A field flow preconcentration system for copper determination in seawater is described. Seawater samples are collected and preconcentrated in situ by passing them using a peristaltic pump through a minicolumn packed with Amberlite XAD-4 impregnated with the complexing agent 1-(2-pyridylazo)-2-naphthol. Thus, copper is preconcentrated without the interference of the saline matrix. Once in the laboratory, the minicolumns loaded with copper are incorporated on a flow injection system and eluted with a small volume of a 20% (v/v) ethanolic solution of 0.5 mol L$^{-1}$ hydrochloric acid into the nebuliser–burner system of a flame atomic absorption spectrometer. The analytical figures of merit for the determination of copper are as follows: detection limit (3σ), 0.06 µg L$^{-1}$; precision (RSD), 1.2% for 2 µg L$^{-1}$; enrichment factor, 30 (using 25 mL of sample and 83 µL of eluent). Analysis of certified reference materials (SLEW-3 and NASS-5) showed good agreement with the certified value. This procedure was applied to the determination of copper in seawater samples from Galicia (Spain).

**Introduction**

Copper is an essential trace element, a component of crustacean respiratory pigments such as hemocyanin, and is commonly present in the coastal marine environment, where it may reach levels toxic to both animals and plants. Increases in copper concentration in estuarine and coastal areas have resulted from industrial and domestic waste discharge, disposal of mining washings, refineries, and the use of copper as a base compound for antifouling paints.1

The determination of extremely low levels of heavy metals in seawater has received special attention as a way to assess the early impact of human sources on the marine environment. However, this evaluation can only be properly performed if the available data are highly precise and accurate. Hyphenation of flow injection sample processing with detection by electrothermal or flame atomic absorption spectrometry (FI-ETAAS or FI-FAAS) is a widely accepted method for trace analysis. Since its introduction, interest has been sustained in the application of flow injection analysis (FIA) techniques to the development of automated, on-line sample pretreatment procedures. Benefits are associated with flow injection separations: preconcentration techniques include high efficiency, simple on-line operation, rapidity, low sample reagent consumption, relatively simple and compact hardware, and freedom from contamination. Most FIA preconcentration methods are based on the use of a minicolumn containing a chelating resin or a solid sorbent, which can significantly reduce sample volume. Therefore, different methods have been applied for the determination of traces of Cu in seawater using FI-AAS methodologies. Sung et al.2 developed a FI accessory for copper preconcentration with Murumac A-1 resin and determination by ETAAS. Ivanova et al.3 described a FI system with on-line sorption of trace metals with ammonium pyrrolidinedithiocarbamate (APDC) or 8-hydroxyquinoline (HQ) in a knotted reactor (KR) coupled with ETAAS. Both reagents were compared for the KR sorption preconcentration of copper and nickel. Ali et al.4 applied 1-nitroso-2-naphthol as a complexing agent for on-line preconcentration of copper using RP-C$_{18}$ material in a microcolumn with FI-FAAS detection. Ferreira et al.5 proposed a procedure for separation and preconcentration of trace amounts of copper in seawater samples. This method is based on the on-line adsorption of copper onto a column of Amberlite XAD-2 loaded with calmagite reagent and determination by FAAS. In all these procedures, traditionally, water monitoring programs collecting discrete volumes of sample in precleaned storage containers, addition of reagents for sample preservation and transporting to the analytical laboratory were proposed. In addition, once at the laboratory, further chemical processes may be necessary before instrumental measurement. These processes tend to be labour intensive, time consuming and incompatible with the highly developed and automated instrumentation that is used in the second stage of the analytical process. Furthermore, the determination of trace metals in seawater is difficult due to various factors, the most important of which are very low element concentrations, high salt content of the sample matrix, and contamination or loss of elements from samples during sampling, preservation and pretreatment. The first two factors are dictated by the seawater medium and cannot be totally controlled, although their effects can be minimized, but any loss or contamination during sample storage and pretreatment is determined by the care taken in sample handling.6 The versatility of FIA is such that experiments need not be confined to the laboratory and preconcentration methods can be accomplished in the same place of sampling.7 Therefore, in order to optimise and improve the first stage of the analytical process (preliminary operations, involving sampling and sample pretreatment) to be placed on the same level of the other stages, the microcolumn field sampling (MFS) technique was proposed. In this technique water samples are processed in flow systems at the sampling site and trace elements of interest are immobilized on microcolumns. The microcolumns may then be returned to the laboratory and directly inserted into a FI system for on-line elution and quantitative analysis. In addition to the advantages.
of FIA methodology, the MFS technique achieved the following: high efficiency, rapidity, cost-effective and environmentally friendly sampling and analysis; improvement in data quality in speciation and ultratrace analysis; collection and transport of water samples (0.5–1 L) back to a laboratory is avoided; and the samples occupy a small space for convenient storage. In this way at present, only one method involving the MFS technique is available in the bibliography for copper determination in seawater. Nickson et al. proposed a field sample unit for the selective in situ preconcentration for 2 h at 0.5 mL min\(^{-1}\) of trace elements from natural waters. The microcolumn contains an imino diacetate resin and elution takes place into an ICP-MS system.

In this work, it is intended to contribute to the development of new MFS methods. Therefore, a new field flow preconcentration system (FFPS) for copper determination in seawater by FI-FAAS was designed. The association of FI-FAAS presents many advantages for trace metals detection and FAAS is not an expensive instrument. The aim of this study is to develop a simple MFS system because this FFPS does not need the incorporation of a channel to introduce a buffer solution. To reach this goal, Amberlite XAD-4 (polystyrene–divinylbenzene polymer with a high surface area of 725 m\(^2\) g\(^{-1}\)) was used as a solid sorbent to prepare a ligand-loaded resin. This substrate was impregnated with 1-(2-pyridylazo)-2-naphthol (PAN), a heterocyclic azo compound capable of forming complexes with copper at the pH of seawater (7.8–8.3), which avoids the modification of the sample pH and as a consequence ensures that the FFPS is the simplest possible. This is very important because the FFPS must be transported to and from the sampling site. This procedure was applied to the determination of copper in seawater samples from Galicia (Spain).

**Experimental**

**Reagents**

All chemicals were of analytical-reagent grade. A standard solution of 1000 \(\mu g\) mL\(^{-1}\) copper(II) was prepared from Cu(II) nitrate in 0.5 mol L\(^{-1}\) nitric acid (BDH Chemicals, Poole, Dorset, UK). From this solution, other diluted standard solutions were prepared daily. Hydrochloric acid (Merck) was diluted to 0.5 mol L\(^{-1}\) HCl in 20% (v/v) ethanol (Merck) was used as an eluent. Amberlite XAD-4 (20 mesh) was from Acros Organics, Morris Plains, NJ, USA. A 2.4 \(\times\) 10\(^{-4}\) mol L\(^{-1}\) solution of 1-(2-pyridylazo)-2-naphthol (PAN) (Acros Organics) was prepared in ethanol. The certified reference materials used were SLEW-3 (estuarine water) and NASS-5 (seawater) from the National Research Council of Canada. Ultrapure water of 18.3 MΩ cm resistivity obtained from a Milli-Q water purification system (Millipore) served for dilution and washing, respectively.

**Instrumentation and analytical procedures**

The FFPS consists of a Gilson Minipuls-3 peristaltic pump, fitted with a poly(vinyl chloride) tube, a Rheodyne (model 5301) switching valve, a 0.45 µm filter (Millipore) and a minicolumn manufactured from a PVC tube (65 \(\times\) 1.4 mm id) packed with 0.05 g of 20 mesh Amberlite XAD-4 impregnated with PAN. A portable alternator model 4600-HN (Honda) was used to connect the peristaltic pump for field preconcentration. A Perkin Elmer 5000 atomic absorption spectrometer, furnished with a copper hollow-cathode lamp, equipped with a deuterium lamp background corrector and an air-acetylene flame (21.0/2.0 L min\(^{-1}\)) as the atomiser was used as the detector for Cu. The peak height was measured at 324.8 nm. The aspiration flow-rate of the nebuliser was adjusted to be the same as the flow-rate of the FI channel (4.5 mL min\(^{-1}\)). The spectrometer output was connected to a Perkin Elmer 50 servograph recorder with a range of 5 mV. The signals measured were the heights of the absorbance peaks. A Crison standard pH meter with electrode Ingold U 455 was used. The flow system comprised a Gilson Minipuls-3 peristaltic pump, fitted with poly(vinyl chloride) tubes and a Rheodyne (model 5041) four-way valve.

**Minicolumns preparation.** Amberlite XAD-4 was kept for one day in methanol, then filtered off and air dried. Laboratory made minicolumns were manufactured from PVC tubing (65 \(\times\) 1.4 mm id) and were packed with 0.05 g of 20 mesh Amberlite XAD-4 (a slurry of copolymer beads was injected into the minicolumn with a syringe); the ends of the tube were fitted with glass wool to retain the copolymer beads in the tube. The resin bed was 45 mm long for a total volume of solid substrate of 70 µL. Once packed, the immobilisation of PAN was performed in dynamics with a flow manifold. A solution of PAN (2 \(\times\) 10\(^{-4}\) mol L\(^{-1}\)) was passed through the minicolumns at a flow rate of 1.5 mL min\(^{-1}\) for 20 min. Later, the minicolumns were rinsed with ultrapure water until any excess reagent was eliminated from the resin, removed from the flow manifold and then kept in a refrigerator. They are stable for at least 1 month stored in a refrigerator until the field sample preconcentration is accomplished. In this stage, eight minicolumns can be prepared at the same time (as many as the channels of the peristaltic pump). Minicolumns could be used repeatedly for several operational cycles (at least ten times). Used minicolumns were cleaned with 1 mol L\(^{-1}\) hydrochloric acid in 20% (v/v) ethanol.

**Field sample preconcentration.** The field sampling and in situ preconcentration procedure of copper was developed using the field flow preconcentration system (FFPS) depicted in Fig. 1. The seawater sample was pumped at 0.5 mL min\(^{-1}\) for a timed period through the minicolumn after on-line filtration with a 0.45 µm filter. Thus, the copper was retained on the minicolumn, and the sample matrix was sent to waste. After loading, the resin was washed with ultrapure water and the residual internal fluid drawn off. The dry minicolumns were then disconnected from the FFPS, placed in a portable refrigerator and returned to the laboratory where they were stored in a refrigerator until the analysis was accomplished. Minicolumn standards were prepared in the same manner by pumping through the appropriate Cu standard solution at pH 8. Minicolumn blanks were prepared by pumping through ultrapure water at pH 8. Calibration and blank columns were prepared in the laboratory using the FFPS shown in Fig. 2.

![Fig. 1] Field flow preconcentration system (FFPS). P, peristaltic pump; SV, switching valve; F, filter; MC, minicolumn; W, waste.
On-line elution and flame atomic absorption determination of copper. In order to determine the copper concentration, each minicolumn was connected sequentially to the FI manifold shown in Fig. 2. This is the simplest FI system, and the minicolumn was located immediately before the detector. The analysis procedure consists of injection of 83 μL of 0.5 mol L⁻¹ hydrochloric acid in 20% (v/v) ethanol into a carrier (ultrapure water pumped at 4.5 mL min⁻¹), equal to the FAAS aspiration flow rate. Thus, copper is released directly into the nebuliser of the spectrometer. Blanks (ultrapure water and artificial seawater) were run in parallel, the absorbance of which ranged between 0.000 and 0.001.

**Results and discussion**

In order to determine the optimum conditions for adsorption of PAN on Amberlite XAD-4, several flow rates were tested. Studies of the effect of the flow rate during minicolumn preparation were conducted with the volume-based system with a constant chelating reagent volume (10 mL), a concentration of 2 × 10⁻⁴ mol L⁻¹ PAN and 0.05 g of Amberlite XAD-4 placed on a minicolumn. The effluent of each solution tested as well as the original solutions of PAN were measured spectrophotometrically at 468.0 nm. The difference between the absorbance of each solution (before and after passing through the resin) provides the quantity of the chelating reagent adsorbed by the resin. Maximum adsorption of PAN on the resin was obtained between 0.5 and 1.5 mL min⁻¹. Adsorption was decreased dramatically at flow rates > 2 mL min⁻¹ owing to very short residence times of the chelating reagent in the minicolumn, which results in its incomplete adsorption (less than 40%).

To determine the optimum concentration of PAN, 10 mL of solutions containing from 5 × 10⁻⁵ to 5 × 10⁻⁴ mol L⁻¹ PAN were passed at 1.5 mL min⁻¹ through 0.05 g of Amberlite XAD-4 (pumping time 6.7 min). The results indicated high dependence of PAN concentration on its adsorption by Amberlite XAD-4. Thus, it was found that 67% of the PAN was adsorbed on the resin with concentrations above 2 × 10⁻⁴ mol L⁻¹ of this reagent. However, smaller concentrations achieved about 100% absorption. Therefore, a PAN flow rate of 1.5 mL min⁻¹ and a concentration of 2 × 10⁻⁴ mol L⁻¹ PAN were selected for subsequent work.

The experimental procedure for field sampling and in situ preconcentration was optimised by using the univariate method to establish the best chemical and flow conditions for the retention of copper. These optimisations were carried out in the laboratory. The chemical and flow variables were studied by continuously introducing a standard solution of 30 μg L⁻¹ copper into the FFPS (sample volume, 2.5 mL). Once the preconcentration step had taken place, the minicolumn was disconnected from the FFPS and then connected to the FI manifold. The eluent used was 3 mol L⁻¹ hydrochloric acid (volume 183 μL and flow rate 3.5 mL min⁻¹). Firstly, the effect of sample pH on copper retention was studied in the range 2–9 by adjusting the copper sample with dilute ammonia or nitric acid as required. The absorbance versus pH graph was plateau-shaped over all the pH range 6–9. As seawater is strongly buffered by the hydrogen carbonate–carbonate–carbon dioxide system at about pH 8.15 and this pH is included within the optimum sample pH range, the seawater sample can be directly preconcentrated into the FFPS with no pH adjustment. The influence of the sample flow rate on Cu(II) retention was examined over the range 0.2–3.5 mL min⁻¹ by using a constant sample volume of 2.5 mL. The maximum retention was obtained between 0.2–0.5 mL min⁻¹. Cu(II) retention decreased dramatically at flow rates > 0.7 mL min⁻¹ owing to very short residence time of the sample in the minicolumn, which results in its incomplete retention. In further studies, the flow rate was kept constant at 0.5 mL min⁻¹ in order to increase sample throughput.

Chemical and flow variables involved in continuous copper elution were also optimised. These variables were studied with minicolumns previously loaded with 0.075 μg of Cu(II). The elution of copper from the minicolumn was studied by using hydrochloric acid solutions at different concentrations as stripping agent. The results showed that elution of copper was quantitative at concentrations greater than 0.5 mol L⁻¹ (183 μL); lower concentrations gave only 30–60% recovery. However, when ethanol was added to the acid eluent (in a proportion of 20% v/v), only 83 μL were enough for the total elution of copper. This is explained because the addition of ethanol to the acid eluent favours the contact between the liquid and the resin beads. No carry-over (incomplete elution) was observed. The influence of the eluent flow rate on the peak height was examined in the range 2–5.5 mL min⁻¹. When changing the flow rate, the aspiration rate on the spectrometer was altered accordingly. The maximum absorbance signals were obtained between 4.0–4.5 mL min⁻¹. The signal decreased dramatically at flow rates > 5.0 mL min⁻¹ owing to the very short residence time of the eluent volume in the minicolumn, which resulted in incomplete elution of copper. A flow rate of 4.5 mL min⁻¹ was thus chosen in order to obtain high peaks and ensure optimal performance of the AAS instrument and to increase sampling frequency.

**Sample volume**

The high capacity of the minicolumn permitted large sample volumes to be preconcentrated without degradation in performance. Quantitative recovery was obtained from a solution of 30 μg L⁻¹ copper and sample volumes up to 15 mL (elucent volume 183 μL), and a solution of 1.0 μg L⁻¹ copper and sample volumes up to 200 mL (elucent volume 83 μL).

**Stability of the minicolumns**

Once loaded with the seawater sample, in order to establish how much time the minicolumns can be stored before the elution step, stability studies at optimum conditions were made. Minicolumns were kept 1, 2, 3, 7 and 15 d at room temperature and at 4 °C (refrigerator). Results obtained indicated that these minicolumns are stable during 2 d at room temperature (greater storage time gave only 40–16% copper recovery) and at least 15 d at 4 °C.

**Sorption capacity**

The sorption capacity of the Amberlite XAD-4 resin loaded with PAN for the retention of copper was also determined. Increasing amounts of copper were passed through a minicolumn containing 0.05 g of loaded resin. The results demonstrated that the resin has a sorption capacity of 2.4 μmol copper per gram of dry resin.
Analytical figures of merit

Under the optimum chemical and flow conditions, the manifolds depicted in Fig. 1 and Fig. 2 were used to run calibration graphs for copper determination with different sample volumes (2.5 and 25 mL). Equations of the calibration curves obtained are as follows: Calibration graph obtained by direct aspiration; absorbance = 1.5 × 10⁻⁴ + 5.8 × 10⁻⁵ C (n = 7), and C = 0–5000 µg L⁻¹ copper. Sample volume 2.5 mL; absorbance = 1.4 × 10⁻⁴ + 1.7 × 10⁻⁴ C (n = 7), and C = 0–75 µg L⁻¹ copper. Sample volume 25 mL; absorbance = 1.4 × 10⁻⁴ + 0.017 C (n = 7), and C = 0–7 µg L⁻¹ copper.

Experimental enrichment factors of 29.1 and 296.1 for 2.5 and 25 mL sample volume, respectively were obtained. These enrichment factors were calculated as the ratio between the slopes of the calibration graphs obtained by each sample volume used and the manual direct aspiration of copper. As the sample volumes used in the method were 2.5 and 25 mL and the injected eluent volume was 83 µL, the theoretical preconcentration factors should be 30.1 and 301, respectively, which demonstrates the good performance and the minimum dispersion of the FIA system.

The detection limits were calculated as three times the standard deviation of the peak height for 30 determinations of the blank (ultrapure water) and were 0.6 and 0.06 µg L⁻¹ copper. The precision of the FIA system demonstrates the good performance and the minimum dispersion of the FIA system.

The precision of the method obtained for standard solutions containing 0.5 (n = 11) and 2 (n = 11) µg L⁻¹ of copper were 4.7 and 1.2%, respectively, expressed as relative standard deviation. The preconcentration factor and detection limit can be further improved by increasing sample loading volume without degradation in the efficiency due to the favourable kinetics of the present system.

Study of interferences

A study of potential interferences and matrix ions of seawater in the determination of copper was performed. A relative error of less than 5% was considered to be within the range of experimental error. Synthetic solutions of 100 mL containing the most important elements present in seawater (concentrations chosen according to the elemental composition of seawater) were used as samples. The results obtained in these experiments (Table 1) demonstrate that the presence of large amounts of alkali and alkaline earth metals in the sample have no significant effect on the preconcentration of copper (1 µg L⁻¹). The effects of other ions at given concentrations are also negligible. When all the potential interferences were examined together to find out their combined effect on copper determination, a relative error of 2% was obtained. This shows that copper can be determined quantitatively in seawater samples.

Accuracy of the method

In order to study the accuracy of the method, certified reference materials (SLEW-3, estuarine water and NASS-5, seawater) with a copper content of 1.55 ± 0.12 µg L⁻¹ and 0.297 ± 0.046 µg L⁻¹, respectively were analysed. The copper content obtained (mean ± s, n = 3) are 1.55 ± 0.04 µg L⁻¹ and 0.30 ± 0.04 µg L⁻¹ and agree with the certified value.

Analysis of seawater samples

The proposed method, involving the use of FFPS and FI-FAAS was applied to the determination of Cu in seawater samples of Galician coast (Atlantic Ocean and Cantabrian Sea, Spain). The results obtained show values between 0.3 and 4.5 µg L⁻¹. The analytical recovery was also calculated by measuring the recovery of standard additions of copper to a seawater sample, which was spiked with different concentrations of copper (0.5 and 2.5 µg L⁻¹). Recovery values obtained are in the range 99.6–103%, which demonstrates the applicability of the method and indicates that the proposed method is essentially free from interferences when applied to the analysis of seawater samples.

Conclusions

The proposed fully portable FFPS shows the following interesting features: simple single-channel manifold because seawater samples can be directly preconcentrated with no pH adjustment, several samples can be preconcentrated at the same time, the minicolumn presents a high stability and the initial immobilisation of the reagent on Amberlite XAD-4 allows the use of the same minicolumn for several operational cycles. This FFPS minimizes the time between sample collection and preconcentration and so avoids the problems associated with sample transport and storage. The portable FFPS using an Amberlite XAD-4 minicolumn coated with PAF for FI-FAAS has been demonstrated to be promising for routine determinations of ultratrace amounts of copper in high saline matrices such as seawater due to its simplicity, high efficiency, high preconcentration factor and good selectivity and accuracy. In addition, sampling time is minimised with respect to the method proposed by Nickson et al. (50 min as compared to the 2 h that these researchers propose).

Acknowledgement

The authors are grateful for the financial support provided by the Galicia Government (Xunta de Galicia) in the framework of Project PGIDT99PX120901A.

Table 1 Interference study

<table>
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<th>Interferent</th>
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<sup>a</sup> All values are given as percentage variation in the atomic absorption signal.
References