

Arsenic quantification techniques and ISO/IEC 17025 accreditation in Brazil

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Abstract. The importance of arsenic (As) quantification in environmental compartments is due to its risks to ecosystems and public health. There are reports of high concentrations of this metalloid in Brazil and technological differences between states are observed. The objective of this work was to present and discuss current scenarios of accreditation and compare the limit of quantification (LOQ) of As by analytical technique in Brazil. Data from accredited laboratories were collected on Inmetro website and in state metrological networks and then grouped and analyzed by state, matrix and analytical technique. There are large discrepancies between the number of laboratories per state and a good correlation with gross domestic product (GDP). Almost all laboratories have a LOQ less than the environmental limits. The observed list of techniques sorted from lowest to highest LOQ values is: for liquid samples ICP MS (inductively coupled plasma mass spectrometry), ET AAS (electrothermal atomic absorption spectrometry), HG AAS (hydride generation combined with atomic absorption spectrometry) or HG ICP OES (hydride generation combined with inductively coupled plasma optical emission spectrometry) and UV VIS (visible ultraviolet spectroscopy); for solids samples HG ICP OES, ICP MS, HG AAS, ET AAS and FAAS (flame atomic absorption spectrometry); and for bioindicators ICP MS, HG ICP OES. Analysis of As species is accredited in only one laboratory, but does not include all species.

Keywords: Hydride generation; Environmental laboratories; Limit of detection; Spectrometry; Speciation; Chromatography.

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Resumo. Técnicas de quantificação de arsênico e acreditação ISO/IEC 17025 no Brasil. A importância da quantificação do arsênico (As) nos compartimentos ambientais deve-se aos riscos para os ecossistemas e para a saúde pública. Há relatos de altas concentrações desse metaloide no Brasil e diferenças tecnológicas entre estados são observadas. O objetivo deste trabalho foi apresentar e discutir os cenários atuais de acreditação e comparar o limite de quantificação (LOQ) de As pelas técnicas analíticas no Brasil. Os dados dos laboratórios credenciados foram coletados no site do Inmetro e nas redes metrológicas estaduais e, em seguida, agrupados e analisados por estado, matriz e técnica analítica. Existem grandes discrepâncias entre o número de laboratórios por estado e uma boa correlação com o produto interno bruto (PIB). Quase todos os laboratórios têm um LOQ menor que os limites ambientais. A lista observada de técnicas classificadas dos menores aos mais altos valores de LOQ é: para amostras líquidas ICP MS (espectrometria de massa de plasma indutivamente acoplado), ET AAS (espectrometria de absorção atômica eletrotérmica), HG AAS (geração de hidreto combinada com espectrometria de absorção atômica) ou HG ICP OES (geração de hidreto combinado com espectrometria de emissão óptica de plasma acoplada indutivamente) e UV VIS (espectroscopia ultravioleta visível); para amostras de sólidos HG ICP OES, ICP MS, HG AAS, ET AAS e FAAS (espectrometria de absorção atômica por chama); e para bioindicadores ICP MS, HG ICP OES. A análise das espécies As é creditada em apenas um laboratório, mas não inclui todas as espécies.

Palavras-chave: Geração de hidreto; Laboratórios ambientais; Limite de detecção; Espectrometria; Especificação; Cromatografia.

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Introduction

The environmental risk of arsenic (As) to ecosystems and public health is a fact in a large number of countries around the world (Bundschuh et al., 2012). The metalloid can be responsible for various dermatological, cardiovascular, pulmonary, reproductive, neurological and tumorigenesis complications in many parts of the body (Abdul et al., 2015).

Analytical techniques for quantification of As on environmental samples typically include atomic absorption, atomic emission and mass spectrometry and, X-ray fluorescence and visible-ultraviolet spectroscopy techniques (Ma et al., 2014; Sankararamakrishnan and Mishra, 2018). These techniques may include flame

atomizers, hydride generators and electrothermal devices, such as the graphite furnace (Sankararamakrishnan and Mishra, 2018). Analytical techniques approved by USEPA include inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP MS), hydride generation combined with atomic absorption spectrometry (HG AAS) and electrothermal atomic absorption spectrometry (ET AAS), with quantification limits ranging from 0.5 to 50 $\mu\text{g L}^{-1}$ (Ma et al. 2014).

Recent studies have used ICP MS (Bolea-Fernandez et al., 2015; Oroian et al., 2016; Kaya and Turkoglu, 2017; Machado et al., 2017; De La Cruz et al., 2018), HG AAS (Waterlot and Douay, 2015), ET AAS (Hassanpoor et al., 2015;

Oliveira et al., 2016; Souza et al., 2016; Pereira et al., 2016), hydride generation combined with inductively coupled plasma optical emission spectrometry HG ICP OES (Kim et al., 2019), hydride generation combined with atomic fluorescence spectrometry (HG AFS) (Wang et al., 2016), microwave induced plasma optical emission spectrometry (MIP OES) (Gallego Ríos et al., 2018), visible ultraviolet spectroscopy (UV VIS) (Gürkan et al., 2015), total reflection X-ray fluorescence (TXRF) (Pierangeli et al., 2015) and portable X-ray fluorescence (PXRF) (García-Rico et al., 2019; Kim et al., 2019).

In addition to total As quantification, speciation techniques are important to detect and quantify many of As species, which may occur in organic or inorganic forms and in different valence states, with implications on their bioavailability and toxicity (Abdul et al., 2015; Moe et al., 2016; Liu et al., 2018). Some hyphenated techniques consider chromatography and capillary electrophoresis (Khan et al., 2015; Ma et al., 2016; Cheng et al., 2018; García-Rico et al., 2019); ion chromatography (Zhu et al., 2017), ultraviolet spectroscopy and capillary electrophoresis (CE UV) (Lee et al., 2018) for the separation of species.

The maximum established limit for drinking water, groundwater and class 1 freshwater is $10 \mu\text{g L}^{-1}$ (Brasil, 2005, 2009, 2017). For effluents, the limit is $500 \mu\text{g L}^{-1}$ (Brasil, 2011). In soils, the value of prevention (VP) is 15 mg kg^{-1} , the value of agricultural investigation is 35 mg kg^{-1} , residential investigation is 55 mg kg^{-1} and the industrial value is 150 mg kg^{-1} (Brasil, 2009). The resolutions of National Environment Council (CONAMA), which enforce the accepted limits, also require that the analyzes for characterization and monitoring be performed by laboratories accredited by the National Institute of Metrology, Standardization and Industrial Quality (INMETRO) (Brasil, 2009, 2011). However, there are no standards for bioindicators, air quality and As species.

Brazil has historical regional differences that are reflected in the access

to technologies (Santos et al., 2014). According to Grochau et al. (2017) there is a strong correlation between the gross domestic product (GDP) of counties in the Americas and the number of ISO 17025 accredited laboratories.

In Brazil, the main high As concentrations occur in Minas Gerais state (Bundschuh et al., 2012), especially correlated to gold deposits in the Iron Quadrangle (Borba et al., 2003; Varejão et al., 2011; Costa et al., 2015; Silva et al., 2018) and in the surroundings the of city of Paracatu (Ono et al., 2012; Rezende et al., 2015; Bidone et al., 2018). In these regions the presence of As is associated with natural deposits of gold, where it is predominantly contained in sulfide minerals such as arsenopyrite and pyrite (Deschamps et al., 2002).

Keeping this in view, the objective of this work was to present and discuss current scenarios of accreditation and compare the limit of quantification (LOQ) of As by analytical techniques in Brazil.

Methodology

Data on accredited laboratories, LOQ and analytical techniques were collected in July, 2018 from Inmetro's website (Inmetro 2018) and state metrological networks (RMMG, 2018; Rede Metrológica do Rio Grande do Sul, 2018). Laboratories were grouped by state, matrix and analytical technique. Matrices were grouped by the sample type as liquid (drinking water, raw water, underground water, for human consumption, treated, saline, brackish, residual, effluent, solubilized extract and leachate and liquid waste), solid (soil, sediment, solid waste, industrial, rock, sludge) and bioindicators (plant tissue, mussel, aquatic, terrestrial and plant organisms). The correlation between state's GDP and number of accredited laboratories was based on Pearson correlation coefficient using Excel software (Office 365, 1903 version). Descriptive analysis of the analytical techniques by state and matrix.

Results and discussion

In Brazil, there are 1081 accredited laboratories, of which 385 offer environmental tests and only 102 analyze As. The highest number of environmental laboratories is concentrated in the Southeast and South regions, which accounts for 89% of the total. For instance, São Paulo (SP) state respond for almost 53%. The number is even higher when considering As analysis, with 96% of the laboratories located in the South and Southeast regions, 67% in SP. Northeast

region has only one laboratory in Bahia (BA) while the North has no. Figure 1 shows the distribution of laboratories and GDP by state.

A strong positive correlation (Pearson correlation) was found between the number of accredited laboratories and GDP, as also observed by (Grochau et al., 2017). The highest correlation occurred with the testing laboratories ($r = 0.97$), followed by testing environmental laboratories ($r = 0.94$) and finally those performing As analyses ($r = 0.92$).

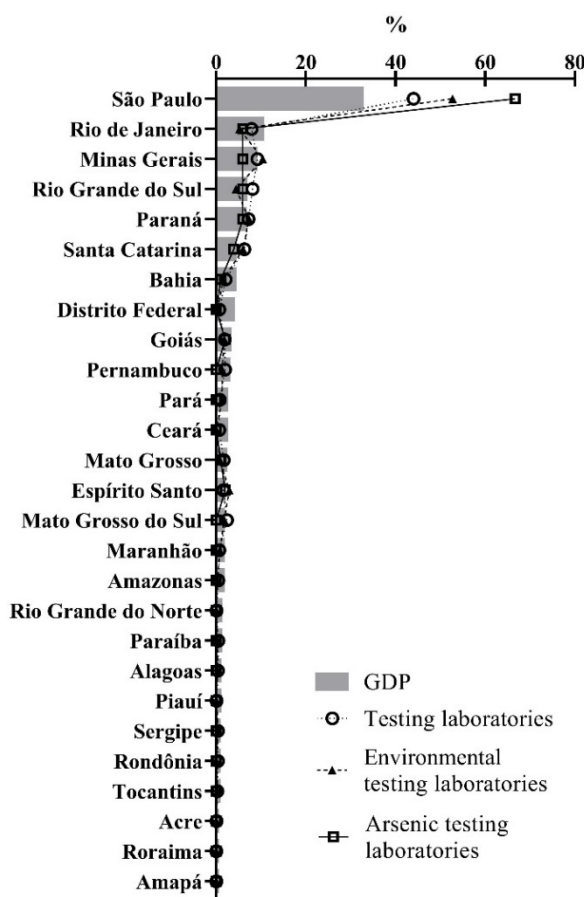


Figure 1. Percentage of the national number of accreditations of testing laboratories (1081), testing environmental (385), arsenic testing (102) and GDP (gross domestic product), by State, in Brazil.

HG ICP OES or HG AAS are most common techniques used for quantify As

in small content (Table 1), corresponding to 80.3% of the accreditations. The ones

with larger investments and with higher analytical sensitivity, such as ICP MS and ET AAS, accounted for 17.2% and those with lower sensitivity, such as flame

atomic absorption spectrometry (FAAS) and UV VIS, only 2.5%. More sensitive techniques are present in only 5 states (SP, MG, RJ, RS and PR).

Table 1. Analytical techniques for As quantification of As used in accredited laboratories in different states from Brazil.

Technique	States									
	SP	MG	RJ	RS	PR	SC	ES	BA	GO	MT
ICP MS	4	2	1	1	1	0	0	0	0	0
ET AAS	8	1	0	2	1	0	0	0	0	0
HG AAS	20	7	3	5	2	1	0	1	1	0
HG ICP OES	41	4	3	0	3	3	2	0	1	1
UV VIS	2	0	0	0	0	0	0	0	0	0
FAAS	0	0	0	0	1	0	0	0	0	0

Considering only laboratories accredited for As analysis, 89% have accreditation in liquid matrices, 42% in solids, 10% in gases and 2% in bioindicators. That distribution probably stems from a greater concern with water potability. Fig. 2 shows the LOQ (Limit of quantification) for As per analytical technique, in the three different matrices: liquid, solid and bioindicator samples.

Almost all laboratories presented a LOQ in accordance with environmental threshold for water, effluent and soil. Many laboratories (31) has a value equal to the potability standard (Brasil, 2017) (Figure 2a), potentially indicating that it is used as a target. Only one laboratory presented a LOQ greater than the potability standard and is therefore not applicable for this purpose (Figure 2a). This laboratory utilizes the HG AAS, but the occurrence does not prove to be a limitation since the other laboratories and other studies (Borba et al., 2004; Akter et al., 2005; Waterlot and Douay, 2015) presented considerably lower values. Three laboratories presented LOQ values greater than the VP (15 mg kg⁻¹) (Brasil, 2009) (Figure 2b), of which two used HG ICP OES and one FAAS. As with other laboratories, which obtained LOQ values below the VP using HG ICP OES, the

occurrence is not a limitation of the technique. Only one laboratory uses FAAS and presents LOQ values above the VP. Other authors also obtained LOQ values near or even above the VP, such as 12.8 mg kg⁻¹ with ICP OES (Paye et al., 2010) and 33.3 mg kg⁻¹ with PXRF (García-Rico et al., 2019).

Techniques sorted from lowest to highest LOQ, considering the lowest LOQ, was similar among the matrices. In the case of liquid matrices, it was: ICP MS (40 ng L⁻¹), ET AAS (50 ng L⁻¹), HG AAS or HG ICP OES (100 ng L⁻¹) and UV VIS (4 µg L⁻¹) (Fig. 2a). In solid matrices: HG ICP OES (1 µg kg⁻¹), ICP MS (1.5 µg kg⁻¹), HG AAS (10 µg kg⁻¹), ET AAS (50 µg kg⁻¹) and FAAS (100 mg kg⁻¹) (Figure 2b). In bioindicators: ICP MS (10 µg kg⁻¹) and HG ICP OES (50 µg kg⁻¹) (Figure 2c). In a study comparing practically the same analytical techniques, Hung et al. (2004) observed a similar sequence (ICP MS, ET AAS, HG AFS, HG AAS and HG ICP OES) compared with the present study, except for UV VIS which was not observed. Yogarajah and Tsai (2015) also obtained a lower LOQ for ICP MS (ICP MS=AFS<AAS) and Akter et al. (2005) observed a lower LOQ for liquid chromatography (LC) combined with ICP MS than for HG AAS (LC ICP MS<HG AAS<CE UV).

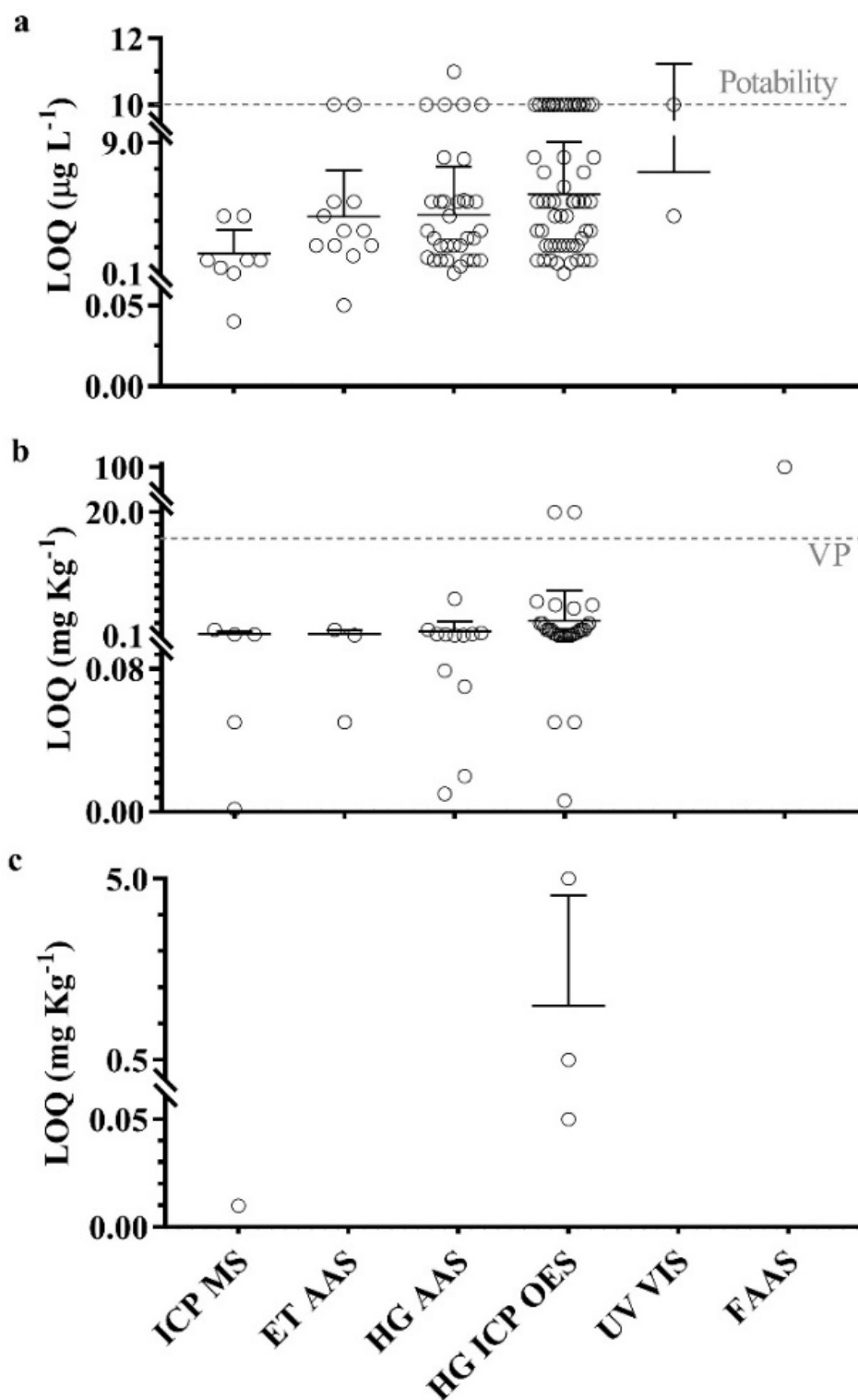


Figure 2. LOQ (Limits of quantification) of As per analytical technique, in liquid (a), solid (b) and bioindicator samples (c) and comparison with legal environmental limits of potability and value of prevention (VP) for soil.

Table 2 present the LOQ for As obtained using different analytical technique and compare it with that showed in studies involving As quantification in the three matrices considered in the present data survey.

Table 2. LOQ (Limits of quantification) of As per analytical technique in liquid, solid and bioindicator samples observed in the present data survey and comparison with other works.

Technique	LOQ	Reference
Liquid samples ($\mu\text{g L}^{-1}$)		
ICP MS	0.0007	(Bolea-Fernandez et al. 2015)
ET AAS	0.006	(Hassanpoor et al. 2015)
ICP MS	0.04 to 4.00	Data survey
ET AAS	0.05 to 10.00	Data survey
HG ICP OES	0.10 to 10.00	Data survey
HG AAS	0.10 to 11.00	Data survey
ICP MS	0.21	(Komorowicz and Barańkiewicz 2016)
ICP MS	0.33	(García-Rico et al. 2019)
HG AAS	0.33	(Akter et al. 2005)
HG AAS	0.41	(Waterlot and Douay 2015)
ICP MS	0.46	(Makowska et al. 2018)
ICP MS	0.70	(Machado et al. 2017)
UV VIS	4.00 to 10.00	Data survey
ET AAS	4.60	(Makowska et al. 2018)
Solid samples ($\mu\text{g kg}^{-1}$)		
HG AAS	0.67	(Gürleyük et al. 2000)
HG ICP OES	1.00 to 20,000	Data survey
ICP MS	1.50 to 1,000	Data survey
ET AAS	7.40	(Nielsen et al. 2011)
HG AAS	10.0 to 6,000	Data survey
TXRF	33.3	(Pierangeli et al. 2015)
HG ICP OES	50.0	(Souza et al. 2016)
HG ICP OES	50.0	(Alcântara et al. 2011)
ET AAS	50.0 to 1,000	Data survey
HG ICP OES	210	(Paye et al. 2010)
HG AAS	300	(Rezende et al. 2011)
GC ECD	480	(Zhong et al. 2019)
HG ICP OES	830	(Kim et al. 2019)
PXRF	1,670	(Kim et al. 2019)
ICP OES	12,800	(Paye et al. 2010)
PXRF	33,300	(García-Rico et al. 2019)
FAAS	100,000	Data survey

Table 2. Continued.

Technique	LOQ	Reference
Bioindicator samples ($\mu\text{g kg}^{-1}$)		
ET AAS	0.08	(Baig et al. 2010)
ICP MS	0.09	(Khan et al. 2015)
ICP MS	0.12	(Kaya and Turkoglu 2017)
ICP MS	2.27	(Oroian et al. 2016)
ICP MS	10.0	Data survey
ICP MS	13.3	(De La Cruz et al. 2018)
HG ICP OES	50.0 to 5,000	Data survey
MIP OES	76.7	(Gallego Ríos et al. 2018)
ET AAS	100	(Pereira et al. 2016)
HG AFS	200	(Wang et al. 2016)
ET AAS	257	(Oliveira et al. 2016)

In our data survey, it was possible to observe that the ICP MS presented a LOQ ranging from 0.04 to 4.00 $\mu\text{g L}^{-1}$ in liquids, 1.50 to 1,000 $\mu\text{g kg}^{-1}$ in solids and 10.00 $\mu\text{g kg}^{-1}$ in bioindicators (Table 2). However, in water samples, some studies have considerably lower LOQ, such as 0.0007 $\mu\text{g L}^{-1}$ (Bolea-Fernandez et al., 2015). But most values observed are close to the range (0.04 to 4.00 $\mu\text{g L}^{-1}$), such as 0.21 $\mu\text{g L}^{-1}$ (Komorowicz and Barańkiewicz, 2016), 0.33 $\mu\text{g L}^{-1}$ (García-Rico et al., 2019), 0.46 $\mu\text{g L}^{-1}$ (Kilic et al., 2018) and 0.70 $\mu\text{g L}^{-1}$ (Machado et al., 2017). In bioindicators, some studies showed values close to those observed in the present data survey, while others showed lower values. For example, Khan et al. (2015) obtained 0.09 $\mu\text{g kg}^{-1}$ when analyzing algae and Kaya and Turkoglu (2017) found 0.12 $\mu\text{g kg}^{-1}$ in fish samples. Oroian et al. (2016) observed 2.27 $\mu\text{g kg}^{-1}$ in honey samples and De La Cruz et al. (2018) found 13.3 $\mu\text{g kg}^{-1}$ in plant tissues.

The ET AAS showed a LOQ between 0.05 and 10.00 $\mu\text{g L}^{-1}$ in liquid samples and between 50.0 and 1,000 $\mu\text{g kg}^{-1}$ in solids (Table 2). Studies using the same technique also present similar results in liquids ranging from 0.006 $\mu\text{g L}^{-1}$ (Hassanpoor et al., 2015) and 4.60 $\mu\text{g L}^{-1}$ (Makowska et al., 2018). In solid samples (soils), Nielsen et al. (2011) obtained a

considerably lower value (7.40 $\mu\text{g kg}^{-1}$) than the present data survey. Baig et al. (2010) obtained 0.08 $\mu\text{g kg}^{-1}$ in bioindicator samples (corn) and Oliveira et al. (2016) reported 257 $\mu\text{g kg}^{-1}$ when analyzing rice. Already Pereira et al. (2016) found 100 $\mu\text{g kg}^{-1}$ when analyzing fish oil.

The two techniques that use HG presented similar LOQ values. The HG AAS had a LOQ ranging from 0.1 to 11 $\mu\text{g L}^{-1}$ in liquid samples and from 10 to 6,000 $\mu\text{g kg}^{-1}$ in solid samples; while the HG ICP OES ranged from 0.1 to 10 $\mu\text{g L}^{-1}$ in liquid samples, from 1.0 to 20,000 $\mu\text{g kg}^{-1}$ in solid samples and from 50 to 5,000 $\mu\text{g kg}^{-1}$ in bioindicators (Table 2). Other studies using HG presented values within the same ranges found. When using HG AAS to analyze water, Akter et al. (2005) obtained 0.33 $\mu\text{g L}^{-1}$ and Waterlot and Douay (2015) 0.41 $\mu\text{g L}^{-1}$. In soils Gürleyük et al. (2000) obtained 0.67 $\mu\text{g kg}^{-1}$, and in sediments Rezende et al. (2011) found 300 $\mu\text{g kg}^{-1}$. When using HG ICP OES to analyze soils, Souza et al. (2016) and Alcântara et al. (2011) obtained 50.0 $\mu\text{g kg}^{-1}$, Paye et al. (2010) 210 $\mu\text{g kg}^{-1}$ and Kim et al. (2019) 830 $\mu\text{g kg}^{-1}$.

Some techniques are used by few laboratories, such as UV VIS and FAAS. The UV VIS had a LOQ ranging from 4 to 10 $\mu\text{g L}^{-1}$ in liquid samples and FAAS presented

100,000 $\mu\text{g kg}^{-1}$ in solid samples (Table 2). These techniques are also less used in scientific works, which in addition to the techniques previously discussed, use techniques that involve fluorescence, microwave induced plasma, electron capture detector and X-ray in diverse matrices. In soil samples, Pierangeli et al. (2015) used TXRF and obtained 33.3 $\mu\text{g L}^{-1}$, Zhong et al. (2019) with gas chromatograph with an electron capture detector (GC ECD) found 480 $\mu\text{g kg}^{-1}$ and Kim et al. (2019) with PXRF reported 1,670 $\mu\text{g kg}^{-1}$. Analyzing samples in fish, Gallego Ríos et al. (2018) obtained 76.7 $\mu\text{g kg}^{-1}$ using MIP OES and in samples of *Eisenia fetida*, Wang et al. (2016) obtained 200 $\mu\text{g kg}^{-1}$ with HG AFS.

Table 3 present the LOQ for As species obtained using different analytical techniques and compare it with that showed in studies involving As quantification in the three matrices considered in the present data survey. Only one laboratory is accredited for As speciation. However, it does not cover all species analyzed in scientific studies, quantifying only the species As III, As V, Monomethyl Arsenic (MMA), Dimethyl Arsenic (DMA) and Arsenic Betaine (AsB). Species such as trimethylarsine oxide (TMAO) found in plants (Bergqvist and Greger, 2012) or Arsenocoline (AsC) found in marine animals (Raber et al. 2012), are not accredited by any Brazilian laboratory.

The LOQ for As species in liquid samples was 0.25 $\mu\text{g L}^{-1}$ (Table 3) for As III, As V, MMA, DMA and AsB. These values are similar to other reports which used similar techniques to determine As species. One study presented a lower LOQ when using solid phase extraction (SPE) coupled to ET AAS, obtaining 0.006 $\mu\text{g L}^{-1}$ in the determination of As(III) and As(V), but it should be noted that other species were not determined (Hassanpoor et al. 2015). Using high performance liquid chromatography (HPLC) combined with ICP MS, Liu e Cai (2013) obtained values between 0.13 and 1.66 $\mu\text{g L}^{-1}$, Komorowicz and Barańkiewicz (2016) between 0.22 and 0.39 $\mu\text{g L}^{-1}$ and Cheng et al. (2018)

between 3.00 and 5.90 $\mu\text{g L}^{-1}$ for the determination of As III, As V, MMA, and DMA. Where in addition to the previous species, Komorowicz and Barańkiewicz (2016) also determined AsB and Liu and Cai (2013) quantified ROX and AsA. Akter et al. (2005) used HG AAS and obtained between 0.33 and 0.63 $\mu\text{g L}^{-1}$ for determination of As III and DMA. Waterlot and Douay (2015) found 0.41 $\mu\text{g L}^{-1}$ when determining As III and V by the same technique. Using LC ICP MS, Akter et al. (2005) obtained between 0.33 and 0.67 $\mu\text{g L}^{-1}$ for the determination of As III, As V, DMA and MMA. Some studies have higher LOQ values because they use less sensitive techniques, such as Gürkan et al. (2015) that obtained 3.00 $\mu\text{g L}^{-1}$ for As V when using UV VIS. With CE UV Lee et al. (2018) obtained values between 7.90 and 20.0 $\mu\text{g L}^{-1}$ for As III, As V, MMA and DMA and Akter et al. (2005) reported between 300 and 1600 $\mu\text{g L}^{-1}$ for As III, As V and DMA.

For As species in solid samples and bioindicators, the LOQ was 12.5 $\mu\text{g kg}^{-1}$ (Table 3) for As III, As V, MMA, DMA and AsB. The LOQ of the laboratories was considerably lower than those achieved by Wang et al. (2018) which obtained values between 400 and 1000 $\mu\text{g kg}^{-1}$ for the determination of As III, V, DMA and MMA in *Eisenia fetida* using HG AFS. Other studies obtained smaller LOQ values in several matrices and analytical techniques, mostly using HPLC HG ICP OES, as in Khan et al. (2015) with LOQ between 0.06 and 0.20 $\mu\text{g kg}^{-1}$ for MMA, AsB, As V, DMA, AsC and As III in algae. For quantification of As(III), As(V), MMA and DMA using same technique, García-Rico et al. (2019) found values ranging from 0.40 up to 0.70 $\mu\text{g L}^{-1}$ in urine. Ma et al. (2016) found values between 0.70 and 3.00 $\mu\text{g kg}^{-1}$ in rice and Al-Assaf et al. (2009) reported values between 1.30 and 3.30 $\mu\text{g L}^{-1}$ in soils. Using HPLC ICP MS, Wolf et al. (2011) obtained 0.05 $\mu\text{g L}^{-1}$ for As III and V in soils. Working with rice samples, Wang et al. (2018) showed As values ranging from 0.70 and 3.00 $\mu\text{g kg}^{-1}$ with HG AFS. Zhu et al. (2017) found lower values between 0.10 and 0.20 $\mu\text{g L}^{-1}$ with ion

chromatography (IC) combined with ICP MS. Using HG AAS, Santos et al. (2018)

obtained values between 0.07 and 0.10 $\mu\text{g L}^{-1}$ for As III and V in fish.

Table 3. LOQ (Limits of quantification) of As species per analytical technique, in liquid, solid and bioindicator samples observed in the present data survey and comparison with other works.

Technique	LOQ	Reference
Liquid samples ($\mu\text{g L}^{-1}$)		
SPE ET AAS	0.006	(Hassanpoor et al. 2015)
HPLC ICP MS	0.13 to 1.66	(Liu and Cai 2013)
HPLC ICP MS	0.22 to 0.39	(Komorowicz and Barańkiewicz 2016)
HPLC ICP MS	0.25	Data survey
HG AAS	0.33 to 0.63	(Akter et al. 2005)
LC ICP MS	0.33 to 0.67	(Akter et al. 2005)
HG AAS	0.41	(Waterlot and Douay 2015)
HPLC ICP MS	3.00 to 5.90	(Cheng et al. 2018)
UV VIS	3.00	(Gürkan et al. 2015)
CE UV	7.90 to 20.0	(Lee et al. 2018)
CE UV	300 to 1,600	(Akter et al. 2005)
Solid and bioindicator samples ($\mu\text{g kg}^{-1}$)		
HPLC HG ICP OES	0.06 to 0.20	(Khan et al. 2015)
HPLC HG ICP OES	0.40 to 0.70	(García-Rico et al. 2019)
HPLC HG ICP OES	0.70 to 3.00	(Ma et al. 2016)
HPLC HG ICP OES	1.30 to 3.30	(Al-Assaf et al. 2009)
HPLC ICP MS	0.05	(Wolf et al. 2011)
HG AFS	0.70 to 3.00	(Wang et al. 2018)
IC ICP MS	0.10 to 0.20	(Zhu et al. 2017)
HG AAS	0.07 to 0.10	(Santos et al. 2018)
HPLC ICP MS	12.5	Data survey
HG AFS	400 to 1,000	(Wang et al. 2016)

Conclusions

There is a wide discrepancy between the number of accredited laboratories and analytical techniques by state and region in Brazil. A strong correlation was observed between the GDP and the number of accredited laboratories. Almost all laboratories were able to confirm environmental contamination, since they presented LOQ values inferior to environmental threshold. Analytical techniques sorted from lowest to highest LOQ values are: ICP

MS, ET AAS, HG AAS or HG ICP OES and UV VIS for liquid matrices; HG ICP OES, ICP MS, HG AAS, ET AAS and FAAS for solids; and ICP MS, HG and ICP OES for bioindicators. Only one laboratory is accredited for the analysis of As species but does not cover all species.

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Conflict of interests

Authors declare that they have no conflict of interests.

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