Determination of As, Se and Hg in fuel samples by in-chamber chemical vapor generation ICP OES using a Flow Blurring® multinebulizer †‡

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Abstract

In this work, a new and simple analytical methodology based on in-chamber chemical vapor generation has been developed for the spectrochemical analysis of commercial fuel samples. A multiple nebulizer with three nebulization units has been employed for this purpose: one unit was used for sample introduction while the other two were used for the necessary reagents introduction. By this way, the aerosols were mixed inside the spray chamber. Through this method, analyte transport, and therefore, the sensitivity, are improved in inductively coupled plasma-optical emission spectrometry.

The factors (i.e., variables) influencing chemical vapor generation have been optimized using a multivariate approach.

Under optimum chemical vapor generation conditions ($[\text{NaBH}_4] = 1.39 \%$, $[\text{HCl}] = 2.97 \text{ M}$, total liquid flow = $936 \mu\text{L min}^{-1}$) the proposed sample introduction system allowed the determination of arsenic, selenium and mercury up to $5 \mu\text{g g}^{-1}$ with a limit of detection of 25, 140 and $13 \mu\text{g kg}^{-1}$, respectively. Analyzing spiked commercial fuel samples recovery values obtained were between 96 % and 113 %, and expanded uncertainty values ranged from 4 % to 16 %. The most striking practical conclusion of this investigation is that no carbon deposit appears on the plasma torch after extended periods of working.

1. INTRODUCTION

Gasoline and diesel are petroleum-derived products which are widely used nowadays as fuels for internal combustion engines,¹ as well as offering other applications, and accordingly they are in great demand. Many elements can appear in fuel samples at a higher level of concentration than that desirable, either occurring naturally or due to additions during the refining processes.² The presence of these elements is inconvenient because it can cause serious damages to different parts of the engine, as well as being a major source of atmospheric pollution when released into the environment after combustion.³ These emissions contribute to a decline in air quality and as a result can affect human health. Moreover, the relatively high levels of concentration can even affect product performance, as the presence of contaminant elements decrease its volatility. Among all troublesome elements, the determination of As, Se and Hg is fundamental owing to different reasons:

Firstly, mercury is a very toxic element recognized as a global contaminant and it is found in trace levels of concentration or even higher in petroleum-derived products.^{4,5} Its presence in fuels might also affect processing as it reacts with metallic surfaces, forming amalgams, impairing the proper operation of the equipment. It might also poison catalysts.⁴⁻⁶

Arsenic, for its part, is also an element of great importance owing to its toxic, cumulative and harmful effects. Importantly, in petrochemical plants and various cracking processes is important as it can cause severe and irreversible catalyst poisoning, even at low concentration levels.⁷

Likewise, the presence of selenium in fuels is a matter of concern as it may inhibit the oxidative process of lubricants, although it is considered an essential element in low concentrations.^{8,9}

The main drawbacks that turns up when determining these three elements in fuels are that they are generally found in low concentrations in such samples, so their determination requires sensitive techniques^{4,5,7} and the organic nature of samples requires appropriate sample pretreatment.

In the past two decades, most analytical methods reported in the literature for the determination and quantification of contaminants in these samples are based on atomic spectrometric techniques such as Flame Atomic Absorption Spectrometry (FAAS),¹⁰ Electrothermal Atomic Absorption Spectrometry (ETAAS),^{7,11-15} Hydride

Generation Atomic Absorption Spectrometry (HGAAS),¹⁶ Cold Vapor Atomic Absorption Spectrometry (CVAAS),^{3,4,17} in addition to inductive coupled plasma-based techniques, which include Optical Emission Spectrometry (ICP OES)^{18,19} and Mass Spectrometry (ICP MS).²⁰⁻²²

There are few reports in the literature involving FAAS due to its low sensitivity. Roldan et al.¹⁰ proposed a method for the determination of metals in gasoline by FAAS. The determination was made after a preconcentration step using silica gel chemically modified with 2-aminotiazole groups. Limits of detection at the low $\mu\text{g L}^{-1}$ level were obtained for Cu, Fe, Ni and Zn.

ETAAS is one of the most useful analytical techniques for metal determination in fuel samples due to its high sensitivity and capability to deal with high organic loads. However, it may present significant analyte losses, memory effects and the discrete sampling makes sample throughput considerably slow. Dos Santos et al.¹⁵ described a procedure for the determination of mercury in petroleum products using ETAAS. This method involved a multiple injection technique for direct preconcentration in the graphite tube and samples were prepared as oil-in-water microemulsions. Reboucas et al.¹⁴ described an analytical method for the determination of trace metals (Cu, Fe and Pb) in naphtha by ETAAS using oil-in-water microemulsions. The most important drawback of these methods is the stability of the microemulsion.

Other authors use acid digestion as sample preparation, for determination of As and Hg in gasoline by HGAAS¹⁶ and CVAAS,^{4,17} respectively. However, it is widely known that acid digestion is usually tedious and extremely time-consuming, with a high risk of sample contamination, volatile analyte losses or incomplete mineralization of the organic matrix.

Among all of the techniques found in the literature for this purpose, it is worth stressing on those based on inductive coupled plasma. Considering the higher cost of equipment and operation of ICP MS, ICP OES in particular is the most appropriate choice due to its relatively low price, high throughput, wide dynamic range, sensitivity and capability for simultaneous determination. Nevertheless, the ICP OES technique may present limitations for determining trace elements specially when working with organic samples, such gasoline or other petroleum products. That is because the introduction of solvents with organic matrices gives rise to the formation of carbon species, which have a direct impact on the plasma fundamental

properties (*i.e.*, thermal conductivity and ionization energy). Up to a given level of carbon content, it can have beneficial effects on excitation temperature and electron number density. However, beyond this level, it dramatically affects the plasma analytical performance and consequently, the analytical figures of merit of the technique.

One of the best known effect of organic solvent introduction in ICP techniques is the formation of soot deposits on the tulip of the torch and the tip of the injector tube due to the incomplete combustion of carbon. This carbon deposition can cause sensitivity losses, instabilities and interferences, as the presence of carbon reduces the intensity of some atomic lines for which excitation energies are lower than 6 eV.²³

To date, the carbon deposition can be avoided by adding a small amount of oxygen to the intermediate gas flow. However, the use of oxygen to support complete combustion of carbon further increases the complexity of the experimental set-up and the cost-per-analysis. Recently, our research group reported that the addition of water to the ICP could reduce carbon deposits on the torch when using multinebulization systems based on the *Flow Blurring*[®] technology (FBMN).²⁴ The additional water eliminates spectral interferences created by carbon compounds and avoids injector clogging and therefore, prevents the resulting loss of sensitivity and precision. This implies an important advantage over conventional systems since it does not require the continuous cleaning of ICP components or the use of expensive additional components such as cooled spray chambers or an auxiliary oxygen supply.

The main purpose of this study was to extend the applicability of this *Flow Blurring*[®] multinebulization systems for the analysis of As, Se and Hg in commercial fuel samples by **ICP OES** without oxygen supply. To this end, an in-chamber chemical vapor generation (CVG) methodology based on the new multinebulizer is developed for the first time.

2. EXPERIMENTAL DESIGN

2.1. Instrumentation

All measurements were performed with an inductively coupled plasma optical emission spectrometer (model 720-ES, Agilent Technologies, Melbourne, Australia) working in axially-viewed plasma mode. **Table S1** in the ESI† shows the optimum operating conditions and emission lines evaluated in **ICP OES**. The RF generator power and gas flow rates (*i.e.*, plasma, auxiliary and nebulizing gas flow rates) were optimized achieving the maximum analyte intensities using a standard solution containing 2 µg g⁻¹ of As, Se and Hg in **petroleum ether (Panreac, Barcelona, Spain. Boiling range: 190–250 °C).**

2.2. Reagents

Five organic calibration standards of 1, 2, 3, 4 and 5 µg g⁻¹ were prepared from mono elemental stock solution (CONOSTAN, SCP Science, Baie D'Urfé, Canada) containing 500 µg g⁻¹ of As and Se and 100 µg g⁻¹ of Hg. The solvent used in these calibration standards was petroleum ether and the blank calibration standard was also prepared using this solvent. HCl solution was prepared by an appropriate dilution of an ultra-pure acid (32 % (w w⁻¹), Merck Pro Analysis, Darmstadt, Germany) in distilled deionized water (18 MΩ cm resistivity). Immediately prior to the analysis, a solution of sodium borohydride (Scharlau, Barcelona, Spain) in 0.1 % potassium hydroxide (Scharlau) was prepared in distilled deionized water.

2.3. In-chamber chemical vapor generation (CVG)

The FBMN used in this study consists of three independent *Flow Blurring*[®] nebulization units and a common gas inlet in a single nebulizer body of polytetrafluoroethylene (**Figure 1**). The in-chamber chemical vapor generation system was composed of the FBMN associated with a conventional cyclonic spray chamber with a volume of 50 mL (model Tracy, Glass Expansion, Victoria, Australia). No special modifications were required on the cyclonic spray chamber or other

components of the standard liquid sample introduction system. The FBMN-spray chamber combination is known as the FBMN-based system.

In this way, aqueous solutions of borohydride and hydrochloric acid and organic calibration standards/samples were introduced separately as aerosols into the spray chamber through the FBMN. The primary aerosols generated by the nozzles then interacted inside the spray chamber generating the conditions for chemical vapor generation (CVG). Volatile species and the tertiary aerosol were transported to the spectrometer without any separation of gas and liquid phases.

2.4. Optimization of in-chamber CVG

In-chamber CVG optimization was performed using a multivariate approach consisting in two steps: (i) a Plackett-Burman factorial design in order to identify the significant factors followed by (ii) a circumscribed central composite design (CCCD) in order to optimize those factors identified as significant in step (i). In both studies, the experiments were randomly performed in order to nullify the effect of extraneous or nuisance factors. A standard solution containing 2 $\mu\text{g g}^{-1}$ of the analytes was used. Data were evaluated with the NemrodW statistical software (NemrodW® version 2007, LPRAI, Marseille, France).

2.5. Analytical figures of merit evaluation

Under optimum conditions, the capability of the **ICP OES** technique for elemental analysis in organic samples is evaluated using the in-chamber CVG. To this end, figures of merit (i.e., sensitivity and detection limit) were studied. The results were compared with those obtained when organic samples were analyzed without in-chamber CVG. When the analysis was performed without in-chamber CVG, deionized water was used instead of NaBH_4 and HCl reagent solutions.

2.6. Commercial fuel sample analysis

The applicability of the analytical method proposed was evaluated using commercial fuel samples of 95 RON gasoline, 98 RON gasoline and diesel. Matrix

effects produced by the different samples and standard matrices were studied. Sample dilution was used as a method for matrix effect reduction. Different 98 RON gasoline sample dilutions (i.e., 50, 90 and 95%) were analyzed by external calibration using organic calibration standards prepared as described in Section 2.2. Lastly, a dilution factor of 95 % was chosen for the analysis of 95 RON gasoline and diesel.

The samples were purchased at a petrol station close to the University of Alicante and were stored in polyethylene terephthalate (PET) containers and kept in the refrigerator until analyzed. Before performing the analysis, the samples were allowed to reach room temperature.

3. RESULTS AND DISCUSSION

3.1. Optimization of in-chamber CVG

Optimization of the different factors involved on in-chamber CVG was carried out using a multivariate analysis. Multivariate analysis consisted of two main steps: screening study and optimization. On this study the individual emission intensities were the responses or dependent variables (y).

3.1.1. Screening study

Investigated factors (i.e., variables) were: NaBH_4 and HCl concentrations and the total liquid flow and the mathematical model for each evaluated emission line (i.e., response) was defined as follows:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3$$

where β_0 was the constant, x_n were the investigated factors and β_n their corresponding linear coefficients.

The constant and linear coefficients were calculated by a software in order to predict the response for any point of the experimental domain by simply replacing x_1 , x_2 and x_3 with actual values. **Table 1** shows the experimental factors and levels considered

in the Plackett–Burman design. The design matrix involved a total of 12 runs which were randomly performed. Pareto charts of this screening study are shown in **Figure 2**.

The length of the bars shown is proportional to the significance of the estimated main factors that affect the emission intensities of the analytes. Bars extending beyond the dashed vertical line indicate statistically significant factors at 95% probability. In addition, the direction of the bar is related to the “sign” of the effect produced by that factor (*i.e.*, rightward bars indicate a positive effect in the response when increasing factor value, while leftward bars indicate a negative effect). In general, all factors show positive effects for the signal with a varying degree of significance depending on the analyte. On the one hand, the total liquid flow is statistically significant for all the analytes. On the other hand, the NaBH₄ and HCl concentrations are only statistically significant for Hg and As, respectively. Since the three factors studied showed a significant and positive effect on the response of some or all of the evaluated analytes, the three factors studied were optimized in the next step.

3.1.2. Optimization study

The factors that have been previously established as significant were optimized in this step. The main objective was to find, if possible, the optimum experimental conditions of the in-chamber CVG in order to provide simultaneously the best response for all analytes evaluated. The **mathematical model** was defined for each emission line as follows:

$$y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_{11}X_1^2 + \beta_{22}X_2^2 + \beta_{33}X_3^2 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{23}X_2X_3$$

as in the previous study, the constant, the investigated factors, and the linear (*i.e.*, β_n), quadratic (*i.e.*, β_{nn}) and interaction (*i.e.*, β_{nm}) coefficients were calculated by a software for multiple regression.

Table 2 shows the factors and levels investigated in the circumscribed central composite design (CCCD). This experimental design involves 5 levels for each factor: a low level (-1), a central level (0), a high level (+1) and two star points located at $\pm\alpha$

($\alpha=1.682$). The CCCD design involved a total of 18 runs which were randomly performed.

The results obtained in this study for As, Hg and Se are shown in **Figures S1-S3** in the ESI[†], respectively, as response surfaces and contour plots. The graphs a), b) and c) for each figure show the relationship between the response and a pair of factors. The third factor is held constant at its optimum value for each element. Pairs of factors were considered separately in order to easily interpret the effect of each one on the response.

As expected, each and every evaluated experimental factor has a positive effect on the response. As noted in **Figures S1-S3** in the ESI[†], the response of the system for all evaluated emission lines increases when the value of one or more experimental factors increase (*i.e.*, the higher the value of the experimental factors, the higher response of the system) until reaching a maximum and then decreases. This occurs because increasing the values of experimental factors leads to a solvent and total dissolved solids overload to the plasma, and therefore produces a decreased response due to plasma instability.

Due to the similarity between the optimum values of each factor obtained for the different analytes, average values were chosen as the common optimum conditions for in-chamber CVG. In short, the results obtained from the overall optimization process lead to the following experimental conditions for in-chamber CVG: 936 $\mu\text{L min}^{-1}$, 1.39 % (w w⁻¹) and 2.97 (mol L⁻¹) for total liquid flow, NaBH₄ and HCl concentrations, respectively.

3.3 Evaluation of the analytical figures of merit

3.3.1. Sensitivity and limits of detection

Under optimum conditions, the analytical figures of merit (*i.e.*, sensitivity and LOD) with and without in-chamber CVG were evaluated and compared. LOD values were calculated following the $3\sigma_{\text{blank}}$ criteria, being σ_{blank} the standard deviation of 10 blank measurements. **Table 3** summarizes the analytical figures of merit obtained with both methods. As noted, the use of CVG provides relative sensitivity values greater than 1 for all emission lines evaluated, evidencing that the generation of

volatile species leads to enhanced sensitivity in ICP OES. This improvement depends on the analyte evaluated, the average sensitivity obtained with in-chamber CVG being approximately 4-7 times higher than that found without in-chamber CVG. This assumption results in a 3-7-fold decrease in the detection limits obtained with in-chamber CVG.

Of the three elements studied, mercury offered the most successful results in the analysis by in-chamber CVG-ICP OES, obtaining a sensitivity of 2606 ± 99 cps g μg^{-1} and a LOD of 13 $\mu\text{g kg}^{-1}$. Conversely, the highest LOD value was obtained for selenium (*i.e.*, 140 $\mu\text{g kg}^{-1}$).

3.3.2. Long-term stability

The presented procedure is based on the procedure of Aguirre et al.²⁴ for long-term stability tests. Long-term stability tests are critical in ICP OES analysis of organic samples. For these samples, incomplete carbon combustion usually gives rise to carbon deposits on the tulip and at the tip of the injector tube. This can lead to both signal drift and signal instability, and therefore deteriorates the long-term stability values. Hence, stability of both sample introduction systems in the analysis of organic samples was evaluated.

In this study, firstly the FBMN-based system was operated by nebulizing 1 $\mu\text{g g}^{-1}$ of organic standard solution through one nozzle and the aqueous solutions of borohydride and hydrochloric acid through the remaining two. Afterwards, the FBMN-based system was operated by nebulizing the same organic standard through one nozzle, keeping the rest of nozzles unused. In both cases, precision was expressed as a percent relative standard deviation of the emission signal obtained from several replicate measurements carried out over the period of time evaluated (*i.e.*, 60 min).

The results of the long-term stability test are shown in Table S2 in the ESI† in terms of RSD values. RSD values ranged from 5 to 8 % with ICP OES and from 4 to 5 % with in-chamber CVG-ICP OES.

As an illustrative example of such emission signal stability, Figure S4 in the ESI† shows the resulting normalized signal of one of the evaluated analytes (As I 188.980

nm) during one hour of continuous organic standard nebulization with the FBMN-based system, with (grey) and without (black) the in-chamber CVG.

The normalized signal is defined as the ratio between the signal value obtained at a given time and the signal value obtained at time zero (initial value). A normalized value of one implies no difference between the two measurements (*i.e.*, no signal drift). In both cases, data were acquired every five minutes over the one-hour nebulization period. Comparison of both emission signals shows that, as indicated above, the signal stability is enhanced when the in-chamber CVG procedure is applied as compared to the only organic standard nebulization.

Inspection of black markers in **Fig. S4** in the ESI† shows a progressive signal depression starting approximately after 15 minutes of continuous only organic standard introduction, which is most probably owing to carbon deposit formation on torch tulip (*i.e.*, the larger the carbon deposit, the less the emission signal). After the one-hour test without in-chamber CVG, emission signal had decreased to 0.87 times its initial value.

In contrast, grey markers (**Fig. S4**) indicate that emission signal remains close to its initial value during the one-hour test. It therefore follows that signal stability applying in-chamber CVG with FBMN-based system is excellent.

On the basis of the results obtained and the progressive visual assessment of the ICP torch and injector tube after every one-hour stability test (**Figure 3**), it is clear that the in-chamber CVG with the FBMN-based sample introduction system achieves a more complete organic sample/solvent combustion and reduces the formation of carbon deposits at the tip of the injector tube and the torch tulip, which results in a signal stability enhancement. Furthermore, the proposed system provides a simple setup which offers facilities as it is less expensive, there is no need of purchase adaptable spray chambers or additional components and it is not necessary to disassemble and clean separate parts.

3.4 Commercial fuel samples analysis

The original concentrations of the analytes in the commercial samples were below the LOD. Hence, in order to assess the applicability of the proposed analytical

method, spiked commercial fuel samples were analyzed. The added concentration of each analyte was $2.5 \mu\text{g g}^{-1}$, approximately.

Firstly, in order to study matrix effects produced by the sample matrix, three spiked samples of one of the fuels, chosen randomly, were prepared. The three spiked samples differed in their degree of dilution: 50 % dilution, 90 % dilution and, lastly, 95 % dilution. The fuel chosen was 98 RON gasoline and the solvent used for dilution was petroleum ether.

Table 4 shows how sample dilution can alleviate the matrix effects produced by the sample matrix. The results show that a dilution of 50 % produced strong matrix effects in As and Se determination and show less pronounced matrix effects for Hg determination. The results shown in **Table 4** indicate that the sample needs to be diluted up to 95 % for the determination of As and Se. By contrast, Hg determination could be satisfactory achieved with a 90% dilution.

Overall, the most successful results are obtained for the most diluted samples (*i.e.* 95 %) and, thus, this degree of dilution was used in the subsequent recovery study. Lastly, in order to assess the applicability of the proposed analytical method in different types of real samples with a complex matrix, a recovery study was conducted with different commercial fuel samples (**Table 5**). The fuels chosen were 95 RON gasoline and diesel. For all samples the added concentration of each analyte was $2.5 \mu\text{g g}^{-1}$, approximately, and all of them were diluted at 95 % with petroleum ether as a solvent. Summarizing, recovery values achieved in all spiked commercial fuel samples evaluated at 95 % of dilution, including 98 RON gasoline (**Table 4**), ranged from $96 \pm 5 \%$ to $113 \pm 12 \%$.

As shown in **Table 6**, several analytical methods using different analytical techniques and sample preparation have been published for the last decade. The limits of detection obtained by the present procedure were higher than those for the analysis of gasoline samples. However, the majority of the method reported used an analytical technique with higher sensitivity than ICP OES, such as GF AAS^{3,25} or ICP MS²⁶. We would like to emphasize that all methods in **Table 6** used a sample preparation in order to increase the sensitivity (*e.g.*, preconcentration procedures) or to remove/reduce the organic solvent loading (*e.g.*, microwave assisted acid digestion or emulsion). In contrast, the present method describes a reliable direct simultaneous analysis of As, Se and Hg (*i.e.*, without sample preparation) easily

applicable to routine analysis with higher sample throughput (*i.e.*, less than 1 minute to measure a sample).

4. CONCLUSIONS

Chemical vapor generation has been revisited for the analysis of As, Se, and Hg in commercial fuel samples by ICP OES. The experimental set-up is based on a new *Flow Blurring*[®] multinebulizer that mixes aerosols generated with different nozzles directly into the spray chamber. This study extends the applicability of this new technology for spectrochemical analysis of commercial fuel samples. With the in-chamber CVG investigated the continuous cleaning of the ICP components or the use of expensive additional components such as cooled spray chambers or an auxiliary oxygen supply are not required. Additionally, there are several advantages over conventional FIA systems used for in-chamber CVG: (i) simple design and low-cost system (*i.e.*, the use of valves, mix coils and gas-liquid phase separator is avoided), (ii) low sample and reagent consumptions, decreasing the total analytical cost, (iii) capability to measure simultaneously forming and non-forming volatile species.

For the analysis of commercial fuel samples, a sample dilution step using petroleum ether as a solvent is needed. For Hg determination in the case of 98 RON gasoline in particular, the sample dilution must be, at least 90 %, while being 95 % for As and Se determination. The recovery study with the three spiked commercial fuel samples proved the analytical methodology to be accurate, because it achieved recovery values which ranged between 96 % and 113 % and combined standard uncertainty values between 4% and 16%.

Finally, multivariate analysis is recommended as an environmentally friendly optimization approach of experimental conditions of both sample preparation and detection on spectrochemical analysis.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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FIGURES

Figure 1: Flow Blurring® multinebulizer (FBMN).

Figure 2: Pareto charts obtained in the screening study of the experimental factors affecting the in-chamber CVG for all the evaluated emission lines.

Figure 3. Real pictures of the ICP torch (a) before the long-term stability test (*i.e.*, initial state); (b) after 1 hour of continuous organic standard introduction with in-chamber CVG and (c) after 1 hour of continuous organic standard introduction without in-chamber CVG.

TABLES

Table 1: Experimental factors and levels of the Plackett–Burman design.

Experimental factor	Level	
	Low (-1)	High (+1)
NaBH ₄ concentration (% w w ⁻¹)	0.5	1.5
HCl concentration (M)	1	3
Total liquid flow rate (μL min ⁻¹)	500	1000

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Table 2: Experimental factors and levels of the Circumscribed Central Composite design (CCCD)

Experimental factor	Level			Star points ($\alpha = 1.682$)	
	Low (-1)	Central (0)	High (+1)	$-\alpha$	$+\alpha$
NaBH ₄ concentration (% w w ⁻¹)	0.5	1.0	1.5	0.2	1.8
HCl concentration (M)	1.0	2.0	3.0	0.4	3.6
Total liquid flow rate (μL min ⁻¹)	500	750	1000	320	1170

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Table 3 Analytical figures of merit obtained with and without in-chamber CVG.

Emission line (nm)	With in-chamber CVG		Without in-chamber CVG		Relative sensitivity ^{b,c}	Relative LOD ^d
	Sensitivity (cps g μg^{-1}) ^a	LOD ($\mu\text{g kg}^{-1}$)	Sensitivity (cps g μg^{-1}) ^a	LOD ($\mu\text{g kg}^{-1}$)		
As I (188.980)	1277 $\pm$ 22	25	182 $\pm$ 11	176	7.0 $\pm$ 0.4	7.0
Hg I (184.887)	2606 $\pm$ 99	13	534 $\pm$ 31	68	4.9 $\pm$ 0.3	5.2
Se I (196.026)	587 $\pm$ 24	140	163 $\pm$ 11	480	3.6 $\pm$ 0.3	3.4

^a Slope $\pm$ standard deviation. The number of calibration standards was six.

^b Sensitivity (with in-chamber CVG) / Sensitivity (without in-chamber CVG).

^c Uncertainty expressed as combined standard uncertainty.

^d LOD (without in-chamber CVG) / LOD (with in-chamber CVG).

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Table 4: Analysis of spiked 98 RON gasoline using the FBMN-based system.

Analyte	Spiked concentration ($\mu\text{g g}^{-1}$)	50 % Sample dilution		90 % Sample dilution		95 % Sample dilution	
		Found value ($\mu\text{g g}^{-1}$) ^a	R (%) ^b	Found value ($\mu\text{g g}^{-1}$) ^a	R (%) ^b	Found value ($\mu\text{g g}^{-1}$) ^a	R (%) ^b
As	2.81	0.60±0.12	21±4	1.93±1.7	69±2.9	2.71±0.10	97±4
Hg	2.52	3.1±0.3	122±12	2.7±0.3	107±12	2.8±0.3	113±12
Se	2.56	n.d. ^c	n.c. ^d	1.3±0.5	49±20	2.5±0.4	98±16

^a In $\mu\text{g g}^{-1} \pm$ confidence interval at 95%.

^b R: Recovery $\pm$ combined standard uncertainty. The combined standard uncertainty was calculated assuming that spiked concentration is free of uncertainty.

^c Not detected.

^d Not calculated.

Table 5. Analysis of spiked commercial fuel samples using the FBMN-based system with 95 % sample dilution.

Analyte	Spiked concentration ($\mu\text{g g}^{-1}$)	Diesel		95 RON Gasoline	
		Found value ($\mu\text{g g}^{-1}$) ^a	Recovery (%) ^b	Found value ($\mu\text{g g}^{-1}$) ^a	Recovery (%) ^b
As	2.57	2.55 ± 0.12	99 ± 5	2.63 ± 0.12	102 ± 5
Hg	2.50	2.7 ± 0.3	107 ± 14	2.5 ± 0.3	102 ± 14
Se	2.59	2.49 ± 0.13	96 ± 5	2.13 ± 0.13	96 ± 5

^a In $\mu\text{g g}^{-1} \pm$ confidence interval at 95%.

^b Recovery $\pm$ combined standard uncertainty. The combined standard uncertainty was calculated assuming that spiked concentration is free of uncertainty.

Table 6. Comparison of some of previously developed method for As, Se and Hg analysis in liquid fuels.

Analyte	LOD	Technique	Details	Ref.
As	10 $\mu\text{g L}^{-1}$	HG-FAAS ^a	Sample preparation: Microwave assisted acid digestion (35 min).	[16]
As	20 $\mu\text{g L}^{-1}$	FAAS	Sample: gasoline. Microwave assisted acid digestion (35 min).	[16]
As	6.4 ng L^{-1}	HG-GFAAS ^b	Sample: gasoline. Microwave assisted acid digestion (60 min and over-night pre-digestion with nitric acid).	[7]
As	0.18 $\mu\text{g L}^{-1}$	ICP OES	Sample preparation: dual-bed solid phase extraction (10 minute per sample).	[27]
As	0.09 $\mu\text{g L}^{-1}$	ICP OES	Sample preparation: hollow fiber-liquid phase microextraction (55 min per sample).	[28]
As	25 $\mu\text{g kg}^{-1}$	CVG-ICP OES	Sample preparation: Direct introduction (less than 1 min per sample)	This work
Hg	0.6 $\mu\text{g L}^{-1}$	PVG-FAAS ^c	Sample preparation: Microemulsion formation (4 min per sample).	[5]
Hg	0.08 $\mu\text{g L}^{-1}$	CV-GFAAS ^d	Sample preparation: preconcentration system using a gold column (15 min per sample).	[3]
Hg	0.2 $\mu\text{g L}^{-1}$	CV- ICP MS	Sample preparation: microemulsions were heated by microwave (35 min).	[26]
Hg	13 $\mu\text{g kg}^{-1}$	CVG-ICP OES	Sample preparation: Direct introduction (less than 1 min per sample).	This work
Se	1.76 $\mu\text{g L}^{-1}$	GFAAS	Sample preparation: emulsion formation (30 min).	[25]
Se	140 $\mu\text{g kg}^{-1}$	CVG-ICP OES	Sample preparation: Direct introduction (less than 1 min per sample).	This work

^a HG-FAAS: hydride generation flame atomic absorption spectrometry.

^b GFAAS: Graphite furnace atomic absorption spectrometry.

^c PVG-FAAS: photochemical vapor generation flame atomic absorption spectrometry.

^d CV-GFAAS: cold vapor graphite furnace atomic absorption spectrometry.