, 0.5 mg/l, in STW were passed through the 0.1 ml column at the flow rates 7.4, 5.2 and 2.7 ml/min. The recoveries were 88.2, 85.2 and 82.0%, respectively. The copper concentrations in the effluents from the column were 3.2, 1.1 and 0.4 µg/l, respectively, which shows that the retention of copper is better than 99% at all flow rates. The recovery for acetate buffered STW was close to 100% under the same conditions. The somewhat unexpected decrease in recovery with flow rate can be explained by adsorption of part of the copper in the flow system at high pH. If the kinetics of this adsorption is slow, the losses would increase with decreased flow rate as observed.

The effect of pH on the recovery was studied for 0.5 mg/l copper(II) solutions in the STW medium. Droplets of 1 M hydrochloric acid or 1 M sodium hydroxide were used for pH adjustment to 8.2, 7.2 and 6.0. The sample with pH 5.5, however, was buffered with 10 mM acetate for sufficient pH stability. The recovery changed from 88% at pH 8.2 to 104% at pH 5.5. The pH dependence of the recovery indicates that a pH adjustment of the tap water sample might be necessary before preconcentration in order to avoid losses.

Analysis of tap water

There are several organic[14] and inorganic substances in tap water, e g. humic substances and heavy metals, that may affect the preconcentration and quantification of copper. It is very difficult or even impossible to simulate such interferences in a synthetic tap water. They must therefore be revealed by analysis of real samples. Subramanian and co-workers[7] developed a two-column method to overcome the effect of metal complexation by humic substances in drinking water. A separation method for tap and sea water was designed by Hernández-Torres and Arias-Leon[9] for removal of potentially interfering ions such as Co(II), Ni(II), Zn(II) and Cd(II). No pretreatment of the tap water was made here.

The absence of matrix effects in the 1 M hydrochloric acid eluate from the column after preconcentration from tap water was confirmed by the agreement between the copper concentrations obtained by evaluation from the calibration curve and by the method of standard additions. Various tap waters, either containing a natural high concentration of copper or after spiking, were analysed directly after acidification by FAAS or after preconcentration at their natural pH of 7.5 with the TraceCon apparatus. These measurements resulted in recoveries around 88% which is surprisingly close to the result obtained for the STW medium and is probably due to the good quality of the water, which contains only 2 mg/l of dissolved organic matter. Analysis of the effluent showed that less than 2% of the copper passed unadsorbed through the column, again suggesting that the incomplete recovery is caused by losses in the TraceCon apparatus.

The effect of pH on the recovery of copper was studied by enrichment of 20 ml aliquots of a tap water sample adjusted to pH 8.3, 7.5, 7.0, 6.0 and 5.5, respectively. The corresponding recoveries found were 87.7, 91.6, 91.7, 97.4 and 100.5%. The decreasing recovery with pH in this pH range can be explained by hydrolysis of Cu(II) with the formation of species which can be adsorbed by the materials used in the equipment.

Acidification of the tap water by hydrochloric acid to pH 2 followed by adjustment to pH 5.5 with 35 mM acetate buffer resulted in the same recovery (100%) as the sample directly adjusted to pH 5.5. This indicates the absence of robust copper complexes which need decomposition.

The influence of flow rates of the eluent between 1 and 5.5 ml/min on the recovery was investigated for tap water samples with pH adjusted to 7.0 and 5.5. The results indicated that the recoveries, 89.2 ± 1.5 and 99.7 ± 2.6%, were independent of flow rate of the eluent.

Manual enrichment and field test of the column enrichment

A small column with an adsorbent permitting a high flow rate is desirable for manual on-site sampling and preconcentration. One of the main problems of the manual enrichment on a column is the fairly high resistance of the PEI-Novarose adsorbent to flow. By reducing the volume of the adsorbent to 0.05 ml (2 mm), the back pressure was diminished sufficiently for unstrained work. A sampling device allowing high flow rates was constructed from a graduated 60 ml plastic syringe and the adsorption column was packed between two frits in the slightly conical outlet from the syringe. The pressure from one hand, resting on the plunger, resulted in a flow of 12 to 15 ml/min. Thus 50 ml of the sample can be enriched in 3 to 4 minutes and yields a preconcentration factor of about 10, which is adequate for most tap waters. Larger volumes can, of course, be sampled by refilling the syringe with additional aliquots of the tap water.

The recovery of the syringe preconcentrator was tested on three tap water samples with the copper concentrations of 35.4, 175 and 277 µg/l as determined directly by ICP-AES. The natural pH of the samples was about 7.5. The pH of aliquots was decreased to 6.0 by addition of 1 M hydrochloric acid or to 6.2 by addition of sodium dihydrogen phosphate. With a flow rate of about 12 ml/min the mean recoveries of 100.6 ± 6.1, 99.5 ± 3.8% and 100.3 ± 7.4, were obtained for the samples with pH 7.5, 6.2 and 6.0, respectively. The high recovery at pH 7.5 is in contrast to previous results using the TraceCon apparatus for the enrichment. A possible explanation is that the extent of adsorption of copper at high pH is less in the syringe preconcentrator due to the fact that the sample is less exposed to surfaces than in previous experiments. At flow rates higher than 15 ml/min the recovery dropped, for instance, to about 90% at 25 ml/min. The results of this experiment suggest that there is no need for a pH adjustment of the sample prior to preconcentration as long as moderately precise results suffice. In this way the sampling and preconcentration procedure is substantially simplified.

A syringe preconcentrator and a 250 ml plastic bottle containing 25 ml of 1 M hydrochloric acid as the preservative were distributed to 22 households in different parts of Uppsala and its neighbourhood. These were instructed to flush the water for 10 minutes before filling the bottle and the syringe to the 50 ml mark. After insertion of the plunger the syringe should be emptied at a rate of 10 to 15 ml/min. The copper concentrations of the tap waters were determined by ICP-AES of the acidified samples and by FAAS after elution of the columns in the laboratory.

Table 2 summarises the results. The value of the copper concentration found for sample no. 22 is probably not far from the concentration in the mains, since it was collected at a site with no copper tubing installed. Most of the data therefore reflect the contamination of the water from the mains by the local distribution system. There is a reasonable agreement between the results from the ICP-AES determinations and the preconcentration procedure for most of the samples. Since the sampling has been done on-site and for each site by a different person, the somewhat large variation in recovery is reasonable. Explanations could be contamination, too fast sample flow rates as well as the fact that the reference and preconcentrated samples were not exactly the same. The reproducibility of the procedure was estimated by a separate experiment in which six syringe preconcentrators were prepared and used to sample water no. 1. The mean of the copper concentration was 111 μg/l with a RSD of 2.1% for the six replicates.

The column becomes coloured by the copper, which is adsorbed as a well defined band, which expands as the amount adsorbed increases. For a given sample volume, the width of the coloured layer is roughly proportional to the copper concentration. Any indication of a very thin blue layer at the top of the column after enrichment of 50 ml

Table 2 Copper concentrations in tap waters from the Uppsala region measured either directly by ICP-AES or, after manual preconcentration on a mini-column, by FAAS.

Sample No.	*Copper concentrations (μg/l)*		*Recovery (from the column) %*
	ICP-AES	*FAAS*	
1	118	113	95.8
2	45.8	47.8	104
3	17.4	14.6	84.1
4	18.7	19.6	105
5	154	148	96.1
6	122	109	89.3
7	655	640	97.7
8	311	285	91.6
9	194	176	91.2
10	403	374	92.8
11	164	161	98.2
12	106	118	111
13	167	129	77.3
14	92.0	106	115
15	149	140	93.8
16	235	239	100
17	79.3	89.7	113
18	191	194	102
19	19.8	23.0	116
20	176	202	115
21	237	227	95.9
22	8.2	8.1	99.0

Mean recovery: 99.3 ± 10.3%

corresponds to about 100 µg/l and the whole column becomes coloured at about 2000 µg/l. Hence the adsorbent can also be used for a simple semiquantitative estimate of copper concentrations in tap water. The column can be generated with a few ml of 0.1 M hydrochloric acid. The life-time is set by the irreversible adsorption of humic matter which discolours the initially white adsorbent.

Direct analysis of suspensions of the adsorbent

The PEI-Novarose adsorbent is quite hydrophilic and can be easily dispersed in an aqueous medium. Direct aspiration into the flame by use of an ordinary nebulizer was therefore tested as an alternative to elution. Since the particles of the adsorbent would be decomposed in the flame, this method should increase the recovery of copper in the case that the eluent did not efficiently desorb the copper from the adsorbent.

Preliminary experiments indicated that it is possible to aspirate a suspension of the adsorbent without clogging the nebulizer. Gentle shaking was sufficient to avoid sedimentation of the particles. No background absorbance was observed from 0.1 to 0.5 ml of absorbent dispersed in 10 ml of 1 M hydrochloric acid. The uptake and recovery of copper from accumulation in the batch mode were investigated in 10 mM acetate buffers. It was found that resuspension of the adsorbent in 0.15 M hydrochloric acid was sufficient to obtain quantitative recovery. In a complementary set of column experiment, 0.1 ml of adsorbent was enriched with copper(II) solutions in 10 mM acetate buffer. The adsorbent was pushed out of the column, suspended in 5 ml of 1 M hydrochloric acid and aspirated into the flame. The mean recovery for initial concentrations between 20 and 500 µg/l was 96.5 ± 3.3%. This figure is based on the calibration curve obtained with standards in 1 M hydrochloric acid.

Despite the good results obtained by direct aspiration of the adsorbent, the method was abandoned. No significant improvement in the recovery was observed from this method compared to elution of adsorbed copper by acid, while it made the analysis more time consuming and complicated. Furthermore, it was found that the adsorbent gradually accumulated in the mixing chamber of the AAS instrument which required regular cleaning.

CONCLUSION

The field experiments indicate that the syringe preconcentrator, or variations thereof, is a simple, cheap and convenient sampling device for monitoring work in which only moderate precision is needed. It requires no training before use and no handling of chemicals is involved. Even in the case that a preconcentration is unnecessary from the analytical point of view, sampling on an adsorbent is advantageous. Sending the analyte to the laboratory fixed on a small column is more handy than as a liquid sample in a container. In addition, copper may be precipitated or adsorbed on the container wall unless the sample is acidified.

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