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Determination of arsenic in agricultural soil samples using High-resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry and direct solid sample analysis.

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ABSTRACT

Soils around coal-fired thermal power plants based on coal combustion can present high concentrations of arsenic. This fact has a direct effect on the food chain. Arsenic can be absorbed by plants and vegetables through the soil, which will then serve as food for different animals, spreading the contamination. A method has been developed using high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GFAAS) for direct determination of arsenic in solid soil samples. Different chemical modifiers were tested to suppress the matrix effects observed.

¹ In memoriam

Among them, the modifier that showed the best results was the Zr, used as a permanent modifier. The optimized pyrolysis and atomization temperatures were 1000 °C and 2200 °C, respectively. A calibration curve was established using aqueous standard solutions which was linear up to 16 ng of arsenic. The characteristic mass and limit of detection were 22 pg and 73 pg As, respectively. The accuracy of the method was verified using two certified reference materials and comparison with results obtained for samples after microwave-assisted digestion. Eleven soil samples were collected around the power plant Complex Jorge Lacerda–Tractebel Suezin, in the south of Santa Catarina, Brazil. The concentration of As ranged from 3.4 mg kg⁻¹ to 9.7 mg kg⁻¹, which is within the limits allowed by Brazilian legislation.

Graphical abstract



Keywords: Arsenic determination; Soil analysis; Thermal power plants; Direct solid sample analysis; Graphite furnace atomization; spectral interference.

1. Introduction

Thermal power plants based on coal combustion (TPC) contribute significantly to the production of electric energy. In 2012, coal-fired generation accounted for 59% of the world's electricity supply; in 2040, its share is projected to remain close to this value [1]. However, the environmental impact caused by such plants needs to be taken into account.

Combustion of coal at TPCs emits mainly carbon dioxide, sulfur oxides and airborne inorganic particulate matter, such as fly ash. The fly ash's finer size components are recovered by collection devices, but the collection efficiency is always less than 100 %, so that some fly ash is released into the atmosphere and deposited

around the TPC. Furthermore, the larger fraction, which has been removed from the stack gases, is typically disposed in nearby landfills or ponds. Discarded fly ash is responsible for environmental pollution of the surrounding area, affecting soil, water bodies and air quality through leaching, windblown or atmospheric deposition [2].

Several investigations were carried out to evaluate the potential risk of waste from thermal power plants, especially in relation to nearby soil and agricultural fields. Different levels of enrichment were observed in trace element concentration, even at distances greater than 5 km. In this context, arsenic is one of the most studied elements, due to its toxic potential [3-7].

Considered the most important thermoelectric complex in South America, the Jorge Lacerda Complex, operated by Tractebel-Suezin, has a power capacity of 857 MW, providing electric energy for approximately 8 million inhabitants [8]. The foundation of this complex was an attempt to promote the consumption of the low-quality coal gathered from local coal mines [9]. The thermoelectric complex is surrounded by farms, which produces vegetables and cereals for the local markets and since the residual ash and the smoke could affect the quality of these crops with hazardous metals contamination and pH alterations, is important to evaluate the soil quality in these farms.

Arsenic is naturally found in soils and sediments, mostly as As (V) and As (III) oxidation states, which may form, among other compounds, inorganic arsenate (H_2AsO_4^-) and arsenite ($\text{As}(\text{OH})_3$), respectively [10]. The most prevailing species is depending on the soil composition and the redox potential of the soil and sediment. Methylation processes may transform arsenic also into monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) [11]. Its natural content may vary considerably according to the geological history of the region, but generally has low-ppm levels. Elevated concentrations in soil are generally associated with contamination by anthropogenic sources [12, 13]. Mining, smelting of non-ferrous metals and burning of fossil fuels – as in the case of TPC – are the major anthropogenic sources of arsenic contamination [14]. This contamination requires special attention because alter the composition and nature of the arsenic in the environment, once deposited in the soil may accumulate rapidly since it is only slowly depleted through plant uptake, leaching or erosion [10]. Its persistence in the soil causes a concern in despite to safety of plants

and animals, and specific limits requirements, varying with the soil purpose, requires measurements down to low mg kg^{-1} concentrations

It is well known that the inorganic forms of arsenic are more toxic than most of the organic forms. Chronic ingestion of inorganic arsenic has been related to increased incidence of skin, bladder, lung, liver and kidney cancer. The International Agency for Research on Cancer (IARC) classifies arsenic as a Category 1 carcinogenic agent for humans [13]. Considering that contaminated soil is the main route of exposure to arsenic, it is important that its presence and concentration be monitored constantly, especially in soils with a high risk of contamination, such as soils near TPCs. There is in particular a problem with elevated arsenic in rice fields since the arsenic is easily taken up and transported into the grain. Hence, the new regulation for the maximum limits of inorganic arsenic in rice by the WHO and implemented in the EU [14].

Several analytical techniques are used for the determination of arsenic in soil, such as inductively coupled plasma optical emission spectrometry (ICP OES) [15], hydride generation atomic absorption spectrometry (HG AAS) [16] and inductively coupled plasma mass spectrometry (ICP-MS) [17]. However, these techniques require pre-treatment, either with acidic extraction or acidic oxidation digestion of the sample, which increase the risk of contamination and/or loss of the analyte, and increase the production of toxic waste. X-ray fluorescence (XRF) is one of the few techniques that can directly measure arsenic in soil without requiring extraction or digestion. Nevertheless, the XRF analysis has relatively low accuracy and sensitivity compared to others analytical techniques[18].

Despite presenting interesting features, such as high sensitivity, good accuracy and the possibility for direct solid sample analysis, graphite furnace atomic absorption spectrometry (GF AAS) is not reported for the determination of arsenic in soil. Difficulties were reported for the analysis of complex matrices, such as severe interferences by large amounts of aluminum, sodium, potassium and sulfate in the samples, and analyte volatilization problems. Several chemical modifiers were investigated to overcome these difficulties, such as mixtures of palladium/magnesium nitrates, nitrate/magnesium nitrates and palladium nitrate/potassium persulfate [19].

The goal of the present study was to develop an interference-free method for the determination of arsenic in soil samples without sample pre-treatment using high-

resolution continuum source GF AAS (HR-CS GF AAS). Special attention has been given to the optimization of analytical conditions to prevent losses of arsenic. The accuracy of the developed method was verified by the application in two different certified reference materials (CRM) and in soil samples collected in rice farms near a coal-fired power plant in Capivari de Baixo, Brazil.

2. Experimental

2.1. Instrumentation

All HR-CS GFAAS experiments were performed on an Analytik Jena Model contrAA-600 atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) equipped with a transversally heated graphite tube atomizer and an MPE-60 (Analytik Jena) autosampler. The primary radiation source used in this equipment is a xenon short-arc lamp, which emits a spectral continuum between 190 and 900 nm.

The spectral line of arsenic 193.696 nm and the integrated absorbance of three pixels ($CP\pm 1$) were selected for the analyses. The method of interactive background correction (IBC) was chosen for signal evaluation and the ASpect CS 2.1.2.0 Software[®] (Analytik Jena AG, Germany) was used for the assignment of atomic lines and molecular bands.

Pyrolytic graphite coated tubes with PIN-graphite platform (Analytik Jena, Part No.: 407-A81.025) were applied for the optimizations with aqueous standards. Solid sampling (SS) graphite tubes without a dosing hole (Analytik Jena, Part no. 407-A81.303) and SS graphite platforms (Analytik Jena, Part no. 407-152.023) were used for all analyses using certified reference materials (CRM) and soil samples. An M2P microbalance (Sartorius, Göttingen, Germany) was used for weighing the samples directly onto the SS platforms, which was transferred to the atomizer with the aid of a pre-adjusted pair of tweezers. High-purity (99.996%) argon (White Martins, São Paulo, Brazil) was used as graphite furnace purge gas.

2.2. Reagents and solutions

All reagents used were of analytical grade or higher purity. Ultrapure water with a resistivity of 18.3 M Ω cm was obtained from a model Milli-Q Integral ultrapure water

system (Bedford, MA, USA). Nitric and hydrochloric acid in ultrapure grade were obtained from Sigma-Aldrich (St. Louis, MO, USA). The both acids were used for microwave-assisted digestion and the nitric acid was used to decontaminate all containers and glassware.

A stock standard solution of 1.0 g L^{-1} arsenic (SpecSol, Ribeirão Preto, SP, Brazil) was used to prepare the calibration curve and aqueous standard solutions. Zirconium, iridium and tungsten (Sigma-Aldrich) were tested as permanent chemical modifiers: $400 \text{ }\mu\text{g}$ of each modifier was deposited onto the SS platform surface by injecting ten successive volumes of $40 \text{ }\mu\text{L}$ of a solution containing 1.0 g L^{-1} and applying the temperature program in Table 1 after each injection. A mixture of palladium/magnesium nitrate solution ($0.5/0.3 \text{ g L}^{-1}$) was also tested as chemical modifier in solution ($10 \text{ }\mu\text{L}$) applied over the samples in combination with permanent modifiers. A combination of tungsten as permanent modifier and tungsten solution/magnesium nitrate solution ($0.5/0.5 \text{ g L}^{-1}$) as a modifier in solution was also tested.

2.3. Certified reference materials and samples

To verify the accuracy of the method, two CRM were used: PACS-2-Marine sediment (National Research Council Canada, Ottawa, Canada) and BCR 142-Soil (Community Bureau of Reference, Brussels, Belgium).

Eleven soil samples were collected around Jorge Lacerda–Tractebel Suezin power plant, in Santa Catarina, southern part of Brazil. This power plant is the largest TPC in Brazil and has an installed capacity of 857 MW. The coal used by the TPC is a blend of different suppliers, mainly from Santa Catarina, mixed with imported coal. The blend is basically composed of bituminous coal with high sulfur content ($>2\%$) and 40% ash [18]. The power plant is surrounded by small farms, which produce, mainly rice and corn. The farms cultivate rice in paddy soils, using as water source the Tubarão river, which also supplies the coal-fired power plant. The soil samples were collected in three rice farms, according to the Figure 1, where the closest sampling point was 2.5 kilometers from the power plant, and the farthest one was 4.2 kilometers far from the power plant. The samples were collected from approximately 10 cm depth with a Teflon spatula and stored in sterile polyethylene bags. After collected, roots and leaves were manually removed, the samples were left to dry at room temperature for 48 hours, then

were mashed in a grail and sieved in a 200 μm mesh.

2.4. Procedure of direct solid sample analysis and microwave-assisted digested samples analysis.

About 0.2 mg of soil CRM or soil sample was weighed directly onto the SS graphite platform, which was inserted into the graphite tube and submitted to the temperature program shown in Table 2. Calibration curve have been established using aqueous standard solution ($50 \mu\text{g L}^{-1}$ As) manually injected onto the SS graphite platform pretreated with Zr as permanent chemical modifier.

For the accuracy evaluation, the samples collected in Capivari de Baixo were submitted to a microwave-assisted digestion. As described by Schneider et al. [21], about 0.15 g of the sample was directly weighed onto Teflon vessel, added 10 mL of *aqua-regia* and submitted to a temperature and pressure program described at Table 2. After this procedure, the samples were transferred to a falcon flask, filled up to 15 mL with ultrapure water and determined by HR-CS GF AAS with the developed method.

3. Results and discussion

3.1. Optimization of temperature program and chemical modifier

The determination of arsenic by GF AAS is commonly hampered by spectral and/or non-spectral interferences. Due to the volatility of arsenic, the pyrolysis temperature should be low to avoid losses of the analyte. Significant As losses at low temperatures (~ 400 °C) have been reported for different types of samples [22]. However, at low pyrolysis temperatures the matrix can't be removed efficiently, which causes that concomitants are volatilized together with the analyte in the atomization stage, increasing the background signal. To overcome this problem, the use of a chemical modifier is mandatory.

The ideal chemical modifier is one that increases the thermal stability of arsenic, allowing higher pyrolysis temperatures to better remove the matrix and reduce the background signals. Thus, pyrolysis and atomization curves were established to obtain the optimum temperatures for the modifiers selected in this work: zirconium, iridium and tungsten as permanent chemical modifiers, and mixtures of palladium/magnesium nitrates ($0.5/0.3 \text{ g L}^{-1}$) and tungsten /magnesium nitrate ($0.5/0.5 \text{ g L}^{-1}$) as modifiers in solution. Combinations of permanent modifiers with addition of palladium/magnesium

were also tested. The pyrolysis and atomization curves for arsenic without chemical modifier were obtained for comparison purposes. The study of modifiers is shown in Fig. 2. The subscript 'per' with the chemical symbol of the modifier, such as Zr_{per} , has been used to indicate a permanent chemical modifier.

Overall, the pyrolysis curves for all modifiers exhibited a plateau between 400 °C and 1400 °C. This indicates that the chemical modifiers tested promote efficient thermal stabilization for arsenic, which sublimates in elemental form at 616 °C [23]. An interruption in the plateau is only observed for temperatures below 400 °C, for Zr_{per} , without modifier and for the combination $Ir_{per} + Pd/Mg$. At these temperatures, the precision between measurements deteriorates significantly, probably due to the increase in background noise.

The pyrolysis curve with palladium/magnesium in solution showed about half the signal intensity of the other modifiers tested. This behavior suggests that the presence of a chemical modifier that prevents early contact of the analyte with the graphite surface is indispensable. Many papers in the literature report a similar behavior [24, 25]. It is possible that the direct contact of arsenic with the surface of the graphite platform allows its migration to the pores and subsequent formation of carbides or intercalation compounds, which will hinder its volatilization. The use of permanent modifiers forms a layer that prevents the migration of arsenic to the pores of the platform.

Zr_{per} and Ir_{per} showed the highest signal intensity in both the pyrolysis and the atomization curve. The maximum atomization temperature observed for Zr_{per} was 2200 °C and for Ir_{per} it was 2300 °C.

To compare the thermal behavior of the analyte in the aqueous standard with that in the solid sample analysis, the same chemical modifiers were tested for CRM PACS-2. The results of this optimization are shown in Fig. 3.

To choose the best conditions, the sensitivity was considered, as well as the peak shape of the atomic absorption and the separation of the background signal. The Fig. 4 reveals that atomic absorption and background transient signals for arsenic varied significantly for each modifier tested. Best transient signal profiles (better separation of background absorption and return to baseline) were obtained for Zr_{per} . Hence, Zr_{per} was

chosen as permanent modifier for this work. An atomization temperature of 2200 °C and pyrolysis temperature of 1000 °C have been chosen as optimal, which is consistent with literature data [26, 27]. The optimized heating program of the graphite tube employed for the direct determination of arsenic in soil is shown in Table 3.

3.2. Evaluation of spectral interference

Figure 4 shows the presence of a significant background absorption near the analytical line of arsenic, even when zirconium is used as a modifier. It is well known that the main absorption line of arsenic is in the range of the strong absorption bands of the PO molecule. Although the presence of phosphates in soil samples might be expected, the correction using the least squares algorithm did not completely resolve the observed interference. Other molecules with absorption bands in the same region, such as NO, were also tested; however, the spectrum continued to exhibit interference. To understand the extension of the spectral interference, the pixels used to monitor the arsenic line were evaluated for sensitivity, precision and accuracy. The result is shown in Table 4.

The center pixel (CP) measures the absorbance at the line core, while the side pixels measure the absorbance at the wings of the line. It is known that the use of the CP combined with two or four side pixels increases the sensitivity when compared to the use of CP only, although the decisive parameter should be the signal-to-noise level [28]. Nevertheless, when a spectral interference overlaps the wing of the line but does not reach the core of the line, it might be of advantage to use only CP or $CP \pm 1$ to avoid errors.

Table 4 shows the influence of side pixels on sensitivity and accuracy. As expected, the increase in the number of pixels used in the absorption measurements increases the sensitivity of the method. On the other hand, when comparing the concentration of arsenic found in CRM PACS-2 and its certified value, a significant discrepancy can be noted. Considering that the quantification is effective when using CP and $CP \pm 1$, it is very likely that the discrepancy for $CP \pm 2$ and $CP \pm 3$ is the consequence of a spectral interference. Thus, signal evaluation using three pixels only ($CP \pm 1$, which is equivalent to about 193.696 ± 0.0025 nm) is sufficient to avoid overlapping between the atomic line and the nearest interfering band.

3.3. Evaluation of the influence of sample mass

The interaction of the analyte with the modified surface of the graphite platform provides the thermal stability, avoiding losses by diffusion. This interaction is associated with the sample mass inserted in the graphite platform – as higher the mass, the lower will be sensitivity since the interaction with the modified surface will be compromised by an excess of matrix. Besides the lower analyte-tube interaction, high masses of matrix inside the tube can cause interferences due to the high concentration of concomitants and poor efficiency of the pyrolysis step. Figure 5 shows the correlation between absorbance and sample mass, which is linear up to a sample mass of about 0.6 mg, which has been considered the maximum sample mass to be used in the experiments.

3.4. Figures of merit

The figures of merit, such as the limit of detection (LOD), limit of quantification (LOQ), and the linear correlation coefficient (R^2) were evaluated. The LOD and LOQ have been calculated as 3 and 10 σ/S ($n = 10$) where σ is the standard deviation of a blank (generated by an empty SS-platform) and S is the slope of the calibration curve. The figures of merit are shown in Table 5.

Comparing the obtained values of LOD with the values presented in the Table 6, the proposed method achieved considerably lower LOD than other published methods for arsenic determination in sediment and soil samples. The direct analysis avoids contaminations from extra reagents, achieving low blank values and permits a higher arsenic concentration inside the graphite tube, since there is no sample dilution. The direct analysis also enhances the analytical throughput, since there are no extra sample preparation steps, being a cheap, safe and quick option for routine laboratories with a great number of samples to be analyzed.

The low LOD and LOQ achieved values allow the application of the developed method in the control of arsenic levels in soil. The Brazilian legislation CONAMA

420/2009 [36] stipulates a guideline value of $15 \mu\text{g g}^{-1}$ for cleanup criterion and $35 \mu\text{g g}^{-1}$ for agricultural soils. The Japanese Ministry of Environment [37] set the maximum value of $15 \mu\text{g g}^{-1}$ for agricultural soils, while Canadian guideline for agricultural soil is $12 \mu\text{g g}^{-1}$ [38].

The accuracy was verified comparing the certified values of two CRM, PACS-2 (marine sediment) and BCR-142 (Light sandy soil) with those obtained with the proposed method. According to the values in the Table 7, applying a t-test with 95% confidence interval, there is no significant difference between the values found and the certified/informed values for both CRM.

3.5. Determination of arsenic in soil samples

The arsenic content in the samples collected near to the Jorge Lacerda – Tractebel Suezin power plant in Capivari de Baixo, Brazil, has been determined and the results are shown in Table 8. According to Fig. 1, the samples 1-4 were collected in the same farm, the closest sampling point, being approximately 2.5 kilometers from the power plant in the direction east-south-east (ESE). The second sampling point, where the samples 5-8 have been collected, was about 3.2 km west of the power plant. The arsenic values found for these samples are considerably higher when compared with the third sampling point, about 4.2 km north-west (NW) of the power plant (samples 9-11). Although more studies would be necessary to verify the environmental impact of the power plant on the safety of the soil and the food produced near to the power plant, is possible to say that there is an enhancement of the arsenic levels near to the power plant. The preferred wind direction obviously also plays a role in transporting the plume of the chimney. Winds blowing from the east (the sea) are quite common, as well as winds from the north-west, whereas winds from the south-east are much less common [35]. Besides the power plant and the wind, samples 1-4 are only 600 meters from an open-air coal waste deposit, which could also be responsible for the higher arsenic values, since the remaining arsenic present in the ashes could be leached by rain and spread through the farm soil.

The farms around the Jorge Lacerda – Tractebel Suezin power plant produce crops and vegetables for the local markets and the environmental impact of the powerplant in the soil is directly related with the quality of the food produced in these farms. Considering the arsenic levels found near to the power plant, it is important to verify the Brazilian legislation CONAMA 420/2009 [36] which stipulates a safe arsenic value below $35 \mu\text{g g}^{-1}$ for agricultural soils. The analyzed soil samples, even those containing the highest levels found for arsenic in the farms, are below the values mentioned in the Brazilian legislation. Thus, in terms of arsenic levels, the soils present safe values for cultivation.

4. Conclusions

This paper is proposing a novel method for arsenic determination, using direct solid sample analysis, where the samples were only dried and sieved with no extra sample preparation steps, avoiding contamination of the sample with extra reagents or losses of the analyte. The fact of no sample preparation was needed, reduces costs and time dispended with sample preparation, being appropriated for a routine laboratory.

The accuracy of the method has been evaluated by comparison of the value found with the proposed method and the certified value for two CRM (PACS-2 and BCR-142) and no significant difference has been found. To avoid interferences, masses lower than 0.6 mg and $CP \pm 1$ for evaluation have been selected. The method achieved satisfactory accuracy and precision. The authors suggests the use of a smaller sieve to warranty the homogeneity and representativeness of the sample.

Low values of LOD and LOQ have been achieved, well below the Brazilian legislation values, which makes the method suitable for an official quality control. As part of an environmental study, the arsenic concentrations in 11 soil samples have been determined. All the soil samples presented As concentrations below the maximum values stipulated by the Brazilian legislation. This means that even the soils closest to the power plant have been found proper for the cultivation, at least with respect to their arsenic content.

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References

- [1] International Energy Outlook, 2016. US Energy Information Administration, Independent Statistics and Analysis. [https://www.eia.gov/outlooks/ieo/pdf/0484\(2016\).pdf](https://www.eia.gov/outlooks/ieo/pdf/0484(2016).pdf) (Accessed 28 March 2017).
- [2] A. Shamshad, M.H. Fulekar, P. Bhawana. Impact of coal based thermal power plant on environment and its mitigation measure, *Int. Res. J. Environment Sci.* 1 (2012) 60-64.
- [3] A. Mandal, D. Sengupta. An assessment of soil contamination due to heavy metals around a coal-fired thermal power plant in India, *Environ. Geo.* 51 (2006) 409-420.
- [4] S. Dragović, M. Čujić, L. Slavković-Beškoski, B. Gajić, B. Bajat, M. Kilibarda, A. Onjia. Trace element distribution in surface soils from a coal burning power production area: A case study from the largest power plant site in Serbia, *Catena* 104 (2013) 288-296.
- [5] A. Rodriguez-Iruretagoiena, S.F.O. de Vallejuelo, A. Gredilla, C.G. Ramos, M.L.S. Oliveira, G. Arana, A. de Diego, J.M. Madariaga, L.F.O. Silva. Fate of hazardous elements in agricultural soils surrounding a coal power plant complex from Santa Catarina (Brazil), *Sci. Total Environ.* 508 (2015) 374-382.
- [6] J. George, R.E. Masto, L.C. Ram, T.B. Das, T.K. Rout, T.K.M. Mohan. Human exposure risks for metals in soil near a coal-fired power-generating plant, *Arch. Environ. Contam. Toxicol.* 68 (2015) 451-461.
- [7] R. Raja, A.K. Nayak, A.K. Shukla, K.S. Rao, P. Gautam, B. Lal, R. Tripathi, M. Shahid, B.B. Panda, A. Kumar, P. Bhattacharyya, G. Bardhan, S. Gupta, D.K. Patra. Impairment of soil health due to fly ash-fugitive dust deposition from coal-fired thermal power plants, *Environ. Monit. Assess.* 187 (2015) 679 - 697.
- [8] Diário do Sul, Cinco décadas de existência do Complexo Jorge Lacerda <http://diariodosul.com.br/SITE2015/noticia/21169/Cinco-decadas-de-existencia-do-Complexo-Jorge-Lacerda-.html> (Accessed 30 December 2017).

- [9] Notícias do Dia, Memória de Santa Catarina - Termelétrica Jorge Lacerda rumo aos 50 anos <https://ndonline.com.br/florianopolis/coluna/carlos-damiao/memoria-de-santa-catarina-termeletrica-jorge-lacerda-rumo-aos-50-anos>. (Accessed 30 December 2017).
- [10] Thomas, D. J. The Chemistry and Metabolism of Arsenic, in *Arsenic: Exposure Sources, Health Risks, and Mechanisms of Toxicity* (ed J. C. States), John Wiley & Sons, Hoboken, New Jersey, 2015.
- [11] F.J. Zhao, E. Harris, J. Yan, J. Ma, L. Wu, W. Liu, S.P. McGrath, J. Zhou, Y.G. Zhu, Arsenic methylation in soils and its relationship with microbial *arsM* abundance and diversity, and As speciation in rice, *Environ. Sci. Technol.* 47 (2013) 7147–7154.
- [12] K.A. Hudson-Edwards, S.L. Houghton, A. Osborn. Extraction and analysis of arsenic in soils and sediments, *Trends Anal. Chem.* 23 (2004) 745-752.
- [13] IARC Working Group on the Evaluation of Carcinogenic Risk to Humans. Arsenic, Metals, Fibres and Dusts. Lyon (FR): International Agency for Research on Cancer; 2012. (IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, No. 100C.) <http://monographs.iarc.fr/ENG/Monographs/vol100C/mono100C.pdf> (Accessed 29 December 2017).
- [14] A.H. Petursdottir, J.J. Sloth, J. Feldmann, Introduction of regulations for arsenic in feed and food with emphasis on inorganic arsenic, and implications for analytical chemistry, *Anal. Bioanal. Chem.* 407 (2015) 8385–8396.
- [15] G. Záray, T.Kántor. Direct determination of arsenic, cadmium, lead and zinc in soils and sediments by electrothermal vaporization and inductively coupled plasma excitation spectrometry, *Spectrochim. Acta Part B At. Spectrosc.* 50 (1995) 489-500.
- [16] M.A. Vieira, B. Welz, A.J. Curtius. Determination of arsenic in sediments, coal and fly ash slurries after ultrasonic treatment by hydride generation atomic absorption spectrometry and trapping in an iridium-treated graphite tube, *Spectrochim. Acta Part B At. Spectrosc.* 57 (2002) 2057-2067.
- [17] S. Akbulut, U. Cevik, A.A. Van, K. De Wael, R.V. Grieken. Precision and accuracy of ST-EDXRF performance for As determination comparing with ICP-MS and evaluation of As deviation in the soil media, *Chemosphere* 96 (2014) 16-22.
- [18] C. Parsons, E. Margui Grabulosa, E. Pili, G.H. Floor, G. Roman-Ross, L. Charlet, Quantification of trace arsenic in soils by field-portable X-ray fluorescence spectrometry: Considerations for sample preparation and measurement conditions, *J. Hazard. Mater.* 262 (2013) 1213–1222.
- [19] S. Xiao-Quan, N. Zhe-Ming, Z. Li. Determination of arsenic in soil, coal fly ash and biological samples by electrothermal atomic absorption spectrometry with matrix modification, *Anal. Chim. Acta* 151 (1983) 179-185.
- [20] L.F. Silva, C.R. Ward, J.C. Hower, M. Izquierdo, F. Waanders, M.L. Oliveira,

L. Zhongsheng, R. Hatch, X. Querol. Mineralogy and leaching characteristics of coal ash from a major Brazilian power plant, *Coal Combustion and Gasification Products* 2 (2010) 51-65.

[21] M. Schneider, E.R. Pereira, I.N.B. Castilho, E. Carasek, B. Welz, I.G. Martens. A simple sample preparation procedure for the fast screening of selenium species in soil samples using alkaline extraction and hydride-generation graphite furnace atomic absorption spectrometry, *Microchem. J.* 125 (2016) 50-55.

[22] E. Becker, R. T. Rampazzo, M. B. Dessuy, M. G. R. Vale, M. M. da Silva, B. Welz, D. A. Katskov. Direct determination of arsenic in petroleum derivatives by graphite furnace atomic absorption spectrometry: A comparison between filter and platform atomizers, *Spectrochim. Acta Part B At. Spectrosc.* 66 (2011) 345-351.

[23] Lide, D. *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, Florida, 2008.

[24] É.R. Pereira, T.S. de Almeida, D.L. Borges, E. Carasek, B. Welz, J. Feldmann, J. del Campo Menoyo. Investigation of chemical modifiers for the direct determination of arsenic in fish oil using high-resolution continuum source graphite furnace atomic absorption spectrometry, *Talanta* 150 (2016) 142-147.

[25] P. Török, M. Žemberyová. Utilization of W/Mg (NO₃)₂ modifiers for the direct determination of As and Sb in soils, sewage sludge and sediments by solid sampling electrothermal atomic absorption spectrometry, *Spectrochim. Acta Part B At. Spectrosc.* 65 (2010) 291-296.

[26] X. Wang, G. Xu, P. Chen, X. Liu, Y. Fang, S. Yang, G. Wang. Arsenic speciation analysis in environmental water, sediment and soil samples by magnetic ionic liquid-based air-assisted liquid-liquid microextraction, *RSC Advances* 6 (2016) 110247-110254.

[27] R.M. de Oliveira, A.C.N. Antunes, M.A. Vieira, A.L. Medina, A.S. Ribeiro. Evaluation of sample preparation methods for the determination of As, Cd, Pb, and Se in rice samples by GF AAS, *Microchem. J.* 124 (2016) 402-409.

[28] U. Heitmann, B. Welz, D.L.G. Borges, F.G. Lepri, Feasibility of peak volume, side pixel and multiple peak registration in high-resolution continuum source atomic absorption spectrometry, *Spectrochim. Acta Part B At. Spectrosc.* 62 (2007) 1222-1230.

[29] S. Murko, R. Milačić, M. Veber, J. Ščančar. Determination of Cd, Pb and As in sediments of the Sava River by electrothermal atomic absorption spectrometry, *J. Serb. Chem. Soc.* 75 (2010) 113-128.

[30] T. Narukawa, W. Yoshimura, A. Uzawa. Determination of total arsenic in environmental and geological samples by electrothermal atomic absorption

spectrometry using a tungsten furnace after solvent extraction and cobalt (III) oxide collection, *Bull. Chem. Soc. Jpn.* 72 (1999) 701-706.

[31] A. de Jesus, A.V. Zmozinski, I.C.F. Damin, M.M. Silva, M.G.R. Vale. Determination of arsenic and cadmium in crude oil by direct sampling graphite furnace atomic absorption spectrometry, *Spectrochim. Acta Part B At. Spectrosc.* 71 (2012) 86-91.

[32] M.V. Reboucas, S.L. Ferreira, B. de Barros Neto. Behaviour of chemical modifiers in the determination of arsenic by electrothermal atomic absorption spectrometry in petroleum products, *Talanta* 67 (2005) 195-204.

[33] L. Husáková, T. Černohorský, J., Šrámková, L. Vavrušová. Direct determination of arsenic in beer by electrothermal atomic absorption spectrometry with deuterium background correction (D₂-ET-AAS), *Food Chem.* 105 (2007) 286-292.

[34] R.M. de Carvalho Jr, J.A. dos Santos, J.A.S. Silva, T.G. do Prado, A.F. da Fonseca, E.S. Chaves, V.A. Frescura. Determination of metals in Brazilian soils by inductively coupled plasma mass spectrometry, *Environ. Monit. Assess.* 187 (2015) 535-544.

[35] Município de Capivari de Baixo. Ventos e Clima. <http://www.capivaridebaixo.sc.gov.br/cms/pagina/ver/codMapaItem/16749> (Accessed 29 December 2017).

[36] CONAMA - Conselho Nacional do Meio-Ambiente. Resolução nº 420 de 28 de Dezembro de 2009. <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=620> (Accessed 17 September 2017).

[37] Ministry of Environment, Government of Japan. Environmental Quality Standards for Soil Pollution. <http://www.env.go.jp/en/water/soil/sp.html> (Accessed 30 December 2017).

[38] Canadian Council of Ministers of the Environment. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health (1999). <http://ceqg-rcqe.ccme.ca/download/en/257/> (Accessed 30 December 2017).

Caption of Figures

Figure 1. Sampling points in Capivari de Baixo, Brazil, near to the Jorge Lacerda – Tractebel Suezin power plant (28°27'18.0"S 48°58'10.6"W). The numbers 1 to 11 represent the points where the samples have been collected.

Figure 2. Pyrolysis and atomization curves obtained for an aqueous solution of 4 ng As

by HR-CS GF AAS at 193.696 nm. For the Pd/Mg modifier in solution (Δ) the pyrolysis temperature (T_{pyr}) chosen for the atomization curve was 1100 °C; for Zr_{per} (\blacktriangle) T_{pyr} was 900 °C; for Ir_{per} (\circ) T_{pyr} was 1000 °C; for $Zr_{\text{per}} + Pd/Mg$ (\bullet) T_{pyr} was 1000 °C; for $Ir_{\text{per}} + Pd/Mg$ (\square) T_{pyr} was 1100 °C; and for $W_{\text{per}} + W/Mg$ (\blacksquare) T_{pyr} was 900 °C; T_{at} was 2100 °C in all cases.

Figure 3. Pyrolysis and atomization curves obtained for about 0.2 mg PACS-2 by HR-CS GF AAS at 193.696 nm. For; for the Pd/Mg modifier in solution (Δ) T_{pyr} was 1100 °C and T_{at} was 2200 °C; for Zr_{per} (\blacktriangle) T_{pyr} was 1000 °C and T_{at} 2300 °C; for Ir_{per} (\circ) T_{pyr} was 1000 °C and T_{at} was 2300 °C; for $Zr_{\text{per}} + Pd/Mg$ (\bullet) T_{pyr} was 1000 °C and T_{at} was 2400 °C; for $Ir_{\text{per}} + Pd/Mg$ (\square) T_{pyr} was 1100 °C and T_{at} was 2400 °C; and for $W_{\text{per}} + W/Mg$ (\blacksquare) T_{pyr} was 900 °C and T_{at} was 2300 °C. The integrated absorbances were normalized in function of the sample mass used to generate the signal.

Figure 4. Comparison of 3D spectra between 193.575 nm and 193.816 nm obtained for approximately 0.2 mg PACS-2 with Ir_{per} (A), $W_{\text{per}} + W/Mg$ (B) and Zr_{per} (C).

Figure 5. Evaluation of sample mass in the sensitivity. The points were generated with a range of masses up to 1.25 mg of CRM PACS-2. The baseline refers to a curve with the same slope of the calibration curve.

Table 1. Temperature program for iridium, zirconium and tungsten coating of the PIN platform. Gas flow 2 L min⁻¹ during all program stages.

Stage	Temperature (°C)	Ramp (°C s ⁻¹)	Hold (s)
1	90	5	40
2	110	1	40
3	130	1	40
4	1200	300	25
5	2100	500	10
6	2100	0	5

Table 2. Microwave-assisted digestion program for soil samples in *aqua-regia* media.

Parameter	Value
Temperature (°C)	190
Pressure (bar)	40
Ramp (min)	1
Hold time (min)	25

Table 3. Temperature programs for arsenic determination using a Zirconium-coated graphite platform.

Stage	Temperature (°C)	Ramp (°C s ⁻¹)	Hold (s)	Gas Flow
Drying	90	10	10	Max
Drying	110	10	10	Max
Pyrolysis	1000	300	15	Max
Atomization	2200	3000	05	Zero
Cleaning	2300	100	05	Max

Table 4. Evaluation of center pixel set in 193.696 nm and side pixels to understand the extension of the spectral interference observed.

	Width (pm)	Slope (s ng ⁻¹)	R ²	Found (µg g ⁻¹)	2 tailed p-value ¹
CP	1.4	5.6 x 10 ⁻⁵	0.9991	25.9 ± 13	0.97
CP ± 1	4.2	15.1 x 10 ⁻⁵	0.9990	25.7 ± 3.8	0.84
CP ± 2	7.0	20.2 x 10 ⁻⁵	0.9992	33.7 ± 5.3	0.08
CP ± 3	9.8	21.4 x 10 ⁻⁵	0.9989	34.0 ± 5.8	0.09

¹ Based on t-test using CRM PACS-2 certified value: 26.2 ± 1.5 µg g⁻¹.

Table 5. Analytical figures of merit for the determination of arsenic in soil samples using HR-CS SS-GF AAS.

Parameter	Value
Linear regression equation	$A_{\text{int}} = 0.01 + 0.0002 \text{ pg As}$
Linear range	0.28 - 16.0 ng
R ²	0.998
LOD	28 pg ^a / 0.04 ng g ^{-1b}
LOQ	184 pg ^a / 0.3 ng g ^{-1b}
Characteristic mass (m ₀)	22 pg

^a Absolute value.

^b Value calculated for 0.6 mg of sample.

Table 6. Comparison between published methods for arsenic determination and their LOD values.

Sample	Technique	Method	Modifier	T _{pyr}	T _{atm}	LOD	REF
Sediment	HG-ET AAS	Slurry	Ir _{per}	1300	2100	0.7 µg g ⁻¹	[16]

Sediment	ET AAS	Acid digestion	Pd/Mg	200	2500	0.25 mg kg ⁻¹	[29]
Soils and sediments	ET AAS	Direct	W _{per} +Mg	1200	2400	0.5 µg g ⁻¹	[25]
Geological	ET AAS	Extraction/slurry	W furnace	1000	2500	12 µg dm ⁻³	[30]
Soil and sediment	GF AAS	MIL-AALLME ¹	Pd/Mg	800	2200	0.029 µg L ⁻¹	[26]
Crude oil	GF AAS	Direct	Pd/Mg	1200	2400	5.1 µg kg ⁻¹	[31]
Petroleum derivatives	ET AAS	Direct	La	800	2400	0.56 µg L ⁻¹	[32]
Petroleum derivatives	GF AAS	Microemulsion	Pd/Mg	1400	2400	1.9 µg L ⁻¹	[22]
Beer	GF AAS	Direct	Pd	1400	2600	1.3 µg L ⁻¹	[33]
Rice	GFAAS	Acid digestion	Pd/Mg	1000	2200	77.2 ng g ⁻¹	[27]
Fish oil	HR-CS GF AAS	Direct	Ru _{per} +Pd	1400	2300	30 pg	[24]
Soil	HR-CS GF AAS	Direct solid sample analysis	Zr _{per}	900	2200	28 pg	This work

¹ Magnetic ionic liquid-based air-assisted liquid–liquid micro-extraction.

Table 7. Arsenic determination in soil CRM using HR-CS GF AAS and direct solid sample analysis with calibration against aqueous standards. The values represent the mean of five measurements ± SD, n=5.

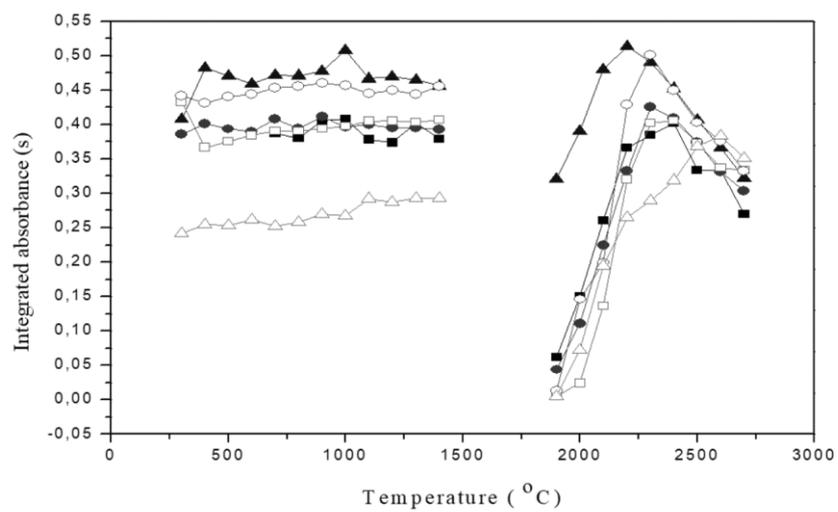
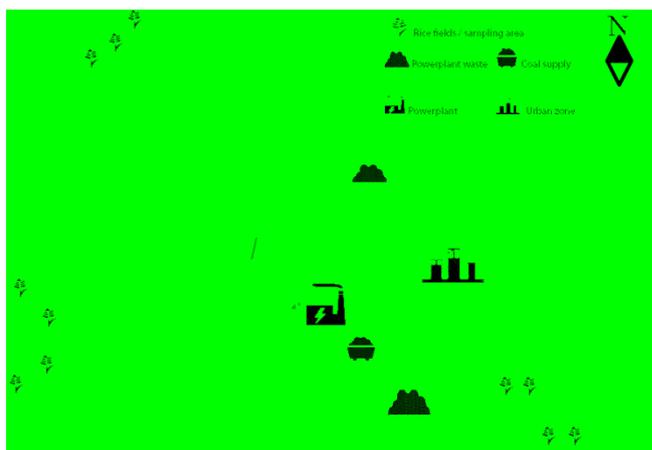
CRM	Found (µg g ⁻¹)	Certified (µg g ⁻¹)
Light Sandy Soil (BCR142)	16.9 ± 0.8	17.05 ± 1.45
Marine Sediment (PACS-2)	27.3 ± 1.5	26.2 ± 1.5

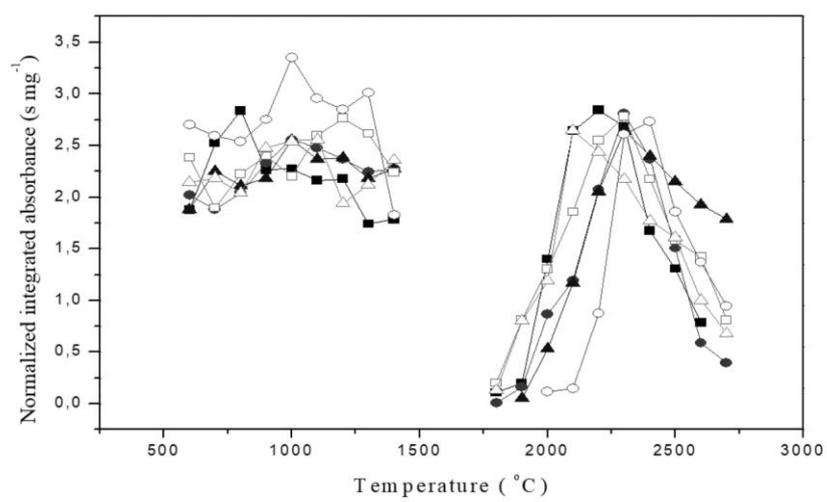
*Informed value [34]

Table 8. Arsenic determination in eleven soil samples by HR-CS GF AAS. The uncertainty is based on a 95 % confidence level (n=5).

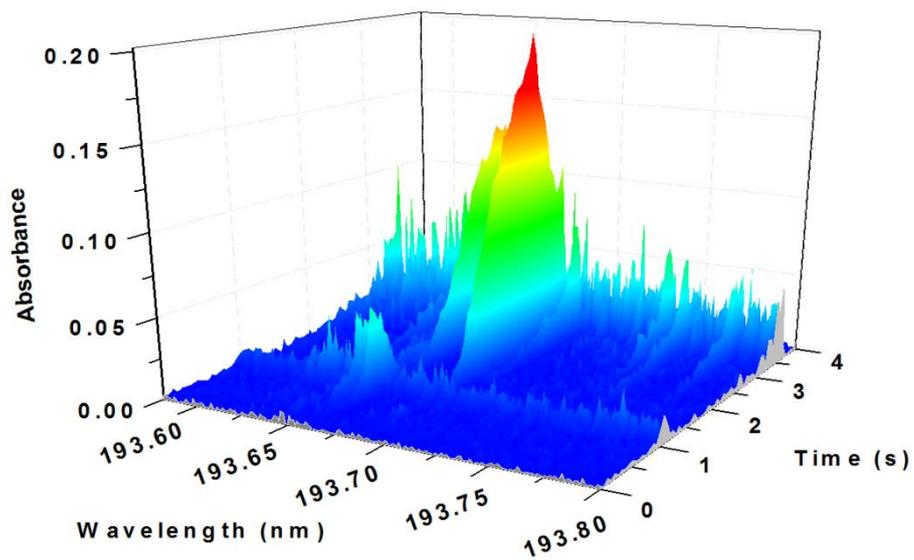
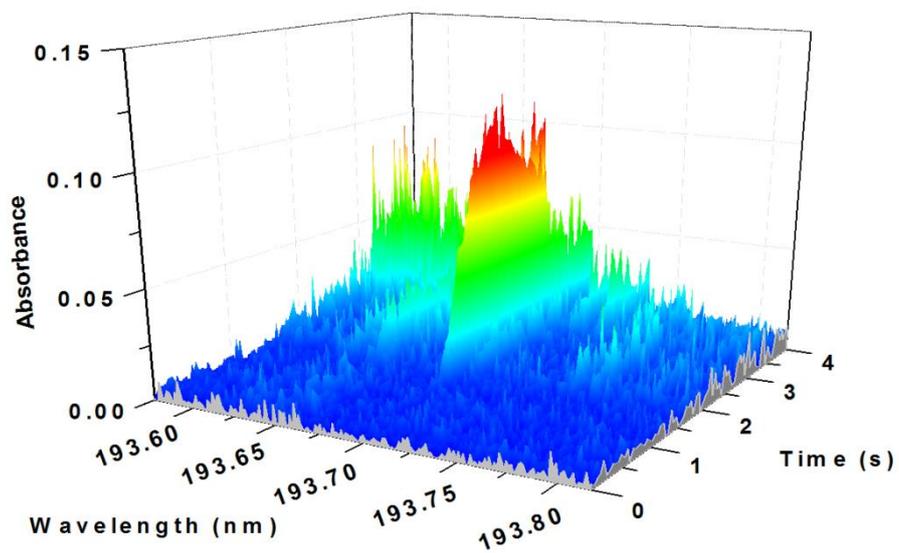
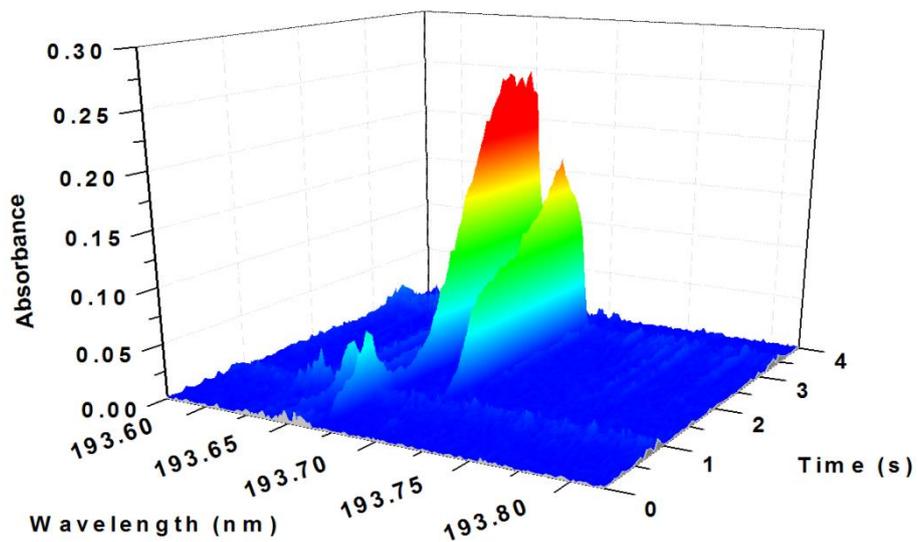
Samples	Arsenic concentration (µg g ⁻¹)
1	6.94 ± 0.64
2	8.98 ± 0.65
3	7.18 ± 0.73
4	9.65 ± 0.003
5	7.13 ± 0.49
6	7.56 ± 0.80
7	6.64 ± 2.36

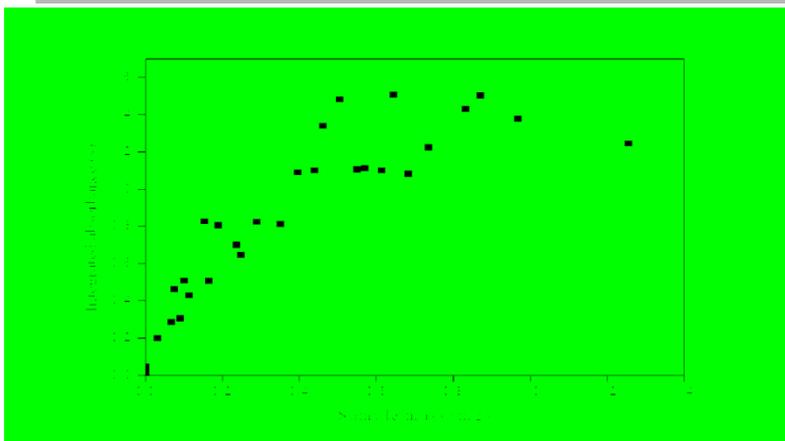
8	7.93 ± 0.94
9	3.37 ± 1.08
10	4.80 ± 1.06
11	5.14 ± 1.30





Accepted manuscript

A**B****C**



HIGHLIGHTS

- A simple method was developed for arsenic determination.
- The method uses direct analysis with no extra sample preparation steps.
- No interferences are found when the correct temperature program, permanent modifier and number of evaluation pixels are set.
- Arsenic levels can be determined with standard aqueous calibration.
- Low limits of quantification can be achieved when compared with microwave-assisted digestion, since the sample is not diluted.

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