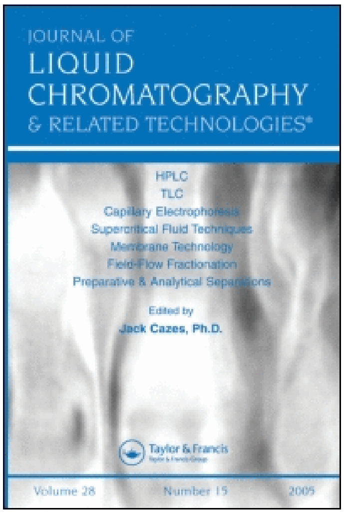

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Flow Analysis Method Using Chelating CIM Monolithic Disks for Monitoring Dissolved Labile Copper in Environmental Water Samples

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Abstract: A low pressure flow analysis system incorporating a chelating monolithic disc for the selective retention and elution of Cu(II) from within environmental samples, is reported. Three monolithic discs were modified with either picolinic acid, dipicolinic acid, or dodecyliminodiacetic acid and the extraction and elution efficiency of Cu(II) on the three chelating phases compared. The dipicolinic acid disc showed the highest capacity and linear range for Cu(II) and was incorporated into a flow analysis system, using chemiluminescence detection based on the measurement of light emitted from the Cu(II) catalysed oxidation of 1,10-phenanthroline by hydrogen peroxide. The system gave a linear response ($R^2 = 0.998$) over the concentration range 0-125 μg L^{-1} in simulated seawater, with detection limits for Cu(II) of 5 μg L^{-1} in a sample volume of just 220 μL. Accuracy was determined using a standard reference material (SRM 1640) and the method applied to estuary and coastal seawater samples.

Keywords: Monolithic chelating disc, Dipicolinic acid, Extraction of copper ions, Saline samples, Chemiluminescent detection

INTRODUCTION

The use of chemiluminescence reactions for the determination of dissolved trace metals has become a popular choice over recent years, requiring only

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simple and inexpensive instrumentation in comparison to more complex instrumental methods such as atomic absorption spectroscopy (AAS), inductively coupled plasma techniques (ICP), and other spectrophotometric techniques, which have traditionally been used for trace metal determinations.[1] Chemiluminescence detection can offer high sensitivity for many target analytes, however complete selectivity is necessary for quantitative analysis and this often requires the inclusion in the method of a separation step. Chemiluminescence is commonly used in flow injection analysis (FIA) due to its low limits of detection, high precision, and fast sample throughput.

One well known chemiluminescence reaction used for the determination of Cu(II) is based on the formation of a complex between Cu(II) and 1,10-phenanthroline.[2–4] The chemiluminescence reaction, which emits between 445 – 450 nm, involves the reaction of Cu(II) in the sample with 1,10-phenanthroline, and the subsequent release of photons from the oxidative destruction of the Cu(II)-1,10-phenanthroline complex by hydrogen peroxide at an alkaline pH. This reaction is popular due to its sensitivity for Cu(II), but metal ions such as Ca(II), Mg(II), Pb(II), Zn(II), Fe(II), and Fe(III), when present in large excess, have all been found to interfere with this chemiluminescence reaction.[2,5] For example, in a study carried out by Coale et al.,[2] it was found that high concentrations of Mg(II) present in seawater (0.05 M) caused a 100-fold reduction in the intensity of chemiluminescence when the seawater sample was injected directly into the system. As a result, a preconcentration step was employed using a packed column of immobilised 8-hydroxyquinoline (8-HQ) to preconcentrate and remove the matrix interference. The analysis of samples containing less than 0.3 $\mu g\ L^{-1}$ Cu(II) in undiluted seawater were successfully carried out, and resulted in low detection limits (0.02 $\mu g\ L^{-1}$) being obtained when this preconcentration step was used. A similar approach was carried out by Tyrrell et al. using an on-line itaconic acid functionalised packed column for the analysis of samples containing 1 $\mu g\ L^{-1}$ Cu(II) and high concentrations of Ca(II) and Mg(II).[6]

For the efficient low pressure extraction of trace metals from high ionic strength samples, monolithic chelating phases offer several advantages over traditional particle packed columns. Monolithic polymer materials consist of a continuous unitary porous structure that is made from in-situ polymerisation or consolidation inside the column or disc housing.[7] Typical characteristics of such materials include a high degree of flow through porosity combined with a relatively large surface area and a structure resistant to void and channel formation. The combination of these characteristics means very short monolithic columns or discs can be readily incorporated into low pressure flow systems such as FIA, and utilised for either simple separations and matrix elimination or rapid sample preconcentration. In the past, such phases have been used in a limited way for rapid bioseparations,[8,9] however, since commercial Convective-Interaction Media (CIM®) monolithic discs became available in 1998[10] other applications have begun to appear.

These commercial monoliths consist of a continuous, homogenous methacrylate or styrene-divinylbenzene rigid polymer structure, crosslinked with three dimensional interconnected channels with over 60% porosity. The macrochannels are approximately 1,500 nm in diameter, with mesochannels of less than 100 nm in diameter. The larger channels result in the low backpressure associated with the material, while the mesochannels provide a large surface area for adsorption or modification.

A large range of well characterised chelating ligands are available, which could be used to modify the above monolithic discs. Commonly used chelating ligands for complexing transition metals often possess carboxylic acid functional groups, due to their favourable complexation kinetics and selectivity for transition metals over alkali and alkaline earth metals.[11] For example, picolinic acid (2-pyridinecarboxylic acid) has been successfully used as an on-column chelating agent for the chromatographic separation of a range of transition metals, including Mn(II), Cu(II), Ni(II), Co(II), Cd(II), and Zn(II) in industrial waste water,[12] as well as the separation of lanthanides[13] and the determination of rare earth metals.[14] Dipicolinic acid (2,6-pyridinedicarboxylic acid) also has strong a complexing ability, and has been used for a number of applications involving the complexation of transition and alkaline earth metals.[15–18]

Iminodiacetic acid (IDA) is also commonly used for the complexation of transition metal cations, as a review by Nickson et al. for the analysis of samples such as seawater, river water, brines, and snow illustrates.[19] Other separation work involving the use of IDA chelating phases includes the separation of trace alkaline earth metals in brines[20] and the separation of lanthanides.[21]

In the work described here, the results of an investigation into the use of three carboxylic acid based chelating ligands, namely picolinic acid, dipicolinic acid, and dodecyliminodiacetic acid, for the modification of CIM® monolithic disks, and the application of these chelating disks for the extraction and elution of Cu(II) ions from saline samples within a flow analysis system is presented. Each 3 mm long disc was coated and characterised for relative copper recovery from simulated seawater matrices, relative disc capacity, and elution behaviour for Cu(II). The most suitable disc was used within the flow analysis system for the selective retention of Cu(II) ions and their rapid elution into a reagent stream for subsequent chemiluminescence detection.

EXPERIMENTAL

Flow Analysis System

A schematic of the flow analysis instrumentation used in this work is shown in Figure 1. Initially, the system consisted of a variable speed, 10 roller model

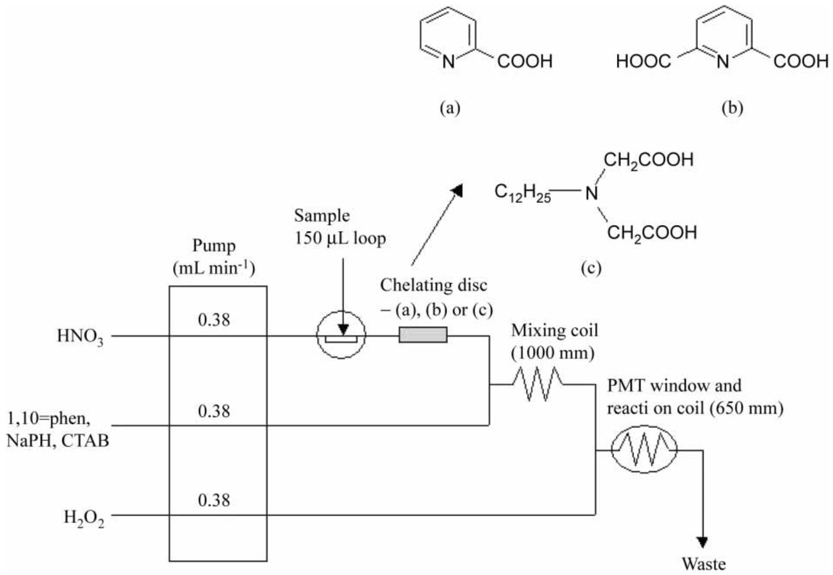

Figure 1. Schematic diagram of the flow manifold used for the determination of Cu(II) incorporating the monolithic disc, and the structures of the three chelating ligands used for modification, (a) picolinic acid, (b) dipicolinic acid, and (c) dodecyliminodiacetic acid.

peristaltic pump (Gilson Minipuls 312, Villiers, France), which provided a combined carrier/eluent and post-disc reagent flow rate of 1.14 mL $\min^{-1}$ (later 1.43 mL $\min^{-1}$), and a six-port Rheodyne Model 7125 rotary injection valve, (Rheodyne, Cotati, CA, USA) fitted with a 150 μL sample loop (later 220 μL). The detection flow cell used consisted of a 650 mm coil of a 0.6 mm I.D. transparent polyethylene (PE) tubing, tightly spiralled in a coil to a diameter of 25.4 mm, total volume 184 μL and fixed onto the front of a photomultiplier tube (PMT) supplied by Hamamatsu Photonics UK (Herts., U.K), so that the spiral flow cell faced the PMT window. The PMT used in this work for detection purposes was the H9319-02 multialkali series. The PMT was approximately 135 mm in height and provided a 22 mm diameter active area. In this work, the chemiluminescence occurred between 445 and 450 nm, and the PMT spectral range was from 300 nm to 850 nm. The PMT was operated in photon counting mode and the signal was recorded, and the data processed using Microsoft Excel. The complete flow manifold and PMT was completely enclosed in a light tight box. All tubing used in this system, except the peristaltic tubing (standard PVC peristaltic tubing) and detection flow cell tubing (PE tubing), was narrow bore PEEK tubing (0.127 mm I.D.) obtained from Alltech Associates Applied Science Ltd. (Lancashire, England).

Monolithic Discs

CIM® monolithic disc columns (BIA Separations, Slovenia) used here were reversed-phase styrene-divinylbenzene co-polymer discs (RP-SDVB). It is possible to accommodate up to four disks per housing, which can be used at a flow rate of up to 10 mL min^{-1} and a back-pressure of up to 50 Barr. They are stable within the pH range of pH 2.0 to 12.0 and at various ionic strengths. The disc dimensions were 16 mm in diameter and 3 mm in thickness, with a total volume of just 0.34 mL. Three different carboxylic acid containing chelating ligands, namely picolinic acid, dipicolinic acid, and dodecyliminodiacetic acid were employed for the modification of the monolithic discs. Picolinic and dipicolinic acid were obtained from Sigma Aldrich Ltd., Dublin, Ireland. Dodecyliminoacetic acid was synthesised in house as follows: 4.77 g of chloroacetic acid was dissolved in 2.50 mL of ethanol (pH 9.5 NaOH). The chloracetate solution was then added to a 5.0 mL ethanol solution containing 4.6 g of dodecylamine. The combined solution was stirred and gently heated for 4 hrs and finally boiled until a solid precipitate resulted. The product was then dissolved in 70 mL of DI. This was once again boiled and then cooled in an ice bath resulting in a pearl like fine grained precipitate, which was filtered and dried in an oven at 60°C for 12 hr.

For disc modification, the acids were prepared as a 10 mM solution in DI water, filtered, and 25 mL of the solution pumped through the monolithic disc using a peristaltic pump. The discs were then washed thoroughly with DI water to remove excess non adsorbed reagent. It was possible to reuse the discs, as the sorbed layer could be quantitatively stripped from the disc by washing with a 1.0 M sodium hydroxide solution, followed by washing with 0.1% trifluoroacetic acid (TFA) in iso-propanol (IPA), allowing further modification of the disc by the same or a different reagent.

Reagents

All reagents were of analytical reagent grade and were used as is unless stated otherwise. All solutions were prepared with ultra pure water obtained from Sigma Aldrich Ltd., Dublin, Ireland, unless otherwise specified. All the solutions were degassed using sonication to ensure reagent dissolution and homogeneity and filtered through a 0.45 μm nylon membrane filter from Gelman Laboratories (Michigan, USA) prior to use. Normal precautions for trace metal analysis were taken, including acid washing of all glassware and plastic containers to remove contamination.

The carrier solution used for sample loading was simply ultra pure water and the eluent used was a 25 mM nitric acid solution (69% w/v, BDH Laboratory Supplies, Poole, England). For chemiluminescence detection, a reagent solution containing 0.06 mM 1,10-phenanthroline (BDH Laboratory Supplies, Poole, England) made from a 12 mM stock solution, 1.3 mM surfactant cetyltrimethylammonium bromide (CTAB) (obtained from BDH Laboratory Supplies, Poole, England), and 0.075 M sodium hydroxide (Sigma Aldrich Ltd., Dublin, Ireland) was prepared. This solution was prepared using ultra pure water and was made up fresh each day. The 12 mM stock solution of 1,10-phenanthroline was found to be stable for several days and was initially purified, prior to use, by recrystalisation using nitric acid (69% w/v, BDH Laboratory Supplies, Poole, England). In addition a 5% w/v hydrogen peroxide solution was made up from a 27.5% w/v hydrogen peroxide solution (Sigma Aldrich Ltd., Dublin, Ireland) in ultra pure water. This was prepared freshly each day as the reagent was unstable over time, which would lead to a decrease in the overall sensitivity of the analysis.

A synthetic seawater sample was made up containing approximately 0.5 M sodium chloride, 400 mg L^{-1} Ca(II) and 1,300 mg L^{-1} Mg(II) (chloride salts obtained from Sigma Aldrich Ltd., Dublin, Ireland). Actual water samples used in this work were taken from a coastal seawater sight (Portmarnock Beach, Co. Dublin) and an estuarine sight (Malahide Estuary, Co. Dublin). For the analysis of Ca(II) and Mg(II) in synthetic seawater mixtures, a post-disc reagent containing 0.4 mM *o*-cresolphthalein complexone (*o*-CPC) (Sigma Aldrich Ltd., Dublin, Ireland), 0.25 M boric acid adjusted to pH 10.5 with sodium hydroxide was used, and mixed with the eluate at a ratio of 1:1, prior to absorbance detection at 570 nm.

Sample Analysis

The sample was introduced into the flowing carrier stream of ultra pure water, which was used to load the set volume of sample onto the chelating monolithic disc. Unretained matrix components were eluted from the disc with the carrier solution. The carrier line was then switched to the nitric acid eluent, which was used to elute the Cu(II) from the disc, which was then mixed with the 1,10-phenanthroline solution at a T piece merging connection. The sample and 1,10-phenanthroline solution were mixed together in a 1,000 mm mixing coil of PEEK tubing prior to merging with the hydrogen peroxide solution through a second T piece connection. The length of tubing between the second T piece, where the sample and reagent streams merge, and the detection flow cell, where the chemiluminescence emission occurs, was kept as short as physically possible (approximately 50 mm) to ensure a rapid passage of solutions into the reaction cell since the chemiluminescence reaction occurs almost instantaneously. The chelating disc was finally switched back to the carrier stream of ultra pure water to equilibrate prior to the next injection.

RESULTS AND DISCUSSION

Optimisation and Selectivity of the Chemiluminescence Reagent

Using a basic flow analysis system, three of the chemiluminescent reagent components were optimised for maximum sensitivity for Cu(II). These were the concentrations of 1,10-phenanthroline, the CTAB surfactant and hydrogen peroxide. The concentrations of 1,10-phenanthroline and CTAB were both optimised simultaneously, to show the combined effects on the Cu(II) signal. By keeping the concentrations of the nitric acid eluent, NaOH and peroxide solution constant, the optimum concentrations of 1,10-phenanthroline and CTAB could be determined. From systematic variation, the highest signal to noise ratio was achieved when using 0.06 mM 1,10-phenanthroline and 1.3 mM CTAB. Following this, the concentration of hydrogen peroxide solution was varied from 2.5% to 15% w/v, while keeping the remaining reagent concentrations constant. Here it was found that a 5% peroxide solution resulted in the highest analytical signal for a Cu(II) standard, with little difference in background noise, even though in some of the literature a 10% hydrogen peroxide solution was used.[3]

The selectivity of the chemiluminecent reaction used in this work is well documented elsewhere.[2,5,6] The reaction shows no response for alkali metal ions and little or no response for Ag(I), Cr(III) or Cr(VI), Hg(II), Mn(II), Zn(II), Ni(II), Cd(II), Co(II), Pb(II), Al(III), Fe(II) or Fe(III), and various other less common metal ions, at concentrations of up to several orders of magnitude above those found in typical seawater samples.[2] However, for solutions containing Ca(II) or Mg(II), such as most natural matrices, strong interference is seen, even for concentrations as low as 1 mg L^{-1},[22] with Coale et al. reporting the concentration of Mg(II) present in seawater causing a 100-fold reduction in the signal for Cu(II).[2] Anions have also been shown to effect the response for Cu(II), although nitrate, carbonate, sulphate, chloride, bromide, oxalate, and arsenate can be tolerated up to 100 mg L^{-1}, with iodide tolerable up to 50 mg L^{-1} and phosphate up to 10 mg L^{-1}.[22] From the above, it is clear that the use of the chelating disc to remove the NaCl matrix and the high concentration of Ca(II) and Mg(II) is required for estuarine and coastal seawater analysis.

Comparison of Chelating Discs

Using the flow analysis system shown in Figure 1 with the optimised detection conditions described above, a sample loading and recovery study was carried out on each of the three chelating discs at concentrations ranging from 0 to 250 μg L^{-1} based upon a sample volume of 150 μL ($n = 6$). All injections were injected in duplicate and recovery and linearity data was based upon average blank adjusted peak heights. Figure 2 shows the resultant peaks for

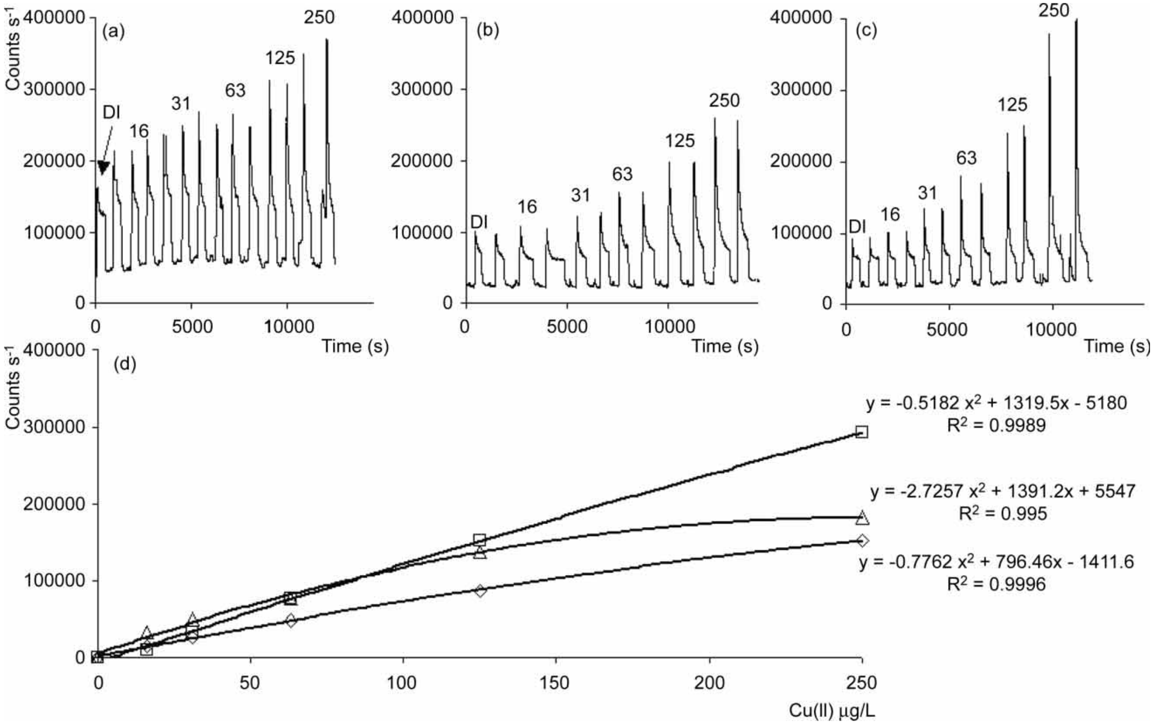

Figure 2. Detector responses for Cu(II) standards obtained using (a) picolinic acid modified disc compared to (b) the dipicolinic acid modified disc, and (c) the dodecyliminodiacetic acid modified disc. Figure 2(d) shows the plotted blank adjusted peak heights. Sample volume = 150 μL, total flow rate = 1.14 mL min^{-1}.

the above calibrations standards for (a) the picolinic acid disc, (b) the dodecyliminoacetic acid disc, and (c) the dipicolinic acid disc. In all cases, the switching from the water carrier to the acid eluent caused a baseline change upon which the signal for the eluted Cu(II) can be seen. All three discs showed acceptable linearity over the concentration range 0 to 125 μg L^{-1}. However, the dipicolinic acid column showed an increased linear response up to 250 μg L^{-1} (linear regression correlation coefficient of $R^2 = 0.998$). Table 1 shows the relative blank adjusted responses (relative recovery) for Cu(II) at each concentration on each chelating disc (relative to picolinic acid coated disc). As Table 1 and Figure 2(d) shows, both the dipicolinic acid and dodecylaiminoacetic acid discs perform similarly well up to 125 μg L^{-1} Cu(II), at which point recovery of Cu(II) on the dodecyliminoacetic acid disc drops off rapidly, indicating an overall lower capacity than the two pyridine based acids. The lower recovery data for the picolinic acid disc across the concentration range is a reflection of a relatively low affinity for Cu(II), due to only the single carboxylic acid group. While the nitrogen present in the pyridine ring of the dipicolinic acid holds the two carboxylate groups rigidly, thus, favouring the formation of metal complexes.

Dipicolinic Acid Discs

From the above comparison study, the dipicolinic acid disc was chosen for further study. First, the selectivity of the disc for Cu(II) under varying concentrations of nitric acid was evaluated. Standards of 50 μg L^{-1} Cu(II) were injected onto the disc in eluents ranging from 2.5 to 50 mM HNO_3. Figure 3(a) shows the responses obtained. At 2.5 mM and below, Cu(II)

Table 1. Comparative linearity and recovery data for chelating monolithic discs

Disc	Picolinic acid	Dipicolinic acid	Dodecyliminoacetic acid	
Linear range μg L^{-1}	0–125	0–250	0–125 (in synthetic seawater)	0–125
R^2	0.981	0.998	0.974	0.995
Slope	1039	1189	799	691
Rel. recovery μg L^{-1}				
16	1.0	0.7	0.5	2.3
31	1.0	1.3	0.9	1.9
63	1.0	1.6	1.1	1.6
125	1.0	1.7	1.2	1.6
250	1.0	1.9	1.3	1.2
Reproducibility N = 10	<3.9%	<4.0%		<2.5%

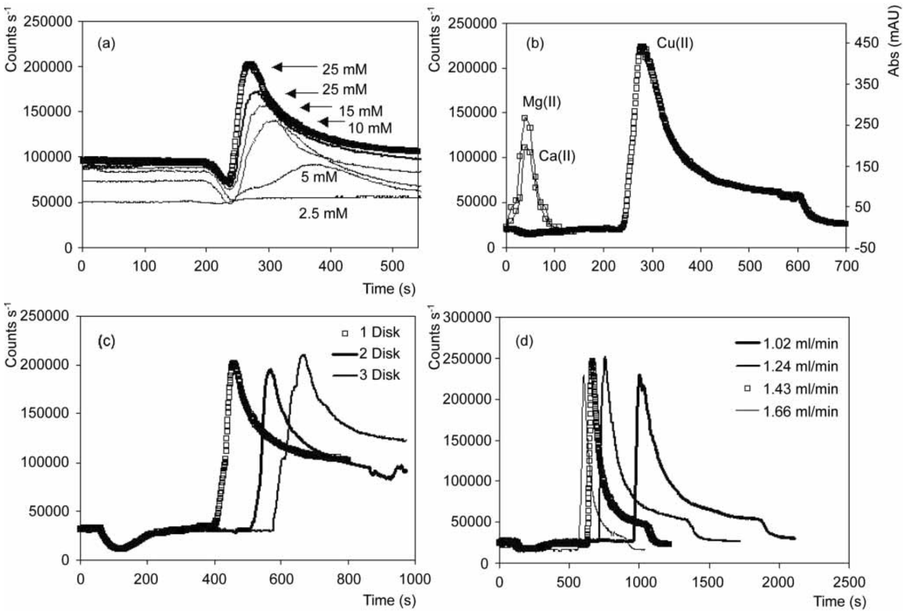

Figure 3. (a) Retention of Cu(II) on dipicolinic acid monolithic disc with increasing HNO_3 eluent concentration. (b) Reaction peaks generated for synthetic seawater sample spiked with 250 μg L^{-1} Cu(II) with unretained Ca(II) and Mg(II) peaks detected by visible absorbance detection. (c) Extraction from synthetic seawater and elution with 25 mM HNO_3 of 50 μg l^{-1} Cu(II) from single (3 mm), double (6 mm), and triple (9 mm) dipicolinic acid modified monolithic discs. (d) Effect of eluent flow rate on peak shape of Cu(II) eluted from single 3 mm dipicolinic acid disc. Other conditions: Total flow rate of 1.14 mL min^{-1} and sample loop size of 150 μL. Chemiluminescence reagents: 0.06 mM 1,10-phenanthroline, 1.3 mM CTAB, 0.075 M NaOH, 5% H_2O_2, and 25 mM HNO_3. Visible reagents: 5 mM HNO_3 and 0.4 mm *o*-CPC with 0.25 M boric acid, detected at 570 nm.

was completely retained on the disc. From 2.5 mM up to 25 mM the retention of Cu(II) gradually decreased. Above 25 mM, the signal for Cu(II) decreased considerably due to a decrease in the pH of the subsequent chemiluminescence reaction. Therefore, Figure 3(a) shows complete Cu(II) removal by the dipicolinic acid disc from the 2.5 mM HNO_3 eluent or water, and its complete elution using the 25 mM HNO_3.

The separation of excess Ca(II) and Mg(II) from Cu(II) using the dipicolinic acid disc was investigated using a synthetic seawater matrix containing 0.5 M sodium chloride, 400 mg L^{-1} Ca(II), and 1,300 mg L^{-1} Mg(II), spiked with varying concentrations of Cu(II), from 0 to 250 μg L^{-1} ($n = 6$). The eluate from the disc following injection of these mixed standards was monitoring using both chemiluminescence and visible absorbance spectrophotometry at 570 nm, following post-disc reaction with *o*-CPC. The resultant peaks showed the synthetic seawater matrix had some effect upon the recovery of Cu(II) by the dipicolinic acid disc. First, the linear range was reduced down from 250 μg L^{-1} to 125 μg L^{-1} (0 to 125 μg L^{-1}, $n = 5$, $R^2 = 0.974$), and secondly, the calibration slope was reduced by ~ 30% (data included in Table 1).

Figure 4(b) shows the Ca(II) and Mg(II) detected using visible detection overlaid on the chemiluminescence signal produced for a 250 mg L^{-1} Cu(II) standard made up in the synthetic seawater matrix. As can be seen, the signals measured for the Ca(II) and Mg(II) correspond well to the negative peak on the Cu(II) chemiluminescence signal, thus verifying the interference in the chemiluminescent detection signal that Ca(II) and Mg(II) present in the seawater matrix can cause, and that both are completely unretained on the monolithic disc.

It is possible to accommodate up to four monolithic discs per housing, and so the effect of increasing the number of chelating discs was investigated. Using three dipicolinic acid coated discs (total length 9 mm), a Cu(II) standard in the synthetic seawater matrix (50 μg L^{-1}) was injected into the carrier stream of ultra pure water at time = 0, then at time = 300 s the carrier line was switched to the nitric acid line for elution purposes. The same was carried out on a double disc and a single disc for comparison. It was found that the retention of the Cu(II) increased with the number of modified discs used in the system, from an unadjusted retention time of 405 s for a single disc up to 621 s for the triple discs. However, as shown in Figure 3(c), the use of increased discs, although resulting in a slight increase in peak area for Cu(II) (higher capacity giving an improved recovery), did not result in any significant peak height increase for Cu(II), due to the eluting peak width increasing by a similar factor, ~25%. Therefore, for simplicity and analysis time, a single chelating disc was deemed appropriate.

Analysis of a Certified Reference Water Sample

The accuracy of this method was verified using an international certified standard reference material from the National Institute of Standards and

Technology (NIST). This sample SRM 1640 freshwater standard was acidified with 0.5 mol L^{-1} nitric acid and was certified to contain 85.2 μg L^{-1} ± 1.2 μg L^{-1} Cu(II), together with 29 mg L^{-1} Na, 5.8 mg L^{-1} Mg(II), and 7.0 mg L^{-1} Ca(II), together with a full spectrum of common transition and heavy metal ions from between 20 and 150 μg L^{-1}. The sample was neutralised using a dilute hydroxide solution and was diluted by 50% with ultra pure water. A sample blank and the diluted sample were analysed in a similar way to the Cu(II) standards and, based on peak heights, the blank adjusted signal for the diluted SRM sample was calculated. The signal for the sample corresponded to approximately 44 μg L^{-1} for the 1 in 2 dilution and approximately 88 μg L^{-1} in the undiluted sample. This compared well to the certified value of 85.2 μg L^{-1}. The results for the analysis of the SRM 1640 sample are shown as Figure 4. As can be seen from Figure 4(b), a positive peak is shown to elute at ~500 s, which is the signal for unretained matrix cations which would otherwise cause a positive interference in the results obtained.

Analysis of Estuary and Coastal Seawater Samples

The method was then used for the analysis of fresh estuarine and coastal seawater samples. Both of the samples were analysed in the same way. Aliquots of each sample was spiked with increasing concentrations of Cu(II) and analysed by the system. The experimental conditions were similar to those used previously. Figure 5(a) shows the reaction peaks generated for the estuarine sample itself, followed by aliquots spiked with increasing Cu(II), (concentration range 0 to 250 μg L^{-1}). The negative detection response due

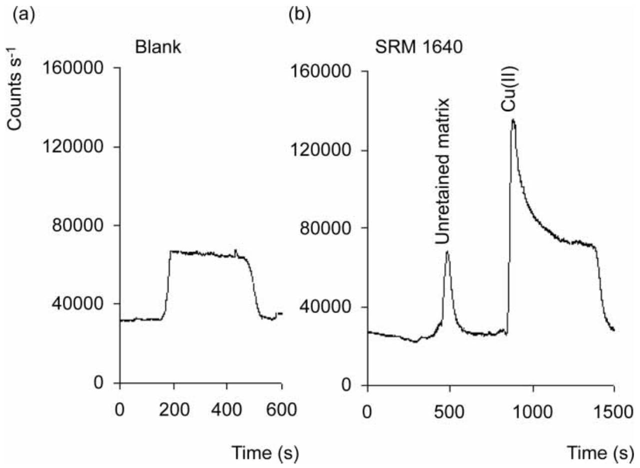

Figure 4. Analysis of a 1 in 2 dilution of SRM sample (n = 2) containing approximately 44 μg L^{-1} Cu(II). Experimental conditions as in Figure 2.

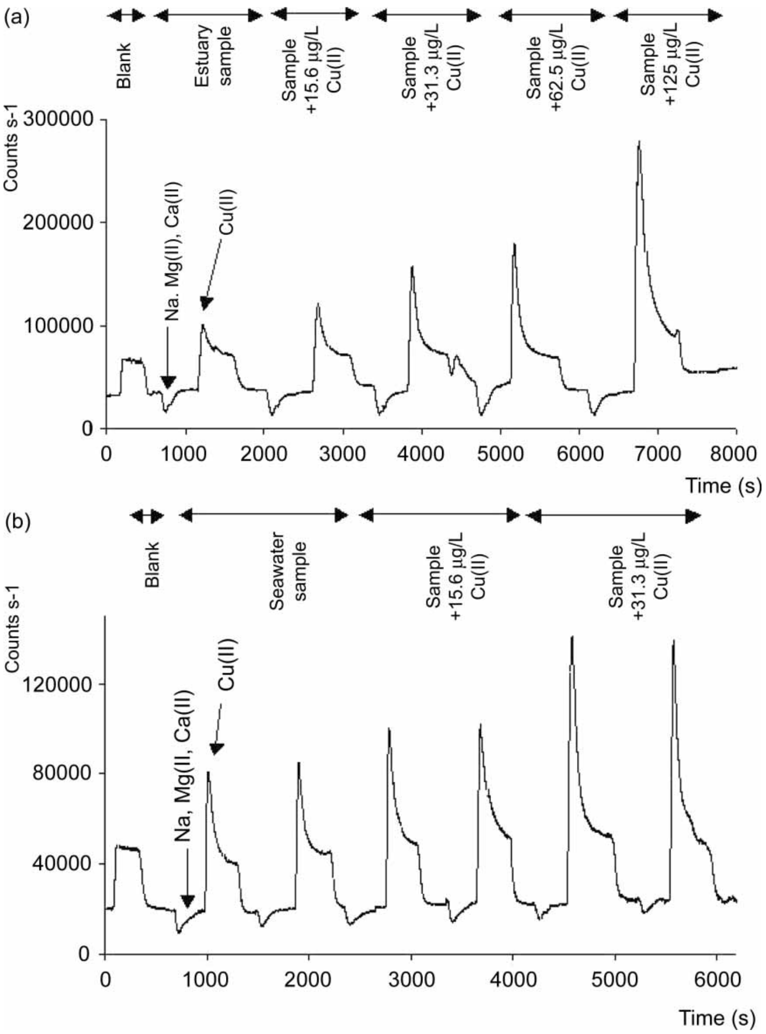

Figure 5. (a) An estuary water sample spiked with varying concentrations of Cu(II), and (b) a coastal seawater sample spiked with varying concentrations of Cu(II), analysed using dipicolinic acid modified disc. Experimental conditions: For 5(a) as in Figure 2. For 5(b) total flow rate of 1.43 mL min^{-1} and sample loop size of 220 µL.

to the unretained sample matrix components can be clearly seen. It was found that the results were linear over the concentration range 0 to 250 $\mu g\ L^{-1}$ ($n = 6$, $R^2 = 0.997$). Using this standard addition method, the amount of dissolved labile Cu(II) present in the estuarine sample was calculated to be ~25 $\mu g\ L^{-1}$.

The same procedure was carried out on the coastal water sample. However, for the developed method to be suitable for analysis of coastal seawater samples, ideally the analysis time needed to be reduced and the detector response increased. Therefore, the system total flow rate was increased systematically from 1.14 mL min^{-1} up to 1.66 mL min^{-1}. A flow rate of 1.43 mL min^{-1} was found optimum, reducing analysis times without causing an increase in backpressure across the monolithic disc (see Figure 3(d)). The sample injection loop was also increased from 150 µL to 220 µL, with a resultant increase in peak height without any significant effect upon linear range of calibration slope observed. Loop sizes up to 2000 µL were investigated, resulting in a three to four-fold increase in peak heights for Cu(II) standards, although linear range was significantly affected above 500 µL. Figure 5(b) illustrates the reaction peaks generated for the coastal seawater sample spiked with varying concentrations of Cu(II) under the modified conditions. Here, the results were found to be linear over the concentration range 0 to 125 µg L^{-1} ($n = 5$, $R^2 = 0.993$). This smaller linear range is due to the more complex sample matrix of the coastal seawater sample and the increased sample size. In this case, the amount of Cu(II) present in the coastal seawater sample was calculated to be ~14 µg L^{-1}.

CONCLUSIONS

An analytical procedure using a chelation exchange separation support based on modified monolithic discs was developed here for the extraction/separation of Cu(II) ions from within environmental water samples. The monolithic chelating disc was successfully incorporated into a standard flow analysis system, using chemiluminescence detection for the determination of trace concentrations of Cu(II) based on the oxidative destruction of the Cu(II)-1,10-phenanthroline complex by hydrogen peroxide at an alkaline pH. The monolithic discs were modified using picolinic acid, dipicolinic acid, and dodecyliminodiacetic acid, and the efficiency of the three acids were compared and contrasted for the extraction and elution of Cu(II). The dipicolinic acid coated disc was found to be the best of the three modified discs, due to its stronger complexing ability over both picolinic acid and dodecyliminodiacetic acid. The combination of the modified disc with the 1,10-phenanthroline reaction, allowed the determination of Cu(II) more selectively than with the 1,10-phenanthroline reaction alone. This system was successfully applied to a certified SRM sample and the results for the Cu(II) analysis were found to be accurate. The procedure was also used successfully for the determination of labile dissolved Cu(II) in both coastal seawater and estuary water samples.

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