HG-ICP-OES Technique, a Useful Tool for Arsenic Determination in Soft Water

ECATERINA ANCA SERBAN¹, GABRIELA GEANINAVASILE¹*, TOMA GALAON¹,
CORINA ENE², LUOANA FLORENTINA PASCU¹
¹National Research and Development Institute for Industrial Ecology - ECOIND, 71-73 Drumul Podul Dambovitei Str., 060652, Bucharest, Romania
²Petroleum-Gas University of Ploiesti, Faculty of Economic Sciences, 39 Bucharest Blvd., 100680, Ploiesti, Romania

Abstract. This paper presents a fast, sensitive, linear and precise method for the determination of arsenic (As) at trace levels, from different types of water (drinking, mineral, surface water and groundwater) using hydride generation and optical emission spectrometry with inductively coupled plasma (HG-ICP-OES). In order to generate the hydride, the initial pretreatment of the samples with a mixture of potassium iodide and ascorbic acid is necessary, in hydrochloric acid medium for reducing the As⁵⁺ to As³⁺ ions and for the subsequent formation of the hydride from As³⁺ ions and sodium borohydride, in a continuous-flow cell. The quantification limit of the method (LOQ = 0.43 µg/L), the precision (3.41%), the recovery yield (95%) and the measurement uncertainty of 24% frame the method within the limits imposed by the acceptance criteria of an analytical method for arsenic determination. The proposed method was tested on several types of water, the obtained results being compared to those obtained by applying two sensitive and selective alternative methods using ICP-MS, respectively ultrasonic nebulizer and ICP-OES.

Keywords: arsenic, hydride generation, ICP-OES, drinking water, groundwater, mineral water

1. Introduction

Heavy metals are naturally occurring in the environment and they are considered pollutants when the values of the concentrations required by the legislation are exceeded and cause a change in the balance of the environmental components [1]. In the environment, heavy metals come from different sources: industrial activities, transport, fossil fuels, agriculture, urbanization and other human activities [2]. Waters pollution with heavy metals occurs due to direct or indirect discharges to the environment of waste leachate, emissions of industrial and domestic waste water, as well as due to natural disasters. The most common sources of heavy metals which reach the aquatic systems are the discharges of untreated wastewater or poorly treated wastewater [1]. As heavy metals existing in the aquatic sector cannot be decomposed or destroyed, some of them end up being dissolved in water, another part being bioaccumulated by aquatic plants and organisms, some settling in the bottom sediments, but most being transported along the watercourse as suspensions [1; 3].

European Directive on drinking water 98/83 / EC, transposed into Romanian Legislation in the form of Law No. 458/2002 updated by Law No. 311 of 2004, imposes a concentration limit for arsenic of 10 µg/L in water intended for human consumption [7]. For mineral water, Romanian legislation in force imposes a maximum permissible limit of 10 µg/L for arsenic [4-6].

In recent years, numerous studies have been conducted to determine the arsenic species (As) in drinking, mineral, surface water and groundwater, in products within the food chain, due to the well-known toxic and carcinogenic effects of its chemical forms and oxidation states [8-10].

The arsenic in natural water is predominant in inorganic forms, these being the trivalent and pentavalent forms, arsenite (As³⁺) and arsenate (As⁵⁺) respectively. Organic forms of arsenic are monomethyl arsenic acid (MMAA) and dimethyl arsenic acid (DMAA) [11-13].

*email: gabriela.vasile@incdecoind.ro
Generally, arsenite is found in anaerobic conditions in groundwater, while arsenate is found in aerobic conditions in surface waters. The valence and inorganic arsenic species depend on the redox conditions and the groundwater pH. The As$^{3+}$ and As$^{5+}$ species can be found in the deep waters either as a mixture or individually according to the pH of the water [11-12]. The arsenate species, As$^{5+}$, is the dominant form in oxidizing conditions, while in reducing conditions, such as in deep water, the As$^{3+}$ species are dominant.

Inorganic forms are more toxic than organic ones, and As$^{3+}$ species are more toxic than As$^{5+}$, hence it is necessary to determine the species in order to determine the water toxicity [11; 13].

Long-term exposure to arsenic by ingesting drinking water, mineral water or groundwater contaminated with arsenic causes various conditions, such as skin, lung, bladder and kidney cancer, etc. [14].

There are a wide variety of analytical techniques that can be used to determine arsenic in the environment, so we can list the following: atomic absorption spectrometry coupled with the hydride generator (HG-AAS); electrothermal atomic absorption spectrometry with graphite furnace (ETAAS); atomic fluorescence spectrometry (AFS); inductive coupled plasma optical emission spectrometry (ICP-OES); inductive coupled plasma mass spectrometry (ICP-MS); X-ray spectrometry; capillary electrophoresis; gas chromatography (GC); high performance liquid chromatography (HPLC); ion chromatography (IC), etc. [8; 15-25]. Some of the techniques mentioned above can be coupled with hydride generation (HG) to increase sensitivity and selectivity by removing interferences from the sample (HG-ETAAS; HG-AFS; HG-ICP-OES; HG-ICP-MS). In the presence of sodium borohydride, As$^{3+}$ ions form volatile hydrides such as arsine, which are transported using an inert gas stream (argon) to the atomizer [21-24; 26-29]. Arsenic is then determined according to the type of detector in a different concentration range (mg/L, µg/L, ng/L) depending on the sensitivity of the detector.

The present study proposes a method for determining arsenic in low-contaminated waters (drinking water, mineral water, groundwater, surface water, spring water, raw water, non-carbonated water and carbonated water) using hydride generation and inductive coupled plasma optical emission spectrometry (HG-ICP-OES) with a state-of-the-art Perkin Elmer spectrometer (AVIO 500). The proposed method was verified by participating in international interlaboratory comparison schemes and by comparative studies on other analytical techniques: USN-ICP-OES technique (AVIO 500) and ICP-MS technique (7900 Agilent Technologies).

2. Materials and methods
2.1. ICP-OES equipment and conditions

For the experimental study, an inductively coupled plasma optical emission spectrometer ICP – OES Avio 500 Perkin Elmer, with UV and VIS detectors, axial plasma view, was used.

As$^{3+}$ determinations were performed using Perkin Elmer FIAS 400 equipment, an automatic flow injection system for hydride generation coupled to ICP-OES.

Comparative studies were performed with an Ultrasonic U6000AT + nebulizer, Teledyne, Cetac Technologies, coupled to ICP-OES and an inductively coupled plasma mass spectrometer ICP-MS model 7900 Agilent Technologies.

High quality water was obtained through an Ultrapure water system ELX Technology Inside MilliQ.

The operating conditions of the ICP-OES spectrometer and the hydride flow generation system are presented in Table 1.

| Table 1. Operational parameters of HG-ICP-OES | Spectrometer parameters |
|-----------------------------------------------|-------------------------|
| **As λ:** 188.979 nm, 197.197 nm               | Replicates 3             |
| Purge gas flow rate: high                     | Transient Read Delay 0.0 s |
| Integration time: 0.05 s                      | Transient Read Time 15.0 s |

Rev. Chim., 71 (7), 2020, 379-390 380 https://doi.org/10.37358/RC.20.7.8255
2.2. Reagents

For calibration, a Certified Reference Material (CRM) Arsenic standard for ICP, 1000 mg/L (Sigma-Aldrich) and a Reference Material (RM) Quality Control Standard 21, 100 mg/L (LGC) were used.

The comparative studies were performed with a 10 mg/L Multi-element Certified Reference Material (Agilent Technologies) and the analytical control was performed with a 100 mg/L Multi-element Certified Reference Material (Merck).

For the determination of As$^{3+}$, the following reagents and chemicals were used: sodium borohydride purum, ≥96%; sodium hydroxide puriss ≥ 98%, pellets; potassium iodide puriss 99-100.5%; L-Ascorbic acid puriss 99.7-100.5% (Sigma-Aldrich); hydrochloric acid 37%; nitric acid ultrapure grade 69% (Merck);

Argon and Nitrogen purity type 5.0 (Linde-Gas) were used.

The quality control of the results was also achieved using a Certified Reference Material Matrix, water, code 5A, sample for hydride generation control of As$^{3+}$, Aquacheck Scheme, LGC.

All calibration, hydride generation solutions and samples were prepared daily.

2.3. Sample pretreatment

**HG-ICP-OES**

The standard solutions for drawing the calibration curve and for the quality control of the results, respectively the water samples (drinking, mineral, surface water and groundwater) were pretreated in order to reduce the As$^{5+}$ ions to As$^{3+}$ ions. The reaction was carried out by adding 2 mL ultrapure HCl 37% (v/v) and 10 mL of 5% potassium iodide solution (w/v) in 5% (w/v) ascorbic acid solution added to an aliquot sample up to 35 mL. Sample and standard solutions were brought to a volumetric flask of 50 mL with ultrapure water, the reduction reaction being carried out at room temperature for 45 minutes.

Hydride vapor generation was performed in a continuous-flow cell in FIAS 400 equipment using two types of solutions: a carrier solution of 10% (v/v) HCl, respectively, as reducing agent, 0.2% NaBH$_4$ (w/v) in NaOH solution (w/v) 0.05%.

**USN-ICP-OES, ICP-MS**

The preparation of the water samples for these techniques was accomplished by filtering and acidifying them to a pH of less than 2 using ultrapure nitric acid.

The calibration curve for USN-ICP-OES was performed on the same concentration range as in HG-ICP-OES (4 - 20 µg/L As), while for ICP-MS a range of 2 - 10 µg/L As was used.
2.4. Method validation experimental tests

The experimental studies performed for the in-house validation of the determination method of As\(^{3+}\) from water samples consisted in the determination of several performance parameters: limit of detection (LOD), limit of quantification (LOQ), linearity (calibration curve and homogeneity of dispersions test), accuracy (repeatability, intermediate precision), recovery test, selectivity (interference study), and uncertainty budget (Table 2). All precision and accuracy tests were performed at the same concentration of 10 µg/L, which represents the maximum permissible limit for arsenic in drinking and mineral water according to the in-force legislation [6, 7].

The calibration curves were drawn using 1000 mg/L As CRM from Sigma Aldrich for ICP-OES (classic Meinhart nebulizer, respectively ultrasonic nebulizer), respectively 10 mg/L CRM from Agilent Technologies for ICP-MS.

The control of the results was performed using a RM type multi-element of 100 mg/L (LGC) for ICP-OES, respectively a CRM type multi-element of 100 mg/L (Merck) for ICP-MS.

The studies were conducted in two accredited laboratories that comply with the requirements of the SR EN ISO 17025: 2018 [30] reference regarding the control of the test results.

| Table 2. Experimental tests for in-house validation studies of arsenic |
|---------------------------------------------------------------|
| **LOD, LOQ** | 1 µg/L, 5 samples |
| Linearity / Calibration curve | 4 µg/L, 8 µg/L, 12 µg/L, 16 µg/L, 20 µg/L |
| Homogeneity of the dispersions test | 4 µg/L and 20 µg/L, 10 determinations for each concentration |
| Repeatability | 10 µg/L, 10 determinations, one analyst, one day |
| Intermediate precision | 10 µg/L, 4 determinations, 3 days, 2 analysts |
| Accuracy / recovery yield | drinking water enriched with 10 µg/L, 5 determinations |
| Equipment precision | 10 µg/L, 8 repeated determinations from the same sample |
| Selectivity - interference studies (Fe, Al) | 10 µg/L, 30 µg/L, 50 µg/L, 100 µg/L, 150 µg/L, 200 µg/L |
| Each recovery test was performed 5 times |

3. Results and discussions

3.1. Linearity tests

The linearity tests, consisting of the dispersions homogeneity test, the linearity test through the calibration curve for the determination of As\(^{3+}\) in drinking water, mineral water, surface water and groundwater were performed at three characteristic wavelengths for the arsenic, namely: 188.979 nm, 193.693 nm and 197.197 nm. The wavelength of 193.693 nm gave aberrant results for the arsenic concentration from real samples, the recovery yields being higher than 200%, probably due to interference given by other metals (eg iron, aluminum). For these reasons, the results obtained at the performance parameters for this wavelength are not shown in this paper.

The calibration curve was performed on the concentration range of 4 – 20 µg/L from a 1000 mg/L MRC (Sigma-Aldrich). The results obtained in the linearity test and the curve parameters are presented in Table 3 (λ = 188.979 nm), respectively Table 4 (λ = 197.197 nm).

| Table 3. Linearity results for As determination (λ=188.979 nm) |
|---------------------------------------------------------------|
| \(x_i (\mu g/L)\) | 4 | 8 | 12 | 16 | 20 |
| \(y_i (\text{peak})\) | 656 | 1342 | 1990 | 2694 | 3419 |
| \(y = -42.9 + 171.928x\) |
| \(a = -42.9\) | \(b = 171.928\) | \(R = 0.9998\) |
| \(S = 15.2215\) | \(S_{y1} = 0.0885\) | \(V_{y1} = 0.74\%\) |

| Homogeneity of the dispersions test |
|-----------------------------------|
| \(Y_{11}\) | \(Y_{10}\) |
| 622.1 | 3050.8 |
| 622.6 | 3076.8 |
| 640.0 | 3110.3 |
| 643.1 | 3202.1 |
| 602.0 | 3087.9 |
| 594.7 | 2981.1 |

(Variance \(y1\))^2 = 466.2649
(Variance \(y10\))^2 = 2197.198
PG 10/1 = 4.712
PG 10/10 = 0.212
In order to verify the linearity, a linearity test was performed, in which the data were obtained from the calibration curve. The accepted linearity limits between which the linear calibration model can be applied with a known confidence level are ± 1% [15]. The linearity is calculated from the relation:

\[(1 - s_b/b) \times 100\]  

(1)

where \(s_b\) is the standard deviation of the slope, and \(b\) is the slope of the calibration curve.

The value \(s_b\) is obtained from the formula:

\[s_b = \sqrt{\frac{S_{y1}^2}{S_{xx}}}\]  

(2)

where: \(S_{y1}\) is the residual standard deviation of the function, and \(S_{xx}\) is the sum of the squares of the differences between \(x_{\text{mean value}}\) and \(x_i\).

The linearity value for the As\(^{3+}\) calibration curve within the 4 - 20 µg/L range at the wavelength of 188.979 nm is 99.3%, while for the wavelength of 197.197 nm it is 99.86%.

In the dispersions homogeneity test, the value \(PG = s_{10}^2/s_1^2\) \((s_1^2 < s_{10}^2)\) was determined, obtaining \(PG = 4.71\). Comparing the PG value with the table values of the F function (Fischer-Snedecor) for 9 degrees of freedom and 99% confidence interval, \(F_{9,99} = 5.35\), it can be observed that \(PG < F_{9,99}\). The deviations of the \(s_1^2\) and \(s_{10}^2\) dispersions are not significant, so there are no differences in the limits of the selected range.

The coefficient of variation of the method (relative standard deviation of the method) is 0.74%. For concentrations higher than 1 ppm and lower than 10 ppm, CV (RSD) is between 7 and 11% [15].

Comparative results at wavelengths of 188.979 nm versus 197.197 nm for As\(^{3+}\) indicated a better sensitivity (higher peak heights) at the wavelength of 188.979 nm, as shown in Figure 1. Figure 2 shows the shape of As\(^{3+}\) peaks at the two wavelengths.
3.2. Limit of detection, limit of quantification

The values obtained when evaluating the parameters LOD and LOQ are presented in Table 5.

| LOD, LOQ test | LOD (µg/L) | LOQ (µg/L) |
|--------------|------------|------------|
| λ=188.979 nm | 0.13       | 0.43       |
| λ=197.197 nm | 0.23       | 0.75       |

The limits of detection and quantification are below the maximum allowable values for drinking water quality [7], respectively of 1 µg/L for LOD and 3 µg/L for LOQ. It can be observed that at the wavelength of 188.979 nm these limits are about 57% smaller than at the wavelength of 197.197 nm.

3.3. Precision and recovery tests

The results obtained in the precision tests (repeatability, intermediate precision) obtained at the maximum allowed concentration for As in drinking water (10 µg/L) are presented in Table 6 for both wavelengths. The repeatability and the intermediate precision expressed in the form of the relative standard deviation (RSDr, RSDI) are well below the value indicated by the specialized literature for this concentration level, namely of maximum 21% [15], the registered values being of maximum 3.4%.
Table 6. Precision and recovery tests results in drinking water

| λ=188.979 nm                  |
|------------------------------|
| Repeatability test           |
| \(X_{\text{measured}}\) (µg/L) | 9.608 | 9.413 | 10.181 | 9.538 | 10.267 |
| \(X_{\text{mean value}}\) (µg/L) | 9.85  | S (µg/L) | 0.28
| Repeatability (µg/L)         | 0.78  | RSD\% | 2.84
| Intermediate precision test  |
| \(X_{\text{measured}}\) (µg/L) | 10.841 | 10.205 | 10.543 | 10.142 | 9.700 |
| \(X_{\text{mean value}}\) (µg/L) | 10.277 | S (µg/L) | 0.35
| Intermediate precision (µg/L) | 0.98  | RSD\% | 3.41
| Recovery test                |
| X\_initial mean (µg/L)       | 0.45  | X\_added (µg/L) | 10.00 |
| X\_final (µg/L)              | 10.840 | 9.481 | 10.743 | 9.267 |
| X\_final mean (µg/L)         | 9.973  |          | \(\eta\) (%) ± s | 95.43 ± 6.44

| λ=197.197 nm                  |
|------------------------------|
| Repeatability test           |
| \(X_{\text{measured}}\) (µg/L) | 9.873  | 9.650 | 9.860 | 9.911 | 10.040 |
| \(X_{\text{mean value}}\) (µg/L) | 10.06  | S (µg/L) | 0.32
| Repeatability (µg/L)         | 0.89  | RSD\% | 3.15
| Intermediate precision test  |
| \(X_{\text{measured}}\) (µg/L) | 10.512 | 10.340 | 10.312 | 9.929 |
| \(X_{\text{mean value}}\) (µg/L) | 10.13  | S (µg/L) | 0.34
| Intermediate precision (µg/L) | 0.95  | RSD\% | 3.36
| Recovery test                |
| X\_initial mean (µg/L)       | 0.45  | X\_added (µg/L) | 10.00 |
| X\_final (µg/L)              | 9.873  | 9.650 | 9.860 | 10.340 |
| X\_final mean (µg/L)         | 9.791  |          | \(\eta\) (%) ± s | 93.69 ± 4.28

Also, the repeatability and the intermediate precision values expressed in µg/L units are less than 1 µg/L, as required by the legislation in force for drinking water quality [7].

For concentrations of 10 µg/L the accuracy must be in the range 60 - 115% [15]. It can be observed that at both wavelengths the registered recoveries are over 93%, at 188.979 nm the recovery is greater than at 197.197 nm, the obtained value being 95.43% with a standard deviation of 6.44%.

3.4. Selectivity of the method, interference studies

The selectivity tests for the As determination method using the HG-ICP-OES technique followed the studies of interference given by Fe and Al at 188.979 nm (Table 7) and 197.197 nm respectively (Table 8). For each recovery test, five separate samples were analyzed, the reported values being the mean values and the associated standard deviation.

Table 7. Recovery percentage for As in interference tests at 188.979 nm

| Iron concentration (µg/L) | 0 | 10 | 30 | 50 | 100 | 150 |
|--------------------------|---|----|----|----|-----|-----|
| Iron concentration (µg/L) | 10.000 | 10.000 | 10.000 | 10.000 | 10.000 | 10.000 |
| Recovered mean           | 10.10 | 10.34 | 10.49 | 9.28 | 8.83 | 8.75 |
| Recovery yield ± standard deviation (%) | 100.1 ± 0.26 | 103.3 ± 0.26 | 104.8 ± 0.37 | 92.7 ± 1.29 | 88.3 ± 1.76 | 87.4 ± 1.87 |
The conclusions of the interference tests indicate that in the case of Fe, at both wavelengths analyzed, the recovery yield decreases as the concentration of Fe in the analyzed sample increases. The selected Fe values for the study ranged from 10 µg/L to 200 µg/L, which represents the maximum concentration allowed in drinking water. For the wavelength of 188.979 nm it is observed that the reduction of the recovery yield is made even by 20% to the value of 200 µg/L Fe, while for 197.197 nm the recovery yield is reduced by 10%. However, the obtained values fall within the recommended range for this concentration level, namely 60 - 115% [15].

Regarding the possible interference given by Al it is observed that at 188.979 nm a maximum decrease of about 8% can be noted, while at 197.197 nm no significant variations of the recovery yield can be noted.

The uncertainty of the extended measurement was evaluated taking into account the data obtained in the linearity, intermediate precision and recovery tests [15,31-32], the calculated values being then compared with the maximum value allowed 3 µg/L [7] according to the in-force legislation (Table 9).

### 3.5 Summary of the in-house validation

The results obtained during the in-house validation tests for As from drinking water are summarized in Table 9.

#### Table 8. Recovery percentage for As in interference tests at 197.197 nm

| Iron concentration (µg/L) | Iron concentration (µg/L) | Recovery yield ± standard deviation (%) |
|---------------------------|---------------------------|----------------------------------------|
| Added | Recovered mean | Added | Recovered mean | Added | Recovered mean |
| 0 | 10.000 | 9.90 | 98.98 ± 0.24 |
| 10 | 10.000 | 10.12 | 102.3 ± 0.09 |
| 30 | 10.000 | 10.43 | 105.4 ± 0.57 |
| 50 | 10.000 | 10.02 | 101.2 ± 0.15 |
| 100 | 10.000 | 9.63 | 97.3 ± 0.60 |
| 150 | 10.000 | 9.52 | 96.1 ± 0.78 |
| 200 | 10.000 | 8.99 | 90.1 ± 1.40 |

#### Table 9. Synthetic results obtained in the in-house validation process compared to the norms imposed for the quality control of drinking water

| Parameter | Acceptance criteria according to drinking water legislation (µg/L) | Obtained values (µg/L) |
|-----------|---------------------------------------------------------------|-----------------------|
| As (λ=188.979 nm) | ≤ 1 | 0.49 |
| Accuracy | ≤ 1 | 0.78 |
| Repeatability (r) | ≤ 1 | 0.78 |

The conclusions of the interference tests indicate that in the case of Fe, at both wavelengths analyzed, the recovery yield decreases as the concentration of Fe in the analyzed sample increases. The selected Fe values for the study ranged from 10 µg/L to 200 µg/L, which represents the maximum concentration allowed in drinking water. For the wavelength of 188.979 nm it is observed that the reduction of the recovery yield is made even by 20% to the value of 200 µg/L Fe, while for 197.197 nm the recovery yield is reduced by 10%. However, the obtained values fall within the recommended range for this concentration level, namely 60 - 115% [15].

Regarding the possible interference given by Al it is observed that at 188.979 nm a maximum decrease of about 8% can be noted, while at 197.197 nm no significant variations of the recovery yield can be noted.

The uncertainty of the extended measurement was evaluated taking into account the data obtained in the linearity, intermediate precision and recovery tests [15,31-32], the calculated values being then compared with the maximum value allowed 3 µg/L [7] according to the in-force legislation (Table 9).
Intermediate precision (Ri) ≤ 1 0.98
Limit of detection (LOD) ≤ 1 0.13
Limit of quantification (LOQ) ≤ 3 0.43
Measurement uncertainty (Ux) ≤ 3 µg/L to 10 µg/L 2.57 µg/L to 10.62 µg/L

| Linearity (R) | Recovery |
|--------------|----------|
| R = 0.9998   | 95.43    |

As (λ=197.197 nm)

| Accuracy    | Repeatability (r) |
|-------------|--------------------|
| ≤ 1         | 0.24               |
|             | 0.89               |

| Intermediate precision (Ri) | Limit of detection (LOD) | Limit of quantification (LOQ) | Measurement uncertainty (Ux) | Linearity (R) | Recovery |
|-----------------------------|--------------------------|-----------------------------|-----------------------------|--------------|----------|
| ≤ 1                         | ≤ 1                      | ≤ 3                         | ≤ 3 µg/L to 10 µg/L          | R = 0.9968   | 93.69    |
|                            |                          | 2.44 µg/L to 10.24 µg/L     |                            |              |          |

Linearity (R) R = 0.9998
Recovery 95.43

The validation data indicated that the proposed method is suitable for the determination of As in drinking water at both wavelengths, specifying that in the case of high Fe concentrations (≥ 200 µg/L) it is indicated that As be quantified at a wavelength of 197.197 nm.

### 3.6. Real samples analyses

Several types of water samples (drinking water, surface water, mineral water and groundwater) were analyzed both by the proposed method and by two other sensitive methods using ICP-MS, respectively USN-ICP-OES. The types of analyzed samples and the sampling locations are presented in Table 10.

| Table 10. Description of the water samples collected |
|-----------------------------------------------------|
| Sample code | Description                  | Sample code | Description                  |
| DW1         | Drinking water, Ilfov        | DW5         | Drinking water, Targoviste,  |
|             |                            |             | Dambovita                    |
| DW2         | Drinking water, Ilfov        | DW6         | Drinking water, Ploiesti     |
| DW3         | Drinking water, Ploiesti     | DW7         | Drinking water, Ilfov        |
| DW4         | Drinking water, Ploiesti     | DW8         | Drinking water, Bucharest    |
| DW5         | Drinking water, Targoviste,  | DW9         | Drinking water, Mioveni, Pitesti |
|             | Dambovita                   | DW10        | Drinking water, Bucharest    |
| DW11        | Drinking water, Bucharest    | DW11        | Raw water, Baia de Arama, Mehmedi |
| DW12        | Drinking water, Craiova, Dolj| DW13        | Raw water, Dunare, zona Turnu Magurele |
| DW14        | Drinking water, Slatina, Olt | DW14        | Raw water, Dunare, zona Turnu Magurele |
| DW15        | Drinking water, Slabozia     | DW15        | Raw water, Dunare, zona Turnu Magurele |
| DW16        | Drinking water, Slabozia     | DW16        | Raw water, Dunare, zona Turnu Magurele |
| DW17        | Drinking water, Slabozia     | DW17        | Raw water, Dunare, zona Turnu Magurele |
| DW18        | Drinking water, Slabozia     | DW18        | Raw water, Dunare, zona Turnu Magurele |
| DW19        | Drinking water, Slabozia     | DW19        | Raw water, Dunare, zona Turnu Magurele |
| DW20        | Drinking water, Slabozia     | DW20        | Raw water, Dunare, zona Turnu Magurele |
| DW21        | Drinking water, Ploiesti     | DW21        | Raw water, Dunare, zona Turnu Magurele |
| DW22        | Drinking water, Ploiesti     | DW22        | Raw water, Dunare, zona Turnu Magurele |
| DW23        | Drinking water, Ploiesti     | DW23        | Raw water, Dunare, zona Turnu Magurele |
| DW24        | Drinking water, Mioveni, Pitesti | GW1         | Groundwater, Vanatori, Vrancea |
| GW1         | Groundwater, Vanatori, Vrancea |            | Osmosis water, Bucharest     |
The results in Table 11 represent the mean of three determinations, each result being presented together with the associated measurement uncertainty.

As noted, the values recorded by the proposed method are comparable to those obtained by the ICP-MS method, which uses a standardized method [33]. All the analyzed water samples had the As concentration below the maximum value allowed by the legislation in force [6,7] except for two spring water samples which had higher values, obtained both by the HG-ICP-OES and also through ICP-MS technique.

| No. | Sample ID | Unit | HG-ICP-OES (µg/L) | USN-ICP-OES (µg/L) | No. | Sample ID | HG-ICP-OES (µg/L) | ICP-MS (µg/L) |
|-----|-----------|------|-------------------|--------------------|-----|-----------|-------------------|--------------|
| 1   | DW₁       | µg/L | 4.75 ± 1.14       | 4.56 ± 0.91        | 26  | DW₁₀     | 1.97 ± 0.47        | 1.78 ± 0.23  |
| 2   | DW₂       | µg/L | 4.60 ± 1.10       | 4.42 ± 0.88        | 27  | DW₁₁     | 1.52 ± 0.37        | 1.41 ± 0.18  |
| 3   | DW₃       | µg/L | 2.23 ± 0.54       | 2.11 ± 0.42        | 28  | DW₁₂     | 1.52 ± 0.37        | 1.69 ± 0.22  |
| 4   | DW₄       | µg/L | <0.43             | <2.0               | 29  | DW₁₃     | 0.84 ± 0.20        | 0.87 ± 0.11  |
| 5   | DW₅       | µg/L | 5.30 ± 1.27       | 5.15 ± 1.03        | 30  | DW₁₄     | 1.13 ± 0.27        | 1.17 ± 0.15  |
| 6   | DW₆       | µg/L | 2.04 ± 0.49       | 2.17 ± 0.43        | 31  | DW₁₅     | 1.55 ± 0.37        | 1.40 ± 0.18  |
| 7   | DW₇       | µg/L | 5.23 ± 1.26       | 5.39 ± 1.08        | 32  | DW₁₆     | 0.89 ± 0.21        | 0.79 ± 0.10  |
| 8   | DW₈       | µg/L | 3.36 ± 0.81       | 3.18 ± 0.64        | 33  | DW₁₇     | 1.28 ± 0.31        | 1.10 ± 0.14  |
| 9   | DW₉       | µg/L | <0.43             | <2.0               | 34  | DW₁₈     | 2.08 ± 0.50        | 2.07 ± 0.27  |
| 10  | DW₁₀      | µg/L | <0.43             | <2.0               | 35  | RW₁      | 1.51 ± 0.36        | 1.59 ± 0.21  |
| 11  | DW₁₁      | µg/L | 4.04 ± 0.97       | 4.23 ± 0.85        | 36  | RW₁₂     | 1.64 ± 0.39        | 1.77 ± 0.23  |
| 12  | DW₁₂      | µg/L | <0.43             | <2.0               | 37  | RW₁₃     | 1.61 ± 0.38        | 1.54 ± 0.20  |
| 13  | DW₁₃      | µg/L | 2.03 ± 0.49       | <2.0               | 38  | RW₁₄     | 1.44 ± 0.35        | 1.31 ± 0.17  |
| 14  | DW₁₄      | µg/L | <0.43             | <2.0               | 39  | GW₁      | 0.82 ± 0.20        | 0.80 ± 0.10  |
| 15  | DW₁₅      | µg/L | <0.43             | <2.0               | 40  | GW₁₂     | 1.58 ± 0.38        | 1.66 ± 0.22  |
| 16  | RW₁       | µg/L | <0.43             | <2.0               | 41  | GW₁₃     | 0.93 ± 0.22        | 0.86 ± 0.11  |
| 17  | RW₂       | µg/L | <0.43             | <2.0               | 42  | GW₁₄     | <0.43             | 0.25 ± 0.03  |
| 18  | GW₁       | µg/L | 2.57 ± 0.62       | 2.56 ± 0.51        | 43  | SpW₁     | 14.33±3.44         | 14.15 ± 1.84 |
| 19  | GW₂       | µg/L | 2.09 ± 0.50       | 2.14 ± 0.43        | 44  | SpW₂     | 16.41±3.94         | 17.07 ± 2.22 |
| 20  | GW₃       | µg/L | 2.11 ± 0.51       | <2.0               | 45  | SpW₁₃    | 1.21 ± 0.29        | 1.18 ± 0.15  |
| 21  | GW₄       | µg/L | <0.43             | <2.0               | 46  | MW₁      | 1.16 ± 0.28        | 1.09 ± 0.14  |
| 22  | GW₅       | µg/L | 3.92 ± 0.94       | 3.83 ± 0.77        | 47  | MW₁₂     | 1.14 ± 0.27        | 1.15 ± 0.15  |
| 23  | BW        | µg/L | <0.43             | <2.0               | 48  | MW₁₃     | 1.07 ± 0.25        | 1.12 ± 0.14  |
| 24  | SW        | µg/L | <0.43             | <2.0               | 49  | SuW₁     | 0.78 ± 0.18        | 0.72 ± 0.09  |
| 25  | OW        | µg/L | <0.43             | <2.0               | 50  | SuW₁₂    | 0.81 ± 0.19        | 0.88 ± 0.11  |

4. Conclusions

This paper proposes a method for As determination from water samples using hydride generation and inductively coupled plasma optical emission spectrometry. Standardized methods for determining As at concentrations expressed in µg/L units usually use ICP-MS, HG-AAS, or ET-AAS. The proposed method (HG-ICP-OES) was verified at two wavelengths (188.979 nm and 197.197 nm), and the results obtained at the tested parameters indicated that at 188.979 nm the method is more sensitive (lower LOD and LOQ), but selectivity is better at 197.197 nm (at Fe concentrations ≥ 200 µg/L, higher recovery percentage than at 188.979 nm). Thus, the proposed method is suitable for determining As at the concentrations required by the in-force laws for the control of both, drinking and mineral water. The method thus developed can be extended to other matrices such as aqueous extracts of plant organs.

Acknowledgments: The authors acknowledge the financial support offered by The National Research Program “Nucleu” through contract no 20N/2019, Project code PN 19 04 01 01.

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