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

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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 As^{5+} to As^{3+} ions and for the subsequent formation of the hydride from As^{3+} 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 (As^{3+}) and arsenate (As^{5+}) respectively. Organic forms of arsenic are monomethyl arsenic acid (MMAA) and dimethyl arsenic acid (DMAA) [11-13].

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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 *p*H. 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

Plasma parameters				
Argon flow rate 15 L/min			Power RF 1350 W	
Agent auxiliary flow rate 0.2 L/min			Plasma view Axial	
Nebulizer flow rate 0.5 L/min			View distance 15.0 mm	
Flow injection program				
Step	Time (s)	Pump 1 (U/min)	Pump 2 (U/min)	Valve
Prefil	15	100	120	Fill
1	10	100	120	Fill
2	15	100	120	Inject
Processing spectral peaks			**Processing time**	
Peak Algorithm: peak height			Peak Algorithm: peak height	
Points per peak: 10 points			Smoothing point: 19 points	
Spectral corrections: background correction				

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 *p*H 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)

Calibration Curve Parameters	x_i (μg/L)	4	8	12	16	20
	$y_i(H_{peak})$	656	1342	1990	2694	3419
	y = -42.9 + 171.928x					
	a = -42.9		b = 171.928		R = 0.9998	
	S_y = 15.2215		S_{x0} = 0.0885		V_{x0} = 0.74%	

Homogeneity of the dispersions test

Y_{1i}	Y_{10i}	
622.1	3050.8	(Variance y1)^2 = 466.2649
622.6	3076.8	(Variance y10)^2 = 2197.198
640.0	3110.3	PG 10/1 = 4.712
643.1	3202.1	PG 1/10 = 0.212
602.0	3087.9	
594.7	2981.1	

566.9	3054.2	F(9,9, 99%)=5.35 PG < F (9, 9, 99%) 4.712 < 5.35
552.8	3132.1	
587.5	3064.5	
579.7	3072.9	

Table 4. Linearity results for As determination (λ=197.197 nm)

Calibration Curve Parameters						
	x_i (µg/L)	4	8	12	16	20
	$y_i(H_{peak})$	314	715	1044	1498	1919
	y = -99.5+99.785x					
	a = -99.5		b = 99.785		R = 0.9968	
	S_y = 22.1573		S_{x0} = 0.2220		V_{x0} = 1.85 %	

Homogeneity of the dispersions test

Y_{1i}	Y_{10i}	
273.1	1634.0	
295.6	1654.2	
297.8	1588.7	(Variance y1)^2 = 1670.505 (Variance y10)^2 = 4508.676 PG 10/1 = 2.699 PG 1/10 = 0.371 F(9,9, 99%)=5.35 PG < F (9, 9, 99%) 2.699< 5.35
309.4	1744.3	
282.8	1694.9	
263.1	1555.5	
269.5	1596.4	
336.0	1715.6	
368.6	1671.6	
378.5	1550.2	

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:

$$(1- s_b/b)\times 100 \qquad (1)$$

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:

$$s_b = \sqrt{\frac{S_{y1}^2}{S_{xx}}} \qquad (2)$$

where: S_{y1} is the residual standard deviation of the function, and S_{xx} is the sum of the squares of the differences between $x_{mean\ value}$ 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^2_{10}/s^2_1 ($s^2_1 < s^2_{10}$) 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, $F_{9.9;\ 0.99}$ = 5.35, it can be observed that PG <$F_{9.9;\ 0.99}$. The deviations of the s^2_1 and s^2_{10} 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.

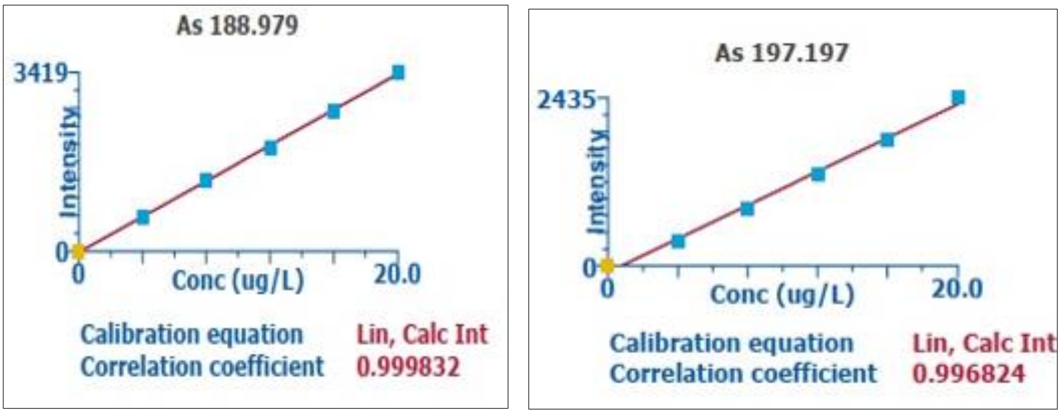

Figure 1. Calibration curve of As^{3+} (λ=188.979 nm, λ=197.197 nm)

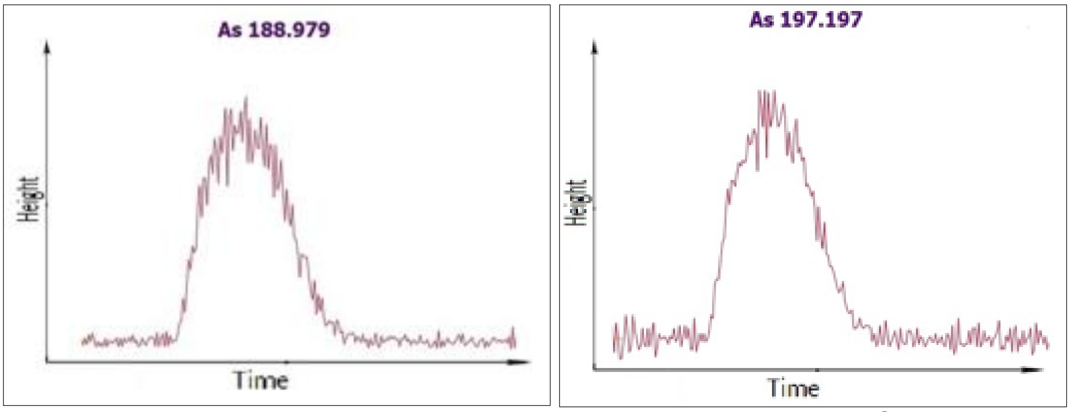

Figure 2. The height of the corresponding peaks for As^{3+}
(λ=188.979 nm, λ=197.197 nm), at the concentration of 10 µg/L

3.2. Limit of detection, limit of quantification

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

Table 5. In-house validation experiments – LOD, LOQ

		***LOD, LOQ test* λ=188.979 nm**			
$X_{measured}$ (µg/L)	1.358	1.392	1.359	1.462	1.415
$X_{mean\ value}$ (µg/L)		**1.39**	**s (µg/L)**		**0.04**
LOD (µg/L)		**0.13**	**LOQ (µg/L)**		**0.43**
		***LOD, LOQ test* λ=197.197 nm**			
$X_{measured}$ (µg/L)	1.286	1.225	1.142	1.152	1.307
$X_{mean\ value}$ (µg/L)		**1.22**	**s (µg/L)**		**0.08**
LOD (µg/L)		**0.23**	**LOQ (µg/L)**		**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 (RSD_r, RSD_R) 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					
$X_{measured}$ (µg/L)	9.608	9.413	10.181	9.538	10.267
	9.991	9.722	9.959	10.018	9.829
$X_{mean\ value}$ (µg/L)		**9.85**	**S (µg/L)**		**0.28**
Repeatability (µg/L)		**0.78**	**RSD_r %**		**2.84**
Intermediate precision test					
$X_{measured}$ (µg/L)	10.841	10.205	10.543	10.142	9.700
	9.942	10.055	10.460	10.492	10.580
	10.237	10.127			
$X_{mean\ value}$ (µg/L)		**10.277**	**S (µg/L)**		**0.35**
Intermediate precision (µg/L)		**0.98**	**RSD_R %**		**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
	9.534				
$X_{final\ mean}$ (µg/L)	**9.973**			Ƞ (%) **± s**	**95.43 ± 6.44**
λ=197.197 nm					
Repeatability test					
$X_{measured}$ (µg/L)	9.873	9.650	9.860	9.911	10.040
	10.413	10.731	10.105	10.217	9.859
$X_{mean\ value}$ (µg/L)		**10.06**	**S (µg/L)**		**0.32**
Repeatability (µg/L)		**0.89**	**RSD_r %**		**3.15**
Intermediate precision test					
$X_{measured}$ (µg/L)		10.512	10.340	10.312	9.929
		10.337	9.993	10.328	10.424
		9.756	9.460	10.059	10.142
$X_{mean\ value}$ (µg/L)		**10.13**	**S (µg/L)**		**0.34**
Intermediate precision (µg/L)		**0.95**	**RSD_R %**		**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
	9.231				
$X_{final\ mean}$ (µg/L)		**9.791**		Ƞ (%) **± 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)	Iron concentration (µg/L) Added	Iron concentration (µg/L) Recovered mean	Recovery yield ± standard deviation (%)
0	10.000	10.01	100.1 ± 0.26
10	10.000	10.34	103.3 ± 0.26
30	10.000	10.49	104.8 ± 0.37
50	10.000	9.28	92.7 ± 1.29
100	10.000	8.83	88.3 ± 1.76
150	10.000	8.75	87.4 ± 1.87

200	10.000	8.10	80.9 ± 2.60
Aluminum concentration (µg/L)	Aluminum concentration (µg/L)		Recovery yield ± standard deviation (%)
	Added	Recovered mean	
0	10.000	9.97	99.74 ± 0.25
10	10.000	9.99	100.2 ± 0.76
30	10.000	9.78	98.0 ± 1.02
50	10.000	9.27	93.0 ± 1.71
100	10.000	9.18	92.1 ± 2.66
150	10.000	9.24	94.7 ± 3.00
200	10.000	9.29	93.1 ± 0.51

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	
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
Aluminum concentration (µg/L)	Aluminum concentration (µg/L)		Recovery yield ± standard deviation (%)
	Added	Recovered mean	
0	10.000	10.03	100.3 ± 0.47
10	10.000	9.91	98.8 ± 0.58
30	10.000	10.41	103.8 ± 0.84
50	10.000	9.97	99.4 ± 1.69
100	10.000	9.95	99.2 ± 2.87
150	10.000	10.60	105.2 ± 3.37
200	10.000	10.16	101.3 ± 0.75

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 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)	
Accuracy	≤ 1	0.49
Repeatability (r)	≤ 1	0.78

Intermediate precision (R_i)	≤ 1	0.98
Limit of detection (LOD)	≤ 1	0.13
Limit of quantification (LOQ)	≤ 3	0.43
Measurement uncertainty (U_{ex})	≤ 3 µg/L to 10 µg/L	2.57 µg/L to 10.62 µg/L
Linearity (R)		R = 0.9998
Recovery		95.43
As (λ=197.197 nm)		
Accuracy	≤ 1	0.24
Repeatability (r)	≤ 1	0.89
Intermediate precision (R_i)	≤ 1	0.95
Limit of detection (LOD)	≤ 1	0.23
Limit of quantification (LOQ)	≤ 3	0.75
Measurement uncertainty (U_{ex})	≤ 3 µg/L to 10 µg/L	2.44 ug/L to 10.24 ug/L
Linearity (R)		R = 0.9968
Recovery		93.69

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
DW_1	Drinking water, Ilfov	GW_2	Groundwater, Galati
DW_2	Drinking water, Ilfov	GW_3	Groundwater, Galati
DW_3	Drinking water, Ploiesti	GW_4	Groundwater, Ploiesti
DW_4	Drinking water, Ploiesti	GW_5	Groundwater, Tulcea
DW_5	Drinking water, Targoviste, Dambovita	GW_6	Groundwater, Brazi, Prahova
DW_6	Drinking water, Ploiesti	GW_7	Groundwater, Brazi, Prahova
DW_7	Drinking water, Ilfov	GW_8	Groundwater, Ciofliceni, Ilfov
DW_8	Drinking water, Bucharest	GW_9	Groundwater, Bucharest
DW_9	Drinking water, Mioveni, Pitesti	RW_1	Raw water, Baia de Arama, Mehedinti
DW_{10}	Drinking water, Bucharest	RW_2	Raw water, Mioveni, Pitesti
DW_{11}	Drinking water, Bucharest	RW_3	Raw water, Dunare, zona Turnu Magurele
DW_{12}	Drinking water, Craoiva, Dolj	RW_4	Raw water, Dunare, zona Turnu Magurele
DW_{13}	Drinking water, Slatina, Olt	RW_5	Raw water, Dunare, zona Turnu Magurele
DW_{14}	Drinking water, Slatina, Olt	RW_6	Raw water, Dunare, zona Turnu Magurele
DW_{15}	Drinking water, Slobozia	MW_1	Mineral water, Timisoara
DW_{16}	Drinking water, Slobozia	MW_2	Mineral water, Timisoara
DW_{17}	Drinking water, Slobozia	MW_3	Mineral water, Timisoara
DW_{18}	Drinking water, Slobozia	BW	Bottled water, Vidra, Ramnicu Valcea
DW_{19}	Drinking water, Slobozia	SW	Sparkling water, Vidra, Ramnicu Valcea
DW_{20}	Drinking water, Slobozia	SuW_1	Surface water, Ploiesti
DW_{21}	Drinking water, Ploiesti	SuW_2	Surface water, Ploiesti
DW_{22}	Drinking water, Ploiesti	SpW_1	Spring water, Valenii de Munte, Prahova
DW_{23}	Drinking water, Ploiesti	SpW_2	Spring water, Valenii de Munte, Prahova
DW_{24}	Drinking water, Mioveni, Pitesti	SpW_3	Spring water, Valenii de Munte, Prahova
GW_1	Groundwater, Vanatori, Vrancea	OW	Osmosis water, Bucharest

Table 11. Arsenic concentration in different types of water and associated uncertainty value

No.	Sample ID	Unit	HG-ICP-OES	USN-ICP-OES	No.	Sample ID	Unit	HG-ICP-OES	ICP-MS
1	DW_1	µg/L	4.75 ± 1.14	4.56 ± 0.91	26	DW_{15}	µg/L	1.97 ± 0.47	1.78 ± 0.23
2	DW_2	µg/L	4.60 ± 1.10	4.42 ± 0.88	27	DW_{16}	µg/L	1.52 ± 0.37	1.41 ± 0.18
3	DW_3	µg/L	2.23 ± 0.54	2.11 ± 0.42	28	DW_{17}	µg/L	1.52 ± 0.37	1.69 ± 0.22
4	DW_4	µg/L	<0.43	<2.0	29	DW_{18}	µg/L	0.84 ± 0.20	0.87 ± 0.11
5	DW_5	µg/L	5.30 ± 1.27	5.15 ±1.03	30	DW_{19}	µg/L	1.13 ± 0.27	1.17 ± 0.15
6	DW_6	µg/L	2.04 ± 0.49	2.17 ± 0.43	31	DW_{20}	µg/L	1.55 ± 0.37	1.40 ± 0.18
7	DW_7	µg/L	5.23 ± 1.26	5.39 ± 1.08	32	DW_{21}	µg/L	0.89 ± 0.21	0.79 ± 0.10
8	DW_8	µg/L	3.36 ± 0.81	3.18 ± 0.64	33	DW_{22}	µg/L	1.28 ± 0.31	1.10 ± 0.14
9	DW_9	µg/L	<0.43	<2.0	34	DW_{23}	µg/L	2.08 ± 0.50	2.07 ± 0.27
10	DW_{10}	µg/L	<0.43	<2.0	35	RW_3	µg/L	1.51 ± 0.36	1.59 ± 0.21
11	DW_{11}	µg/L	4.04 ± 0.97	4.23 ± 0.85	36	RW_4	µg/L	1.64 ± 0.39	1.77 ± 0.23
12	DW_{12}	µg/L	<0.43	<2.0	37	RW_5	µg/L	1.61 ± 0.38	1.54 ± 0.20
13	DW_{13}	µg/L	2.03 ± 0.49	<2.0	38	RW_6	µg/L	1.44 ± 0.35	1.31 ± 0.17
14	DW_{14}	µg/L	<0.43	<2.0	39	GW_4	µg/L	0.82 ± 0.20	0.80 ± 0.10
15	DW_{24}	µg/L	<0.43	<2.0	40	GW_5	µg/L	1.58 ± 0.38	1.66 ± 0.22
16	RW_1	µg/L	<0.43	<2.0	41	GW_6	µg/L	0.93 ± 0.22	0.86 ± 0.11
17	RW_2	µg/L	<0.43	<2.0	42	GW_7	µg/L	<0.43	0.25 ± 0.03
18	GW_1	µg/L	2.57 ± 0.62	2.56 ± 0.51	43	SpW_1	µg/L	14.33±3.44	14.15 ± 1.84
19	GW_2	µg/L	2.09 ± 0.50	2.14 ± 0.43	44	SpW_2	µg/L	16.41±3.94	17.07 ± 2.22
20	GW_3	µg/L	2.11 ± 0.51	<2.0	45	SpW_3	µg/L	1.21 ± 0.29	1.18 ± 0.15
21	GW_8	µg/L	<0.43	<2.0	46	MW_1	µg/L	1.16 ± 0.28	1.09 ± 0.14
22	GW_9	µg/L	3.92 ± 0.94	3.83 ± 0.77	47	MW_2	µg/L	1.14 ± 0.27	1.15 ± 0.15
23	BW	µg/L	<0.43	<2.0	48	MW_3	µg/L	1.07 ± 0.25	1.12 ± 0.14
24	SW	µg/L	<0.43	<2.0	49	SuW_1	µg/L	0.78 ± 0.18	0.72 ± 0.09
25	OW	µg/L	<0.43	<2.0	50	SuW_2	µg/L	0.81 ± 0.19	0.88 ± 0.11

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.

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.

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