Slurry sampling of sediments for direct determination of Cu, Mn, Ni, Sn and Zn by graphite furnace atomic absorption spectrometry

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Summary: *In this study, methodologies were developed for the determination of metals (Cu, Mn, Ni, Sn and Zn) in sediments prepared as slurries, which were maintained homogeneous by the introduction of air supplied by an aquariam pump by GF AAS (Graphite Furnace Atomic Absorption Spectrometry). The optimization of the pyrolysis and atomization temperatures were done through pyrolysis and atomization temperature curves using Ir, Rh, Ru, Zr, W and the condition with non-modifier use for generating each curve. To determine Cu, Mn, Ni, Sn and Zn in sediments by slurries, the sample was first dried, then crushed and sifted in a 65 μm sieve and weighed (~ 0,1 g) directly in the auto-sampler cup of the GF AAS, and finally, a 1 mL mixture of 3% H_2O_2 and 5% HNO_3 was added. The slurry was maintained homogeneous by an air flow created using a simple and inexpensive air pump. The optimized methodologies did not present matrix effects, which allowed for use of aqueous calibration of all the examined slurry metals. The relative standard deviation values of the measurements and their correlation coefficients were sufficient to attest the good precision and linearity for the methodologies. The study for accuracy was conducted using standard reference materials (NIST 1944 and 2709 e NRCC PACS-2 and MESS-3), which were in agreement with the certified values for the analyzed metals. The recovery values were between 80 and 120%. The achieved limits of quantification (LOQ) are in compliance with Brazilian federal legislation.*

Keywords: *Copper, Manganese, Nickel, Tin, Zinc, Graphite furnace atomic absorption spectrometry, Slurries, Sediments, Permanent modifiers.*

I. Introduction

The distribution and abundance of total metal concentrations are useful indicators of the extent of soil contamination, but as the risk from metals depend on their bioavailability, total concentrations fail to provide sufficient information regarding their potential environmental impact [1]

To prevent exposure to the population from metals that exceed health and safety limits, Brazilian legislation stipulates maximum allowable levels of these inorganic constituents in soils, sediments, food products, tributaries and drinking water. The Brazilian National Environmental Council (CONAMA) also requires rigid guidelines and procedures for evaluation of dredged sediments [2].

Considering the concerns above, it is justifiable to conduct studies, as described in the present study aimed at developing methodologies to quantify metals in low concentrations in sediments. The results of this work may contribute to the achievement of a viable model for tracking regions suffering from anthropogenic impacts.

Sediment layers are organic and inorganic particles that are deposited on the bottom surfaces of rivers, lakes and oceans [3]. The sediments originate as part of processes of weathering, erosion and transport, and deposition of loose aggregates of particles in a sedimentary basin [4]. Sediments may be considered as resulting from the integration of the sum of the processes that occur in the aquatic environment and act as important metal reservoirs [5]. The principal sediment fractions responsible for the accumulation of metals are small particles, such as silt (0.0039 to 0.0625 mm) and clay (<0.0039 mm). The large surface area and high cathion exchange capacity explain the greater retention capacity of metals in particles of these sediment fractions. The metal species that are retained in the sediments can be dislocated in water by several factors which may include a change of redox conditions and medium pH and material turn over on water surfaces (mechanical effect). The study of sediments provides scientists with information regarding the mobilized stock of contaminants, as well as exposure of water and aquatic organisms [6].

These specificities have encouraged the use of sediments in various natural study environments. Shutar and colleagues studied the presence of metals in sediments in the Hindon River, in India. The classification of contamination levels used in their work was done using the geo accumulation (Igeo) index and results indicated that sediments were unpolluted to moderately polluted with Mn, Pb and Zn, moderately polluted with Cu, Cr and Fe, and heavily polluted with Cd [7].

Vicent-Martorell and colleagues [8] determined Cu, Zn, Cd, Pb and As concentrations in water and sediments samples from two rivers in polluted regions of the Huelva province, Spain. These results indicated that the concentrations of the five analytes exceeded the reference limits in some water samples, and for almost all the sediment samples. The presence of these metals in water and sediment samples was associated with metallurgical industry activities in the region [8]. Chinese researchers evaluated the spatial distribution of toxic metals in an important industrial region north of the country by means of the determination of Hg, As, Cr, Pb, Cu, Zn and Cd in samples of water, sediments and plants [9]. All these studies reported a correlation between the concentration of metals present in water and sediments.

In Brazil, recent studies have evaluated sediment contamination by Cd, Cu, Ni, Pb and Zn in a tributary of the São Francisco River, as a result of intensive zinc mining exploration in the region. The results suggest the need for further assessment of source metals, given that other factors, such as fertilizers use, may influence the presence of metals in water and sediments [10].

We evaluated the Cd, Cr and Pb concentrations present at the bottom surface of Lake Pampulha, located in the southeastern state of Minas Gerais, Brazil. The analytes were determined by Graphite Furnace Atomic Absorption Spectrometry (GF AAS) and results suggest that the Cr and Pb concentrations were above the threshold, an indication of a probable biota adverse effect, this according to the CONAMA Resolution 344. A study of the bioavailability of Al, Ba, Ce, Co, Cr, Fe, K, La, Mn, Na, Rb, Sc and Zn by neutron activation analysis in sediments of Lake Pampulha found that the concentration of trace elements in sediments may not represent a public health risk to the population that was exposed to the material dredged from its waters. This could be explained because the concentrations found for these metals were similar or lower than those of other areas that did not suffer an impact [11].

Slurries of insoluble particles allow the release of analytes associated with the solid phase. The liquid medium used to prepare suspensions may contain organic surfactants such as Triton X-100 and acids or acid mixtures [12].

Slurries have been used in studies to determine metals by GF AAS in different matrices. In a review article by Cal-Pietro *et al*. [13], the authors review different preparation and stabilization of slurries by GF AAS. Several strategies are presented to maintain the homogeneity of slurries: use of surfactants, ultrasonic agitation, mechanical agitation, organic solvents such as glycerin, among others.

Fernandes and colleagues [14] compared several strategies for preparing slurries by the determination of V in hair samples using GF AAS. The employed investigated strategies weakly concentrated nitric acid medium (0.1% v / v) Triton X-100 (0.1% v / v) and water-soluble tertiary amines (CFA-C, pH 8). The values for the relative standard deviation were less than 8.0%[15]. One study evaluated the presence of contaminants in electronic components by slurry analysis. The plastic pieces were ground and weighed directly into a polytetrafluoroethylene tube (PTFE), followed by the addition of dimethylformamide (DMF) and the volume was completed with deionized water. The elements Cd, Cr, Pb and Sb were determined by GF AAS with use of universal modifier (a Pd and Mg nitrate mixture). The values of the relative standard deviations were less than 2.5% [16].

Therefore, the objective of the following study was to development a new method that is simple, easy to implement, secure, presents accuracy, precision and sensitivity for the determination of Cu, Mn, Ni, Sn and Zn by graphite furnace atomic absorption spectrometry.

II.   Experimental

Instrumentation

All measurements were conducted using a GF AAS (GBC Scientific Equipment Pty Ltd), Model 906 AA (Victoria, Australia) equipped with a graphite furnace (GF 3000), auto-sampler (PAL 3000) and a deuterium lamp for background correction. We used hollow cathode lamps for all elements supplied by Varian (Mulgrave, VIC, Australia).

A multi-element, hollow cathode lamp (HCL) (Co/Cr /Cu/Fe/Mn/Ni) by Varian, (Mulgrave, VIC, Australia, Part No. 5610107600) was used for copper, manganese and nickel. The element programing data in this study was as follows: copper was operated at 4.0 mA with a 0.5 nm slit width and a 324.8 nm wavelength; manganese was operated at 5.0 mA with a slit width of 0.2 nm and a wavelength of 279.5 nm; nickel was operated at 4.0 mA with a 0.2 nm slit width and a 232.1 nm wavelength; a hollow cathode lamp for tin (Varian Part. No. 5610106100) was operated at 8.0 mA with a slit width of 0.5 nm and a wavelength of 286.3 nm and a

hollow cathode lamp for Zn (Varian Part No. 5610109800), was operated at 5.0 mA with a 0.5 nm slit width and a 213.9 nm wavelength.

Argon, 99.999% purity, was used as the purge gas (White Martins, Belo Horizonte-MG, Brazil). The purge gas flow was 250 ml min^{-1}. The pyrolytic graphite tubes with L'vov platforms were provided by Varian (Part Number 01-900327-0) were used for all studies. All measurements were done by integrating the area of the absorption signal (integrated absorbance, s).

Mass measurements were done on a Shimadzu model AX-200 analytical balance with a resolution of 0.0001 g and a maximum weight of 200g. For preparation of the sediment samples, a Tecnal model TE-354/1 oven was used (Piracicaba, Brazil), the temperature controlled manually and the working range was between 50 and 250 ^{o}C, using a 65 micrometer fine mesh sieve opening (RETSCH - Solutions in Milling & Sieving, Haan, Germany).

The determination of sediment metals was done by suspending a sample as described below. The slurries were maintained homogeneously with an air flow produced by a Superpamp model A320 commercial aquarium pump (Aquarius hobby, Campinas, Brazil).

Reagents and solutions

All reagents were of analytical grade. Nitric acid 65% (w/w) was supplied by Merck (Darmnstad, Germany). Hydrogen peroxide, 30% m / m, used in the suspension diluent preparation for the sediments, was supplied by Vetec (São Paulo, Brazil).

Standard element solutions were used as permanent modifier: 0.996 g L^{-1} of iridium in 10% (v/v) of hydrochloric acid and 1.011 g L^{-1} of rhodium in 5.0% of hydrochloric acid (v/v), both supplied by Aldrich; 1.000 g L^{-1} of ruthenium in 1 mol L^{-1} of hydrochloric acid and 1.000 g L^{-1} of zirconium in 2 mol L^{-1} of hydrochloric acid, were both supplied by Sigma-Aldrich (St. Louis, MO, USA); and 1.000 g L^{-1} of tungsten in 2 mol L^{-1} of nitric acid were provided by Vetec.

The standard solutions for Cu, Mn, Ni, Sn and Zn were prepared from a 1000 mg L^{-1} stock solution from Merck in 2% (v / v) nitric acid. Deionized water was used to prepare the samples and the solutions were obtained using a Milli-Q system (18 MΩ cm^{-1} resistivity).

The following certified reference materials were used to assess the accuracy of the proposed methodologies: NIST (National Institute of Standards and Technology) 1944 New York/New Jersey Waterway Sediment; 2709 San Joaquin Soil and NRCC (National Research Council of Canada): PACS-2 Marine Sediment; and MESS-3 Marine Sediment.

Materials

Glass bottles and plastic containers, such as micro pipette tips, centrifuge tubes, and auto-sampler equipment cups were left immersed in 10% (v/v) HNO$_3$ solution for at least 24 hours and then rinsed several times with Milli-Q water and dried in a laminar flow hood. The cleaning solution of the automatic pipette sampler of the GF AAS was prepared by mixing 0.1% (v/v) of Triton® X-100 (Merck) and 0.2% (v/v) nitric acid (Merck). This solution was used to prevent adsorption of the solubilized sample in the inner surface of the auto-sampler capillary, in addition to enhancing dispersion of the platform around the graphite tube.

Sample preparation

The sediment samples were collected along the shores of Lake Pampulha (Belo Horizonte, MG, Brazil), close to the water depth in an area that was recently covered by water as a result of tidal oscillations. A polyethylene spoon was used to collect the material and packed in 300 mL wide mouth polyethylene containers. Excess water was allowed to drain from the sediments before placing in the containers. The containers were sealed and transported to the laboratory where they were cold stored at about - 5 ° C until analysis.

The sediment samples were dried at 60 °C for 24 hours. The unwanted material, such as twigs, rock particles, leaves, were previously separated with the aid of a plastic spatula. The samples were homogenized with a trowel to separate dirt, then crushed in a mortar and pestle, previously decontaminated, and finally, screened through a 65 micrometer fine mesh sieve opening.

The slurry samples were prepared by weighing the variable masses (10-100 mg) of sediment directly into the auto-sampler cups of the atomic absorption spectrometer. The variable masses were used due to the different analyte concentrations in the matrix, and consequently, the analytical signal produced by each constituent. The preparation of suspension sediments for Mn, for example, required a lower sediment mass, due to the high metal concentration in the sample that could produce analytical signal intensity above the integrated absorbance limit of 0.7, s (Beer's Law).

A 1.00 mL aqueous diluent (3% v/v H$_2$O$_2$ and 5% v/v HNO$_3$) was added to the sediment. The purpose of H$_2$O$_2$ is to oxidize organic matter present in the matrix, and the release of HNO$_3$ adsorbed metal, or chemically associated with the surface sediment particles, though this acid also has oxidant characteristics.

The formed slurry was maintained homogenous using an air flow created by an aquarium pump.

In this study, the preparation of slurries of the certified reference materials NIST 1944 and 2709 and NRCC PACS-2 and MESS-3 was done in the same fashion as was done for the Lake Pampulha sediment samples used in the optimization of analytical conditions for each investigated metal.

Treatment of the graphite furnace

The interior of the graphite tubes were treated with a volume equal to 50 μL of the permanent modifier solution. The tube was subjected to a furnace temperature program as shown in Table 1. The procedure was repeated 10 times to obtain a treated surface with about 500 μg of modifying substance. This program was applied to obtain surfaces with iridium, rhodium, ruthenium, tungsten and zirconium. The program used is similar to that applied in other studies with GF AAS by Silva *et al.* [17, 18].

Three conditions were initially optimized: (a) the liquid sample volume added to the graphite tube, (b) drying stage duration and (c) "time constant". The "time constant" is the condition related to the number of readings made by the device per unit time. The greater the "time constant" value, the more attenuated or amortized will be the resulting analytical signal format. This feature is available using the GBC spectrometer employed in this study. The optimization of these parameters was performed on the operating conditions (furnace temperature program) as suggested by the equipment manufacturer.

We evaluated which liquid volumes to be introduced into the tube: 20 or 40 μL. Projection or non-projection of liquid to the exterior of the tube was observed.

Liquid volumes introduced into the graphite tube less than 20 μL could generate insufficient analytical signals of intensity during the studies, considering the integrated absorbance (peak area, s). Therefore, the evaluation was limited to two volume levels.

The duration of the drying stage began optimizing itself at a time equal to 3 s. Next, the time was gradually increased from 2 s until a valor that no longer resulted in boiling without loss of the confined liquid within the tube.

The "time constant" readings between 0.1 and 0.9 s, at 0.1 s intervals, were taken to evaluate at which analytical peak time would be more attenuated and without extending the base.

The instrumental parameters used in GF AAS of the GBC to construct the pyrolysis curves and the atomization for the determination of sediment metals, are presented in Table 2.

The optimization furnace program for determination of Cu, Mn, Ni, Sn and Zn in sediments by GF AAS, in addition to choice of permanent modifier, were done by means of pyrolysis temperature curves and atomization.

Analytical validation
Matrix effect

The evaluated analytical figures of merit were: limits of detection and quantification, linearity, selectivity, precision and accuracy. There were three calibration curves prepared in Milli Q water (aqueous calibration) and three sediment calibration curves (standard addition). Figures of merit calculations were done to arrive at the average values of three readings from the resulting calibration curves in each medium.

Limits of detection and quantification

The limits of detection (LOD) and quantification (LOQ) were calculated using Equations 1 and 2, respectively: *LD = 3 σ / b* and *LQ = 10 σ / b*, where σ is the estimated standard deviation for 10 readings of the blank reagent calibration curve selected in the previous study and *b* is the slope of this curve.

Linearity

The evaluation of linearity was done by calculating the correlation coefficient of the calibration curve (r). Curves with r values greater than or equal to 0.99 were considered satisfactory.

Selectivity

The selectivity of the proposed methodologies was made by comparing the aqueous calibration curves slopes and the curves by analyte addition. Comparison was done using the Fischer-Snedecor distribution and Student's t-test set at a 95% significance level. Statistical differences between the curve slopes of the two calibration strategies indicated that there were matrix components interfering in the analytical signal, thus preventing the use of aqueous calibration.

Precision

Precision was determined by metal analysis of 10 consecutive readings of replicate samples. The methodologies were considered accurate when RSD% presented values less than 15%.

Accuracy

The evaluation of accuracy was done by calculating the percentage recovery concentration found in relation to the analyte concentration in the certified reference material. A recovery range 80-120% was considered sufficient accuracy for the investigated methodology.

III. Results and Discussion

Initial optimization of the operating conditions of the Atomic Absorption Spectrometer

The slurry samples began to boil inside the graphite tubes before the heating program reached the pre-drying temperature. Next, the added suspension volume and time duration of the pre-drying step were optimized. Volumes greater than 20 μL sputtered inside the tube causing the material to project outside of the tube resulting in sensitivity loss and a decreased accuracy. As a result of this circumstance, we decided to introduce a 20 μL suspension to the tube. Although a smaller volume, analytical signals were produced in sufficient intensity to continue our work.

The duration of the pre-drying step was 20 seconds, and not 3 seconds, as recommended by the GBC equipment manufacturer. This was achieved in optimal time, so the evaporation sample would appear in a bland and progressive form, thereby avoiding sample loss, discussed earlier, for sensitivity and accuracy. Table 2 presents the optimized apparatus operating conditions as described above, in addition to the mass and pellet type used for preparation of 1 mL slurry.

Manganese was the only metal that used a 10 mg mass, while other metals used 100 mg. The rationale behind using a smaller mass was due to the fact that the Lake sediment composition presented a relatively higher Mn concentration. This relatively higher concentration produced an analytical signal above the proportionality threshold (Beer's Law), and therefore, it was necessary to use a smaller sediment mass. We used the NRCC MESS - 2 sediment, and not the Lake Pampulha sediment to optimize the methodologies for determination of Cu and Zn, because, in its composition, the Lake sediment presented a higher metal concentration. Even if a smaller sediment mass was used in the slurry preparation, it would not be enough to produce a proper intensity analytical signal.

The "time constant" factor was optimized to obtain a signal format that was as attenuated as possible. The "time constant" values for each analyte are presented in Table 2. Nickel required a greater "time constant" than the other elements. Figures 1 through 3 illustrate the analytical signal change effect on the "time constant" value for Mn determination in sediments.

Univariate optimization methodologies for determination of sediment metals

All measurements conducted in the optimization methodologies step for each metal, in addition to studies for obtaining the merit parameters, demonstrated properly corrected background signals by the deuterium lamp. Considering this aspect of the analytical signals, presented in the tables for optimization of pyrolysis and atomization temperatures, the signals are properly corrected. Pyrolysis and atomization curves were used to choose the best permanent modifier for each analyte, as well as to optimize the pyrolysis and atomization temperatures.

The slurries were prepared as previously described. The Sn (100 μg L^{-1}) and Ni (200 μg L^{-1}) slurries were contaminated because the sediments did not possess an adequate concentration of these metals to produce the proper analytical signal intensity. It was not necessary to perform contamination in the Cu, Mn and Zn slurries.

Figures 4 to 8 present the pyrolysis and atomization curves for each modifier and non-modifier use. The curve related to the element symbol containing the apostrophe shows the obtained absorbance values in the optimized atomization temperature with the fixed pyrolysis temperature, in this example, Rh'. The curve related to the element symbol without apostrophe shows the absorbance values obtained from the pyrolysis temperature optimization with the fixed temperature atomization, in this example, Rh.

Methodology for determination of copper sediments

The pyrolysis and optimization curves of the optimization program oven temperature for Cu sediments determination are presented in Figure 4.

The best performance was achieved without the use of permanent modifier. The maximum observed absorption for Cu was between 700 and 2100 °C for pyrolysis and atomization temperatures, respectively. The use of non-permanent modifier for Cu determination was reported in an early technique application stage. In these initial studies with Cu, pyrolysis temperatures were found to be around 1000 °C [19].

The better performance of Cu in the absence of modifiers can be associated with the element chemical form of the matrix. When metals appear associated as nitrate, a decomposition of salt in nitrogen and metal oxides occurs. The oxide metal decomposes in oxygen and elemental metal at temperatures above 1800 °C [20].

Other researchers have obtained better results using a mixture of W-Rh in determining Cu in sediment samples digested with hydrochloric and nitric acid [21]. Based on the pyrolysis and optimization temperature curves, and optimizing the remaining steps, an oven temperature program was created and is presented in Table 2.

Method for determining manganese in sediments

The pyrolysis and optimizing curves of the oven temperature program to determine Mn in sediments are presented in Figure 5.

Using permanent ruthenium (500 µg) as a modifier resulted in the best pyrolysis and atomization temperatures of 1200 and 2500 °C, respectively. The analyte signal stability at pyrolysis temperatures up to 1200 °C is suitable for method implementation, because it may ensure removal of concomitants in matrix. The 1200 °C temperature for the pyrolysis step and Ru use as a permanent modifier, were reported elsewhere [22]. Ruthenium's effectiveness as a Mn modifier may be associated to Pearson´s Hard Soft Acid Base Theory, where Mn (soft acid) may preferably combine to Ru (soft base) for the formation of intermetallic compounds that thermally stabilize analyte atoms so the matrix can be effectively eliminated during the pyrolysis step [22].

Methodology for determination of nickel in sediments

The pyrolysis and atomization curves for optimizing the oven temperature program for Ni determination in sediments are presented in figure 6.

The permanent modifier rhodium (500 µg) demonstrated the best performance with an optimum atomization temperature of 2500 °C, and a pyrolysis temperature of 600 °C. As was observed, pyrolysis temperatures greater than 600 °C resulted in a significant drop of the analyte signal.

This fact can be associated with nickel's relative volatility when compared to other GF AAS determined metals. According to previous studies, the Ni atomization temperature is determined in graphite tubes with transversal heating equal to 2500 °C, which is consistent with the results in our study [19]. The use of Rh as a modifier in Ni determination in sediments has also been reported by other authors as part of their scientific review [22].

Methodology for determination of tin in sediments

The pyrolysis and atomization curves for the oven temperature program, optimized for Sn determination in sediments, are presented in Figure 7.

Tin demonstrated a maximum absorption of 2500 °C atomization temperature with permanent iridium (500 µg) as its modifier. The pyrolysis curve behavior was typical for the GF AAS temperature at an 800 °C temperature resulting in a significant attenuation of the analytical signal. However, the greater analytical signal intensity for Sn optimization, during the pyrolysis temperature, was observed with the use of Zr modifier. This fact can be explained by the Zr characteristic to form Sn compounds, which are thermally stable, thus allowing for higher pyrolysis temperature interventions. However, with optimal pyrolysis temperature, seen during the study of atomization temperatures, permanent iridium once again demonstrated higher integrated s, absorbance values, and thus, it was the chosen modifier for further tin studies. The Sn behavior, in the presence of Ir, in the optimization of the atomization temperature, may be related to the ability of Sn to form more stable compounds at higher temperatures with this modifier. Iridium was observed as a chemical modifier with the highest boiling point between those used in this study [20].

Studies by Volysky and collaborators showed that an Ir + Mg mixture performed better as a modifier for Sn determination in sediment and plants samples [24]. The number of graphite tube firings, or atomization cycles, (1520) in our study, when using Ir, was compatible with the values (1750) observed by Silva and colleagues in a study using Ru modifier to determine tin in sediment samples after extraction with aqua regia [18]. This study contributes to further highlight a characteristic favorable for using permanent modifiers: to increase graphite tube life, even under aggressive acid and peroxide matrix mixture conditions, contrary to what is normally obtained with solution modifier use [18].

Method for determination of zinc in sediments

The pyrolysis and atomization curves for optimizing the oven temperature program for Zn determination in sediment are presented in Figure 8.

The best modifier for Zn determination in sediments was permanent rhodium (500 µg). The atomization temperature was equal to 1800 °C, and the pyrolysis temperature was 600 °C, a temperature sufficient for the elimination of concomitant matrix that can interfere with analyte determination. This temperature is consistent with the maximum pyrolysis temperature obtained by other researchers working with a Zn modifier using Rh [22].

The scientific literature indicates that, regardless of type of graphite tube heating, transverse or longitudinal, the atomization temperature step is usually employed between 1600-1800 °C, which is consistent with the results observed in this study [19]. The Zn absorption intensity, at 400 °C, during pyrolysis temperature optimizing without modifier use, showed a higher value than for the same temperature measured in the presence of Rh. However, the readings without modifier use presented analytical signals that did not return to baseline, and with inadequate background signal correction, this resulted in a difficult interpretation of the obtained signals.

Table 3 shows the oven program for determining Cu, Mn, Ni, Sn and Zn in sediment slurries by GF AAS.

Characteristic masses

The characteristic mass values for each analyte and the investigated permanent modification strategies are presented in Table 4.

It was observed that characteristic mass values of all elements were close to those recommended by the equipment manufacturer, except for Ni, which was equal to 6 pg, using rhodium as permanent modifier, which was higher than the 5 pg recommended value. However, this should not be considered, separately, as evidence suggests that optimization of the methodology has been insufficient. The recommended values of characteristic mass are obtained under optimal conditions, such as ultrapure reagents use, use of graphite tubes in excellent conditions and a newly manufactured apparatus, or under ideal operating conditions. In addition, the recommended characteristic mass is independent of the matrix and is evaluated by measuring the analyte signal using a standard solution of each analyte. In the present study, we worked with sediment samples that were complex matrices and could cause interference that provoked analytical signal attenuation: an example was the presence of organic matter [19]. Moreover, the manner which the sample is introduced inside the graphite tube by means of suspension without the use of previous sample digestion may not be sufficient enough to achieve adequate Ni sensitivity.

Linearity and matrix effect

To evaluate the linearity and matrix effect, six calibration curves were constructed: three in Milli-Q water (aqueous curve) and three in sediment matrix using the cited diluent for slurry preparation (mixture of HNO_3 and H_2O_2 and standard addition curves). The results of the average inclinations for each element of the curve, prepared in the diluent and of the aqueous curve, are presented in Table 5.

The calibration curves were considered linear with correlation coefficients values greater than 0.99 for all elements. There was no statistically significant difference between the two calibration strategies. These results demonstrate that it is possible to determine all the evaluated metals in this study using aqueous calibration prepared in HNO_3 and H_2O_2.

Limits of Detection and Quantification (LOD and LOQ)

The limits of detection and quantification for the elements, in addition to the maximum allowed values for each sediment metals, according to Brazilian legislation, are presented in Table 6.

We conclude from the results presented in Table 6 that it is possible to implement the methodologies with good sensitivity for determination of metals in sediment. The LOQ values are less than the maximum permitted by CONAMA, Resolution 344 [23].

The LOD result for Sn (20.0 μg kg^{-1}) was lower than that found from other reported studies (57 μg kg^{-1}) [14]. In this study, a Triton X-100 solution was used to maintain the suspension homogeneous and the modifier used was a mixture of Pd and Mg nitrate.

Accuracy and precision

The evaluation of method accuracy was done by means of comparative studies using certified material samples. The results are shown in Table 7.

The results show that the developed methodologies demonstrated sufficient accuracy to determine, with reliability, the studied elements sediments using GF AAS, by use of sample introduction in suspension form. The values found for the metal concentrations of the reference materials were in agreement at the 95% significance level with the certified values, which confirms good accuracy of the proposed methodologies. The relative standard deviation values for the determinations were less than 15%, which is the acceptable value for the concentration range of 100 μg kg^{-1}. For lower concentrations, between 10 and 100 μg kg^{-1}, the acceptable value for RSD (%) is 21% [24].

The resulting RSD values for Cu and Ni in this study, using air flow produced by an aquarium pump, was equal to 2.35 and 2.89%, respectively, lower than the result reported in the literature (3.13%), which uses an ultrasonic probe to maintain the homogeneous suspensions [14]. Furthermore, the published study used

digestion with aqua régia for preparing the sediment samples, contrary to the proposed sediment sample preparation used in this study, which did not use pre-digestion of the samples. In both studies, the literature and present work, the samples were passed through a 65 μm sieve.

IV.   Conclusions

The sample preparation method of sediment by suspension by GF AAS is an alternative technique for the preparation of acid digestion samples, which normally use large quantities of supra-pure reagents, and less often, with the use of microwave equipment. The disadvantages of the acid digestion method includes increased analytical cost of analysis, it requires more expensive and sophisticated equipment, in addition to the need for specially trained technicians.

The air flow produced by the aquarium pump was adequate for maintaining the homogeneous sediments in suspension with good RSD for all the studied analytes. The values were always lower than 15%, which is the acceptable value for the range of metal concentrations of analyzed sediments. The obtained RSD% values in this study are consistent with those observed in the literature, but employ more expensive strategies for maintaining suspension homogeneity, such as using ultrasonic probes, to cite an example. The commercial aquarium pump cost about $10.00 (ten US dollars). Commercially available ultrasonic probes can cost more than a thousand dollars. Furthermore, the sample preparation proposed in this work consisted in weighing sediment in the GF AAS glass auto-sampler equipment, followed by addition of diluent mixture, making it unnecessary for good accuracy and precision of the investigated metals.

The limits of quantification methodology values, developed for the determination of metals in sediments by GF AAS, were sufficient at adhering to Brazilian legislation requirements, in addition to other parameters such as merit, linearity, accuracy and precision, which were in accordance with the specified requirements for considering the validated methodologies.

The use of permanent modifiers was sufficient at ensuring the determination of metals in sediment suspension with adequate correction of matrix interferences, thus allowing for use of aqueous calibration for all metals (external calibration).

Acknowledgments

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List of tables

Table I. Graphite furnace temperature program for treatment with permanent modifier.

Stage	Temperture (°C)	Ramp (s)	Time duration (s)	Air flow (mL min^{-1})
Pre-drying	90	5	15	250
Drying	140	5	15	250
Pyrolysis	1000	10	10	250
Atomization	2000	0	5	0
Cooling	20	1	10	250

Table 2. Instrumental parameters employed in gbc gf aas to construct pyrolysis and atomization curves for the determination of metals in sediment.

Element	λ (nm)	Curve (nm)	Current (mA)	Time constant (s)	Sediment mass (mg)
Cu	324.0	0.5	3.0	0.1	100 *
Mn	279.5	0.2	5.0	0.2	10.0 **
Ni	232.1	0.2	4.0	0.5	100 **
Sn	286.3	0.5	8.0	0.3	100 **
Zn	213.9	0.5	5.0	0.2	100 *

* NRCC MESS - 2

** Lake Pampulha sediment.

Table 3. Optimized univariate oven temperature program for determination of metals in sediments by GF AAS.

Stage	Temperature (ºC)	Ramp (s)	Time held (s)	Argon flow rate (mL min^{-1})
Pre-drying	90	15.0	20.0	250
Drying	140	3.0	4.0	250
Pyrolysis	700 [a]; 1200 [b]; 600 [c]; 800 [d]; 600 [e]	4.0	20	250
Atomization	2100 [a]; 2500 [b, c, d]; 1800 [e]	1.0 [a,b]; 0.4 [c, d, e],	2.0	0.0
Cleaning	2800	2.0	2.0	250

a = Cu; b = Mn; c = Ni; d = Sn; e = Zn.

Table 4. Characteristic masses obtained under the best pyrolysis and atomization temperature conditions for the determination of metals in sediment suspensions by GF AAS.

Analyte	(pg)					
	Zr	Rh	Ir	Ru	Non modifier	Recommended
Cu	4.8	5.0	3.5	3.4	**3.3**	2.5
Mn	1.8	1.0	1.5	**0.9**	1.2	0.7
Ni	120	**36**	132	240	85	25
Sn	32	176	**38**	59	180	22
Zn	1.4	**1.1**	1.3	1.7	1.3	0.8

Table 5. Evaluation of the inclination of aqueous calibration curves and in solvent for the determination of metals in sediment suspensions by GF AAS.

Element	Aquosa curve (n = 9)		Curve in diluent (n = 9)	
	Slope	R^2	Slope	R^2
Cu	0.0262	1.00	0.0281	0.999
Mn	0.00714	0.999	0.00709	0.999
Ni	0.00485	0.999	0.00476	0.998
Sn	0.000991	0.997	0.000996	0.993
Zn	0.0391	0.998	0.0388	0.999

R^2 = correlation coefficient.

Table 6. Detection and quantification limits for determination of metals in sediment suspensions by gf aas and the maximum permitted values according to brazilian legislation

Element	LOD		LOQ		
	(μg L^{-1})	(μg kg^{-1})	(μg L^{-1})	(μg kg^{-1})	CONAMA 344 (mg kg^{-1})
Cu	0.631	6.39	2.05	20.5	400
Mn	4.01	40.1	13.0	130	-
Ni	0.902	9.00	3.00	30.0	35.9
Sn	2.00	20.0	6.66	66.6	-
Zn	0.133	1.30	0.434	4.30	315

Table 7. Accuracy and precision study with certified material for determination of metals in sediment suspensions by GF AAS

Element	Mean ± standard deviation (n = 5)		Certified material	RSD (%)
	Found (μg kg^{-1})	Certified (μg kg^{-1})		
Cu	34.1 ± 0.8	34.6 ± 0.7	NIST 1944	2.35
Mn	444 ± 16	440 ± 19	PACS - 2	4.32
	365 ± 21	357 ± 11	MESS – 2	5.75
Ni	41.5 ± 1.2	39.5 ± 2.3	PACS – 2	2.89
	50.5 ± 0.9	49.3 ± 1.8	MESS - 2	1.78
Sn	19.1 ± 2.8	19.8 ± 2.5	PACS – 2	14.7
Zn	98 ± 4	106 ± 3	NIST 2709	4.08

Figure Captions:
Fig. 1. Analytical signal for Mn in water without use of permanent modifier and "time constant" equal to 0.0 s.
Fig. 2. Analytical signal for Mn in water without use of permanent modifier and "time constant" equal to 0.1 s.
Fig. 3. Analytical signal for Mn in water without use of permanent modifier and "time constant" equal to 0.2 s.
Fig. 4. Pyrolysis temperature and atomization curves for Cu sediment slurry.
Fig. 5. Pyrolysis and atomization temperature curves for Mn determination in sediment slurry.
Fig. 6. Pyrolysis and atomization temperature curves for Ni determination in sediment slurry.
Fig. 7. Pyrolysis and atomization temperature curves for Sn determination in sediment slurry.
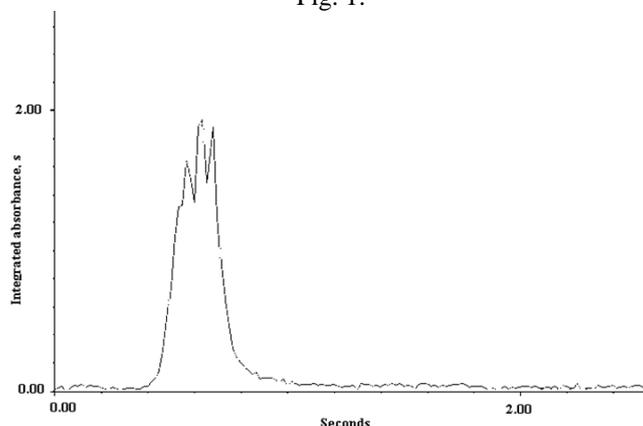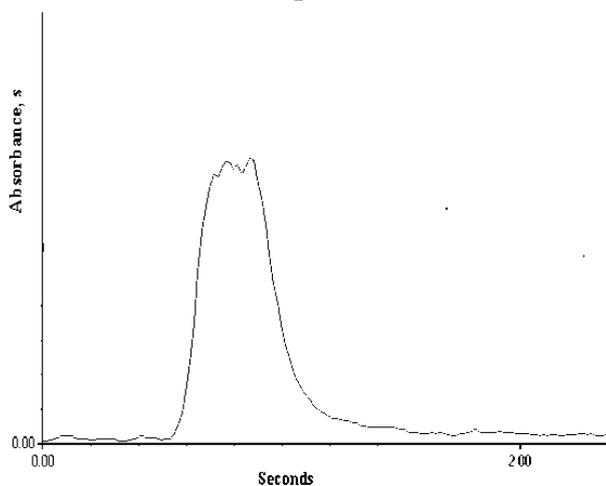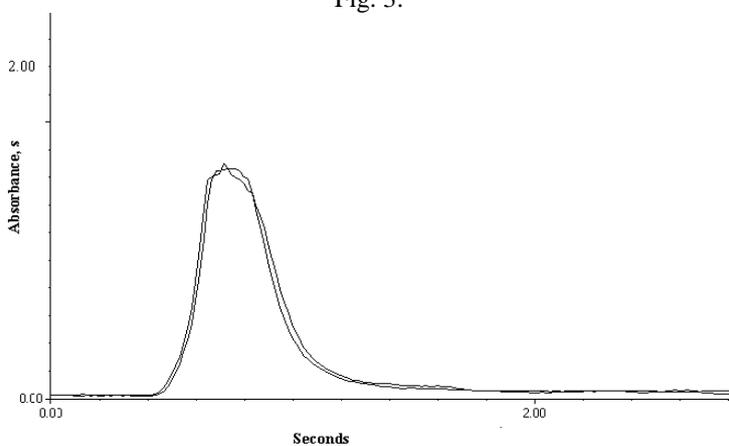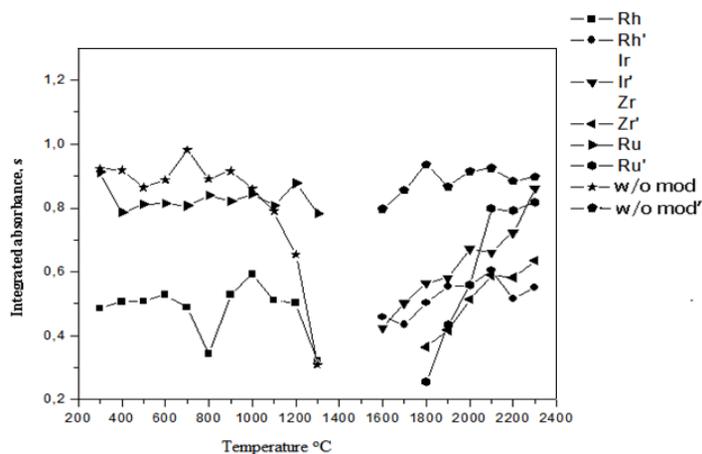**Fig. 8**. Pyrolysis and atomization temperature curves for Zn determination in sediment slurry.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.