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Solid Phase Extraction of Trace Elements in Water and Tissue Samples on a Mini Column with Diphenylcarbazone Impregnated Nano-TiO₂ and Their Determination by Inductively Coupled Plasma Optical Emission Spectrometry

Sıtkı Baytak^{a,*} and Zikri Arslan^b

^aDepartment of Chemical Engineering, Faculty of Engineering, Süleyman Demirel University, Isparta 32260, Turkey

^bDepartment of Chemistry and Biochemistry, Jackson State University, Jackson, MS 39217, USA

Abstract

This study presents a simple, robust and environmentally friendly solid phase preconcentration procedure for multielement determination by inductively coupled plasma optical emission spectrometry (ICP-OES) using diphenylcarbazone (DPC) impregnated TiO₂ nanopowder (*n*-TiO₂). DPC was successfully impregnated onto *n*-TiO₂ in colloidal solution. A number of elements, including Co(II), Cr(III), Cu(II), Fe(III), Mn(II) and Zn(II) were quantitatively preconcentrated from aqueous solutions between pH 8 and 8.5 at a flow rate of 2 mL min⁻¹, and then eluted with 2 mL of 5% (v/v) HNO₃. A mini-column packed with 0.12 g DPC impregnated *n*-TiO₂ retained all elements quantitatively from up to 250 mL multielement solution (2.5 µg per analyte) affording an enrichment factor of 125. The limits of detection (LOD) for preconcentration of 50 mL blank solutions (*n* = 12) were 0.28, 0.15, 0.25, 0.22, 0.12, and 0.10 µg L⁻¹ for Co, Cr, Cu, Fe, Mn, and Zn, respectively. The relative standard deviation (RSD) for five replicate determinations was 0.8, 3.4, 2.6, 2.2, 1.2 and 3.3% for Co, Cr, Cu, Fe, Mn and Zn, respectively, at 5 µg L⁻¹ level. The method was validated with analysis of Freshwater (SRM 1643e) and Lobster hepatopancreas (TORT-2) certified reference materials, and then applied to the determination of the elements from tap water and lake water samples by ICP-OES.

Keywords

Trace element; TiO₂ nanoparticle; Diphenylcarbazone; Solid phase extraction; Inductively coupled plasma optical emission spectrometry

1 Introduction

Trace metals are continuously released to the biosphere from natural and anthropogenic processes, including agriculture, volcanic eruptions, mining, power plants, and plating

*Corresponding author. Tel: +90 246 211 1390; Fax: +90 246 237 0859, sitkibaytak@sdu.edu.tr.

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industries. Some trace elements, such as copper (Cu), iron (Fe) and zinc (Zn) are essential to living organisms for biological processes. However, even essential elements would induce adverse health effects above a threshold concentration which varies with the physicochemical properties of the element, environmental factors and species [1]. Therefore, development of sensitive and affordable methods for monitoring and determination of trace element concentrations in environmental samples (e.g., water and sediments) and biological materials (tissues and body fluids) is important, especially in the assessment of occupational and environmental exposure to toxic elements [2].

Flame atomic absorption spectrometry (FAAS) [3–5], electrothermal atomic absorption spectrometry (ETAAS) [6, 7], inductively coupled plasma optical emission spectrometry (ICP-OES) [8–11] and inductively coupled plasma mass spectrometry (ICP-MS) [12, 13] have been most often employed in trace elements determinations. Among these techniques, ICP-OES has gained strong recognition in analysis of biological and environmental samples owing to its multi-elemental analysis capability, large linear dynamic range, and tolerance to the matrix effects of complex samples [8–11]. Despite these advantages, direct determination of trace elements in water and biological fluids by ICP-OES is limited by low elemental concentrations and matrix interferences. Preconcentration procedures, especially solid phase extraction (SPE), have been indispensable tools to analyte enrichment to bring the elemental concentrations in solution to the detection range of the ICP-OES instrument [11–16]. Higher enrichment factors could be achieved via both on-line and off-line SPE procedures. Off-line SPE procedures are attractive for ICP-OES determinations because of the capability for handling large volumes of samples for accurate measurement, reducing cost of analysis and instrument runtime. To date various synthetic [17–22] and natural materials [23–25], and chemically modified surfaces [26–34] and target-imprinted sorbents [35–37] have been explored as solid phase supports. A number of chelating agents have been used to modify the surfaces of support materials, which include amino thioamidoanthraquinone [14], 2,4,6-trimorpholino-1,3,5-triazin [15], 3-ferrocenyl-3-hydroxydithioacrylic acid [26], curcumin [27], 1-phenyl-3-methyl-4-benzoyl-5-pyrazone [28], 5-sulfosalicylic acid [29], carboxymethylated pentaethylene hexamine [30], 1-nitroso-2-naphthol [33], gallic acid [34], and L-tyrosine [38].

Nanoscale materials, such as carbon nanotubes, titanium dioxide (TiO₂) nanopowder and silicon dioxide (SiO₂) nanopowder possess significantly larger surface area in comparison to bulk counterparts, besides their excellent chemical and physical stability. As a consequence, the application of these and similar metal oxide nanomaterials as solid supports have received popularity to develop improved SPE procedures in environmental and biological trace analysis [2, 11, 18, 28, 29, 38–40].

In this study, we report a simple, cost effective and efficient off-line SPE procedure using TiO₂ nanopowder (*n*-TiO₂) for multielement determination by ICP-OES.

Diphenylcarbazone (DPC), a strong chelating agent, was successfully adsorbed onto colloidal *n*-TiO₂ particles in aqueous solution and the resulting DPC impregnated *n*-TiO₂ was utilized as chelating sorbent for multielement preconcentration of trace elements including, Co, Cr, Cu, Fe, Mn, and Zn. Experimental conditions, including pH, eluent concentration and volume, flow rates of sample and eluent solutions, and volume of sample

solution were optimized using mini column packed with DPC-impregnated *n*-TiO₂ to achieve quantitative preconcentration of the elements. The developed method was validated by determination of the elements in Fresh water (SRM 1643e) and Lobster hepatopancreas (TORT-2) certified reference materials by ICP-OES and then applied to the analysis tap water and lake water samples.

2 Experimental

2.1 Instrumentation

A Perkin Elmer (Shelton, CT, USA) Optima 3300 DV ICP-AES instrument was used throughout. The instrument is optimized for sensitivity with 2 µg mL⁻¹ Mn solution as needed. Data collection was achieved by ICP-Win Lab software package (version 3.1). Elemental measurements were made in axial view mode using the recommended wavelengths. The operation conditions for the instrument are summarized in Table 1. An OAKTON 510 model digital pH meter with glass electrode was used to adjust the pH of the solutions.

2.2 Standard solutions and reagents

All reagents used were of analytical and spectral purity. Deionized water obtained from Barnstead E-pure system (18.0 MΩ cm) was used to prepare all solutions. Standard stock solution of Co(II), Cr(III), Cu(II), Fe(III), Mn(II), and Zn(II) (1000 µg L⁻¹) were purchased from Spex Certiprep (Metuchen, NJ). A 10 µg mL⁻¹ multielement solution was prepared in 2% (v/v) HNO₃ from individual single element standard solutions and used throughout the study. Titanium oxide nanopowder (D₅₀ = 100 nm TiO₂) was purchased from Sigma Aldrich. Diphenylcarbazone and sodium dodecyl sulfate were purchased from Fisher Scientific as reagent grade chemicals. Trace metal grade nitric acid (HNO₃, Fisher Scientific), hydrochloric acid (HCl, Fisher Scientific), hydrogen peroxide (H₂O₂, Sigma Aldrich) and ammonium hydroxide (NH₄OH, Sigma Aldrich) were used in preparation of samples and standard solutions.

2.3 Sorbent preparation

Sodium dodecyl sulfate (SDS) and 1,5-diphenylcarbazone (DPC) were used without further purification. A 0.2% solution of DPC was prepared by dissolving 0.2 g of the reagent in 100 mL ethanol. A sample of *n*-TiO₂ powder (100 nm) was cleaned before use by shaking in 50 mL of 10% (v/v) HNO₃ and then washed with water until all acid was removed and finally dried in oven at 80 °C overnight.

A sample of 1.5 g of cleaned *n*-TiO₂ powder was added to a 50 mL solution of 0.1 g of sodium dodecyl sulfate (SDS). The solution was stirred vigorously for about 3–4 min and then 4 mL of 0.2% (m/v) solution of DPC was added. The pH was adjusted to approximately 7. The contents were stirred for 30 min and then filtered through Millipore filter paper (0.45 µm). The color of *n*-TiO₂ changed from white to reddish orange indicating successful impregnation (e.g., adsorption) of 1,5-diphenylcarbazone onto *n*-TiO₂ powder. The wetting and drying steps were repeated to maximize the adsorption efficiency of DPC onto *n*-TiO₂.

2.4 Preparation of column and preconcentration procedure

A 15-cm long glass column (0.5 cm i.d.) utilizing a flow-control valve at the bottom and a 250-mL capacity sample reservoir at the top were used for preparation of analytical column. A layer of glass wool was placed above the flow valve. Onto the glass wool, a sample of 0.12 g of DPC impregnated *n*-TiO₂ powder was placed uniformly and then covered with another layer of glass wool. Before use, 5% (v/v) HCl solution, 5% (v/v) HNO₃ solution and deionized water were passed through the column for cleaning the column.

For preconcentration, the pH of 50 mL 20 µg L⁻¹ multielement solution was adjusted to the desired pH with 5% (v/v) HCl and 10% (v/v) NH₄OH. The resulting solution was passed through the column at a flow rate adjusted to the desired value. The retained metal ions were then eluted from the solid phase with 2 mL of 5% (v/v) HNO₃ solution. This solution was analyzed for the trace elements by ICP-OES. The column was used repeatedly after washing with 2 mL of 5% (v/v) HNO₃ solution and distilled water, respectively.

2.5 Samples and preparation

The procedure was verified with analysis of freshwater and tissue certified reference materials. Freshwater certified reference material (SRM 1643e) was purchased from National Institute of Standards & Technology, Gaithersburg, MD. The pH of 25 mL of SRM 1643e was adjusted to pH 8.2–8.3 with 5% (v/v) HCl and 10% (v/v) NH₄OH and then diluted to 50 mL with water. Tap water samples were obtained from Jackson State University campus. Lake water samples were collected from local lakes in Jackson Mississippi, USA. Each water sample was acidified to 0.2% (v/v) HNO₃ (ca. pH 1.7) at the sampling location. In the laboratory, they were filtered through 0.45-µm Millipore cellulose nitrate membrane to remove particulate matter, bottled and stored until use. For analysis, the pH of 100 mL sub-samples (n = 3) of bottled lake water sample was adjusted to pH 8.2 for pre-concentration. Tap water samples were filtered immediately after collection through 0.45-µm Millipore cellulose nitrate membrane. The pH of the filtered sample was raised to pH 8.2–8.3. A volume of 100 mL sub-samples (n = 3) of this tap water solution was used for preconcentration.

In application to biological samples, Lobster hepatopancreas certified standard reference material (TORT-2) was analyzed using the procedure. About 0.2 g sub-sample of TORT-2 (n = 4) was digested in 60-mL PTFE tube with 3 mL concentrated HNO₃ and 2 mL H₂O₂ using a digestion block (Digiprep MS, SCP Science Champlain, NY USA) at 160 °C for 2 h. At the conclusion of this step, additional 2 mL of H₂O₂ were added slowly and the contents were heated until a clear solution was obtained. In order to facilitate the adjustment of pH, the lids were opened and the digests were heated gently to evaporate excess acid until about 1 mL liquid remained. At the end, all digests were cooled to room temperature, first diluted to 40 mL with water, then the pH was brought to 8.2–8.3 with 10% (v/v) NH₄OH and then completed to 50 mL with water.

3 Results and discussion

3.1 Effect of pH

DPC is a bidentate ligand that form complexes with divalent and trivalent metal ions through N-N and N=N groups. The scheme for the formation metal-DPC complex for a divalent metal ion is shown in Fig. 1. The metal-DPC complexes are neutral in nature, therefore, the pH of a solution is an important variable on the retention process. In other words, the pH of the medium mediates the charge on the complexing sites on the column, the chemical forms and species of the metal ions in solution, and consequently the magnitude of interaction between the metal ions and the chelating sites on the column. The effect of solution pH on the retention of Co(II), Cr(III), Cu(II), Fe(III), Mn(II) and Zn(II) was studied between pH 2 and 10. The elemental recoveries are illustrated in Fig. 2 as a function of pH. Cr(III), Cu(II) and Fe(III) were retained quantitatively between pH 6 and 8, whereas the recoveries for Mn(II), Co(II) and Zn(II) were approximately 60% at pH 6. At pH 8, the recoveries for all elements ranged between 95% (Co) and 100% (Mn, Zn). The retention profile at pH 9 was also similar with recoveries ranging between 94% (Cu) and 98% (Mn). The results clearly indicated that the pH range from pH 8 to 9 was optimum for simultaneous preconcentration of the elements. Highly alkaline pHs could lead to formation of colloidal metal hydroxides which may be adsorbed physically on the column rather than sorption via covalent interaction. Therefore, a pH range between pH 8 and 8.3 was chosen as the optimum working pH to avoid the risks associated with precipitation of metal ions at higher pHs (e.g., pH 9).

3.2 Effect of amount of solid phase, eluent type and volume

Unlike micrometer size porous solid supports, nanopowders exhibit two to three orders of magnitude smaller size range and substantially higher surface area. These benefits, however, impart limitations on the flow of solutions through the column. Large amount of support undoubtedly reduces the flow rate and hence the throughput whereas small amount of support would lead to loss of analyte ions due to inadequate interaction with chelating sites. Therefore, the amount of solid support is vital to ensure quantitative retention and optimum throughput. The amount of sorbent placed into the column was optimized at pH 8.2. The results indicated that 0.1 g of sorbent was the minimum amount to achieve quantitative recoveries (Fig. 3). As expected, the retention was lower for 0.05 g support because of loss of the metal ions from the column during loading. A mass of 0.15 or 0.2 g support did not deteriorate the performance, yet it did not provide any apparent advantage in comparison to 0.1 g support. Therefore, a mass of 0.12 g DPC-impregnated *n*-TiO₂ was used in further experiments to maintain precision among replicate measurements.

3.3 Optimization of eluent type and volume

Elution was examined with 2 and 5 mL volumes of 1, 2 and 5% (v/v) trace metal grade HCl and HNO₃. The former is the preferred eluent for removal of elemental species from analytical columns when determinations are performed by FAAS since the atomization of metal chlorides are more efficient than their nitrates. Conversely, HNO₃ is frequently used for determinations in ICP-OES and ICP-MS because of the simpler background spectra. During the course of the elution experiments, both acids performed equally for the removal

of the retained metals ions from the minicolumn of DPC impregnated *n*-TiO₂. Copper was retained relatively strongly on the column; hence, recoveries were lower around 87% and 89%, respectively, when elution was made with 2 mL of 2% (v/v) HCl and HNO₃. Increasing the volume of eluent acids to 5 mL improved the recoveries to about 96%, but at cost of reduced enrichment factor. Similar results were obtained with 2 mL of 5% (v/v) HCl and HNO₃. The recoveries for Cu(II) were better than 95% affording not only quantitative removal of Cu(II) from the column but also higher enrichment factors. In subsequent experiments, elution was made with 2 mL of 5% (v/v) HNO₃, which afforded a preconcentration factor of 50 for a sample volume of 100 mL.

3.4 Effect of sample flow rate and sample volume

The flow rate of sample solution was investigated within a range from 0.5 to 2.5 mL min⁻¹ by passing 50 mL of multielement solution of 20 µg L⁻¹ of each metal ion at the optimum pH through the column. Fig. 4 illustrates the effect of sample flow rate on the retention of the analytes on the DPC impregnated *n*-TiO₂ support. As can be seen, maximum flow rate for quantitative retention was 2 mL min⁻¹ at which elemental recoveries ranged between 95% (Mn) and 98% (Cu). The recoveries declined to 85 to 90% range when solutions were loaded at 2.5 mL min⁻¹. Additional studies performed at 2 mL min⁻¹ exhibited consistent results suggesting that a flow rate of 2 mL min⁻¹ was optimal for quantitative sorption.

The volume of sample solution affects the rate of enrichment and in due course the limits of detection (LOD) of the procedure. A large volume of sample solution is required to achieve high enrichment factors; nonetheless, total volume of solution containing a certain mass of analyte elements is limited by the sorption capacity of the support material. To determine the effect of volume of sample solution on the elemental recoveries, 25, 50, 100, 250 and 500 mL solutions containing 2.5 µg of Co(II), Cr(III), Cu(II), Fe(III), Mn(II) and Zn(II) as multielement solution were passed through the column according to the procedure described above. Fig. 5 illustrates the variation in elemental recoveries as a function of sample volume. Up to a volume of 250 mL solution could be preconcentrated on the column quantitatively (*R* > 95%). Sorption efficiency of the column degraded with increasing sample volumes. Elemental recoveries declined slightly to 90–93% range at 350 mL sample volume. The column did not possess sufficient capacity for sorption of the metal ions from 500 mL solution such that the recoveries ranged between 78% for Mn(II) and 85% for Cr(III). These results indicated that the breakthrough volume of the column was around 300 mL. Further, 125-fold enrichment could be readily attained from preconcentration of 250 mL sample solution into 2 mL 5% (v/v) HNO₃. In this work, analyses were performed with either 50 or 100 mL solutions for real samples to ensure an adequate preconcentration factor and sample throughput.

3.5 Effect of coexisting ions

The effect of some coexisting ions, including Na⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺, SO₄²⁻, Cl⁻, NO₃⁻, PO₄³⁻ were studied to determine the tolerance levels of the DPC impregnated *n*-TiO₂ column. These ions were chosen on the basis of their abundances in the natural water samples, such as estuarine water and lake water samples. The tolerance limit to the coexisting ions was defined as the highest concentration of matrix ion resulting in less than

90% elemental recoveries. For this purpose, a series of solutions (50 mL) were prepared with varying concentrations of the coexisting ions in the presence of $50 \mu\text{g L}^{-1}$ of each metal ion. The solutions were then passed through the column. The tolerance limits of the coexisting ions were found to be $1000 \mu\text{g mL}^{-1}$ for Na^+ , K^+ , Cl^- and NO_3^- , $500 \mu\text{g mL}^{-1}$ for PO_4^{3-} , and $250 \mu\text{g mL}^{-1}$ for Ca^{2+} , Mg^{2+} , and Al^{3+} . These results suggested that the presence of major coexisting ions had no significant deleterious effect on the quantitative preconcentration of the elements from water and biological samples under the optimal experimental conditions.

3.6 Column lifetime and analytical performance

A column retention test was performed daily during the course of the experiments. A 50 mL, $50 \mu\text{g L}^{-1}$ multielement solution at pH 8.2 were loaded onto the column in triplicate and eluted with 2 mL 5% (v/v) HNO_3 followed by column conditioning with 10 mL deionized water. The eluates were then analyzed for the elements by ICP-OES. No significant degradation in the elemental recoveries was observed for up to 30–35 loading-elution cycles suggesting that the column possessed adequate stability affording repetitive uses for cost effective analyses.

External calibration was performed for determinations with 0, 1, 2, 5, 10, 20, 50 and $100 \mu\text{g L}^{-1}$ (50 mL) multielement standard solutions. The standard solutions were preconcentrated as for the samples. Each solution at the optimum pH was passed through the column and the retained elements were eluted with 2 mL of 5% (v/v) HNO_3 . The limits of detection (LOD) were calculated by 3s method; metal ion concentration ($\mu\text{g L}^{-1}$) equivalent to 3 times the standard deviation (s) of blank signals (cps) ($n = 12$) from preconcentration of 50 mL blank solution (pH 8.2–8.3). The LODs were 0.28, 0.15, 0.25, 0.22, 0.12, and $0.10 \mu\text{g L}^{-1}$ for Co, Cr, Cu, Fe, Mn, and Zn, respectively. Preconcentration factor of the method was calculated by the ratio of the sample volume ($V_{\text{initial}} = 50 \text{ mL}$) and the final elution volume ($V_{\text{final}} = 2 \text{ mL}$). Under the optimum conditions, a preconcentration factor of about 25 was achieved from preconcentration of 50 mL sample solution into a final volume of 2 mL with sampling rate of 25 min per sample. The relative standard deviation (RSD) for five replicate ($n = 5$) determinations was 0.8% for Co, 3.4% for Cr, 2.6% for Cu, 2.2% for Fe, 1.2% for Mn and 3.3% for Zn at $5 \mu\text{g L}^{-1}$ level.

A comparison of the operating conditions and analytical performance of the preconcentration method with those of relevant reports is provided in Table 2. In general, the performance of the method was comparable to those reported by others using ICP-OES. As can be seen, off-line approaches require relatively large volumes sample solutions to attain acceptable detection limits for ICP-OES measurements. In this method, comparable detection limits were achieved using smaller volumes of sample solutions. On-line approaches often provide better sampling rate due to smaller volumes used. Yet, the operating conditions (pH and flow rates) and detection limits are not very different from those of off-line approaches. It is also clear that studies involving ICP-MS determinations provide lower detection limits because of the inherent sensitivity and lower background of ICP-MS technique.

3.7 Real sample analysis

In order to validate the method, sub-samples of certified reference materials of freshwater (SRM 1643e) and Lobster Hepatopancreas reference material (TORT-2) were analyzed. The samples were prepared as described in section 2.6 in a total volume of 50 mL. The results are summarized in Table 3 for SRM 1643e and TORT-2. For all elements, the experimental concentrations obtained using the preconcentration procedure was within the 95% confidence interval of the certified values. The determinations in tap water and lake water samples were made for 100 mL samples pre-concentrated into 2 mL of 5% (v/v) HNO₃ and the results are summarized in Table 4. The recoveries from spiked water samples varied between 92 to 101% which were deemed accurate at 95% confidence interval demonstrating that the preconcentration method by using a minicolumn of DPC-impregnated *n*-TiO₂ would afford quantitative determination of the trace elements in water samples by ICP-OES.

4 Conclusions

In this study, a simple and cost effective preconcentration method has been developed and validated using a mini-column of diphenylcarbazone impregnated *n*-TiO₂ for solid phase preconcentration of Co, Cr, Cu, Fe, Mn and Zn from water and biological samples. The method utilizes environmentally friendly procedures and materials. The DPC-impregnated *n*-TiO₂ sorbent possesses high stability and long lifetime for up to 35 runs against treatment with dilute mineral acids without any significant change in the recoveries. The trace elements could be removed from the column with 2 mL of 5% (v/v) HNO₃ or HCl, which is also advantageous to achieve higher enrichment factors in analysis samples with very low elemental concentrations. In most applications, both ICP-OES and FAAS lack the detection power for determination of the selected metal ions and other heavy metals in natural water samples and biological materials. The preconcentration procedure presented here affords high capacity and capability for achieving the desired sensitivity for accurate determination of trace metals by ICP-OES and FAAS.

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Fig. 1.
The mechanism of formation of neutral DPC complexes with divalent metal ions (M^{2+}).

Fig. 2. The effect of pH on the recoveries for a $20 \mu\text{g L}^{-1}$ solution (50 mL) of Co, Cr, Cu, Fe, Mn and Zn. Mass of solid phase = 0.1 g; flow rate = 1.0 mL min^{-1} ; eluent = 2 mL, 5% (v/v) HNO_3 .

Fig. 3.

The effect of amount of solid phase on the recoveries for a $20 \mu\text{g L}^{-1}$ solution (50 mL) of Co, Cr, Cu, Fe, Mn and Zn. Flow rate = 1.0 mL min^{-1} ; eluent = 2 mL, 5% (v/v) HNO_3 .

Fig. 4. The effect of solution flow rate on elemental recoveries for preconcentration of 50 mL, 20 $\mu\text{g L}^{-1}$ multielement solution. Mass of solid phase = 0.12 g; eluent = 2 mL, 5% (v/v) HNO_3 .

Fig. 5.

The effect of sample volume on recoveries. Analyte mass was kept constant at 2.5 μg in each volume. Mass of solid phase = 0.12 g; eluent = 2 mL, 5% (v/v) HNO_3 .

Table 1

Operating conditions for Optima 3300 DV ICP-OES instrument

RF power/kW	1.5
Nebulizer	Cross-flow
Spray chamber	Concentric glass
Plasma Ar / L min ⁻¹	16
Auxiliary Ar / L min ⁻¹	0.4
Nebulizer Ar / L min ⁻¹	0.6
Sample uptake / mL min ⁻¹	1.5
Delay time (s)	45
Scanning mode	Continuous, axial
Integration time (s)	Automatic (min. 0.5 – max. 5 s)
Readings/replicate	3
Wavelength (nm)	Co: 228.616; Cr: 267.716; Cu: 324.752; Fe: 259.940; Mn: 257.610; Zn: 213.856

Table 2

Comparison of analytical performance of DPC impregnated *n*-TiO₂ chelating column with other chelating supports utilized for trace element preconcentration

Sorbent	Analyte (LOD, $\mu\text{g L}^{-1}$)	Load pH (Approach)	Sample volume and flow rate	Eluent	Sampling rate (min sample ⁻¹)	Technique	Reference
DPC impregnated <i>n</i> -TiO ₂	Co(0.28), Cr(0.15), Cu(0.25), Fe(0.22), Mn(0.12), Zn(0.10)	pH 8.2–8.3 (off-line)	50 mL - 2 mL min ⁻¹	2 mL 5% v/v HNO ₃	25	ICP-OES	This work
8-HQ chelates on TiO ₂ nanotubes	Cd(1.0), Ni(0.25)	pH 8.0 (off-line)	200 mL - 1.25 mL min ⁻¹	3 mL HNO ₃ -EtOH (1:9 v/v)	160	FAAS	[18]
5-sulfosalicylic acid modified <i>n</i> -SiO ₂	Fe(0.09)	pH 3.5 (off-line)	200 mL - 1 mL min ⁻¹	2 mL 0.01 M HCl	200	ICP-OES	[29]
1-nitroso-2-naphthol impregnated alumina	Pb, Cu, Cr, Fe	pH 6–7 (off-line)	1.0 L - 10 mL min ⁻¹	5 mL 15 M HNO ₃	100	FAAS	[33]
Ion imprinted polymer	Ni (0.26)	pH 9.0 (off-line)	100 mL - 3 mL min ⁻¹	2.5 mL 2 M HNO ₃	33	ICP-OES	[36]
Single-walled carbon nanotubes (SWCN)	Cu(0.039), Co(0.0012), Pb(0.0054)	pH 8.0 (off-line)	100 mL - 1.2 mL min ⁻¹	2 mL 0.5 M HNO ₃	83	ICP-MS	[39]
Mesoporous TiO ₂	Co(0.09), Cd(0.36), Cr(0.17), Cu(0.12), Mn(0.026), Ni(0.28), V(0.11), Ce(0.35), Dy(0.10), Eu(0.07), La(0.16), Yb(0.03)	pH 8.5 (on-line)	3.0 mL - 2 mL min ⁻¹	0.3 mL 2 M HCl	3	ICP-OES	[40]
Ion imprinted polymer	Cu(0.15), Ni(0.14), Pb(0.18), Zn(0.03)	pH 8.5 (off-line)	250 mL - 3 mL min ⁻¹	2.5 mL 2 M HNO ₃	85	ICP-OES	[41]
1-(di-2-pyridyl)methylene thiocarbonohydrazide modified silica gel	Cd(0.24), Co(0.006), Cr(0.53), Mn(0.004) Ni(0.13), Zn(0.030)	pH 8.6 (on-line)	4.2 mL - 1.4 mL min ⁻¹	1.3 mL/min 2% (v/v) HNO ₃	10	ICP-MS	[42]

Method limits of detection (LOD) and the results from analysis of Freshwater (SRM 1643e) and Lobster hepatopancreas (TORT-2) certified reference materials

Table 3

Element	LOD ^a (µg L ⁻¹)	SRM 1643e			TORT-2		
		Found ^b (µg L ⁻¹)	Certified (µg L ⁻¹)	Relative error (%)	Found ^b (µg g ⁻¹)	Certified (µg g ⁻¹)	Relative error (%) ^c
Co	0.28	25.60 ± 1.40	27.06 ± 0.32	-5	0.48 ± 0.08	0.51 ± 0.09	-6
Cr	0.15	18.80 ± 1.24	20.04 ± 0.40	-6	0.72 ± 0.18	0.77 ± 0.15	-6
Cu	0.25	21.68 ± 0.86	22.76 ± 0.31	-5	98 ± 12	106 ± 10	-7
Fe	0.22	92.40 ± 4.62	98.1 ± 1.4	-6	98 ± 9	105 ± 13	-7
Mn	0.12	36.80 ± 2.50	38.97 ± 0.45	-6	12.8 ± 1.3	13.6 ± 1.2	-6
Zn	0.10	75.20 ± 3.40	78.5 ± 2.2	-4	173 ± 8.4	180 ± 6.0	-4

^a Limits of detection are for 50 mL blank solutions (n = 12).

^b Values are mean ± 95% confidence level of four replicate determinations $\bar{x} \pm ts / \sqrt{N}$.

^c Relative error (%) is calculated as $[(C_{\text{found}} - C_{\text{certified}}) / C_{\text{certified}}] \times 100$.

Table 4

Results for Co, Cr, Cu, Fe, Mn and Zn from tap water and lake water samples

Element	Tap water			Lake water		
	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Co	–	12.0 ± 1.2	–	–	18.6 ± 1.4	–
	20.0	31.0 ± 2.6	95	20.0	37.2 ± 2.1	93
Cr	–	25.4 ± 1.3	–	–	38.4 ± 2.0	–
	20.0	43.6 ± 3.2	93	20.0	58.6 ± 4.2	101
Cu	–	35.2 ± 1.4	–	–	40.4 ± 1.6	–
	20.0	54.0 ± 3.0	94	20.0	58.8 ± 4.0	92
Fe	–	40.5 ± 1.6	–	–	50.2 ± 2.6	–
	20.0	60.4 ± 2.8	97	20.0	70.0 ± 4.2	99
Mn	–	14.2 ± 0.8	–	–	25.4 ± 2.2	–
	20.0	32.6 ± 2.4	92	20.0	44.0 ± 3.2	93
Zn	–	34.0 ± 1.6	–	–	40.0 ± 2.0	–
	20.0	53.2 ± 2.6	96	20.0	59.3 ± 3.4	96

^aValues are mean $\pm$ 95% confidence limit for three replicate determinations.