

ARTICLE

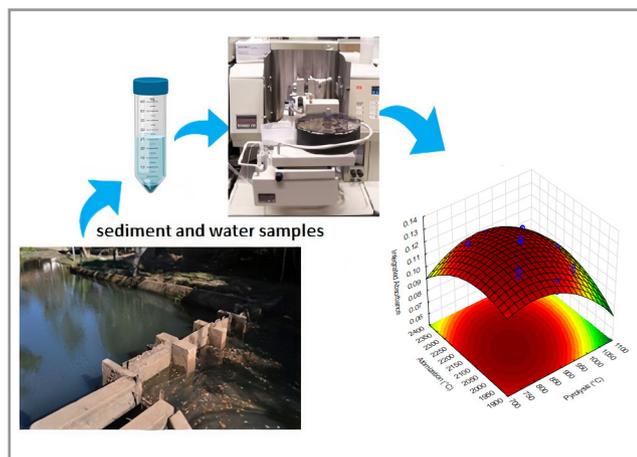
Footprint of Arsenic Contamination in Sediments and Water from Mining Sites

A case study based on multivariate optimization by GF AAS

Glenda Máris Mesquita De Filippis¹, Bruno Elias dos Santos Costa² , Simone Soares de Oliveira Borges², Waldomiro Borges Neto² , Nivia Maria Melo Coelho² , Luciana Melo Coelho^{1*} 

¹Universidade Federal de Catalão, Av. Dr. Lamartine Pinto de Avelar, 1120, Setor Universitário, 75704-020, Catalão, GO, Brazil

²Universidade Federal de Uberlândia, Av. João Naves de Ávila, 2121, Campus Santa Mônica, 38400-902, Uberlândia, MG, Brazil



Arsenic contamination is worrisome in mineral exploration regions. Efficient arsenic monitoring is dependent on detectability at trace level in environmental matrices. This paper presents a procedure to evaluate the occurrence of arsenic in environmental sediment and water samples collected from a mining area in Catalão, Goiás State (GO), Brazil. The water and sediment samples were analyzed by graphite furnace atomic absorption spectrometry (GF AAS) after appropriate chemical treatment. For the arsenic determination, analytical performance was improved employing multivariate tools. The instrumental conditions were optimized using a 2³ factorial design and the response surface

methodology (RSM) was applied with a central composite design (CCD). Iridium was used as a permanent modifier. The results for the sediment samples showed arsenic concentrations below the threshold for adverse effects ranging from 2.06 to 3.82 mg Kg⁻¹. The concentrations in water samples were below LOD. The LOD and LOQ were, respectively, 0.33 and 1.09 µg L⁻¹ to water and digested sediment samples. Under the optimal conditions, the dynamic working range was linear of LOQ to 50.0 µg L⁻¹. The method was applied to determine concentrations of arsenic in water and sediments collected from mining sites, which can be used to assess the availability of arsenic in the region.

Keywords: total arsenic, Samambaia stream, mining sites, permanent modifier, graphite furnace

Cite: Filippis, G. M. M.; Costa, B. E. S.; Borges, S. S. O.; Borges Neto, W.; Coelho, N. M. M.; Coelho, L. M. Footprint of Arsenic Contamination in Sediments and Water from Mining Sites: A case study based on multivariate optimization by GF AAS. *Braz. J. Anal. Chem.*, 2021, 8 (33), pp 42–56. doi: <http://dx.doi.org/10.30744/brjac.2179-3425.AR-71-2020>

Submitted 22 December 2020, Resubmitted 30 March 2021, Accepted 16 April 2021, Available online 14 May 2021.

INTRODUCTION

The presence of arsenic in environmental samples has been extensively reported due to a variety of sources of anthropogenic contamination. This is a matter of great concern since this pollutant can have a subtle but alarming toxic effect.

Arsenic occurs naturally as part of the composition of certain minerals, such as arsenopyrite (FeAsS), realgar (AsS), and orpiment (As_2S_3). It can also be incorporated into the lattice of various other minerals, for instance, during the replacement of Al^{III} and Fe^{III} oxides. Possible host minerals are feldspar, magnetite, galena, blende and apatite. In the form of organic compounds, arsenic is manifested primarily as metabolites derived from marine organisms [1,2].

The toxicity of arsenic compounds is dependent on the nature of the chemical species, and the inorganic forms are around hundred times more toxic than organic compounds [3]. In the case of inorganic species, As^{III} and As^{V} are predominantly found in the aquatic environment, and they are a cause for concern since they can become potentially toxic even in very low concentrations.

In the aquatic environment, the predominant species of inorganic arsenic are strongly dependent on pH and redox potential. Under oxidative conditions (aerobic) and at pH above 2.0, arsenate oxoanions (As^{V}) are the predominant species. In slightly reducing conditions, the neutral specie of As^{III} predominates, manifesting as arsenious acid (H_3AsO_3). This neutral specie converts to anionic species deprotonated with increasing pH. Oxoanions of As^{III} become predominant only at pH above 9.2 [4]. Once released into the water, part of the arsenic is immobilized by adsorption in compounds containing iron, aluminum, manganese and in clay minerals. A small part is complexed to organic compounds. As^{III} is commonly complexed with sulfur amino acids residues like L-cysteine in some peptide metabolites [5].

The presence of arsenic in water has been related to the occurrence of dermatitis, skin cancer, heart problems, cancer and poisoning. The US Environmental Protection Agency (USEPA) revised the regulated limit for arsenic in drinking water from 50 to 10 $\mu\text{g L}^{-1}$ [6,7]. As a result of these revised standard, new technologies have been developed to provide more appropriate monitoring and reduce the levels of this contaminant.

The evaluation of the level of arsenic contamination in a water resource is dependent not only on its determination in water but also in sediment samples. Sediments have a high capacity for the sorption and accumulation of pollutants, especially heavy metals and metalloids such as arsenic. The availability of these contaminants in the aquatic environment can increase by several orders of magnitude, depending on their mobility and environmental changes [8-12].

In Brazil, arsenic has been found in several regions, notably the Iron Quadrangle region in Minas Gerais State, where critical contamination levels have been recorded. It has been reported that total arsenic levels in groundwater samples collected in the cities of Ouro Preto and Mariana, Minas Gerais State, can reach 2980 mg L^{-1} [8].

The occurrence of environmental disasters related to mining activities, such as the rupture of the dam in Brumadinho in January 2019, warns of cases of incorporation and accumulation of arsenic in sediments. Lithogenic compartments are affected by a chain propagation during the course of the mineral waste, spreading out to increasingly distant regions. Parameters such as acidity, oxygen demand and corrosivity of manure can facilitate the availability of arsenic accumulated by leaching over time [13].

Mining is the main economic activity in the city of Catalão, in the state of Goiás, Brazil. Catalão has been the target of investments by large mining companies to explore deposits of phosphate, niobium and rare earths in the region. The water supply in the city occurs through the drainage of the Samambaia Hydrographic Basin. The Samambaia stream constantly suffers from processes of erosion, leaching and silting, which can drag sediments to the riverbed, which are not constantly monitored [14].

Studies on the characterization of sediments point to aluminum, iron, potassium and titanium as the main constituents in addition to silicon [14]. There is still no study aimed at monitoring arsenic in sediments and waters of Samambaia stream. The lack of this information encourages investigations that may reveal history of contamination in recent years.

Due to the above-mentioned factors, it is important to develop a routine methodology for the determination of arsenic in water samples and sludge obtained from mining regions [15], to enable better quality control and reduce the inherent risk of contamination.

In general, the most sensitive analytical techniques for the detection of arsenic are hydride generation atomic absorption spectrometry (HG AAS) and inductively coupled plasma mass spectrometry (ICP-MS). Although the HG AAS technique offers simple and affordable instrumentation, the hydride generation system is restricted to only a few species, and may become unstable under highly reducing conditions. In addition, sample preparation procedures are required, which can lead to losses and contamination [9]. The ICP-MS technique has the advantage of multielement determination, obtaining detection limits of less than $1 \mu\text{g L}^{-1}$. However, it has the disadvantage that samples with a high content of dissolved salts are difficult to analyze, and also this method is costly for routine analysis [10]. The graphite furnace atomic absorption spectrometry (GF AAS) technique has proven to be one of the most powerful methods for the determination of trace and ultra-trace levels. This technique has become increasingly attractive in view of the relative simplicity of operation, automation and minimal requirements for processing of the sample.

For the determination of arsenic and heavy metals by GF AAS, the stages of the temperature program (pyrolysis and atomization) are conventionally optimized univariate [16-20]. This study is limited because it does not explore the effects of interaction between the variables in addition to requiring greater amounts of heating cycles for each increase in temperature. These limitations can be critical in determining volatile elements such as arsenic in complex matrix samples. Optimal temperature programs obtained by modeling from data multivariate become efficient tools to ensure analytical performance in GF AAS [21]. In this context, resources such as factorial design and multivariate optimization are applied to achieve more efficient conditions for the determination of arsenic in trace levels.

The aim of this study was to apply a method for the determination of arsenic in environmental sediment and water samples collected from mining sites in Catalão, GO, Brazil. The determination of total arsenic in the water and sediment samples was performed by GF AAS, combining the efficiency of permanent modifiers with an appropriate temperature program, obtained from multivariate optimization.

MATERIALS AND METHODS

Sampling

Sediment and water samples were collected on the banks of the “Samambaia” Stream, in the north and northeast areas of the city of Catalão located in the southeastern region of Goiás State, Brazil.

The samples were collected at 7 points so as to be representative of the influence of the different human activities carried out along the creek, that is, livestock grazing, crop growing, water harvesting and urbanization: *i*) Point 1 ($18^{\circ}05'13''\text{S}$, $47^{\circ}59'05''\text{W}$) near the bridge along the road GO-330, being representative of the entire basin area, *ii*) Point 2 ($18^{\circ}05'13''\text{S}$, $47^{\circ}58'41''\text{W}$), stretch where water is collected by the Catalão City Superintendent of Water and Sewage (SAE) in order to assess the quality of the water for public supply, *iii*) Point 3 ($18^{\circ}05'16''\text{S}$, $47^{\circ}58'29''\text{W}$) along a tributary of the “Samambaia” Stream, *iv*) Point 4 ($18^{\circ}05'08''\text{S}$ and $47^{\circ}58'23''\text{W}$) in an area used for pasture, *v*) Point 5 ($18^{\circ}06'34''\text{S}$, $47^{\circ}57'05''\text{W}$) along a tributary of the “Samambaia” Stream in an area where there is the presence of urban activities, this point being the stretch closest to the city, *vi*) Point 6 ($18^{\circ}05'11''\text{S}$ and $47^{\circ}54'53''\text{W}$) in an agricultural area and with the presence of livestock in this area and in the vicinity; and *vii*) Point 7 ($18^{\circ}07'08''\text{S}$, $47^{\circ}53'47''\text{W}$) on the edge of the road BR-050. This is the point closest to the head of the “Samambaia” Stream. Figure 1 shows the location of the sampling points along the stream and the study area.

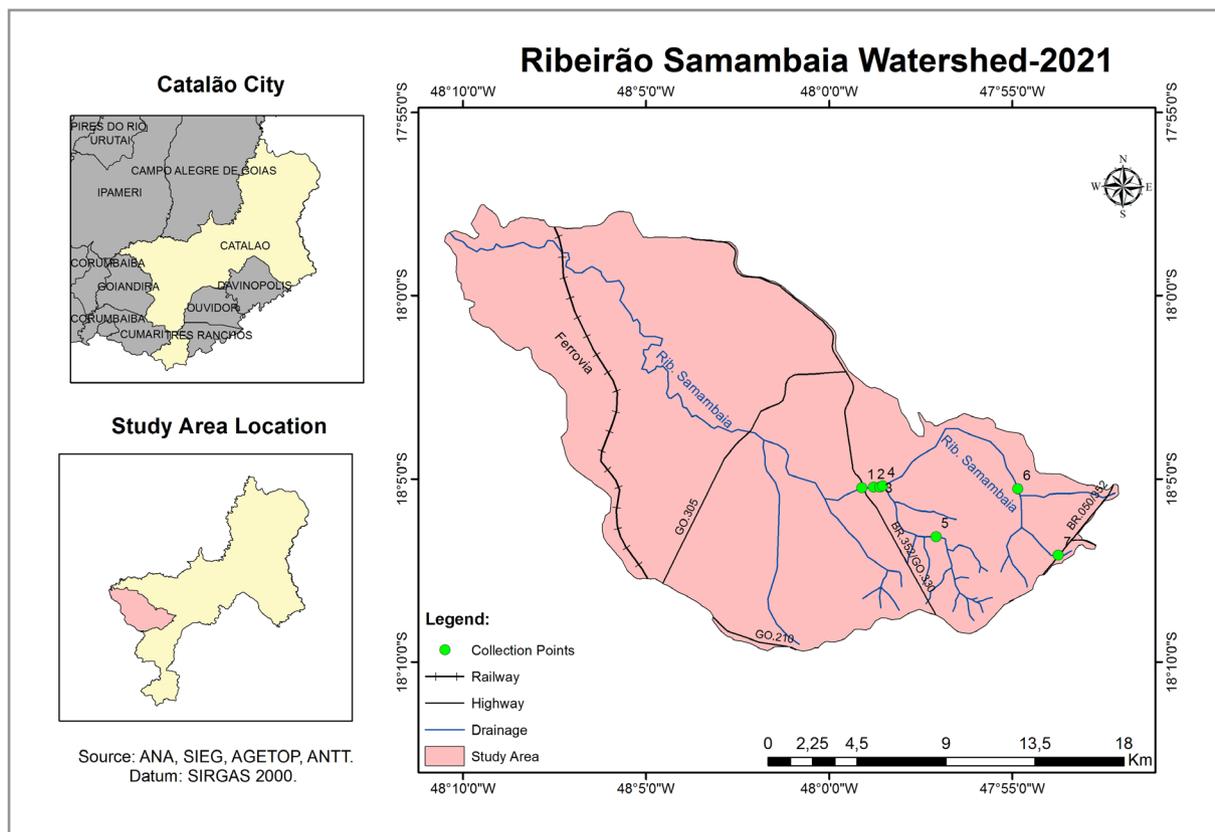


Figure 1. Location of the study area along the Samambaia Stream (Catalão-GO), indicating the points where water and sediment samples were collected.

For each point, one sampling was performed during the collection of sediment and adjacent water. Single sampling was performed, since sediment composition remains stable over an interval of 3 to 5 years [22]. The sampling of water aimed reflecting probable interactions established at the interface, by the diffusion of the analyte in the layer of stagnant water immediately in contact with the collected sediment, in a punctual way.

The water samples were collected in polyethylene bottles previously decontaminated in 10% (v/v) nitric acid for a period of 24 h and washed several times with deionized water. In the sampling procedure, the bottle was washed by placing the mouth of the bottle against the current and filling it about half with water. After this operation, the bottle was completely immersed in the water, leaving only a small gap for sample acidification and homogenization. Then, the samples were preserved by the addition of nitric acid until $\text{pH} < 2.0$. In the laboratory, the water samples were cooled to approximately 4 °C and stored for up to 28 days before analysis [22,23].

Sediment samples were collected only from the first 10 cm of the sediment column (about 2 kg per sampling point). When the sediment is sampled at a depth of 10 cm, it is possible to obtain data for up to last 10 years of deposition [24]. This depth was chosen since it is expected to correspond to the relatively recent occupation history of the area. The sediment was collected manually using a plastic grip. The samples were placed in properly labeled plastic bags and transported to the laboratory.

Study of chemical parameters

The chemical parameters pH, conductivity, dissolved oxygen, temperature and salinity were measured at all collection points using a previously-calibrated multiparameter probe (Horiba - Water Quality Checker U-10).

The sediment samples were homogenized and dried at 40 °C to constant weight. They were then pulverized using a porcelain mortar and pestle and sieved using an electromagnetic sieve shaker with a mesh size of 0.062 mm. The samples were packed into plastic bags until the extraction, which was assisted by microwave acid digestion in a Provecto, DGT 100 plus digester.

Sediment sample preparation

In the sediment preparation procedure, 200 mg of sediment sample and 5 mL of 10% (v/v) HNO₃ were placed in a 100 mL decomposition flask. The flask was placed in a microwave oven and subjected to the digestion program. The program consisted of four stages: *i*) 200 W (8 min); *ii*) 400 W (7 min); *iii*) 600 W (1 min) and *iv*) 0 W (20 min). These conditions were obtained by studies developed from works involving acid digestion by microwave applied to environmental samples [25,26]. Microwave digestion of sediment sample is adequate to promote extraction of elements strongly associated with the crystalline structures of the mineral fraction [12]. After digestion, the solution was filtered using filter paper. The flasks were washed with deionized water and the volume was completed to 20 mL.

Instrumentation

The integrated absorbance signal was obtained using a Varian atomic absorption spectrometer AAnalyst 240Z equipped with an electrothermal graphite furnace atomizer GTA 120 and Zeemann background corrector. A Varian arsenic hollow cathode lamp (Part No.: 5610122200; Serial/Lot No.: 12HO796) was operated at 193.7 nm with a spectral band-pass of 0.5 nm. Argon (99.999%) obtained from White Martins® (Uberlândia - Minas Gerais, Brazil) was used as the purge gas at a flow rate of 300 mL min⁻¹. Pyrolytic graphite coated tubes with a L'Vov platform (Varian Part No: 63-100037-00, Batch: 101816924) were used. In all experiments, the total volume of sample introduced into the graphite tubes was 20 µL. The temperatures applied for drying and cleaning were 85-120 °C for 55.0 s and 2800 °C for 2.0 s, respectively.

Reagents and Solutions

All solutions were prepared using water deionized in a Milli-Q system (Gehaka®). Nitric acid (65%; Suprapur®) purchased from Merck (Darmstadt, Germany) was used to prepare the aqueous solutions. Calibration solutions were prepared from a 1000 ± 0.002 mg L⁻¹ arsenic stock solution (Merck) in 0.6% v/v HNO₃. Autosampler vials and glassware were cleaned by immersion in 10% (v/v) HNO₃ for at least one day, rinsing several times with Milli-Q water and drying. An autosampler washing solution containing a mixture of 1% (v/v) of nitric acid and 0.1% (w/v) Triton X-100 was used in order to prevent the autosampler sampling capillary tip from clogging due to analyte adsorption and improve the sample solution dispersion on the platform. During the optimization and analysis procedures, water samples and digested sediment were transferred directly into the autosampler vials.

Treatment of graphite tubes with permanent modifiers

Six graphite tubes with integrated platforms were treated by pipetting 25 µL of a specific modifier (palladium, iridium, rhodium, niobium, titanium and tantalum) into each tube. The treatment includes 20 consecutive injections of modifier successively subjected to a specific temperature program [27,28]. The procedure resulted in the deposition of 500 µg of modifier on the inner wall of the tube and the platform.

Optimization the furnace temperature program

A factorial design (2³) was used to evaluate the pyrolysis variables, atomization temperatures and modifier. A central composite design (CCD) was performed to determine the critical conditions for the pyrolysis and atomization temperature after selecting the best modifier. The experimental data were processed using STATISTICA 6.0 [29].

RESULTS AND DISCUSSION

Study of modifiers

A preliminary study was performed to evaluate the arsenic signal using tubes treated with permanent modifiers. The furnace temperature program recommended by the manufacturer (1500 °C for pyrolysis temperature and 2600 °C for atomization temperature) was used. Arsenic determination by methods involving electrothermal atomization requires greater care. The use of modifiers is crucial to prevent volatilization losses and minimize problematic matrix interference.

The use of chemical modifiers, such as magnesium nitrate or combined with elements of the platinum group such as tungsten are the most traditionally used for arsenic determinations by GF AAS [30]. However serious phosphorus interferences were reported in the sediment analysis, even using this modifier [25,31]. The use of permanent modifiers is more advantageous than those injected in solution [32]. The literature reports that graphite tubes modified with W-Rh were suitable for determination of arsenic in sediments through slurry sampling, however the temperature program was defined by univariate optimization [33].

In this work, palladium, iridium, rhodium, niobium, tantalum and titanium were tested as permanent modifiers. The atomization profile for 50.0 $\mu\text{g L}^{-1}$ arsenic obtained using GF AAS with each permanent modifier are shown in Figure 2.

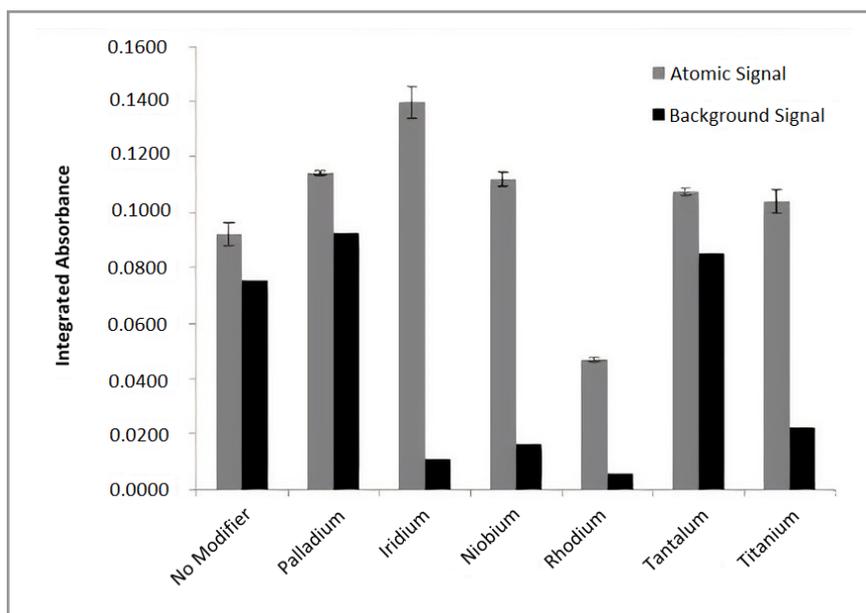


Figure 2. Atomic and background signals for the scan using permanent modifiers for the detection of arsenic. Detail shows the atomization profile for 50.0 $\mu\text{g L}^{-1}$ arsenic obtained using GF AAS with iridium as a permanent modifier.

Elements of the platinum group generally show good performance as permanent modifiers. Intercalation compounds formed with the carbon atoms of the graphite surface could activate the modifier to become an electron donor for the metalloid [34]. This proposed action suggests the thermal stability of arsenic.

The permanent modification of graphite tubes was satisfactorily performed and was necessary to improve the detection. The best signal/noise ratio results were obtained using the tubes modified with iridium and niobium. Although the modification with palladium, tantalum and titanium provided a good analytical signal, were not considered for future studies due to the high background signal. Background signals can be easily corrected by the equipment however they can affect the sensitivity. Iridium and niobium were thus selected for the experimental design and the optimization of the temperature program.

Optimization of temperature program

Optimization experiments were performed to establish the optimal thermal conditions in the determination of arsenic by GF AAS. Aliquots (20.0 µL) of a 50.0 µg L⁻¹ standard solution of arsenic were injected into the graphite tube using the auto-mix auto-sampler function. The experiments were performed randomly and in triplicate.

A 2³ factorial design was run for the initial screening of the pyrolysis and atomization temperatures in a joint action with the selected modifiers. The values for each parameter are shown in Table I. The lower and upper levels were normalized to (-1) and (+1), respectively, and the results were expressed as an integrated absorbance.

Table I. Factorial design (2³) for screening of pyrolysis temperature, atomization temperature and modifier

Experiment	Pyrolysis Temperature / °C	Atomization Temperature / °C	Modifier	Integrated Absorbance (n=3)		
1	800 (-1)	1400 (-1)	Ir (-1)	0.1130	0.1138	0.1140
2	1400 (+1)	1400 (-1)	Ir (-1)	0.0829	0.0831	0.0852
3	800 (-1)	2400 (+1)	Ir (-1)	0.1165	0.1163	0.1158
4	1400 (+1)	2400 (+1)	Ir (-1)	0.0748	0.0750	0.0752
5	800 (-1)	1400 (-1)	Nb (+1)	0.0822	0.0821	0.0861
6	1400 (+1)	1400 (-1)	Nb (+1)	0.0633	0.0633	0.0639
7	800 (-1)	2400 (+1)	Nb (+1)	0.0937	0.0933	0.0938
8	1400 (+1)	2400 (+1)	Nb (+1)	0.0695	0.0706	0.0708

The effects of each variable were evaluated by analysis of variance (ANOVA) at the 95% confidence level. The main and interaction effects are represented on the Pareto chart shown in Figure 3. The data were treated statistically using Statistica 6.0 software.

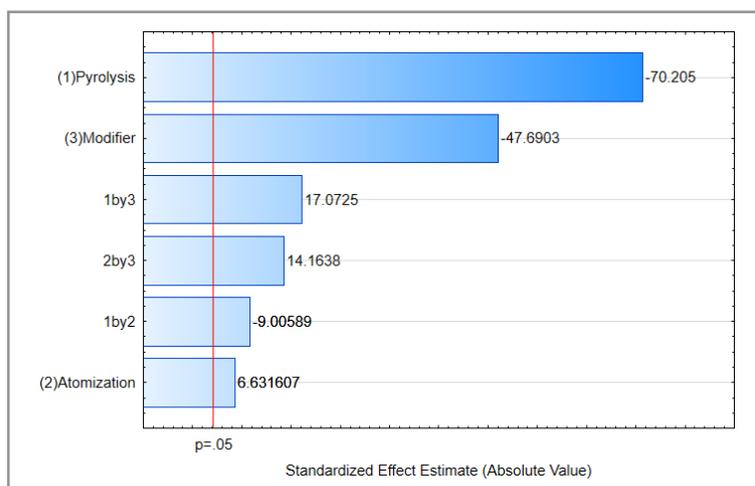


Figure 3. Pareto chart of the effects of different variables and their interaction for the optimization of temperature program.

According to the Pareto chart, all main and interaction effects were significant at the 95% confidence level ($p < 0.05$). The Pareto chart shows the importance of multivariate optimization to determine the occurrence of significant interactions that are neglected in univariate methods. The pyrolysis temperature is the variable with the most significant effect, and the analytical signal is more favorable at the lower temperature level. A high atomization temperature was shown to increase the analytical signal; however, the effect of interaction between the pyrolysis temperature (PT) and atomization temperature (AT) was more significant than the corresponding individual effects.

The modifier also demonstrated a strong contribution, and effective operation occurs at the lower level. When iridium was represented by level (-1) better results were obtained, so this level was fixed in the next steps of the experiment. Figure 2 clearly indicates iridium as the best modifier; however, it is important to check its significance level in relation to the GF AAS temperature program. The inclusion of modifiers as a qualitative variable in multivariate experimental designs showed that the action of iridium does not depend on the interaction with the other variables investigated. This confirms the information obtained from the univariate assay shown in Figure 2. Permanent modification with iridium has been reported as satisfactory for determining arsenic in environmental samples by GF AAS in similar work. It was observed that the graphite tube could be used for at least 200 cycles without any re-treatment [35].

To obtain the optimum values for the pyrolysis and atomization temperatures, experimental modeling of the response surface based on a 2^2 central composite design (CCD) was performed. In this experiment, PT and AT were explored using tubes permanently treated with iridium. The results obtained are shown in Table II.

Table II. Central composite design for optimization of the temperature program using iridium as a permanent modifier

Experiment	Pyrolysis Temperature / °C	Atomization Temperature / °C	Integrated Absorbance ($n=3$)		
1	800 (-1)	2000 (-1)	0.1278	0.1246	0.1310
2	800 (-1)	2300 (+1)	0.1191	0.1193	0.1188
3	1000 (+1)	2000 (-1)	0.1089	0.1129	0.1049
4	1000 (+1)	2300 (+1)	0.1121	0.1114	0.1128
5	759 (-1.41)	2150 (0)	0.1197	0.1197	0.1196
6	1041 (+1.41)	2150 (0)	0.1065	0.1047	0.1083
7	900 (0)	1938 (-1.41)	0.1136	0.1091	0.1181
8	900 (0)	2362 (+1.41)	0.1112	0.1101	0.1122
9	900 (0)	2150 (0)	0.1243	0.1233	0.1252
10	900 (0)	2150 (0)	0.1244	0.1233	0.1254
11	900 (0)	2150 (0)	0.1250	0.1229	0.1232
12	900 (0)	2150 (0)	0.1259	0.1228	0.1289
13	900 (0)	2150 (0)	0.1259	0.1278	0.1281

The response surface was obtained (Figure 4) and the occurrence of the maximum point was verified according to the criterion of Lagrange. The model was tested by Analysis of Variance (ANOVA) with 95% confidence. The quadratic regression model offered a good fit, explaining 93% of the variance explained. The optimum values indicated for the pyrolysis and atomization temperatures were 835 °C and 2106 °C, respectively. The quadratic model was expressed according to Equation 1, where Abs is the integrated absorbance response, PT is the pyrolysis temperature, and AT is the atomization temperature:

$$\text{Abs} = -0.9140 + (4.0779 \times 10^{-4})(\text{PT}) - (4.9531 \times 10^{-7})(\text{PT})^2 + (8.2672 \times 10^{-4})(\text{AT}) - (2.3569 \times 10^{-7})(\text{AT})^2 + (1.9916 \times 10^{-7})(\text{PT})(\text{AT}) \quad \text{Equation 1}$$

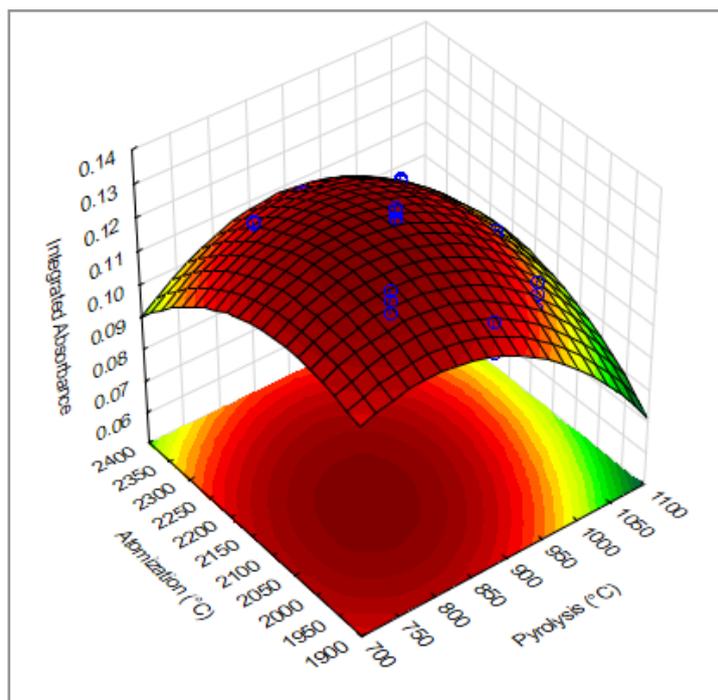


Figure 4. Response surface obtained applying central composite design to optimize the temperature program.

Figures of merit

The optimized method can be assessed by means of the figures of merit shown in Table III. The limits of detection and quantification were calculated, respectively, as three and ten times the standard deviation of the analytic measurement of fifteen blanks divided by the slope of the calibration curve [36]. The limits of detection and quantification were found to be 0.33 $\mu\text{g L}^{-1}$ and 1.09 $\mu\text{g L}^{-1}$, respectively. Under these conditions, it was possible to achieve a characteristic mass which was less than the recommended value, corresponding to 3.4 pg of arsenic in 20 μL of sample. This confirms the satisfactory sensitivity of the proposed method. The method has a working dynamic range and good linearity ($R^2 > 0.99$) with satisfactory precision with a relative standard deviation of less than 5%.

Table III. Figures of merit obtained for the proposed method

Calibration equation	Abs = 0.0023C _{As} + 0.0041	
Coefficient of determination / R ²	0.9995	
Linear working range / µg L ⁻¹	1.10 – 50.0	
Limit of detection (LOD)	µg L ⁻¹	0.33
	mg Kg ⁻¹	0.033
Limit of quantification (LOQ)	µg L ⁻¹	1.09
	mg Kg ⁻¹	0.109
R.S.D. / % (10.00 µg L ⁻¹ , n=10)	4.1	
Characteristic mass / pg (m _o) ^a	3.4	

^aReference value according to the manufacturer's recommendations = 10.00 pg.

Study area, characterization and analysis of water samples

The “Samambaia” Stream is of great importance since it is the water source which ensures the public water supply of the city of Catalão, Goiás State (population of ca. 90,000). It is also used in other activities including irrigation, ensuring the maintenance of various farming activities practiced in the region. Considering that this municipality is also recognized as the largest mineral region in Goiás, the “Samambaia” Stream was selected as the subject of this research, its monitoring being of fundamental importance.

The “Samambaia” Stream is continually subjected to several consequences of human intervention which are of great concern. These include the degradation of riparian forests, the drying up of springs, pressures from urban growth, construction works in the area, the intensive use of pesticides and the disposal of packaging materials, which is performed irregularly.

The economy of Catalão is mainly based on the extraction of niobium and phosphate minerals, which are abundantly distributed, and are also used as raw materials in the manufacture of fertilizers. The investigation of the occurrence of traces of arsenic in this region merits attention given the risk of contamination from the intense extraction of phosphate, due to the chemical similarity between these species.

The physical-chemical parameters of water samples, such as pH, conductivity, dissolved oxygen and temperature, are important since they strongly influence the content of adsorbed contaminants in sediments [37]. The pH values ranged from 4.10 (point 7) to 5.50 (point 6), with the range deliberated by the legislation being 6.0 to 9.0. The standard limits for conductivity, dissolved oxygen, temperature and salinity are respectively: ≤ 0.1 mS cm⁻¹; ≥ 5.0 mg L⁻¹; 0-30 °C and ≤ 0.5%. A variation in conductivity from 0.010 mS cm⁻¹ (point 7) to 0.088 mS cm⁻¹ (point 2) was observed. Regarding the dissolved oxygen, point 7 showed 4.69 mg L⁻¹, while the other points varied in concentration from 8.23 mg L⁻¹ (point 5) to 9.76 mg L⁻¹ (point 6). Salinity in all samples was equal to zero. The average water temperature was 19.3 °C between points 1 to 4, and 20.4 °C between points 5 to 7. Based on the results, it can be observed that the pH values are outside the acceptable levels established by Brazilian legislation (CONAMA 357) for all samples analyzed [38,39]. This factor can greatly affect the occurrence of contamination in both water bodies and sediments.

It was found that the concentration of arsenic in all sampling points are below the limit of quantification (<1.09 µg L⁻¹). In the case of dissolved oxygen only one value was outside the acceptable levels established by CONAMA (point 7). In the location of Point 7 there is the presence of a high amount of organic matter and this could result in a high consumption of dissolved oxygen during its degradation.

Analysis of sediment

The sediment fraction analyzed was that composed of particles of less than 0.062 mm (silt and clay). According to the resolution CONAMA 454/12, this fraction is the most suitable for the extraction of metals. The finer the texture of the sediment the higher the metal concentrations found, due to the greater tendency toward adsorption provided by the high surface area/grain size ratio [40].

This resolution defines two levels for the limits of the amount of a metal present in the sediment: threshold effect level (TEL) and probable effect level (PEL). The TEL represents the concentration below which adverse effects on organisms are rarely expected and the PEL represents the concentration above which there is a potential for adverse effects on organisms and the biota. For arsenic, the TEL and PEL values are, respectively, 5.9 and 17 mg Kg⁻¹. In the range between TEL and PEL such effects can occasionally be observed. The results for the sediment samples are shown in Table IV.

Table IV. Quantification of arsenic in the sediment samples ($n=3$)

Sampling point	[As] / mg Kg ⁻¹
P1	2.30 ± 0.01
P2	2.24 ± 0.02
P3	2.12 ± 0.01
P4	2.20 ± 0.01
P5	2.45 ± 0.03
P6	2.06 ± 0.01
P7	3.82 ± 0.01

The arsenic concentrations at all points were below the threshold of potential adverse effects (PEL). The sample obtained from point 7 had the highest arsenic concentration. This point is located along the road BR-050 which may have influenced the overall results, since this is the point at which the urban area exerts an influence.

The mining activities associated with visible contamination at some sampling points contribute to the bio-accumulation of arsenic in sediments. These can then act as metal transporters and the partitioning of the arsenic in water bodies can be affected by changes in the physicochemical properties of these environments. A similar study was conducted in the city of Paracatu in Minas Gerais, recognized for its gold mining activities and indiscriminate use of mercury. The study revealed that all of the analyzed sediment samples and 37% of the water samples from the rivers and streams presented arsenic concentrations greater than the quality standards established by CCME and USEPA [41]. The results this work highlight the need for environmental monitoring in order to avoid future adverse effects from this bioavailable fraction.

Comparison with methods and recovery test

The obtained parameters from analytical performance of this procedure demonstrate suitability in relation to similar works found in the literature, with comparable or even better detection limits. For these works, the GF AAS technique was used to determine As in drinking water [42], natural waters [17] and underground mineral waters [43], with detection limits equal to 0.26; 1.4 and 0.42 µg L⁻¹ respectively. It is also verified that the characteristic mass achieved here is less than the values reported in Table V, even compared to using high-resolution continuous source solid sampling (HR-CS SS-GF AAS) [18,44]. The present method also showed an advantage even in relation to some electroanalytical techniques. In this case, the study addressed the use of disposable gold screen-printed for voltammetric determination of arsenic in waters, with a reasonably high value for the detection limit (2.5 µg L⁻¹) [45].

Table V. Comparison of analytical parameters involving similar studies for determining As by GF AAS

Sample	PT (°C)	AT (°C)	Optimization Mode	Modifier	LOD ^a	m_o^b (pg)	Reference
Natural waters	1350	2250	Univariate	Pd/Mg(NO ₃) ₂	1.4 µg L ⁻¹	13.4	[17]
Fish oil	1400 ^c	2300 ^c	Univariate	Ru and Pd	0.03 µg g ⁻¹	43	[18]
Groundwater and hemodialysis water	700	2300	Univariate	Mg(NO ₃) ₂	0.13 µg L ⁻¹	26,4	[19]
Sediment and soil	1200	2100	Univariate	W-Rh	0.3 µg g ⁻¹	39	[33]
Drinking water	1200	2400	Univariate	Pd/Mg(NO ₃) ₂	0.26 µg L ⁻¹	4.2	[42]
Mineral groundwaters	1300	2300	Univariate	Pd/Mg(NO ₃) ₂	0.42 µg L ⁻¹	N.I. ^d	[43]
Fish and Seafood	1200 ^c	2400 ^c	Univariate	Pd/Mg/Triton X-100	0.05 µg Kg ⁻¹	20	[44]
Hemodialysis water	800 ^e	2200 ^e	Multivariate	Pd/Mg(NO ₃) ₂	1.0 µg L ⁻¹	N.I. ^d	[46]

^aLimit of Detection; ^bcharacteristic mass; ^cHigh-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS); ^dnot informed; ^eSimultaneous Graphite furnace AAS spectrometer (SIMAA).

It is important to note that the references cited in Table V address univariate assays in the development of methods for determining As by GF AAS. From this comparison, the suitability of experimental designs for multivariate optimization is highlighted once again, as used here.

During the review, just only a similar method involving simultaneous determination of As, Cd and Pb in water for hemodialysis was developed, resorting to the use of factorial designs to obtain the best pyrolysis and atomization temperatures. Response surface modeling experiments have been carried out to refine the screening results even more since it is a GF AAS equipment that operates in simultaneous mode, which is critique and not well established in most laboratories [46].

In order to verify the analytical applicability of the proposed method, addition and recovery tests were performed on the water and sediment samples. Recovery values were obtained in the range of 82.7 - 108.5% (Table VI).

Table VI. Recovery of spiked samples in the determination of arsenic under GF AAS optimized conditions

Sample	Spiked (µg L ⁻¹)	Found (µg L ⁻¹) ^a	Recovery (%) ^b
Water (<i>mix</i>)	3.00	2.91 ± 0.0008	97.00
	7.00	6.74 ± 0.0003	96.28
	10.00	10.06 ± 0.0006	100.60
Tap Water	3.00	2.89 ± 0.0016	96.33
	7.00	8.78 ± 0.0021	96.85
	10.00	10.85 ± 0.0012	108.50
Sediment (<i>mix</i>)	3.00	2.48 ± 0.0014	82.66
	7.00	7.04 ± 0.0004	100.57
	10.00	8.82 ± 0.0013	88.20

^aMean of three experiments ± standard deviation. ^bAcceptable recovery values in the range of 80-120% according to AOAC [36].

Experiments of external calibration and standard addition in the sample, showed that there is no significant difference ($p > 0.05$) in the slopes of the calibration curves. The results did not indicate problematic effects of substances present concomitantly in the samples and confirmed that the matrix does not significantly interfere in the analysis. The results were acceptable, based on a calibration curve automated constructed with a standard aqueous solution of arsenic at $50.0 \mu\text{g L}^{-1}$ employing the self-dilution GF AAS technique [36].

CONCLUSIONS

The method was successfully applied to determine concentrations of arsenic in samples of water and sediment collected from mining sites and could be used to monitor for arsenic contamination. The use of multivariate optimization tools for the conditions of determination by GF AAS were efficient for the precise determination of arsenic and obtaining limit of detection appropriate to the values tolerated by current legislation.

The results reported herein indicate that human activities carried out in the region of the Samambaia Stream, such as the growing of crops using pesticides, agro-pastoral activities and the advancement of urbanization, have led to an enhancement of arsenic in the environment. The contamination of water resources due to these activities can change the constitution of the surface sediments, increasing the risk of bioavailable arsenic being present in the water body.

The results for the chemical parameters of the water showed that the pH values at all sampling points were outside of the acceptable limits established by CONAMA Resolution 357/05 and this can be considered as a particular characteristic of this location. In the case of dissolved oxygen, one value was below the limit permitted by the legislation, and this result may be due to the presence of a large amount of organic matter at that site. The other parameters were within the limits established by current legislation.

The results for the sediment samples showed arsenic concentrations below the adverse effects threshold. The water samples showed concentrations below the limit of quantification, indicating that this element does not pose a risk at the sampling sites.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors are grateful for financial support from the Brazilian governmental agencies “Conselho Nacional de Desenvolvimento Científico e Tecnológico” (CNPq – 477825/2007-9) and “Coordenação de Aperfeiçoamento de Pessoal de Nível Superior” (CAPES – Finance Code 001), the MG state government agency “Fundação de Amparo à Pesquisa do Estado de Minas Gerais” (FAPEMIG), and the GO state government agency “Fundação de Amparo à Pesquisa do Estado de Goiás” (FAPEG). The authors appreciate the contribution of Silas Pereira Trindade (Department of Geography - State University of Goiás) in the elaboration of the location map of the study area of this work.

REFERENCES

1. Henck, K. E. *Arsenic: Environmental Chemistry, Health Threats and Waste Treatment*, 1st ed. Wiley, New York, USA, **2009**.
2. Garcia-Ordiales, E.; Covelli, S.; Rico, J. M.; Roqueñi, N.; Fontolan, G.; Flor-Blanco, G.; Centifuegos, P.; Loredó, J. *Chemosphere*, **2018**, *198*, pp 281-289 (<https://doi.org/10.1016/j.chemosphere.2018.01.146>).
3. Ma, Z.; Lin, L.; Wu, M.; Yu, H.; Shang, T.; Zhang, T.; Zhao, M. *Aquaculture*, **2018**, *497*, pp 49-55 (<https://doi.org/10.1016/j.aquaculture.2018.07.040>).
4. Litter, M.; Morgada, M. E. Formas arsenicales en agua y suelos. In: Litter, M. I.; Armienta, M. A.; Farías, S. S. (Eds.). *Metodologías analíticas para la determinación y especiación de arsénico en aguas y suelos*. CYTED, Buenos Aires, AR, **2009**, Chapter 1, pp 19-28.

5. Faita, F.; Cori, L.; Bianchi, F.; Andreassi, M. G. *Int. J. Environ. Res. Public Health*, **2013**, *10* (4), pp 1527-1546 (<https://doi.org/10.3390/ijerph10041527>).
6. Haider, A. F. M. Y.; Ullah, M. H.; Khan, Z. H.; Kabir, F.; Abedin, K. M. *Opt. Laser Technol.*, **2014**, *56*, pp 299-303 (<https://doi.org/10.1016/j.optlastec.2013.09.002>).
7. Fagundes, T.; Bachmann, A. W. L.; Tomaz, H. S. O.; Rodrigues, C. A. *Quim. Nova*, **2008**, *31* (6), pp 1305-1309 (<https://doi.org/10.1590/S0100-40422008000600006>).
8. Borba, R. P.; Figueiredo, B. R.; Cavalcanti, J. A. *Rev. Esc. Minas*, **2004**, *57* (1), pp 45-51 (<https://doi.org/10.1590/S0370-44672004000100009>).
9. Wang, G.; A, Y.; Jiang, H.; Fu, Q.; Zheng, B. *J. Hydrol.*, **2015**, *520*, pp 37-51 (<https://doi.org/10.1016/j.jhydrol.2014.11.034>).
10. Ma, Y.; Gong, M.; Zhao, H.; Li, X. *Sci. Total Environ.*, **2018**, *613-614*, pp 1130-1139 (<https://doi.org/10.1016/j.scitotenv.2017.09.174>).
11. Brady, J. P.; Kinaev, I.; Goonetilleke, A.; Ayoko, G. A. *Mar. Pollut. Bull.*, **2016**, *106* (1-2), pp 329-334 (<https://doi.org/10.1016/j.marpolbul.2016.03.029>).
12. Silva, L. A.; Coelho, L. M.; Rosolen, V.; Coelho, N. M. M. *J. Braz. Chem. Soc.*, **2011**, *22* (11), pp 2094-2100 (<https://dx.doi.org/10.1590/S0103-50532011001100011>).
13. Rosolen, V.; De-Campos, A. F.; Govone, J. S.; Rocha, C. *Catena*, **2015**, *128*, pp 203-210 (<https://doi.org/10.1016/j.catena.2015.02.007>).
14. Purificação, M. M.; Marchi, M. I.; Amado, N. M. P. *Ciências Exatas e da Terra: Exploração e Qualificação de Diferentes Tecnologias*. Atena, Ponta Grossa, **2020**, Chapter 3, p 22.
15. Ono, F. B.; Tappero, R.; Sparks, D.; Guilherme, L. R. G. *Environ. Sci. Pollut. Res.*, **2016**, *23* (10), pp 638-347 (<https://doi.org/10.1007/s11356-016-6137-z>).
16. Vieira, A. L.; Ferreira, A. C.; Oliveira, S. R.; Barbosa Jr, F.; Gomes Neto, J. A. *Microchem. J.*, **2021**, *160*, 105637 (<https://doi.org/10.1016/j.microc.2020.105637>).
17. Thermo Scientific Application Note: 40851. *Arsenic in Natural Waters by Graphite Furnace Atomic Absorption using EPA Method 200.9*, **2016**.
18. Pereira, E. R.; Almeida, T. S.; Borges, D. L. G.; Carasek, E.; Welz, B.; Feldmann, J.; Menoyo, J. C. *Talanta*, **2016**, *150*, pp 142-147 (<https://doi.org/10.1016/j.talanta.2015.12.036>).
19. Santos, L. M. G.; Jacob, S. C. *Ciênc. Tecnol. Aliment.*, **2009**, *29* (1), pp 120-123 (<http://dx.doi.org/10.1590/S0101-20612009000100019>).
20. Rezende, H. C.; Coelho, N. M. M. *Anal. Methods*, **2014**, *6* (24), pp 9705-9711 (<https://doi.org/10.1039/C4AY01443J>).
21. Pereira, L. A.; Windmüller, C. C.; Silva, J. B. B.; Borges Neto, W. *Quim. Nova*, **2011**, *34* (7), pp 1167-1172 (<https://doi.org/10.1590/S0100-40422011000700012>).
22. Nogueira, A. R. A.; Souza, G. B. *Manual de laboratórios: solo, água, nutrição vegetal, nutrição animal e alimentos*. Embrapa Pecuária Sudeste, São Carlos-SP, **2005**, p 334.
23. Borba, R.; Coscione, A. R.; Figueiredo, B. R.; Zambello, F. *Quim. Nova*, **2009**, *32* (4), pp 970-975 (<https://doi.org/10.1590/S0100-40422009000400027>).
24. Costa, R. A.; Rosolen, V. *Hygeia*, **2012**, *8* (15), pp 222-231.
25. Sakan, S.; Popović, A.; Škrivanj, S.; Sakan, N.; Đorđević, D. *Environ. Sci. Pollut. Res.*, **2016**, *23*, pp 21485-21500 (<http://doi.org/10.1007/s11356-016-7341-6>).
26. Güven, D. E.; Akinci, G. *Gazi University Journal of Science*, **2011**, *24* (1), pp 29-34.
27. Giacomelli, M. B. O.; Lima, M. C.; Stupp, V.; Carvalho Júnior, R. M.; Silva, J. B. B.; Barrera, P. B. *Spectroc. Acta Part B*, **2002**, *57* (12), pp 2151-2157 ([https://doi.org/10.1016/S0584-8547\(02\)00205-7](https://doi.org/10.1016/S0584-8547(02)00205-7)).
28. Costa, B. E.; Coelho, N. M. M.; Coelho, L. M. *Food Chem.*, **2015**, *178*, pp 89-95 (<http://dx.doi.org/10.1016/j.foodchem.2015.01.014>).
29. Statsoft Inc., *Statistica 6.0*, **2007**.
30. Török, P.; Žemberyová, M. *Spectroc. Acta Part. B*, **2010**, *65* (4), pp 291-296 (<https://doi.org/10.1016/j.sab.2010.03.007>).

31. Sardans, J.; Montes, F.; Peñuelas, J. *Soil Sediment Contam.*, **2011**, *20* (4), pp 447-491 (<https://doi.org/10.1080/15320383.2011.571526>).
32. Lima, E. C.; Barbosa, R. V.; Brasil, J. L.; Santos, A. H. D. P. *J. Anal. At. Spectrom.*, **2002**, *17* (11), pp 1523-1529 (<https://doi.org/10.1039/B205905C>).
33. Barbosa Jr., F.; Lima, E. C.; Krug, F. J. *Analyst*, **2000**, *125* (11), pp 2079-2083 (<https://doi.org/10.1039/B005783P>).
34. Ortner, H. M.; Bulska, E.; Rohr, U.; Schlemmer, G.; Weinbruch, S. *Spectroc. Acta Part B*, **2002**, *57* (12), pp 1835-1853 ([https://doi.org/10.1016/S0584-8547\(02\)00140-4](https://doi.org/10.1016/S0584-8547(02)00140-4)).
35. Matusiewicz, H.; Mroczkowska, M. *J. Anal. At. Spectrom.*, **2003**, *18* (7), pp 751-761 (<https://doi.org/10.1039/B302217J>).
36. Association of Official Analytical Chemists (AOAC). *Official Methods of Analysis*. 16th ed.; Arlington, USA, **1995**.
37. Lemes, M. J. L.; Filho, P. M. F.; Pires, M. A. F. *Quim. Nova*, **2003**, *26* (1), pp 13-20 (<https://doi.org/10.1590/S0100-40422003000100004>).
38. Conselho Nacional do Meio Ambiente (CONAMA). Resolução N° 357, 17 de março de **2005**. Available at: <http://www.mma.gov.br> [Accessed 12 August 2019].
39. Conselho Nacional do Meio Ambiente (CONAMA). Resolução N° 454, 01 de novembro de **2012**. Available at: <http://www.mma.gov.br> [Accessed 20 November 2019].
40. Ribeiro, F. A. L.; Ferreira, M. M. C.; Morano, S. C.; Silva, L. R.; Schneider, R. P. *Quim. Nova*, **2008**, *31* (1), pp 164-171 (<https://doi.org/10.1590/S0100-40422008000100029>).
41. Rezende, P. S.; Costa, L. M.; Windmüller, C. C. *Arch. Environ. Contam. Toxicol.*, **2015**, *68*, pp 588-602 (<https://doi.org/10.1007/s00244-015-0134-y>).
42. Michon, J.; Deluchat, V.; Shukry, R. A.; Dagot, C.; Bollinger, J. *Talanta*, **2007**, *71* (1), pp 479-485 (<https://doi.org/10.1016/j.talanta.2006.06.016>).
43. Tudorache, A.; Marin, C.; Badea, I. A.; Vladescu, L. *Environ. Monit. Assess.*, **2011**, *173*, pp 79-89 (<https://doi.org/10.1007/s10661-010-1372-0>).
44. Zimozinski, A. V.; Llorente-Mirandes, T.; Damin, I. C. F.; López-Sánchez, J. F.; Vale, M. G. R.; Welz, B.; Silva, M. M. *Talanta*, **2015**, *134*, pp 224-231 (<https://doi.org/10.1016/j.talanta.2014.11.009>).
45. Laschi, S.; Bagni, G.; Palchetti, I.; Mascini, M. *Anal. Lett.*, **2007**, *40* (16), pp 3002-3013 (<https://doi.org/10.1080/00032710701645703>).
46. Santos, L. M. G.; Gonçalves, J. M.; Jacob, S. C. *Quim. Nova*, **2008**, *31* (5), pp 975-979 (<http://dx.doi.org/10.1590/S0100-40422008000500006>).