

Aerosol generation of As and Se hydrides using a new *Flow Blurring*[®] multiple nebulizer for sample introduction in Inductively Coupled Plasma Optical Emission Spectrometry

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Abstract. A new *Flow Blurring*[®] multiple nebulizer (FBMN) has been used for the efficient generation of As and Se hydrides directly into the aerosol formed inside the spray chamber before detection by inductively coupled plasma optical emission spectrometry (ICP OES). The FBMN allowed the hydrides generation directly into the spray chamber without using any additional device either for solution and gases control or for gas phase separation. Synthetic solutions containing As and Se plus Ca, Mg and K were used for evaluating matrix effects and Ge was suggested as internal standard. Limits of detection of 2.7 and 5.8 $\mu\text{g L}^{-1}$ were obtained for As and Se, respectively, when keeping the nebulization gas flow rate at 0.60 L min^{-1} and the liquid flow rate at 0.67 mL min^{-1} . The developed procedure was applied for spiked digests of food samples and quantitative recoveries were attained. The combination of FBMN, internal standard and hydride generation is a robust and simple approach for generating As and Se hydrides directly into the aerosol.

Keywords: hydride generation direct; arsenic; selenium; multiple nebulizer; ICP OES

1. Introduction

Arsenic is widely and naturally distributed in the environment. Depending on its chemical form, it is considered toxic for all living organisms and it has any known biological function. The main route of exposure to arsenic is by ingestion of foods and beverages [1]. Selenium also occurs in all earth's crust and it is considered an essential element, but it can be toxic at high concentrations [2]. Generally, these elements are found in low concentrations and their determinations require the use of sensitive techniques. Inductively coupled plasma optical emission spectrometry (ICP OES) is widely used in chemical analysis because of its multielemental character, high throughput, and capability for simultaneous determination. However, ICP OES may present limitations for determining trace elements when using its conventional liquid sample introduction system [3,4]. The most common route for introducing samples into the plasma is by converting them into solutions in diluted acid medium. A conventional liquid sample introduction system is composed by a nebulizer and a spray chamber. Usually an aerosol is generated by a nebulizer and transported to the plasma through a spray chamber [4,6]. However, most commonly used systems show some drawbacks such as low transport efficiency, high sample consumption, clogging with high salt content matrices and matrix effects in As and Se determination in presence of easily ionized elements (EIEs) [4,7-10]. Many strategies were developed in order to overcome these limitations, such as hydride generation (HG) for hydride-forming elements and modified sample introduction systems. Frequently HG is used for improving sensitivity because of the higher transport efficiency of the gas phase and the separation of the analyte from the matrix. These advantages made HG a routine sample introduction technique in atomic spectrometry [11]. Pohl *et al.* developed a procedure for determining As and Sb using continuous flow HG coupled to microstrip plasma (MSP)

for emission spectrometry [12]. Savio *et al.* proposed a procedure combining flow injection (FI) and HG-ICP OES. The developed procedure was suitable for determining As, Bi, Sb and Se as hydrides in airborne particulates [13]. Other authors also proposed the use of modified nebulizers such as V-groove, ultrasonic and concentric Meinhard as direct hydride generation nebulizers [14-16]. Rojas *et al.* proposed the use of a direct hydride generation nebulizer (DHGN) as sample introduction system for As, Sb and Se determination [17]. Maldonado *et al.*[18] and Gómez *et al.*[19] reported a dual nebulizer sample introduction system in which two nebulizers were coupled to the spray chamber. Matusiewicz and Ślachciński described the development of the SS-CVG-NEB-MIP OES (*i.e.*, slurry sampling - chemical vapor generation - pneumatic nebulization - microwave induced plasma optical emission spectrometry) for As, Bi, Ge, Sb, Se, Sn, Hg, Ca, Fe, Mg, Mn, and Zn determination [20,21]. These same authors also evaluated the performance of a commercial, specially designed continuous-microflow ultrasonic nebulizer dual capillary system for determination of volatile species by MIP OES [20,21]. Asfaw and Wibetoe [22] developed a procedure for the simultaneous analysis of hydride and non-hydride-forming species using the commercial multimode sample introduction system[®] (MSIS) by ICP OES. Wiltsche *et al.*[23] used the same MSIS for multielemental analysis of high alloy steels using masking agents by ICP OES. It must be pointed out that in all these works the HG systems require the use of other devices for solutions management, for controlling reactions and for gas-liquid separation. The majority of these systems are relatively expensive, difficult to handle, high sample consumption and their applications could be limited to the analysis of simple environmental and biological samples because they did not employ the combination of internal standard and masking agents.

Recently, Aguirre *et al.* reported the performance of a new and efficient multiple sample introduction device based on the *Flow Blurring*[®] nebulization principle. These authors adopted on-line internal standard calibration to determine several elements in complex matrices obtaining good precision, accuracy and limits of detection [24]. Also, it was reported the successful elimination of matrix effects in As and Se determination using a multiple nebulizer [25].

The aim of the study here described was to develop a simple and robust system for hydride generation and on-line internal standardization based on the new *Flow Blurring*[®] multiple nebulizer (FBMN). The performance of this device for aerosol generation of As and Se hydrides and on-line internal standardization followed by determination by ICP OES was studied. The first focus was the development of a straightforward and efficient approach for hydride generation directly into the aerosol inside the nebulization chamber without requiring any additional device either for solutions control or for gas phase separation. The second one was to use the FBMN for correcting matrix effects caused by Ca, K, Mg and a mixture of all them for the determination of As and Se by ICP OES using on-line internal standardization.

2. Experimental

2.1. Reagents and solutions

All reagents used were of analytical grade. Stock solutions of 1000 mg L⁻¹ As and Se were purchased from High-Purity Mono Element Standard Solutions (Charleston, USA). Four analytical calibration solutions containing 50, 100, 150 and 200 µg L⁻¹ As and Se were prepared by dilution of the respective stock solutions. Taking into account the concentration of nitric acid in the diluted food digests, all calibration solutions were acidified to 0.14 mol L⁻¹ by adding proper volume of HNO₃ 65% w w⁻¹ high purity

grade (Merck, Darmstadt, Germany). A calibration blank containing the same amount of HNO_3 was also prepared.

Arsenic and Se solutions containing $100 \mu\text{g L}^{-1}$ of each element were also prepared in media containing 0.050 and 0.100 mol L^{-1} K, Ca, Mg and a mixture of them as nitrate salts (Merck).

Measurements using internal standard (I.S.) was performed using solutions of $100 \mu\text{g L}^{-1}$ of Ge prepared from 1000 mg L^{-1} stock solutions (High-Purity Mono Element Standard Solutions). This internal standard solution was acidified to 3 mol L^{-1} HCl (Merck) for proper generation of hydrides.

A $2.2\% \text{ w v}^{-1}$ sodium borohydride (Scharlau, Barcelona, Spain) solution in $0.1\% \text{ w v}^{-1}$ potassium hydroxide (Scharlau) and $5\% \text{ w v}^{-1}$ thiourea (Merck) was daily prepared immediately prior to analysis.

2.2. On-line hydride generation

The geometry of the FBMN allowed easy and simple coupling with the conventional spray chamber. The on-line hydride generation system used in this work was composed by the new FBMN prototype, previously described [25-27] associated with a conventional baffled cyclonic spray chamber with a volume of 50 mL (model Twister, Glass Expansion, West Melbourne, Victoria, Australia). The combination of FBMN and the spray chamber was named as the FBMN-based system. Figure 1 shows the schematic diagram of the on-line hydride generation system using the FBMN-based system. Reagent solutions (*i.e.*, borohydride and hydrochloric acid), masking agent (*i.e.*, thiourea), internal standards and calibration standards/samples were simultaneously aspirated and flowed through the three capillaries of the FBMN and they were inserted into the spray chamber. Then the primary aerosols generated by the nozzles interact inside the spray chamber generating the conditions for hydrides formation. The tertiary

aerosol is transported to the spectrometer without any separation of gas and liquid phases.

2.3. Instrumentation

All measurements were made using an ICP OES with dual view capacity but operated in axially-viewed plasma mode (Perkin Elmer, Model Optima 4300DV, Norwalk, CT, USA). The operating conditions are shown in Table 1. The sample introduction system is outside of the instrument providing easy access. The quartz torch used is removable and has a ceramic injector. Figure 2 shows a photograph of the FBMN-based system.

2.4. Optimization of CP OES parameters

It is important to mention that the liquid uptake flow rate and all reagent concentrations, e.g. the optimum concentration of thiourea, were optimized in a previous study using experimental design for eliminating interferences caused by transition metals, i.e., Cu, Cd, Co, Ni and Fe. Data were evaluated with the NemrodW version 2007 software (LPRAI, Marseille, France) [27]. On the other hand, the fine adjustment of the concentrations of HCl and sodium borohydride solutions is relevant because both have a strong influence on HG. The total liquid flow rate used was 0.67 mL min^{-1} (i.e., 0.22 mL min^{-1} for each nozzle, approximately) and total nebulizer gas flow rate was 0.60 L min^{-1} (i.e., 0.20 L min^{-1} for each nozzle). The optimum operating conditions are summarized in Table 1.

2.5. Digestion of food samples

All tested food samples (i.e., viscera, processed food, hamburger, wrapped food, jam, pate and soy food) were microwave-assisted acid-digested using an Ethos 1 microwave oven (Milestone, Sorisole, Italy). A mass of 250 mg of a lyophilized sample is inserted in the microwave vessel and a volume of 5 mL HNO_3 concentrated was added. The mixture is left in contact without heating during 2 h. Afterwards, the vessels are closed

and the rotor is inserted inside the microwave oven cavity. The following heating program was applied: (1) heat up to 95 °C during 3 min, (2) heat up to 165 °C during 15 min, (3) heat up to 190 °C during 5 min, (4) hold at 190 °C during 15 min.

Since As and Se concentrations in the tested samples were below the limits of detection, all digests were spiked with 20 µg L⁻¹ of As and Se. Recoveries of As and Se in these spiked solutions will show the accuracy of the developed procedure.

3. Results and discussion

3.1. Hydride generation and matrix effects

The formation of As and Se hydrides was studied in media containing Ca, Mg, K and all them for evaluating matrix interferences. The performance of the system was assessed by using addition-recovery experiments. Figure 3 shows the recoveries for 100 µg L⁻¹ of As and Se in 0.100 mol L⁻¹ K, Mg, Ca, and a mixture of all them using external calibration without internal standardization and on-line internal standardization with the FBMN-based system. When external calibration was used, signal depression in the different matrices evaluated was observed. For all As emission lines evaluated the mean recoveries using external calibration were 94% for Ca, 92% for Mg, 91% for K and 79% for a mixture of them. The mean recoveries obtained for the Se emission lines were 70% for Ca, 87% for Mg, 77% for K and 50% for the mixture. It is known that these EIEs interfere in the generation and transport of aerosol as well as in the stability of the plasma. So it is necessary to use internal standardization in order to compensate for matrix effects. Since hydrides from the analytes are formed inside the spray chamber, the internal standard to be used should present similar behavior for proper correction of eventual matrix effects on HG. For this reason, Ge was tested as internal standard.

Higher recoveries and lower standard deviations were obtained when using Ge(I) 303.906 nm emission line. Addition-recovery experiments indicated that a solution

containing $100 \mu\text{g L}^{-1}$ of Ge presented the best performance for correcting for matrix effects and improving accuracy. When on-line internal standardization was applied, the mean recoveries for As emission lines using Ge as I.S. were 96% for Ca, 94% for Mg, 99% for K and 99% for a mixture of them. For the most sensitive As emission line (*i.e.*, As(I) 228.812 nm) recoveries were 97% for Ca, 92% for Mg, 99% for K and 101% for the mixture. The mean recoveries obtained for the two Se emission lines were 90% for Ca, 94% for Mg, 103% for K and 108% for the mixture. For the most sensitive Se emission line (*i.e.*, Se(I) 196.026 nm) recoveries were 99% for Ca, 91% for Mg, 103% for K and 104% for the mixture. Data presented show quantitative recoveries for most emission lines in different media, but As(I) 228.812 nm and Se(I) 196.026 nm lines presented higher recoveries in Ca, Mg, K and a mixture of them 0.100 mol L^{-1} medium. The same behavior was observed using solutions containing 0.050 mol L^{-1} of each concomitant.

Comparing the system proposed by Maldonado et al. [18] and this work, we observe some difference between them. The work proposed here used a new multiple nebulizer, a commercial spray chamber and a peristaltic pump while Maldonado et al. used two nebulizers, a spray chamber that is not commercially available and two peristaltic pumps. Therefore our system does not change appreciably from a conventional sample introduction system used in ICP OES. Internal standard approach and thiourea were used here to compensate matrix effects, on the other hand Maldonado et al. just used thiourea. The LOD for As I (188.979 nm) showed by this study was lower than that found previously[18].

3.2. Analytical figures of merit

Limits of detection (LOD), calculated using the IUPAC recommendation (based on 3σ blank criterion, determined by 10 consecutive measurements of the blank involving the entire process), are summarized in Table 2. Table 2 also shows LOD values previously presented in the literature and for the FBMN without hydride generation. It can be observed that with the combination of HG and FBMN better LOD values were achieved for all emission lines of As and Se in comparison with those obtained without HG (*i.e.*, higher sensitivity was reached using HG). As expected, the introduction of As and Se as hydrides directly generated into the spray chamber led to a gain of sensitivity around 15-fold when compared to the direct introduction of solutions of these analytes using FBMN.

Table 2 also shows LOD values obtained using different hydride generation systems. Despite the fact that the use of masking reagent results in a significant reduction of volatile hydride intensities [17,23,27], this reagent is needed to analyze real samples. On this study masking agent has been used on the LOD values calculations and they are comparable to those obtained by Wiltsche *et al.*[23] and slightly higher than those obtained by Matusiewicz and Ślachciński [21] (both works using masking agent). On the other hand, there are different works with LOD values lower than this study [17,28]. This could be related with the high sample consumption (higher than 2 mL min^{-1}). If there is not limitation in sample amount, an increment in the sample flow rate may help to decrease LOD values. Nevertheless, in this work the use of a sample flow rate as small as possible was chosen because both the analysis of samples with limited volume, e.g. some biological fluids, and without any limitation can be tackled. The μ -USN-DCS-HG-MIP OES is especially interesting since it provides better LOD values with a sample consumption only of $15 \text{ }\mu\text{L min}^{-1}$ [21]. Nevertheless, this system is not

commercially available and it may be complex to handle (*i.e.*, home-made ultrasonic nebulizer and torch electrically heated).

3.3. Real samples

In order to assess the applicability of the new hydride generation device, different real samples were analyzed.

All samples were mineralized using closed vessel pressurized system assisted by microwave energy using nitric acid. Usually, acids such as HNO₃, that is used for wet sample digestion is responsible by oxidation of the analytes to their higher oxidation states, *i.e.* pentavalent form for arsenic (As(V)) and hexavalent form for selenium (Se(VI)). Thus it is necessary to use pre-reducing reagents to ensure that analytes are present in the solutions at their lower oxidation states. For pre-reduction of As(V) to As(III) the reagents normally used are: KI, thiourea and ascorbic acid. For reducing Se(VI) to Se(IV) the use of a mixture of HCl and HBr under heating is common[11].

In multi-elemental analysis it is essential to use only one procedure for all analytes. Thiourea in combination with HCl was shown as a convenient pre-reducing agent for simultaneous determination of As, Bi, Sb, Se, and Te [11].

In this study a mixture of thiourea and HCl was used as pre-reducing agent for hydride generation. The HCl and thiourea concentrations were optimized considering that the degree of reduction is also dependent on the concentrations of both.

Considering the analytical application for food analysis, As is a contaminant in foodstuff, but there are no maximum levels established by Codex Alimentarius for this element in some foodstuffs, such as meats. According to the Mercosul Technical Regulation on maximum levels of inorganic contaminants in foods, the maximum level of As in foodstuff (processed food) is 0.5 mg kg⁻¹ [29]. There is no maximum level for Se concentration in foodstuff.

Despite the good LOD values obtained with HG associated with FBMN, all digests of food samples did not contain detectable amounts of As and Se. Further, these digests were spiked with $20 \mu\text{g L}^{-1}$ of As and Se. Recoveries using HG and FBMN ranged from 102 to 114 % for As and from 77 to 107% for Se (Table 3). Recoveries for Se varied in a relatively broad range because the spiked concentration is close to the limit of quantification obtained for this analyte. A diluted solution of nitric acid ($0.14 \text{ mol L}^{-1} \text{ HNO}_3$) was inserted between samples for preventing the occurrence of any memory effects.

4. Conclusions

The aerosol hydride generation system proposed in this work using the new FBMN offers a simple and robust alternative for generation of As and Se hydrides without requiring any special device for solutions control and gas-liquid separation. The FBMN is a straightforward device for fast and simple generation of hydrides. Limits of detection for As and Se with the FBMN-HG-ICP OES are of the same order of the best ones reported in the literature using masking agent. The combination of internal standard calibration and the masking agent could permit the analysis of complex metallurgical, environmental and biological samples. It was demonstrated that the FBMN is suitable for generation of As and Se hydrides taking into account the versatility and transport efficiency of this new multiple nebulizer.

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FBMN prototypes provided. The authors are also grateful to the “Laboratorio de Salud Pública de Alicante, Centro de Salud Pública” for the food samples provided.

Table 1. Operating conditions of the ICP OES.

Generator frequency (MHz)	40
Radio-frequency applied power (kW)	1.35
Plasma gas flow rate (L min ⁻¹)	15
Auxiliary gas flow rate (L min ⁻¹)	0.20
Total nebulizer gas flow rate (L min ⁻¹)	0.60
Total liquid flow rate (mL min ⁻¹)	0.67
Read time (ms)	10
Nebulizer	<i>Flow Blurring</i> [®] multiple nebulizer
Spray chamber	Baffled cyclonic-type
Wavelength (nm)	As(I) 228.812, Se(I) 196.026

Table 2. Limits of detection ($\mu\text{g L}^{-1}$) for various sample introduction techniques.

Emission lines (nm)						I.S.	Masking agent	Sample flow rate (mL min ⁻¹)	Source
AsI (188.979)	AsI (193.696)	AsI (197.197)	AsI (228.812)	SeI (196.026)	SeI (203.985)				
2.8	4.7	5.0	2.7	5.8	6.2	Yes	Yes	0.22	Present work
44	43	103	48	53	125	Yes	No	0.30	FBMN-based system ^a
0.1	-	-	-	0.4	-	No	No	2.2	Chemifold system, PerkinElmer ^b
0.4	-	-	-	0.1	-	No	No	2.2	[16] ^c
5.3	-	-	-	4.9	-	No	No	0.24	[17] ^d
3	-	-	-	10	-	No	No	0.60	[18] ^d
-	-	-	1.2	3.3	-	No	Yes	0.015	[20] ^e
0.5	1.8	-	-	0.5	0.9	No	No	0.85	[22] ^f
2.5	-	-	-	4.9	-	No	Yes	0.85	[22] ^f

^aWithout HG.^bConventional flow hydride system [27].^cDHGN (Direct Hydride Generation Nebulizer).^dDual nebulizer system.^e μ -USN-DCS-HG-MIP OES (microflow ultrasonic nebulizer dual capillary system hydride generation by MIP OES).^f(MSIS) Multimode sample introduction system.

Table 3. Recoveries of AsI (228.812 nm) and SeI (196.026 nm) for spiked digests of food samples.

Samples	Recovery (%) ^{a,b}	
	As	Se
Viscera	113 ± 11	107 ± 5
Processed food	107 ± 1	88 ± 7
Hamburger	102 ± 8	82 ± 4
Wrapped food	113 ± 2	90 ± 10
Jam	111 ± 1	91 ± 6
Pate	114 ± 7	96 ± 11
Soy food	105 ± 5	77 ± 7

^aMean ± standard deviation, n = 3.

^bSpiking level: 20 µg L⁻¹.

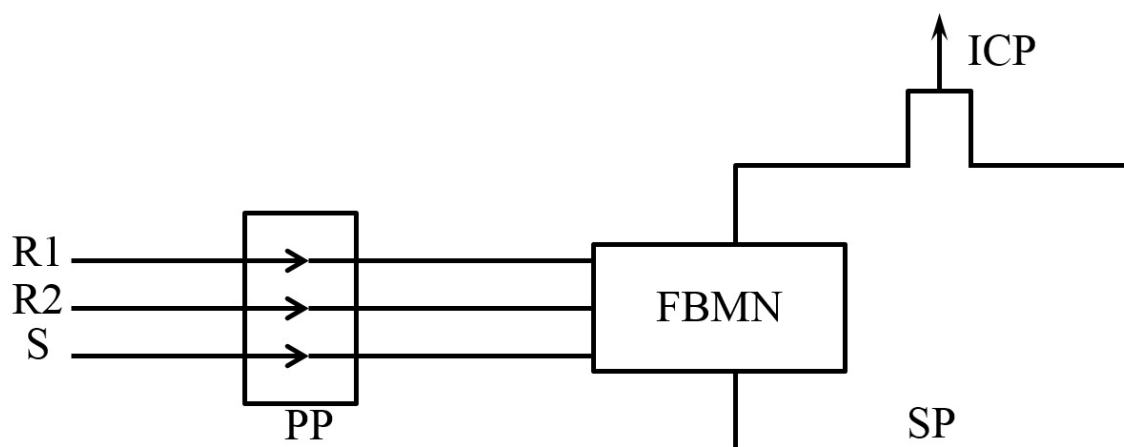


Fig 1. Schematic diagram of the on-line hydride generation system using the FBMN-based system: R1, NaBH₄, KOH and thiourea; R2, HCl and internal standard; S, calibration standards and samples; PP, peristaltic pump; SP, spray chamber.

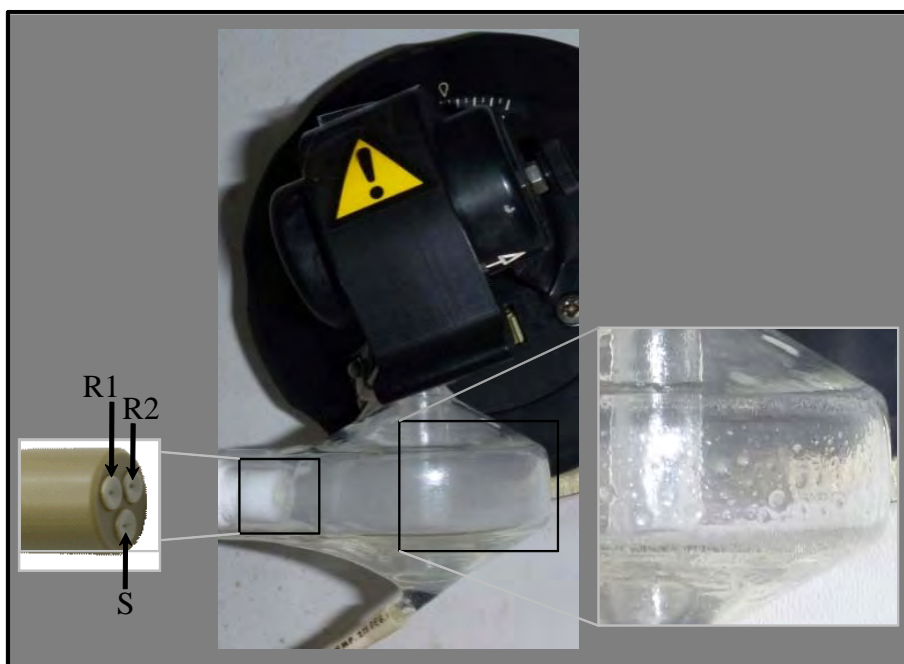


Fig 2. Photograph of FBMN coupled with baffled cyclonic spray chamber and blow up of the nebulizer tips (left) and bubbles (right) formed by hydride generation reaction inside the spray chamber. R1: NaBH_4 , KOH and thiourea; R2: HCl and internal standard; S: calibration standards and samples.

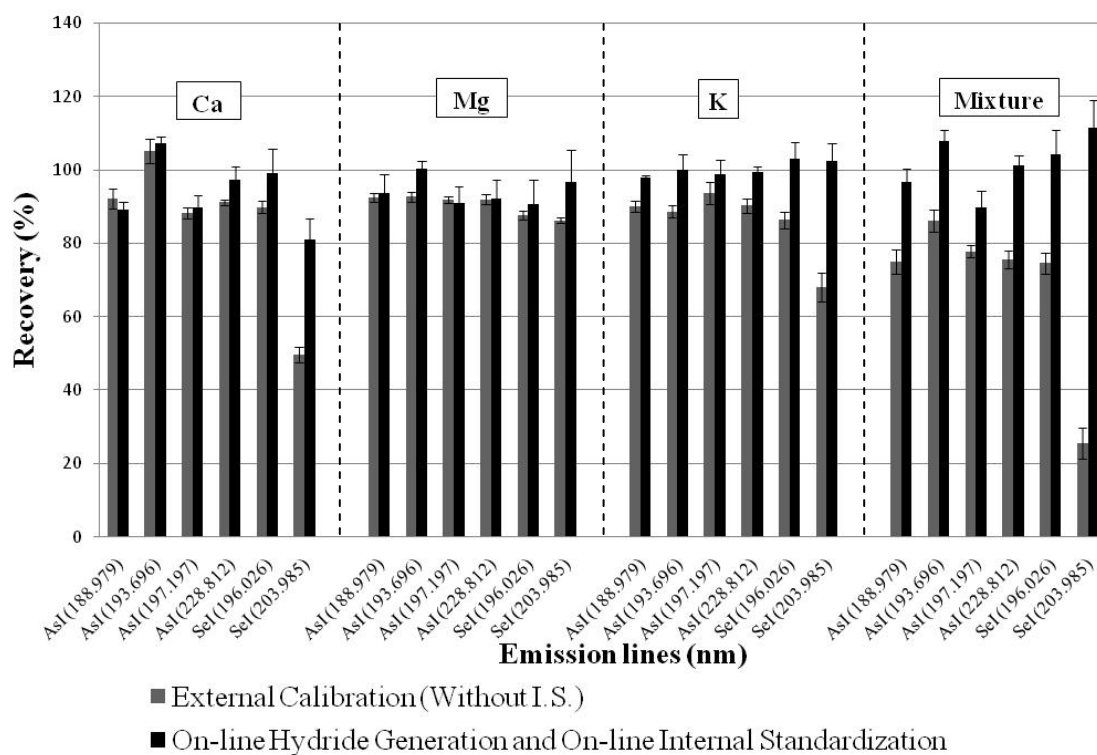


Fig 3. Recoveries of As and Se hydrides in 0.100 mol L^{-1} solutions of Ca, Mg, K and mixture of them using external calibration (grey bars) and the combination of on-line hydride generation and on-line internal calibration (black bars). I.S.: Ge(I) 303.906 nm; $[\text{Ge}] = 100 \mu\text{g L}^{-1}$. The error bars are the standard deviation of three measurements.

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