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Article

Analytical Performance of New Mixed Oxide ($SiO_2/TiO_2/ZnO$)-Based Sorbent for Development of a Reliable Mechanized Enrichment System for Copper Determination in Water and Food Samples

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No presente estudo, um novo material compósito ($SiO_2/TiO_2/ZnO$) foi avaliado para pré-concentração de cobre em amostras de água e alimentos. O sorvente foi caracterizado por microscopia eletrônica de varredura (SEM), infravermelho com transformada de Fourier (FT-IR), análise de dados texturais, fluorescência de raios X por energia dispersiva (EDXRF) e difratometria de raios X (XRD). A pré-concentração em linha e determinação espectrofotométrica na região visível foi baseada na pré-concentração de 20,0 mL de amostra em pH 7,0 através de 50 mg do sorvente, numa vazão de 6,4 mL min^{-1}. Um volume fixo de 0,3 mL de HNO_3 0,5 mol L^{-1} elui os íons cobre que reagem com dietilditiocarbamato (DDTC) 0,3% (m/m) cujo complexo formado ($Cu(DDTC)_2$) é monitorado a 452 nm. A seletividade do sorvente foi examinada avaliando o efeito de íons interferentes. O método proposto forneceu linearidade variando de 20,0 a 230,0 µg L^{-1} (r = 0,998), fator de pré-concentração de 35,9 e limite de detecção de 5,6 µg L^{-1}. Amostras de água e alimentos foram analisadas com sucesso pelo método proposto e a exatidão foi checada por meio de análises de materiais certificados de referência de proteína e fígado de peixe.

In the present study, a new composite material ($SiO_2/TiO_2/ZnO$) for copper preconcentration in water and food samples was evaluated. The sorbent was characterized by scanning electronic microscopy (SEM), Fourier transform infrared spectrophotometry (FT-IR), textural data analyses, energy dispersive X-ray fluorescence (EDXRF) and X-ray diffractometry (XRD). The on-line preconcentration and visible spectrophotometric determination was based on loading 20.0 mL of sample at pH 7.0 through 50 mg of sorbent at a flow rate of 6.4 mL min^{-1}. A fixed volume of 0.3 mL of 0.5 mol L^{-1} HNO_3 elutes copper ions, in which react with 0.3% (m/m) diethyldithiocarbamate (DDTC) whose complex formed ($Cu(DDTC)_2$) is monitored at 452 nm. The selectivity of sorbent has been examined by assessing the effect of interfering ions. The proposed method provided linearity ranging from 20.0 to 230.0 µg L^{-1} (r = 0.998), preconcentration factor of 35.9 and limit of detection of 5.6 µg L^{-1}. Water and food samples were successfully analyzed by proposed method and the accuracy was checked by analysis of certified reference materials of protein and liver of fish.

Keywords: $SiO_2/TiO_2/ZnO$, flow solid phase extraction, spectrophotometry, protein, vegetables

Introduction

The monitoring of copper levels in drinking water and food samples is of great importance, since this element is considered an essential mineral nutrient for humans, playing an important role in carbohydrate and lipid metabolism.[1] On the other hand, copper can be toxic in excessive amounts, mainly by oral ingestion, which can cause nausea, diarrhea, vomiting and disturbances in liver or kidney.[2] Copper is a trace mineral in the body associated to Wilson's disease, a hereditary disorder in which the body retains too much copper. Patients with Wilson's disease

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must avoid the intake of copper-rich foods, such as meats and shellfish.[3] Actually, there is no evidence that elevated copper intake is related with cancer, but more estimates of high inhalation and ingestion exposures need to be carefully investigated to achieve more accurate responses.[4]

Based on these features, levels recommended for dietary intake of copper in the United States of America is approximately 1.0-1.1 mg day^{-1} for adult women and 1.2-1.6 mg day^{-1} for adult men.[5] In drinking water, the maximum allowed contaminant level according to U.S. Environmental Protection Agency[6] is 1.3 mg L^{-1}, whilst the European Commission[7] and Brazilian Health Surveillance Agency[8] have fixed the value as 2.0 mg L^{-1}. Usually, concentrations of copper in unpolluted natural waters and food samples are very low, generally in the range ≤ µg L^{-1} or ≤ µg g^{-1},[4,9] thus the use of sensitive and selective analytical technique is required for a reliable analysis. UV-Vis molecular spectrophotometry presents low cost and simplicity regarding flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma-mass spectrometry (ICP-MS) for copper determination, but it suffers from low sensitivity and selectivity. However, highly improved performance of UV-Vis molecular spectrophotometry for reliable determination of copper at trace levels can be achieved by inserting a preconcentration step prior to analysis. Preconcentration based on solid phase extraction (SPE) coupled to flow injection analysis (FIA) is considered an efficient tool for copper preconcentration, because of its simplicity, fast recovery of solid phase, high preconcentration factor and high sample throughput.[10] For copper determination by UV-Vis molecular spectrophotometry, many sorbents have been developed, such as microcrystalline naphthalene,[11] chitin,[12] carbon nanotubes,[13] silica gel modified with 2-aminomethylpyridine[14] and 1,3-diaminepropane-3-propyl[15] and ion imprinted sorbent.[16] Among these materials, modified silica has gained great interest due to its high surface area, high mechanical strength and low resistance to fluid passage at a high flow rate.[17] Another examples of silica functionalized with various chelating ligands include 3-(1-imidazolyl)propyl,[18] dithizone[19] and 2-aminoethyl-3-aminobutylmethyldimethoxysilane.[20] Such modification improves the selectivity as well as makes better pH stability range of silica. A kind of material based on highly dispersed metal oxides (M_xO_y) on silica surface prepared by sol-gel process has been proposed as sorbent for metal ion preconcentration.[21,22] More recently, composite materials based on $SiO_2/M_xO_y/N_zO_w$ have been also synthesized and applied by our research group to the development of solid phase preconcentration methods on-line coupled to FAAS for cadmium, lead, copper and cobalt determination.[23-26] In general, composite materials prepared by metal oxides or the mixture of them, such as Al_2O_3, ZrO_2, Nb_2O_5, MnO, TiO_2 and ZnO incorporated in silica network, exhibit amphoteric properties due to presence of Lewis and Brønsted acid/base binding sites, which depending upon pH, can promote selectivity to the material toward metal ion.[27] In addition, the preparation of composite material provides higher stability and adsorption capacity to silica matrix in a wide pH range with quick adsorption rate. Another advantage is related to the better orientation and availability of active groups of mixed oxides on silica matrix, which may increase their acidic and basic properties. From an analytical point of view, aiming at application in the field of solid phase extraction, the use of metal oxides loaded on silica matrix is also much more attractive over the bulk physical form, because the fine powder particles of metal oxides promote the formation of flocks or gels due to high-swelling effect when packed into a separation column, thus providing low resistance to fluid passage.[26] Thus, researches on preparation of $SiO_2/M_xO_y/N_zO_w$ as sorbents for metal ions, although quite promising, are still quite limited and unexploited, whose preconcentration methodologies developed up to now have been focused only by on-line coupling to FAAS.

According to comments, the main purpose of this study is to evaluate the selective and adsorptive performance of a new mixed oxide (SiO_2/TiO_2/ZnO) for copper by online coupling to UV-Vis molecular spectrophotometry, a technique naturally less selective and cheaper than FAAS. Powders of TiO_2[28] and ZnO[29] have been used as sorbents for metal ions, but until now, there has been no report on the development of mixed oxide TiO_2/ZnO dispersed in a silica matrix for copper preconcentration. The real applicability of the proposed method was checked from analysis of water and food samples, whose accuracy was confirmed by analysis of certified reference materials.

Experimental

Apparatus

A single beam spectrophotometer Femto (São Paulo, Brazil), model 435 equipped with a flow cell of 1.0 cm optical path was employed in the development of FIA. The data acquisition was done through a PCL 711 interface with programming in Visual Basic macro (Microsoft Excel). A peristaltic pump Ismatec, Model IPC-08 (Glattbrugg, Switzerland) with eight channels, Tygon tubes of different diameters and 0.8 mm internal diameter polyethylene tubes was used for propulsion of the standards, samples and reagents. A proportional injector made of three pieces constructed with poly(methyl metracrylate) was used for standards and samples introduction in FIA system.

Reagents and solutions

All solutions were prepared by using deionized water, from a system of water purification Milli-Q® (Millipore®, Bedford, MA, USA) resistivity of 18.2 MΩ cm. All reagents were of analytical grade. In order to avoid contamination, all glassware utilized in experiments were decontaminated in a 10% nitric acid (Vetec, Rio de Janeiro, Brazil), for 24 h, rinsed with ultrapure Milli-Q® water and dry-cleaned. Copper solutions were prepared from a 1000 mg L^{-1} Cu^{2+} standard stock solution (Merck, Darmstadt, Germany) by making appropriate dilutions with deionized water. Ethanol, concentrated nitric acid (HNO_3), sodium hydroxide (NaOH) were acquired from Merck and used without pre-purification. Tris-HCl and phosphate buffer solutions were prepared from their salts (Merck), without prior purification. Stock sodium diethyldithiocarbamate (DDTC) solutions (Merck) were prepared by dissolving a known amount in ethanol (Impex) and further dilutions were made in purified water. Tetraethylorthosilicate (TEOS, 98%), tetrabutyl orthotitanate (IV) (99%), zinc acetate dihydrate (98%) were acquired form Sigma-Aldrich (Steinheim, Germany). National Research Council of Canada (NRCC) reference materials Dolt-4 (Dogfish liver) and Dorm-3 (Fish Protein) were employed to evaluate the accuracy of the method.

Synthesis of $SiO_2/TiO_2/ZnO$ material

The mixed oxide was synthetized by mixing TEOS in 62 mL of ethanol with 5.7 mL of deionized water and 0.35 mL of concentrated HNO_3. This mixture was stirred during 2 h under reflux. In the following step, the mixture was cooled until room temperature and mixed with a solution containing 42 mL of tetrabutyl orthotitanate in 324 mL of ethanol. The mixture was stirred at room temperature during 2 h. At the end of this step, a solution containing 13.6 g of zinc acetate dehydrate dissolved in 43 mL of deionized water and 1.6 mL of concentrated HNO_3 was added to the reaction mixture. The solution was stirred at room temperature during 2 h. In order to ensure total hydrolysis and gel formation, the resulting mixture was heated at 60 °C without stirring. The ethanol was slowly evaporated at 110 °C during 24 h until formation of xerogel. The resulting material was ground, sieved (particle sizes between 150 and 250 μm) and calcined at 500 °C for 120 h.

Characterization of $SiO_2/TiO_2/ZnO$ material

The morphology of the mixed oxide was evaluated by scanning electron microscopy (SEM) using a scanning electron microscope, model Phillips FEI QUANTA 200 (Amsterdam, Netherlands) with acceleration voltage of 20 kV. Prior to analyses, the samples were coated with an Au/Pd alloy in a Bal-Tec MED 020. The spectra in the infrared region were recorded from 4000 to 400 cm^{-1} with infrared spectrometer model Shimadzu FTIR-8300 (Kyoto, Japan). The experiments were performed using the KBr conventional method. The SiO_2, TiO_2 e ZnO contents in the material were determined by energy dispersive X-ray fluorescence (EDXRF) on a Shimadzu EDX-720 HS Ray-Ny instrument (Kyoto, Japan) in the channels Na-U and Ti-Sc using the lines $K\alpha$ under atmosphere of air and collimator of 10 mm. The X-ray powder diffraction was performed from a Panalytical XPERT PRO MPD diffractometer (Michigan Drive, Natick, MA), with incident X-rays ($\lambda = 1.54060$ Å), 2θ angle varying between 5 and 70° and angular resolution of 0.05°. Certified reference materials (protein and liver of fish) and parsley, chive and lentil were digested in a microwave oven (Multiwave Anton Paar 3000, Graz, Austria).

Sample preparation

Tap water was collected at State University of Londrina campus and mineral water was obtained from local supermarkets. Lake water was collected from Igapó Lake, Londrina, Brazil. After sampling of lake water, it was filtered through a 0.45 μm membrane (Schleicher & Schuell Brazilian Industry, Brazil), acidified with HNO_3 (pH 2.0) and stored in polypropylene bottles at 4 °C, until analysis. Before analysis, the samples pH was adjusted with Tris-HC buffer.

About 0.4000 g of parsley or chive and 0.3000 g of lentil were placed in Teflon® flasks and decomposed with a mixture of concentrated HNO_3 (10.0 mL) and H_2O_2 30% (v/v) (5.0 mL). The flasks were kept overnight followed by three steps microwave digestion: (1) 5 min in 250 W; (2) 5 min in 400 W; and (3) 5 min in 500 W. After digestion, the content was *quasi*-dried on a hot plate and cooled at room temperature. Then the dried residue was transferred to a 100.0 mL volumetric flask and buffered at pH 7.0 with 0.05 mol L^{-1} Tris-HCl.

For certified reference materials, about 0.3200g of DOLT-4 and DORM-3 were digested following the same steps, except for the concentrated HNO_3 and H_2O_2 volumes, that were 20.0 mL and 10.0 mL, respectively. Any contamination source was checked by using blank solutions.

General procedure for flow preconcentration

Figure 1 shows the on-line preconcentration diagram. In the first step (injector on loading position, Figure 1a), 20.0 mL of copper solution (pH 7.0 buffered with 0.05 mol L^{-1} Tris-HCl) (S) are loading through a poly(ethylene) mini-column (C) containing 50 mg of packed material at a 6.4 mL min^{-1} flow rate. At the same time, 0.5 mol L^{-1} HNO_3 (E_1) fills the eluent loop (0.3 mL) and in another line, 1.0 mol L^{-1} HNO_3 (E_2) merges at 2.6 mL min^{-1} flow rate to first confluence zone with 0.3% (m/v) DDTC (1.0 mL min^{-1} flow rate) (CR), which are transported to the second confluence zone. On the second step (Figure 1b), by switching the central part of injector, copper is eluted with a fixed volume of 0.3 mL of 0.5 mol L^{-1} HNO_3 using water as carrier at 6.4 mL min^{-1} flow rate. Copper than react with 0.3% (m/v) DDTC at 1.6 mL min^{-1} flow rate and the complex formed is monitored at 452 nm. All absorbance signals were taken as peak height.

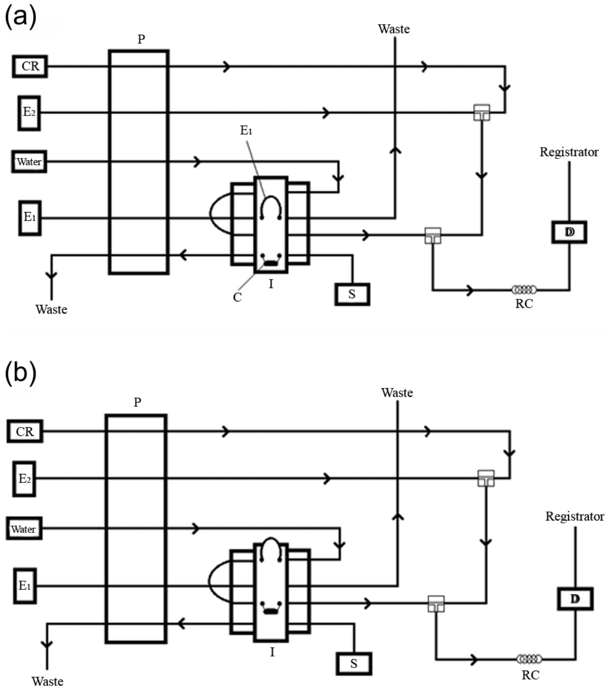

Figure 1. On-line preconcentration diagram: loading step (a) and elution step (b). S: sample; E_1: eluent (HNO_3 0.5 mol L^{-1} and water); E_2: eluent (1.0 mol L^{-1} HNO_3); CR: chelating reagent (DDTC 0.3% m/V); P: peristaltic pump; I: injector; C: mini-column containing 50 mg of $SiO_2/TiO_2/ZnO$; D: spectrophotometric detector; RC: reaction coil.

Results and Discussion

Physical and chemical characterization of $SiO_2/TiO_2/ZnO$

The images of SEM and the corresponding energy dispersive spectra (EDS) mapping for Si, Ti and Zn elements are shown in Figure 2. The prepared material exhibited a morphology containing a flat surface without porosity in the magnification used, together with an uniform dispersion of mixed oxides, as illustrated by absence of phase's segregation or islands in the EDS elemental mapping. The good dispersion of mixed oxides (SiO_2, TiO_2 and ZnO) can be attributed to strong interaction of the siloxane groups of silica surfaces by means of covalent bonds with oxides in the material. The white points observed from EDS mapping assures the presence of Si, Ti and Zn elements. The amounts of SiO_2, TiO_2 and ZnO determined by EDFRX were found to be 38.92, 38.38 and 22.70% (wt.%) respectively, showing the similar reactivity of metallic alcooxides in the sol-gel process.

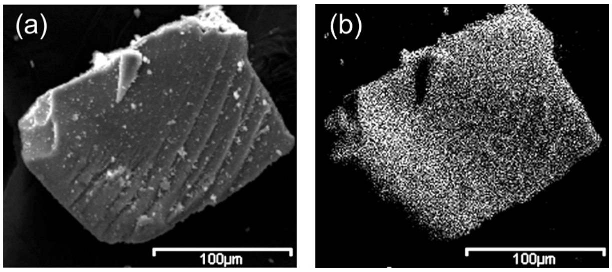

Figure 2. SEM image (a) and EDS mapping (b) of $SiO_2/TiO_2/ZnO$ material.

The X-ray diffraction spectrum depicted in Figure 3 showed a halo typical for the glass silica network in the range varying from $2\theta = 20$ to 30°, with absence of crystalline phases. Thus, the material synthesized is characterized as a non-crystalline solid.

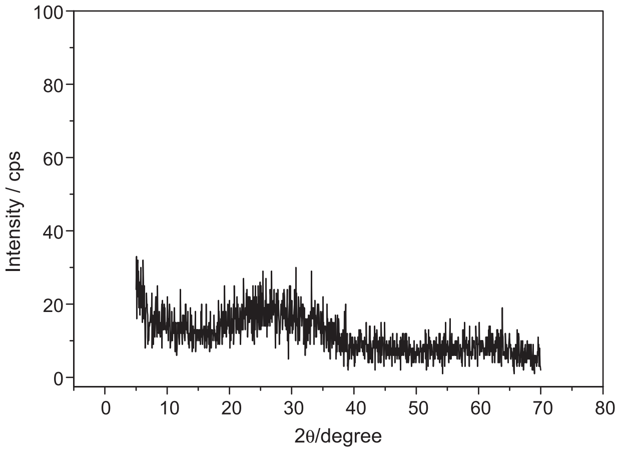

Figure 3. X-ray diffractogram of the $SiO_2/TiO_2/ZnO$ material.

The infrared spectrum of $SiO_2/TiO_2/ZnO$ exhibited a band at 3436 cm^{-1} attributed to OH stretching vibrational mode, whilst the band at 1635 cm^{-1} is related to overtone of O-H bond of water, physically adsorbed on the sorbents[30] and the band at 952 cm^{-1} is related to stretching and bending modes of the Si-OH groups.[31] The bands observed from 1100 to 450 cm^{-1} are attributed to the SiO_2 network, whereas the signals at 1100 cm^{-1} and 800 cm^{-1} correspond, respectively, to the asymmetric and symmetric stretching of Si-O-Si bonds. Finally, the band at 450 cm^{-1} is attributed to angular deformation of Si-O-Si.[30]

Influence of pH, type and buffer concentration

The pH effect was studied in the 3.75 to 10 range. For pH 3.75 and 4.75 samples were buffered with acetate buffer, 7 and 8 with Tris-HCl buffer and 10 with ammoniacal buffer. The concentration of buffer solutions was set at 0.01 mol L^{-1}. As shown in Figure 4, a considerable increase of analytical signal was observed with increasing pH up to 7.0 followed by decreasing after this value.

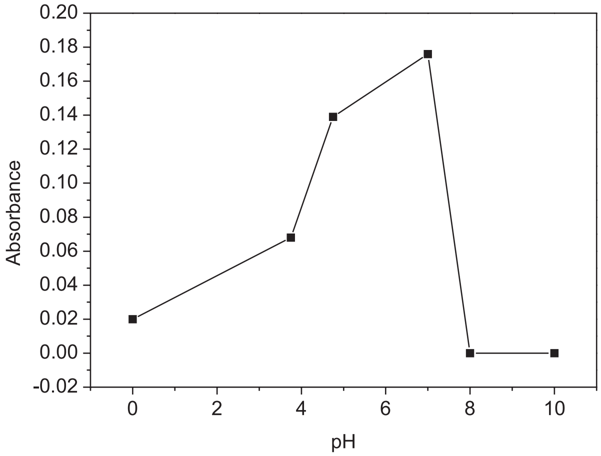

Figure 4. Effect of pH on preconcentration of 200.0 µg L^{-1} copper on 50 mg of the $SiO_2/TiO_2/ZnO$. Conditions: 20 mL of preconcentration volume at 5.2 mL min^{-1}; eluent concentration of 0.75 mol L^{-1}; and DDTC concentration of 0.5 % (m/v) at 0.8 mL min^{-1}.

The sample pH plays an important role in metal adsorption on oxides surface. As $SiO_2/TiO_2/ZnO$ material has acids and bases properties according to Brønsted concept, the available binding sites depends on the pH range. Thus, at low pH values, the oxygen atoms will be protonated, leading to a weak interaction with copper. On the other hand, at high pH values, a high adsorption rate can be noticed, which can be related to electrostatic attraction and/or possible formation of copper complexes with oxygen atoms disposed in the network of material. At pH extremely high, copper can precipitate in the $Cu(OH)_2$ form. According to the comments, all further works were carried out at pH 7.0.

In order to verify the influence of buffer solution type on the preconcentration method, phosphate and Tris-HCl were evaluated. There were no differences in the analytical signal when Tris-HCl and phosphate buffers were compared. Thus, Tris-HCl was chosen in detriment of phosphate in order to avoid posterior drawbacks related to precipitation of other cations present in real samples. Once the pH and buffer were optimized, the Tris-HCl concentration was studied in the 1.0×10^{-3} to 2.0×10^{-1} mol L^{-1} range (Figure 5).

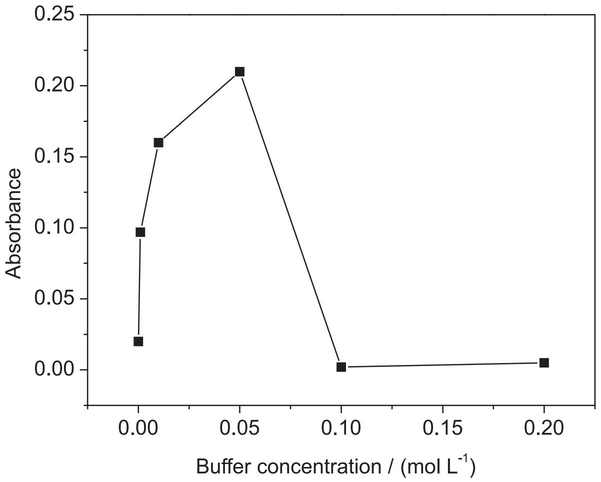

Figure 5. Effect of buffer concentration on preconcentration of 200.0 µg L^{-1} copper on 50 mg of the $SiO_2/TiO_2/ZnO$. Conditions: 20 mL of preconcentration volume at 5.2 mL min^{-1}; pH 7.0; eluent concentration of 0.75 mol L^{-1}; and DDTC concentration of 0.5% (m/v) at 0.8 mL min^{-1}.

The concentration of buffer solution in the medium increases the analytical signal up to 5.0×10^{-2} mol L^{-1}, due to best buffering capacity. For the higher buffer concentration, the analytical signal is suddenly decreased probably due to high ionic strength, which makes more difficult the retention of copper onto surface of material. According to the results, pH 7.0 buffered with 5.0×10^{-2} mol L^{-1} Tris-HCl was chosen for further experiments.

Influence of eluent and DDTC concentration

Nitric acid solution was chosen as eluent of copper from mini-column packed with $SiO_2/TiO_2/ZnO$. Hydrochloric acid was not investigated once previous publication by our research group has pointed out that this eluent is not indicate for reactions of copper with DDTC chelating.[16] Thus, nitric acid concentrations were studied in a range of 0.5 to 1.3 mol L^{-1} and an insignificant difference in the analytical signal was observed, indicating analytical robustness of this variable. For further experiments 0.5 mol L^{-1} HNO_3 was chosen.

The chelating (DDTC) concentrations were investigated in the 0.01 to 0.8% (m/v) range. The analytical signal increased with increasing of DDTC concentration until 0.3% (m/v), being this value adopted for posterior studies. Concentrations higher than 0.3% (m/v) can decrease slightly the molar absorptivity of the complex Cu(DDTC)$_2$, thus justifying the reduction of the analytical signal.

Influence of length of reaction coil, preconcentration, eluent and chelating flow rate

The length reaction coils were evaluated from 30 to 100 cm. The highest analytical response was observed for reaction coil of 60 cm. By using reaction coil higher than 60 cm, an enhanced dispersion of sample zone is observed, with consequent decreases of the analytical signal. In this way, 60 cm of length of reaction coil was chosen for subsequent experiments.

Preconcentration flow rate was ranged from 2.6 up to 10.0 mL min^{-1}. Within this experimental domain, an accentuated reduction of the analytical signal was verified for higher flow rates. Such result indicates that the kinetics of mass transfer of copper towards SiO$_2$/TiO$_2$/ZnO surface is not so fast. The choice of a low flow rate would imply in reduced sample throughput, whereas high flow rates lead to decrease of detectability. Therefore, 6.4 mL min^{-1} was the value adopted as a compromise between analytical signal, sample throughput and waste generation. It is worth emphasizing that problems of leakage due to the swelling of the sorbent are avoided by using lower preconcentration flow rates.

The eluent flow rate was investigated by varying the carrier flow rate (water) in the 2.6 to 10.0 mL min^{-1} range. A pronounced increase of analytical response was observed by increasing the flow rate from 2.6 up to 4.5 mL min^{-1}, and from 4.5 up to 10.0 mL min^{-1} the analytical signal remained unchanged. Such result is attributed to the low broadening of analytical signal when higher flow rate values are used owing to low dispersion of sample zone in the flow system. Thus, taking into account the fixed eluent volume (300 µL) and the eluent concentration previously optimized (0.5 mol L^{-1}); the highest eluent flow rate (10.0 mL min^{-1}) was not employed in the subsequent studies to avoid any memory effect after several preconcentration/elution cycles. Hence, the eluent flow rate of 6.4 mL min^{-1} was chosen.

The chelating flow rate exerts great influences on kinetic of complex formation, Cu(DDTC)$_2$. For this study, the flow rate was varied from 1.0 to 4.15 mL min^{-1}, whose best analytical signal was achieved at 1.6 mL min^{-1}. At low flow rate, the dispersion of sample zone is enhanced, whilst for high flow rate there is kinetic limitation in the complex formation.

Effect of different metal ions on preconcentration procedure

The effect of different metal ions on copper preconcentration onto SiO$_2$/TiO$_2$/ZnO surface, as well as on spectrophotometric determination using DDTC as chelating agent were evaluated under optimized conditions. Binary solutions containing copper and the possible interfering metal ions (Mn^{2+}, Zn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, Ca^{2+} and Mg^{2+}) were prepared in different proportions and submitted to preconcentration procedure. This study was carried out by preconcentrating 20.0 mL of a binary solution containing copper at concentration of 200.0 µg L^{-1}. Interferences were evaluated by comparison of copper recovery from single and binary solutions considering a relative error of ± 10% in the analytical response. It was observed no interference for Mg^{2+}, Ca^{2+} in the 1:100 (m/m, analyte:interference) proportion and Mn^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+}, Ba^{2+} and Cr^{3+} in the 1:10 (m/m, analyte:interference) proportion. The absence of interference can be attributed to Pearson's acidity and basicity definitions,[32] reactivity of interfering ions with DDTC and binding sites available in the material. Mg^{2+}, Ca^{2+}, Cr^{3+}, Fe^{3+}, Mn^{2+} and Ba^{2+} are considered as hard acids, so they will have few interactions with oxygen atoms from Ti-O or Zn-O bonds, both characterized as borderline base. Ni^{2+}and Zn^{2+} ions are borderline acids and, thus, it would be expected some interference on solid phase extraction procedure and spectrophotometric determination once Ni-DDTC and Zn-DDTC complexes are usually monitored at 430 nm.[33] As DDTC form highly stable complexes with copper in comparison to Ni^{2+} and Zn^{2+}, this fact can explain the low interference in this case.[34] Finally, Co^{2+}, Pb^{2+} and Cd^{2+} (borderline and soft acids) positively interfered on analytical signal in the 1:10 proportion, thus suggesting a competitive adsorption onto SiO$_2$/TiO$_2$/ZnO surface and reaction with DDTC. In this case, the Pearson's acidity and basicity theory cannot be applied, mainly for Pb^{2+} and Cd^{2+}, where the retention of these metals ions can take place by complexes formation with oxygen atoms in adequate coordination geometry occupying both interlayer and surface edge sites. It is worth state that, despite the little interference observed, the application of the method in water and food samples will not suffer from concomitant interference.

Analytical features and application of the method

The analytical performance of the developed method was determined under optimized conditions. The calibration equation was found to be Abs = –0.00362 (± 1.8 × 10^{-4}) + 7.0 × 10^{-4} (± 4.9 × 10^{-5}) [Cu^{+2} µg L^{-1}] (r = 0.998) for concentrations ranging from 20.0 to 230.0 µg L^{-1}, whilst the equation for the system without preconcentration step was found to be Abs = 0.00135 (± 4.0 × 10^{-5}) + 1.95 × 10^{-5} (± 9.7 × 10^{-7}) [Cu^{+2} µg L^{-1}]

Table 1. Analytical performance of different solid phase preconcentration methods for copper determination by UV-Vis spectrophotometry

Adsorbent	Preconcentration modality	Volume / mL	Chelating agent	Eluent	LOD / (μg L^{-1})	Reference
Octadecylsilica membrane disks	off-line	500	Neocuproine	3-methyl-1-butanol	0.12	36
1,3-diaminepropane-3-propyl grafted onto a silica gel	on-line	13	DDTC	HNO_3	8.4	15
Lewatit TP807’84 resin	on-line	100	Sulfarsazene	HCl	2.0	37
Microcrystalline benzophenone	off-line	100	Cupferron	Ethanol	5.5	38
Polyurethane foam	on-line	7.5	Me-BDBD	HCl	3.4	39
$SiO_2/TiO_2/ZnO$	on-line	20	DDTC	HNO_3	5.6	This work

LOD: limit of detection (μg L^{-1}); Me-BDBD: 6-[20-(60-methyl-benzothiazolylazo)]-1,2-dihydroxy-3,5-benzenedisulfonic acid.

(r = 0.998) for concentrations ranging from 2000.0 to 15000.0 μg L^{-1}. From the slopes ratio of the calibration equation, a preconcentration factor (PF) of 35.9 was achieved. In addition, the processing method by sol-gel employed for preparation of the $SiO_2/TiO_2/ZnO$ composite can be considered satisfactory to enhance the detectability of the preconcentration method, once no analytical signal was obtained by preconcentrating copper from 20.0 up to 230.0 μg L^{-1} through a mini-column packed with pure SiO_2. The limits of detection and quantification provided by proposed method, determined according to IUPAC definition[35] were found to be 5.6 and 18.8 μg L^{-1}, respectively. The precision was estimated in terms of repeatability for 10 measurements analyzing copper standard solution containing 200.0 μg L^{-1}. A relative standard deviation (RSD) of 0.68% was obtained. The concentration efficiency (CE) defined as the preconcentration factor achieved in one minute of preconcentration, consumption index (CI) as the preconcentrated volume required to achieve one unit of preconcentration factor were found to be 11.5 min^{-1}, 0.55 mL, respectively. A high sample throughput of 17.6 h^{-1} was also obtained for the proposed method. Compared with the other solid phase preconcentration methods for copper determination by UV-Vis spectrophotometry using on-line mode (Table 1), the analytical performance of the $SiO_2/TiO_2/ZnO$ as sorbent was, in general, very similar. However, a low sample consumption, high sample throughput and satisfactory limit of detection can be noticed when compared with those ones using off-line mode. Moreover, the reusability of the $SiO_2/TiO_2/ZnO$ synthesized material has been considered very high, once only one mini-column has been used throughout the study including the optimization and application of the method without apparent losses of adsorptive performance.

In order to evaluate the potential of the preconcentration method for practical applications, it was applied for copper determination in water and vegetables samples, using external calibration. Table 2 shows the results regarding application of the method.

Table 2. Application of the proposed method for copper determination in water and food samples

Water samples			
Sample	Copper added / (μg L^{-1})	Copper found[a] / (μg L^{-1})	Recovery / %
Tap water	30.0	28.00 ± 0.01	93
	60.0	55.90 ± 0.72	93
Mineral water	30.0	30.40 ± 0.67	101
	60.0	63.70 ± 0.01	106
Lake water	30.0	32.30 ± 1.16	108
	60.0	54.60 ± 0.67	91
Vegetable samples			
Sample	Copper added / (μg g^{-1})	Copper found[a] / (μg g^{-1})	Recovery / %
Lentil	–	3.67 ± 0.42	–
	4.0	7.57 ± 0.29	99
Parsley	–	10.19 ± 0.54	–
	10.0	19.98 ± 0.26	99
Chive	–	13.76 ± 0.15	–
	15.0	27.49 ± 0.32	96

[a] Results are expressed as mean value ± standard deviation based on three replicates (n = 3).

Once for water samples the levels of copper were below the limit of detection, the accuracy was checked from addition of known amount of copper followed by recovery tests. The results pointed out recoveries above 91%. Copper was quantified in vegetable samples and satisfactory recovery percentages ranging from 96 to 99% were also achieved. Furthermore, the applicability of the method for determination of copper in animal protein was assured by analysis of Dolt-4 (Dogfish liver) and Dorm-3

(Fish protein) certified reference materials, as exhibited in Table 3. From test *t*-student with 95% confidence level, no statistical difference ($t_{\text{calculated}}$ = 0.806 and 1.90 < t_{critical} = 4.303) was observed between certified value and those determined by the proposed method.

Table 3. Application of the proposed method for copper determination in certified reference materials

Sample	Copper certified / (mg kg^{-1})	Copper found[a] / (mg kg^{-1})	Recovery / %
DOLT-4	31.2 ± 1.1	31.75 ± 1.10	102
DORM-3	15.50 ± 0.63	15.61 ± 0.10	103

[a] Results are expressed as mean value ± standard deviation based on three replicates (n = 3).

Conclusions

In this study, a new mixed oxide $SiO_2/TiO_2/ZnO$ sorbent was synthesized, characterized and used for copper preconcentration from water and digested food samples with posterior flow injection spectrophotometric determination. Compared with the other solid phase spectrophotometric methods for copper determination mainly with those ones using off-line mode, the method herein developed showed low sample consumption, high sample throughput and satisfactory limit of detection. Sorbent presented high reusability and desirable selectivity towards copper, which was confirmed from successfully analysis free-interference with precision and accuracy of water and food samples. The $SiO_2/TiO_2/ZnO$ material can be used as a new and efficient solid phase aiming at improving the detectability and selectivity for copper determination by UV-Vis spectrophotometry.

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