Silica-Alumina-Niobia (SiO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$) Matrix Obtained by the Sol-gel Processing Method: New Material for Online Extraction of Zinc Ions

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In the present work, a new material, SiO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$ (designated as SiAlNb), was evaluated as an adsorbent in a flow injection spectrophotometric method for online preconcentration and determination of trace amounts of Zn$^{2+}$ ions. The preconcentration method is based on Zn$^{2+}$ adsorption onto the surface of SiAlNb in an alkaline medium (pH 9.0). The elution step is carried out using HNO$_3$ solution, followed by reaction of the Zn$^{2+}$ ions with 1-(2-piridilazo)-2-naphthol (pan) in an ammoniacal buffer solution (pH 9.3) containing Tween-80. The [Zn(pan)$_2$] complex formed is determined at 560 nm. The method presented a linear range between 7.6 and 180.0 µg L$^{-1}$ ($r = 0.9992$) and limits of detection and quantification of 2.3 and 7.6 µg L$^{-1}$, respectively. According to the Langmuir linear model, the maximum adsorption capacity was found to be 7.0 mg of Zn$^{2+}$ per gram of SiAlNb. The proposed method was successfully applied to the Zn$^{2+}$ determination in water samples (lake, mineral, tap) and certified reference material (TORT-2 Lobster Hepatopancreas).

Keywords: adsorbent preconcentration system, zinc ions, silica-alumina-niobia, sol-gel process

Introduction

Current research in the field of analytical sciences has basically been focused on the enhancement of technique performance, such as in miniaturization, automation capabilities and enhanced power detection, as well as on sample preparation, aiming at solving instrumental problems.¹ Undoubtedly, solid phase extraction (SPE) is considered one of the most representative techniques for sample preparation, enabling both the removal of severe matrix interferences and the achievement of accentuated enrichment factors. Moreover, other advantages can be pointed out, such as easy automation with flow injection systems, easy recovery of solid phase and, in many cases, no requirement for the use of toxic solvents.²,³ These features enable SPE to be widely used in combination
with relatively simple detection techniques as well as sophisticated equipments. Literature presents a great number of adsorbents which are traditionally classified as inorganic-based ones, mainly \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \); organic-based ones, including natural adsorbents; organic polymers (chelating resins or non-polar polymers); hybrid organic-inorganic polymers and carbonaceous adsorbents (activated carbon, fullerene and carbon nanotubes).\(^5\) Bearing in mind the application of SPE for metal ions, depending upon the choice of materials (mainly those organic polymers with medium polarity), it is necessary to use chelating agents for metal ions so that selectivity can be achieved. Other adsorbents, such as the natural ones, do not usually present selectivity and chemical stability. Therefore, there have been attempts to develop materials with novel and interesting properties through variation of their chemical composition and physical dimensions. New solid adsorbents should possess an excellent specific surface area, highly stable chemical structure over a wide pH range, high adsorption capacity, excellent swelling resistance in different solvents at high pressure, fast and quantitative adsorption and elution, high mass exchange and easy and low cost synthesis. These features are somewhat observed in silica (\( \text{SiO}_2 \)), but the silica matrix used to adsorb metal ions in aqueous solution presents some limitations associated to low selectivity, since the silanol groups (Si-OH) are weakly acidic, and reduced chemical stability in alkaline medium due to hydrolysis of siloxane groups, which is favoured at high pH values.\(^6\) Thus, close attention has been widely paid for searching organically and inorganically modified silica. This later approach has been based on preparation of \( \text{SiO}_2/\text{MO}_x \) binary oxides obtained by the sol-gel processing method, in which the mechanical properties of the silica matrix are combined with the chemical properties of bulk of the metal oxides (\( \text{MO}_x \)).

The sol-gel process also permits to obtain a solid with controlled porosity, and the metal oxide can be obtained as highly dispersed particles in the matrices.\(^7\) Basically, the procedure consists in the reaction between tetraethylorthosilicate, \( \text{Si}(\text{OEt})_4 \), and the metal oxide precursor, \( \text{M} (\text{OR})_x \), shown in equation 1:

\[
\text{Si}(\text{OEt})_4 + x\text{M} (\text{OR})_x \xrightarrow{\text{sol-gel}} \text{SiO}_2/\text{MO}_x + 4\text{EtOH} + xy\text{R}’\text{OH} \quad (1)
\]

The product, \( \text{SiO}_2/\text{MO}_x \), has found many applications in recent years.\(^8\)\(^-\)\(^22\) One of the greatest interests is its use as a porous substrate to immobilize electroactive species and the possibility to prepare a series of electrochemical sensors (chemically modified electrodes).\(^8\)\(^-\)\(^11\)\(^,\)\(^23\)\(^-\)\(^26\) The metal oxides dispersed in the silica matrix are usually refractory, including \( \text{TiO}_2, \text{Al}_2\text{O}_3, \text{Sb}_2\text{O}_5 \) and \( \text{Nb}_2\text{O}_5 \). They present acid and basic properties and therefore can be used for adsorbing metal ions and anionic species depending upon the pH range.\(^27\) It is also important to emphasize that the metal oxide dispersed on the silica matrix presents chemical and physical properties different from those observed for bulk metal oxide, including a higher capacity for ion exchange.\(^28\)

The use of \( \text{SiO}_2/\text{MO}_x \) binary oxides in analytical approaches has been reported for silica-niobia (\( \text{SiO}_2/\text{Nb}_2\text{O}_5 \)),\(^29\) silica-titania (\( \text{SiO}_2/\text{TiO}_2 \)),\(^30\) silica-zirconium(IV)-phosphate (\( \text{SiO}_2/\text{Zr}(\text{H}_2\text{PO}_4)_2 \))\(^31\) and silica-zirconia (\( \text{SiO}_2/\text{ZrO}_2 \)),\(^32\) where they were successfully used for extraction/preconcentration of trace metals. Nevertheless, to the best of our knowledge, the oxide mixture dispersed on the silica matrix, \( i.e. , \text{SiO}_2/\text{MO}_x/ \text{NO}_x \), has not been investigated for analytical purposes concerning metal preconcentration. Therefore, as \( \text{Al}_2\text{O}_3 \) and \( \text{Nb}_2\text{O}_5 \) present Brønsted acid and base properties, besides being used as catalysts\(^33\) and ion exchangers,\(^34\) we highlight, in the present work, the use of this oxide mixture dispersed onto silica matrix (SiAlNb) as a new adsorbent for metal ions for the first time. The \( \text{Al}_2\text{O}_3 \) and \( \text{Nb}_2\text{O}_5 \) oxides are chemically stable in a wide pH range, and \( \text{Nb}_2\text{O}_5 \), in particular, is soluble only in HF and hot \( \text{H}_2\text{SO}_4 \).\(^35\) Thus, the presence of these oxides on the silica matrix (mainly at high \( \text{Nb}_2\text{O}_5 \) concentration) makes the SiAlNb material chemically stable at high pH values.

Particular interest was given to zinc ions owing to their intrinsic importance in various biological systems, where it is found in more than 80 enzymes (as in carboxypeptidase, carbonic anhydrase, bovine superoxide dismutase, etc.)\(^36\) and environmental samples, as well as to their trace amount commonly found in these samples. For example, the active site of the alcohol dehydrogenase (ADH) consists of a zinc atom, and ADH catalyzes the transfer of a hydride ion from NADH to acetaldehyde, forming ethanol.\(^37\) Zinc deficiency can produce hair loss, diarrhea, impotence and sexual immaturity, apathy, chronic liver disease, chronic renal disease, amnesia, fatigue, and other chronic illnesses.\(^38\) Also, zinc compounds such as zinc chloride, sulfide and oxide are widely employed in the industry. Thus, there is great interest in determining the presence of zinc in various types of samples, such as environmental, biological, industrial, etc. The feasibility of the new SiAlNb adsorbent for zinc ions was investigated by the development of an adsorbent flow preconcentration system coupled to UV-Vis spectrophotometry. The proposed method shows attractive features as a new and efficient system for zinc determination in trace levels in water and biological samples.
Experimental

Apparatus

A Femto UV-Vis spectrophotometer (São Paulo, Brazil), model 482, equipped with a flow cell of 1 cm optical length, was used for FIA measurements. Data acquisition was carried out from an interfaced (Advantech) PCL 711S mode and a computational program was developed in an EXCEL® spreadsheet, using macros of Visual Basic®. An Ismatec Model IPC peristaltic pump (Ismatec IPC-08, Glattbrugg, Switzerland) furnished with Tygon® tubes was used to propel all sample and reagent solutions. The preconcentration/elution steps were selected by using a home-made injector commutator made of Teflon® (PTFE, polytetrafluoroethylene). Adjustment of sample pH was done by using a Handylab 1 Schott pHmeter (Stafford, UK). A Shimadzu AA-6800 flame atomic absorption spectrophotometer, where the absorbance measurements were continuously made at 560 nm. All absorbance signals are continuously made at 560 nm. All absorbance signals were taken as peak height. The chelating pan was adopted as peak height. The chelating agent 1-(2-piridylazo)-2-naphtol (pan) and the surfactant Tween-80 were acquired from Vetec (Rio de Janeiro, Brazil). For the preparation of SiAlNb, tetraethylorthosilicate at 98%, aluminum isopropoxide at 98%, niobium(V) chloride at 99% and trifluoroacetic acid, all from Aldrich (St. Louis, USA), were used.

Preparation of SiAlNb mixed oxide

The new material SiO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$, designated as SiAlNb, was prepared according to the following procedure: Into 100.0 mL of a 50% (v/v) solution of ethanol/TEOS (TEOS = tetraethylorthosilicate), 5.6 mL of 3.5 mol L$^{-1}$ HCl were added. The mixture was stirred for 3 h at 60°C. After the pre-hydrolysis step, 4.4 g of aluminum isopropoxide (dissolved in small amounts of trifluoroacetic acid) and 6.7 g of NbCl$_5$, (previously solubilized in ethanol under a nitrogen atmosphere) were added and the resulting mixture was stirred for 2 h at 60°C. The mixture was stirred for another period of 12 h at room temperature. The solvent was slowly evaporated at 60°C until gel formation. The gel so obtained was ground (≤ 250 µm) and the resulting particles were washed with ethanol in a soxhlet extractor for 4 h. Finally, the material was washed with 100 mL of 0.1 mol L$^{-1}$ HNO$_3$, deionized water and ethanol, followed by drying under vacuum (1.3 × 10$^{-2}$ Pa) for 2 h at room temperature and then stored.

Adsorbent flow preconcentration system

The diagram of the flow preconcentration system is displayed in Figure 1. At the preconcentration step position (Figure 1a), 20.0 mL of the sample buffered at pH 9.0 were percolated through a minicoloumn of SiAlNb (150 mg) at 4.0 mL min$^{-1}$ flow rate. After this stage, by switching the central part of the injector commutator, a stream of 0.50 mol L$^{-1}$ HNO$_3$ displaces the zinc ions at 1.0 mL min$^{-1}$ flow rate. Afterwards, the eluted zinc ions react with 100.0 µmol L$^{-1}$ pan solution (pH 9.3) at 2.0 mL min$^{-1}$ flow rate. The [Zn(pam)$_2$] complex is pumped into the spectrophotometer, where the absorbance measurements are continuously made at 560 nm. All absorbance signals were taken as peak height. The chelating pan was adopted in this work because it is a reagent broadly applicable to heavy metals and very common in laboratory.
Adsorption isotherm

The zinc adsorption experiments onto SiAlNb were carried out at 298 K using the batch technique. 20.0 mL of zinc solution, with concentrations increasing from 0.1 up to 10 mg L\(^{-1}\), were shaken during 10 min in 0.05 mol L\(^{-1}\) ammoniacal buffer (pH 9.0). At the end of this equilibrium time, the zinc adsorption by SiAlNb was determined by measuring the initial and final concentration of zinc by FAAS. In order to determine the maximum adsorption capacity (MAC), all batch experimental data were fitted to the linear Langmuir and Freundlich isotherm models.\(^{39}\)

Sample preparation

The devised method was applied for zinc determination in lake water, mineral water and tap water. Mineral and tap water samples were acquired from local supermarkets and from UNIFAL-MG campus and analyzed immediately after pH adjusting with buffer solution. Lake water samples were collected in polypropylene flasks from a lake near Alfenas city and immediately acidified with HNO\(_3\) solution until a pH sample of 2.0 was attained. Afterwards, the samples were filtered through 0.45 \(\mu\)m cellulose acetate membranes under vacuum and the pH was adjusted with buffer solution. Besides these samples, the feasibility of the methodology was also evaluated by analysis of certified reference material (TORT-2 Lobster Hepatopancreas). About 100 mg of the sample were placed into Teflon\(^{®}\) flasks, followed by addition of 10 mL concentrated HNO\(_3\) and 4 mL 30% (v/v) H\(_2\)O\(_2\). The heating program of the microwave oven was then employed in two steps. A 400 W power was applied during 5 min, with further increase to 700 W, which was maintained during 10 min. After this step, 4 mL 30% (v/v) H\(_2\)O\(_2\) were added to the sample, which was heated on a hot plate to near dryness, then cooled to room temperature and dissolved in ammoniacal buffer solution. Any contamination source was checked by using blank solutions.

Results and Discussion

Characterization of SiAlNb

The sample presented characteristics of a porous material and a remarkable surface area around 309 m\(^2\) g\(^{-1}\), obtained by the BET (Brunauer, Emmet, Teller) method.
In addition, it revealed mesopores, which contribute to a higher surface area and allow Zn²⁺ ions diffusion into the pores. These features are highly desirable for the proposed application of this solid adsorbent in flow preconcentration system for metal determination.

The results obtained for the Al₂O₃ and Nb₂O₅ amounts incorporated in the material SiAlNb, obtained by EDFRX, were 2.1 wt.% and 33.6 wt.%, respectively. The value of the 2.1 wt.% for the Al₂O₃ was somewhat lower than expected, probably owing to the pH of the reaction medium, which was not favorable to the complete hydrolysis of aluminum isopropoxide. However, the material SiAlNb is an excellent ion exchanger.

A typical SEM micrograph of the SiAlNb material is shown in Figure 2. The image indicates that the particles of Al₂O₃ and Nb₂O₅ are dispersed on the SiO₂ surface within the magnification used. A few white agglomerated particles are due to Al₂O₃ and Nb₂O₅ and can be detected on the surface as isolated islands in Figure 2A. At the studied level, the material seems homogeneous, as can be seen in Figure 2B (the energy dispersive scanning image, EDS). The Figure 2B showed that the Al and Nb atoms are dispersed without any detectable phase segregation of the oxide particles in the matrix and are present on the SiAlNb surface under the magnification used. A good dispersion of the metal oxides in the matrix is an important feature for the application of the material as a new adsorbent for trace metals using flow injection spectrophotometry.

Figure 3 shows the infrared spectra of SiO₂ (——) and SiAlNb (——) obtained by the sol-gel process. The two spectra are very similar, although the bands recorded for SiAlNb are somewhat broader and some of them shift toward lower frequencies. This behavior is consistent with the infrared spectra obtained by Aronne et al.⁴⁰ for Nb₂O₅-SiO₂ obtained by the sol-gel process with different concentrations of Nb₂O₅ [between (Nb₂O₅)₀.025(SiO₂)₀.975 and (Nb₂O₅)₀.2(SiO₂)₀.8], suggesting that the bands are progressively influenced by the amount of Nb₂O₅. The infrared spectra indicate that the SiO₂ network is only slightly disturbed by the presence of the metal oxides, suggesting that Al₂O₃ and Nb₂O₅ are dispersed on the matrix, as observed from EDS data.

**Optimization of Adsorbent Preconcentration System**

The influence of sample pH on the adsorption of zinc ions onto SiAlNb was studied from pH 4.0 to 10.0. For this study, the zinc standard solutions were buffered with different types of buffers, whose concentrations were maintained at 0.05 mol L⁻¹. Acetate for pH 4.0 and 5.0, phosphate for pH 6.0 up to 8.0 and borate for pH 9.0 and 10.0 were used. The oxides grafted on silica surface present Brønsted acid and base properties. Therefore, the retention of Zn²⁺ ions takes place by electrostatic interaction with oxygen atoms bonded to metal.
(Si-O-Al-O-H and Si-O-Nb-O-H). As a consequence, the adsorption is very low at low pH values owing to the protonation of the oxygen centers. On the other hand, higher adsorption of Zn$^{2+}$ is observed in alkaline medium. As can be seen in Figure 4, an increase in the analytical signal was observed by increasing the sample pH. Moreover, the electrostatic retention of CH$_3$COO$^-$ or H$_2$PO$_4^-$ anions onto the positively charged surface material also contributes to the reduced adsorption rate of Zn$^{2+}$ ions. At pH values above 7.0, the adsorption increases significantly because the SiAlNb acquires negative charge and, as a consequence, an effective retention of Zn$^{2+}$ ions occurs. It must be emphasized that, within the pH range from 8.0 and 9.0, the presence of PO$_4^{3-}$ and BO$_3^{3-}$ can lead to the precipitation of Zn$^{2+}$ ions or their complexation, respectively, and it would imply a decrease in adsorption rate. However, the very high analytical signal observed even in alkaline medium confirms that adsorption takes place, in fact, by retention of Zn$^{2+}$ ions onto the negatively charged adsorbent surface. Above pH 9.0, the adsorption was less effective, probably due to the formation of [Zn(OH)$_4$]$^{2-}$, which is not retained by the adsorbent. Thus, the sample pH of 9.0 was chosen for further experiments.

The effect of the sample flow rate was examined in the 2.0-8.0 mL min$^{-1}$ range. As shown in Figure 5, by employing a low preconcentration flow rate ranging from 2.0 up to 4.0 mL min$^{-1}$, differences in the analytical signal were observed. However, when the work was carried out with a preconcentration flow rate higher than 4.0 mL min$^{-1}$, the analytical signal was unsatisfactory, indicating that the kinetic of mass transfer of Zn$^{2+}$ towards the adsorbent sites is not so fast and depends on the flow rate. Therefore, the preconcentration flow rate of 4.0 mL min$^{-1}$ was chosen for this study.

In order to assess the effect of the type of buffer on the adsorption of zinc ions onto SiAlNb, the preconcentration step was carried out by buffering the sample with ammoniacal or borate buffers at 0.05 mol L$^{-1}$. An increase of ca. 30% in the analytical signal was observed when ammoniacal buffer was used instead of borate buffer. This result can possibly be explained by a higher zinc borate complex formation at pH 9.0 than ammoniacal complex formation. Therefore, ammoniacal buffer was selected for further experiments.

The effect of buffer concentration was studied by ranging ammoniacal buffer from 0.001 up to 0.2 mol L$^{-1}$. Figure 6 illustrates the effect of increasing concentrations of buffer solution on the retention of Zn$^{2+}$ ions onto SiAlNb and, as can be seen, the increase of the buffer concentration up to 0.05 mol L$^{-1}$ increases the analytical signal. A lower buffer concentration could not be used because it would not be feasible to maintain the sample buffered when the nitric acid solution is employed as eluent. The analytical signal decreases significantly as the buffer concentration exceeds 0.05 mol L$^{-1}$. These results suggest that the formation of [Zn(NH$_3$)$_4$]$^{2+}$ may influence the adsorption rate of Zn$^{2+}$ ions onto SiAlNb. Thus, a buffer concentration of 0.05 mol L$^{-1}$ was selected as the best condition.

The concentration of pan plays an important role in the analytical signal. Its concentration must be sufficiently high to guarantee the total complexation of zinc. The studied range was from 100.0 to 800.0 µmol L$^{-1}$ (Figure 7). For all
studied values, there is an excess of pan as compared to zinc ions. However, the excessive concentration of chelating agent in the medium can reduce the molar absorptivity of the [Zn(pan)_2] complex. Thus, the concentration of 100.0 μmol L⁻¹ pan was adopted for further experiments.

The effect of eluent concentration on complete desorption of Zn²⁺ from SiAlNb was studied using nitric acid solutions at different concentrations (0.05-0.5 mol L⁻¹). As shown in Figure 9, for concentrations lower than 0.2 mol L⁻¹, a dramatic decrease in the analytical signal is observed, associated with memory effect after each preconcentration/elution step. Under these conditions, the eluent is not able to disrupt sufficiently the interaction of Zn²⁺ with the SiAlNb surface and subsequently release the metal ion. Quantitative elution is obtained by using concentrations higher than 0.2 mol L⁻¹ HNO₃. Nevertheless, above this concentration, the buffering capacity of the ammoniacal buffer is seriously diminished. So, 0.2 mol L⁻¹ HNO₃ as desorption agent was used in the system.
Effect of foreign ions on preconcentration method

In order to investigate the selective separation and determination of zinc ions from real samples containing different metal ions, a 100 µg L⁻¹ zinc solution and increasing amounts of possible interfering ions were taken and submitted to the preconcentration procedure. The ratios analyte:concomitant employed were 1:1, 1:10 and 1:100 (m/v) for all metals evaluated. The results were compared with zinc preconcentration in the absence of concomitant. When the analytical signal was changed positively or negatively above 10%, the presence of interference in the procedure was considered. The maximum limit of each concomitant metal ion that did not interfere with zinc concentration was: Ni²⁺ (100 µg L⁻¹), Cd²⁺ (1000 µg L⁻¹), Co²⁺ (100 µg L⁻¹), Ca²⁺ (100 mg L⁻¹), Sb³⁺ (1000 µg L⁻¹), Hg²⁺ (100 µg L⁻¹), Pb²⁺ (1000 µg L⁻¹) and Mn²⁺ (100 µg L⁻¹). The absence of interference when using an analyte:concomitant ratio of 1:1 (m/v) is probably attributed to Pearson’s definition of acids and bases.⁴⁴ Co²⁺, Ni²⁺, Mn²⁺ and Zn²⁺ are considered borderline cations and possess affinity for both hard ligands containing oxygen (O) and soft ligands containing sulfur (S). However, as Zn²⁺ is more polarizable and bigger than Co²⁺, Ni²⁺ and Mn²⁺ ions, it is considered a very soft acid. Thus, as the oxygen atom bonded to the metal in Si-O-Al-O and Si-O-Nb-O becomes more polarizable, and as consequence a very soft base, explains fairly the preference of Zn²⁺ in detriment of Co²⁺, Ni²⁺ and Mn²⁺ towards those oxygen atoms of SiAlNb. It can be inferred, from these results, that the method presents reasonable selectivity, once the amounts of these metals are lower in drinking and lake waters. This means that Zn²⁺ can be determined by UV-Vis spectrophotometry even in the presence of these metals, as will be demonstrated from the application of the method in real samples.

Adsorption isotherm

In order to determine the equilibrium time for transfer of Zn²⁺ ions between the solid and liquid phases, extractions in batch experiments for a series of solutions in a medium containing 0.05 mol L⁻¹ ammoniacal buffer (pH 9.0) and 2.0 mg L⁻¹ Zn²⁺ ions were carried out, according to the conditions optimized in the adsorbent flow preconcentration system. Results showed that the equilibrium time, ranging from 1 to 25 min, is attained in 10 min (data not shown). Thus, the mixtures have been shaken for 10 min to reach the equilibrium in the subsequent adsorption isotherm experiments.

Figure 10 shows the adsorption isotherm of Zn²⁺ ions onto SiAlNb, where a plateau was achieved when the equilibrium concentration in the mixture was 6.0 mg L⁻¹. The maximum amount of Zn²⁺ adsorbed per unit of surface area of SiAlNb, i.e., the maximum adsorption capacity, was determined by employing the following linear Langmuir or Freundlich isotherm models.

The Langmuir linear model is given by: $\frac{C}{Q} = \frac{1}{Q_m} + \frac{1}{Q_m K}$, where $Q_m$ is the adsorbed amount of Zn²⁺ (mg g⁻¹), $C$ the Zn²⁺ equilibrium concentration (mg L⁻¹) and $K$ and $M$ are, respectively, the maximum zinc adsorption capacity and the binding constant. This model establishes that adsorption takes place at a monolayer of adsorbent.

The Freundlich linear model is given by: $\log(Q_e) = \log(K_f) + \log(C)$, where $Q_e$ is the adsorbed amount of Zn²⁺ (mg g⁻¹), $C$ the Zn²⁺ equilibrium concentration (mg L⁻¹), $K_f$ is a constant and $K$ is the Freundlich adsorption isotherm. This model establishes that adsorption is not restricted to the formation of a monolayer. According to Figure 11, the best correlation coefficient indicates that the experimental data fit very well the Langmuir linear model ($r = 0.99465$). Thus, the Langmuir model is the most favorable one and this result is somewhat expected, taking into consideration that, according to SEM and EDS data, the Al₂O₃ and Nb₂O₅ particles are dispersed onto silica matrix surface as isolated islands.

From the Langmuir linear model, the MAC, determined from the inverse of the angular coefficient, was 7.0 mg g⁻¹. This result shows that the adsorption capacity of SiAlNb towards Zn²⁺ ions is higher than that reported for other adsorbent materials such as amberlite XAD-2000 (4.80 mg g⁻¹).⁴⁺ zinc(II) ion-imprinted polymer (3.90 mg g⁻¹),⁴⁺ amberlite XAD-2 resin-pyrocatechol (1.85 mg g⁻¹),⁴⁺ silica gel-silicylaldoxime (2.61 mg g⁻¹)⁴⁺ and amberlite XAD-2 resin-o-aminophenol (2.94 mg g⁻¹).⁴⁺
Characteristics of the adsorbent preconcentration flow system

The calibration graph (run for triplicate measurements at each point) for preconcentrating 20.0 mL of sample gave a linear range from 30.0 to at least 180.0 µg L\(^{-1}\) (\(r = 0.99926\)), whose linear equation was \(\text{Abs} = 3.45 \times 10^{-2} + 6.68 \times 10^{-3}[\text{Zn}\text{\(^{2+}\), µg L}\text{\(^{-1}\)}]\). The precision of the method, expressed as the R.S.D., for the determination of 20.0 and 170.0 µg L\(^{-1}\) Zn\(^{2+}\), were 3.25 and 1.71\%, respectively (\(n = 10\)). The linear equation obtained without the preconcentration system was \(\text{Abs} = 3.64 \times 10^{-2} + 1.27 \times 10^{-4}[\text{Zn}\text{\(^{2+}\), µg L}\text{\(^{-1}\)}]\). Therefore, the enrichment factor (EF), defined as the ratio of the slopes of the linear equation of the calibration graphs before and after the preconcentration, was 52.6. The concentration efficiency (CE) defines the preconcentration factor attained by an adsorbent flow preconcentration system during 1 min of preconcentration. Thus, as the entire time of preconcentration step was 5 min, the calculated CE was found to be 10.5 min\(^{-1}\). The limits of detection and quantification, defined, respectively, as the concentration of analyte leading to a signal equivalent to three and ten times the S.D. of the blank signal plus the net blank intensity, were measured as 2.3 and 7.6 µg L\(^{-1}\). The performance of the present adsorbent flow preconcentration method was compared with other methods for zinc preconcentration.

**Table 1.** Features of different preconcentration systems for zinc determination and evaluation with the proposed method using SiO\(_2\)/Al\(_2\)O\(_3\)/Nb\(_2\)O\(_5\) as solid sorbent

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<th>Chelating agent/Modifier</th>
<th>Eluent</th>
<th>PF</th>
<th>CI (mL)</th>
<th>SV (mL)</th>
<th>LD (µg L(^{-1}))</th>
<th>Linear range (µg L(^{-1}))</th>
<th>Detector</th>
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<td>1-100</td>
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<td>Dowex 1X8-50</td>
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<td>HNO(_3)</td>
<td>5</td>
<td>-</td>
<td>50-200</td>
<td>23</td>
<td>-</td>
<td>FAAS</td>
<td>58</td>
</tr>
<tr>
<td>Amberlite XAD-7</td>
<td>ARS</td>
<td>HNO(_3)</td>
<td>50</td>
<td>1</td>
<td>50</td>
<td>29</td>
<td>250-2000</td>
<td>FAAS</td>
<td>59</td>
</tr>
<tr>
<td>Silica gel</td>
<td>2-aminothiazole</td>
<td>HCl</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>97</td>
<td>-</td>
<td>FAAS</td>
<td>60</td>
</tr>
<tr>
<td>SiO(_2)/Al(_2)O(_3)/Nb(_2)O(_5)</td>
<td>pan</td>
<td>HNO(_3)</td>
<td>52.6</td>
<td>0.38</td>
<td>20</td>
<td>2.3</td>
<td>30 – 180</td>
<td>Spectrophotometry</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Notes:**
- PF = preconcentration factor; CI = consumptive index; SV = sample volume; LOD = limit of detection; pan = (1-(2-piridylazo)-2-naphthol); DPTH = 1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide; ARS = Alizarin red S; oVTSC = vanillinthiosemicarbazone; 8-BSQ = 8-(benzenesulfonamido)quinoline; FAAS = flame atomic absorption spectrometry; ICP-OES = inductively coupled plasma optical emission spectrometry.
coupled to different spectroanalytical techniques (Table 1). As observed, the adsorbent preconcentration method presented here shows better or similar performance when compared with the works previously published in terms of limits of detection, sample consumption and sample throughput.²⁻⁶⁰

**Determination of Zn²⁺ in water samples and certified reference material**

The method was applied to the direct determination of Zn²⁺ using external calibration in different types of water samples. Based on recovery studies with percentages varying from 96.0 to 106.7%, it is possible to conclude that the presence of foreign ions in these samples has no effect on the recovery of Zn²⁺ ions, thus attesting the accuracy of the method (Table 2). Moreover, the method was also successfully applied to Zn²⁺ determination in a certified reference material (TORT-2 Lobster Hepatopancreas) submitted to acid decomposition. The analytical results for this material (166.4 ± 4.6 mg kg⁻¹) are in good agreement with the certified values (180.0 ± 6.0 mg kg⁻¹), with 95% confidence level (t-student test), thereby also attesting its accuracy.

**Conclusions**

In this contribution, we reported for the first time the synthesis of a new material based on silica prepared by the sol-gel process and modified with an oxide mixture (Al₂O₃ and Nb₂O₅), as well as its characterization by SEM, EDS, surface area determination and infrared spectroscopy. The material exhibited outstanding features for use as a new solid adsorbent material, homogeneous dispersion of Al₂O₃ and Nb₂O₅ in the silica matrix, excellent swelling resistance and high adsorption capacity towards Zn²⁺ ions. Taking into account these features, a simple and sensitive flow injection spectrophotometric method for online preconcentration and determination of trace amounts of zinc was developed. The method presented feasibility for different types of samples (water and biological samples) with good precision and accuracy. Finally, the results of this study demonstrate that the research on the development of new materials based on preparation of multiple oxides dispersed on silica matrix obtained by the sol-gel process deserves to be more exploited, aiming at improving the performance of the analytical protocol for solid phase extraction.

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**References**
