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# Determination of trace labile copper in environmental waters by magnetic nanoparticle solid phase extraction and high-performance chelation ion chromatography



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## ABSTRACT

Cobalt magnetic nanoparticles surface functionalised with iminodiacetic acid were evaluated as a nanoparticulate solid phase extraction absorbent for copper ions ( $\text{Cu}^{2+}$ ) from environmental water samples. Using an external magnetic field, the collector nanoparticles could be separated from the aqueous phase, and adsorbed ions simply decomplexed using dilute  $\text{HNO}_3$ . Effects of pH, buffer concentration, sample and sorbent volume, extraction equilibrium time, and interfering ion concentration on extraction efficiency were investigated. Optimal conditions were then applied to the extraction of  $\text{Cu}^{2+}$  ions from natural water samples, prior to their quantitation using high-performance chelation ion chromatography. The limits of detection (LOD) of the combined extraction and chromatographic method were  $\sim 0.1 \text{ ng ml}^{-1}$ , based upon a 100-fold preconcentration factor (chromatographic performance;  $\text{LOD} = 9.2 \text{ ng ml}^{-1} \text{ Cu}^{2+}$ ), analytical linear range from 20 to 5000  $\text{ng mL}^{-1}$ , and relative standard deviations = 4.9% ( $c = 1000 \text{ ng ml}^{-1}$ ,  $n = 7$ ). Accuracy and precision of the combined approach was verified using a certified reference standard estuarine water sample (SLEW-2) and comparison of sample determinations with sector field inductively coupled plasma mass spectrometry. Recoveries from the addition of  $\text{Cu}^{2+}$  to impacted estuarine and rain water samples were 103.5% and 108.5%, respectively. Coastal seawater samples, both with and without prior UV irradiation and dissolved organic matter removal were also investigated using the new methodology. The effect of DOM concentration on copper availability was demonstrated.

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## 1. Introduction

Copper (Cu) is an essential micronutrient required for a wide variety of physiological processes [1]. However, like many such essential elements, Cu is also considered potentially toxic when present at elevated concentrations [2]. In natural waters excess Cu may prove toxic to sensitive aquatic organisms, or if present in potable waters, have an impact not only on taste, but also human health. Copper overabundance can negatively affect plant chloroplast function, leading to the formation of reactive oxygen species, which can result in reduced biomass and altered nutrient content [3–5]. It has also been reported, for *Lemna minor*, a common aquatic plant species, that elevated Cu can negatively affect the uptake of other essential metals, growth, and pigmentation [6]. In addition, a wealth of studies have demonstrated that environmentally relevant concentrations of Cu can be toxic to

fresh water snails and other aquatic organisms [7]. Furthermore, excessive ingestion of inorganic Cu from drinking water and Zn deficiency have recently been suggested as contributing factors in cognitive loss associated with Alzheimer's disease [8].

Consequently, there remains an interest in reliable analytical methods for Cu (and indeed other such transition metal ions) in natural and potable water samples, for reasons of both environmental control and public health. Atomic absorption spectroscopy (AAS), and inductively coupled plasma based methods (optical emission spectroscopy (ICP-OES), and mass spectrometry (ICP-MS)), are common instrumental approaches currently applied to elemental analysis. However, excluding high resolution instruments, most atomic spectroscopic methods are prone to significant interferences when dealing with complex sample matrices, particularly samples of high ionic strength, and those with excess concentrations of alkali and alkaline earth salts (e.g. estuarine waters) [9]. Sample dilution is often required, or a process of matrix removal/elimination employed prior to ICP analysis [10].

As an alternative to atomic spectroscopic methods, high-performance chelation ion chromatography (HPCIC) was specifically

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developed to analyse high ionic strength samples for trace levels of transition and heavy metal cations [11–12]. The chelating ion-exchange phases employed within HPCIC exhibit cation selectivity resultant from the formation and dissociation of complexes between metals ions and an immobilised chelating functional group on the surface of the stationary phase. In most cases alkali metal cations are very weakly retained, and alkaline earth metals moderately so, under acidic conditions [13,14]. Divalent and trivalent transition metal ions are strongly retained and so can be selectively separated. However, despite attractive selectivity, the sensitivity (and detection limits) of most published HPCIC methods are insufficient for the direct determination of most transition metals in non-polluted natural waters. For example, recently, a HPCIC method for the direct determination of trace transition metals in fuel ethanol was developed, and the LOD for  $\text{Cu}^{2+}$  was quoted as  $7.4 \text{ ng ml}^{-1}$  [15]. Although this LOD for  $\text{Cu}^{2+}$  is relatively low, it is still higher than dissolved Cu concentrations typically found in clean water bodies, which are generally  $< 5 \text{ nM}$  [16].

Thus, for most of the above mentioned analytical approaches, some preliminary solute preconcentration and matrix elimination is often required. Solid-phase extraction (SPE) is commonly used, typically applying chelating resins for trace metals [17,18]. However, standard SPE can be rather time consuming and demand high volumes of both sample and eluents. More recently, functionalised magnetic nanoparticles have been employed for selective extraction, in what has now been termed magnetic solid-phase extraction (MSPE) [19,20]. These magnetic extraction phases take various forms, and have been successfully applied to the preconcentration of both inorganic and organic target solutes [21–22]. The process itself sees the addition of the ‘collector phase’ of functionalised nanoparticles directly to the sample solution, and then uses the application of an external magnetic field to physically concentrate the magnetic nanoparticles, providing a means for the efficient and rapid separation of sorbed solutes (e.g. metal ions) from the matrix, without additional centrifugation or filtration steps. To-date MSPE, using nanoparticles functionalised with metal ion chelating groups, has been successfully applied to the preconcentration of trace transition and heavy metal ions from biological and environmental samples prior to their determination by AAS [23], ICP-AES [24], and ICP-MS [25]. However, a disadvantage of this procedure is that the magnetic nanoparticle itself, typically based upon functionalised iron oxide nanoparticles, can also contaminate the sample (e.g. with relatively high concentrations of  $\text{Fe}^{3+}$ ), particularly as strong acid eluents are used to liberate complexed target metal cations, thus causing partial dissolution of the core nanoparticle. To-date this issue has restricted the application of iron oxide based magnetic chelating nanoparticles in combination with HPCIC, as the excess  $\text{Fe}^{3+}$  in the concentrated extract is strongly adsorbed upon the HPCIC chelating column, rapidly fouling the column and requiring strong acid washes to elute the  $\text{Fe}^{3+}$  between sample assays [26].

Recently a new chelating magnetic nanoparticle has become available, based upon iminodiacetic acid (IDA) functionalised cobalt nanoparticles. These magnetic cobalt nanoparticles are coated with a thin ( $\sim 2 \text{ nm}$ ) layer of graphitic carbon, upon which the IDA groups are covalently attached. These cobalt based particles exhibit greater compatibility with cation exchange and chelating ion-exchange chromatography columns, such as those used within HPCIC, as  $\text{Co}^{2+}$  contamination emanating from nanoparticles during extraction can be more easily pre-eluted from the analytical column under less acidic conditions (than is the case for  $\text{Fe}^{3+}$ ). Therefore in the current study, magnetic cobalt nanoparticles functionalised with IDA were investigated as a magnetic solid phase extraction absorbent for the concentration of  $\text{Cu}^{2+}$  ions from environmental waters prior to their quantitation using HPCIC. The effects of sample pH, the volume and pH of desorption solution used, the amounts of magnetic sorbent and

sample volume, adsorption equilibrium time, and the concentration of potentially interfering ions, and dissolved organic matter on the extraction efficiency, have each been investigated in detail. The method was then successfully applied to the determination of  $\text{Cu}^{2+}$  in natural waters, including coastal seawater, and method recovery and accuracy was confirmed using sector field inductively coupled plasma-mass spectrometry (ICP-MS).

## 2. Experimental

### 2.1. Instrumentation

The chelation ion chromatography system used for sample quantitation was based upon a modular Dionex ion chromatograph, comprised of an AS25 absorbance detector, IP25 pump, AS50 autosampler, and AS50 column heater (Dionex, Thermo Scientific, Sunnyvale, USA). Post-column reaction detection was achieved using 4-(2-pyridylazo) resorcinol (PAR) as the post-column reagent (PCR), delivered by peristaltic post-column pump. The detection wavelength employed was 510 nm. Chromeleon software (Dionex, Thermo Fisher Scientific, Sunnyvale, CA, USA) was used for data acquisition and processing of chromatograms. A PEEK 150 mm length and 4.0 mm I.D. column packed with  $5 \mu\text{m}$  spherical IDA bonded silica particles was purchased from JPP Chromatography (Plymouth, UK).

A sector field inductively coupled plasma mass spectrometer (ICP-MS, Thermo Fisher Element 2, Bremen, Germany), equipped with a CETAC autosampler (ASX-500, Ohmaha, USA) was employed for the determination of total Cu and other matrix elements in sample extracts. Multiple spectral resolutions were used to help separate signals of interest from potentially overlapping polyatomic interferences [9,27]. The method of external calibration was used for quantification, using a series of standards prepared from commercially available premixed solutions (QCD Analysts, Environmental Science Solutions, Spring Lake, USA). Indium (High Purity Standards, Charleston, USA) was added as an internal standard to all samples and standards at a final concentration of  $100 \mu\text{g l}^{-1}$ . Calibration accuracy was verified via the analysis of independent NIST 1640 “Trace Elements in Natural Water” SRM (Gaithersburg, MD, USA).

### 2.2. Reagents and solutions

Stock solutions of  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  ( $1 \text{ mg ml}^{-1}$ ) were prepared from the following salts;  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (Ajax chemicals Ltd., Sydney, Australia),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (BDH, Poole, UK), and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (May and Baker, London, UK), prepared in diluted  $\text{HNO}_3$ . Calibration and test solutions were prepared by stepwise dilution of their stock solutions. Magnetic cobalt nanoparticles functionalised with IDA were purchased from Turbobeads (Zurich, Switzerland), marketed as Turbobeads Complexon. The magnetic nanoparticles exhibited diameters of below 50 nm, with the surface of the particles covalently functionalised with IDA ( $> 0.1 \text{ mmol/g}$ , immobilised IDA).

The magnetic nanoparticles were purified and regenerated by the following procedure: The nanoparticles were first washed with 4 M  $\text{HNO}_3$  to remove adsorbed metal ions, then with several deionised water washes, followed by 50 mM NaOH, and further deionised water, until the pH value of the suspension was in range 7–8. All other chemicals were of analytical reagent or higher grade. Deionised water from a Milli-Q water supply (Millipore, Bedford, MA, USA) was used throughout this work.

Eluents were prepared from  $\text{KNO}_3$  (BDH, Poole, UK), and 2-pyridinecarboxylic acid (picolinic acid) (Sigma, St. Louis, USA), and acidified using dilute  $\text{HNO}_3$ . The post-column reagent was 0.15 mM PAR (Kodak, Rochester, NY, USA), prepared in 0.4 M ammonia, and

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