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Multivariate optimization of photochemical vapor generation for direct determination of arsenic in seawater by inductively coupled plasma mass spectrometry

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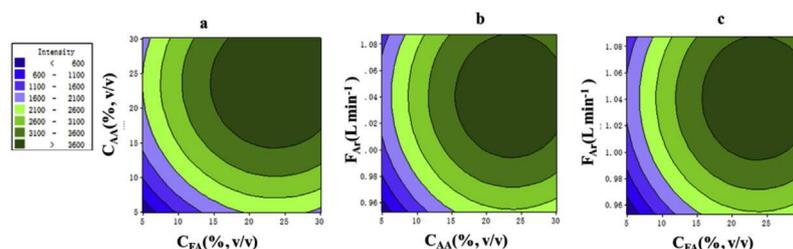
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HIGHLIGHTS

- Direct and accurate determination of ultra-trace level of total As in heavy matrix seawater using PVG ICPMS.
- The impact of the saline matrix on the suppression of analyte signal is efficiently eliminated by use of a mixture of 20% (v/v) formic and 20% acetic acid (v/v) as the photochemical reductants.
- Proposed method provides a 13-fold enhancement in sensitivity and 15-fold improvement in detection limit.

GRAPHICAL ABSTRACT



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ABSTRACT

Photochemical vapor generation (PVG) sample introduction coupled to inductively coupled plasma mass spectrometry (ICPMS) is described for the determination of As in seawater. A Plackett–Burman design (PBD) and central composite design (CCD) were employed to evaluate the significance of experimental variables relevant to the optimization of PVG-ICPMS detection. The impact of the saline matrix on the suppression of analyte signal was eliminated by use of a mixture of 20% (v/v) formic and 20% acetic acid (v/v) as the photochemical reductants. Optimized conditions yielded equivalent PVG generation efficiencies for As(III), As(V), monomethylarsonic acids (MMAs) and dimethylarsinic acids (DMAs), permitting direct and rapid determination of total arsenic in seawater without any other sample pre-treatment. Quantitation was accomplished using one point gravimetric standard addition along with a spike of ^{82}Se internal standard to compensate for signal drift and fluctuation during analysis. The resulting method detection limit of 3 pg g^{-1} (3σ) provided a 15-fold improvement over that obtained using direct solution nebulization, and is comparable to that for conventional chemical hydride generation (HG)-ICPMS. Accuracy was demonstrated by analysis of two Certified Reference Materials (NASS-6 and CASS-5 seawater) with satisfying results characterized by precisions of 3.5% and 3.2% RSD for CASS-5 and NASS-6, respectively.

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1. Introduction

Arsenic is a well-known toxic element present in the natural environment. Human exposure commonly occurs through ingestion of food and/or drinking water [1–3], and at high levels it may cause skin, lung and bladder cancers [1,3,4]. Whereas the World Health Organization has established a limit of 10 ng g^{-1} arsenic in drinking water [5], more recent findings reveal that consumption of water with levels as low as 0.017 ng g^{-1} over long periods of time may lead to arsenicosis [3,4]. Detection of arsenic in natural waters and environmental samples has thus become one of most frequently performed analyses to monitor environmental pollution and investigate its role in marine chemistry.

Among atomic spectrometric techniques, inductively coupled plasma mass spectrometry (ICPMS) provides low detection limits, wide dynamic range and multi-element capability [6]. However, the low sample introduction efficiency associated with classical pneumatic nebulization (typically 2–5%) and low concentration of arsenic present in seawater deteriorate the performance for trace arsenic detection. Furthermore, the elevated background due to $^{40}\text{Ar}^{35}\text{Cl}^+$ on m/z 75 also causes a severe problem for quantification. High resolution sector-field ICPMS or instrumentation equipped with a reaction/collision cell and dilution of seawater (typically 10-fold) may be used to alleviate this problem [7,8] but with compromised analytical performance. In addition, significant deposition of salt on interface cones may remain a problem for continuous sample introduction of even diluted seawater. Moreover, as a result of the extent formation of As hydride species in the plasma being dependent on the oxidation state of As, differences in responses between inorganic As(III) and As(V) occur during sample nebulization with either ICPMS or with ICP optical emission (ICPOES) detection [9,10]. Additionally, response from inorganic As(V) in a 1% (v/v) HCl medium by ICPMS was elevated 11% compared to that of As(III) due to partial formation of AsCl_3 [9,11]. In a solution of 1% HNO_3 , this difference was reduced to 4.0%. However, for analysis of seawater, the high concentration of Cl^- in the sample may remain a source of uncertainty during quantitation despite use of a 1% HNO_3 medium. Furthermore, it has been reported that use of reaction/collision cells may further enhance this sensitivity gap between As(III) and As(V) [9].

Chemical hydride generation (HG) has been widely used with ICPMS to enhance detection power and accuracy for the determination of As [12,13], principally due to efficient matrix isolation and enhanced introduction/ionization efficiency. However, because of the species-dependent efficiencies of reduction of the different forms of arsenic by reaction with $\text{NaBH}_4/\text{KBH}_4$, pre-conversion all As species to a single form is required [14–17]. Alternatively, by prolonging the reaction time to allow complete conversion of all As species, identical vapor generation efficiencies can be achieved [18]. Despite this, use of unstable solutions of $\text{KBH}_4/\text{NaBH}_4$ reductants and instability of the plasma due to the large amounts of hydrogen generated during HG remain drawbacks.

Photochemical vapor generation (PVG), utilizing free radicals generated by photo-redox reactions in the presence of low molecular weight organic compounds has become a powerful alternative to chemical HG for sample introduction [19,20]. PVG not only retains the principle advantages of conventional HG, but also provides for simpler reactions and greener analytical chemistry [20,21]. Currently, there are few reports concerning the mechanism of photochemical alkylation of inorganic arsenic [22,23], and its application to quantitation in real samples is rare [24], possibly due to the issue of species-dependent generation efficiencies. Indeed, a two-fold difference in PVG efficiency between As(III) and As(V) has been reported [24]. In addition, the kinetics of reduction of As(V) was found to be quite slow [22], making its direct determination

complicated. As for the PVG of organoarsenic compounds, related information is not available. Generally, exposure of a thin film of sample to the UV field more efficiently delivers radiation and minimizes the required exposure time for PVG, leading to enhanced analytical performance for many elements [25]. Additionally, the elevated temperature experienced by the sample solution passing through the PVG reactor may facilitate the reduction, as in the case of Se(VI) [26]; however, severe matrix effects remain, as reported for the determination of Se in seawater by PVG [27], necessitating a several-fold dilution of the sample prior to analysis. In addition, in the presence of low concentration of chloride, signal suppression was noted for the determination of Ni and Sn when attempting PVG [28,29], preventing their direct determination in seawater. Most recently, it was noted that the low recovery of analyte from real sample matrices may be due to use of optimum conditions developed for PVG with calibration standards which are different from those required with the sample matrix [30].

The purpose of this work was to develop a sensitive and greener method for the direct determination of total As in seawater using thin film PVG coupled to collision cell qICPMS for detection. The influence of several experimental parameters on response from spiked seawater was investigated using multivariate methods. For this purpose, Plackett–Burman (PBD) and central composite designs (CCD) were undertaken to optimize the analytical procedure. The accuracy of the proposed methodology is demonstrated by successful analysis of two seawater certified reference materials.

2. Experimental section

2.1. Instrumentation

A model 7500 ICPMS equipped with a collision cell (Agilent Technologies, Mississauga, ON, Canada) was used for all measurements. An ESI spray chamber having two inlets to simultaneously permit sample introduction of both gaseous and nebulized liquid samples was used. Solution nebulization was undertaken with a PFA ST nebulizer (ES-2040, Elemental Scientific; Omaha, NE, USA) operating at 0.40 mL min^{-1} . During PVG optimization and sample analysis, gas flow to the nebulizer was stopped in order to achieve best sensitivity of As using PVG. A schematic of the UV-PVG photoreactor interfaced to the ICPMS has been presented earlier [30]. The UV-PVG system consists of a 19 W thin film flow-through lamp (Beijing Titan Instruments Co., Beijing, China) loosely covered with aluminum foil to shield the operator from exposure to the UV. Argon carrier gas was introduced through a “Y” connection between the outlet of the photoreactor and a homemade gas–liquid separator (GLS, ~2 mL internal volume) maintained at 0°C by immersion in an ice bath to minimize any transport of liquid droplets derived from condensation of water vapor to the ICP. The generated analyte vapors were directed from the outlet of the GLS to the gas inlet port of the spray chamber via a 0.25 m length of Teflon lined Tygon tubing (0.25 in o.d., VWR International).

2.2. Reagents and solutions

Nitric and hydrochloric acids were purified in-house prior to use by sub-boiling distillation of reagent grade feedstock in a quartz still. High purity de-ionized water (DIW) was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp, Iowa, USA). High purity formic (88%), and glacial acetic acids were obtained from GFS Chemicals Inc. (Powell, OH, USA). A 5% HNO_3 (v/v) rinse solution was prepared and introduced between samples to efficiently eliminate any carry-over. High-purity NaCl (trace SELECT, >99.999%) was obtained from Sigma–Aldrich Canada (Oakville,

Ontario, Canada).

A 3000.5 $\mu\text{g g}^{-1}$ primary stock solution of arsenic was prepared by dissolution of 0.3 g of the high purity metal (Johnson, Matthey & Co. Limited, London, UK) in 6 mL of HNO_3 and 2 mL HCl followed by dilution in DIW. A working standard solution containing 100 ng g^{-1} for As was prepared by a serial dilution of the stock with DIW. An internal standard was prepared from ^{82}Se (as metal, 99.7%, Trace Sciences International, Richmond Hill, Ontario, Canada) by dissolution in a mixture of HNO_3 and HCl followed by dilution with DIW, from which a working standard solution of 2.0 $\mu\text{g g}^{-1}$ ^{82}Se was prepared by dilution in 2% HCl. The impact of As species on PVG was investigated using solutions of As(V), As(III), MMAs(V) and DMAs(V). Stock solutions of 1000 $\mu\text{g g}^{-1}$ As(V) and As(III) were prepared by dissolving Na_2HAsO_4 and As_2O_3 (Aldrich, 99.95%) in DIW and 3 M HCl, respectively. Stock solutions of 1000 $\mu\text{g g}^{-1}$ (as As) in the form of MMAs(V) and DMAs(V) were made by dissolution of $\text{Na}_2\text{CH}_3\text{AsO}_3 \cdot 6\text{H}_2\text{O}$ (Chem Service, USA) and $(\text{CH}_3)_2\text{As}(\text{O})\text{OH} \cdot 6\text{H}_2\text{O}$ (Strem Chemicals Inc., USA) in DIW, respectively.

National Research Council Canada (NRCC, Ottawa, Canada) seawater CRMs CASS-5 and NASS-6 were used for method validation and analysis.

2.3. Sample preparation and analysis procedure

Standard additions calibration was applied for the determination of As in the seawater samples. Three replicate subsamples of 40 g of each seawater CRM were weighted into pre-cleaned polyethylene bottles. Samples were gravimetrically spiked with internal standard by adding 0.4 g of a solution of 2.0 $\mu\text{g g}^{-1}$ ^{82}Se (VI) followed by 16 g acetic acid (AA) and 16 g formic acid (FA). The samples were then diluted to 80 g with DIW, resulting in the final solutions containing 20% FA and 20% AA. Three sample blanks were prepared containing 1.75% NaCl in a mixture of 20% FA and 20% AA in an effort to matrix match the seawater solutions. A standard additions calibration curve for the determination of As in these seawater samples was generated by weighing 15 g aliquots of the above solutions into pre-cleaned polyethylene bottles. Appropriate masses of the 100 ng g^{-1} primary standard solution of As were added to each of the three sub-samples so as to result in approximately a 1-, 2- and 4-fold increase in the As concentration, respectively.

Optimization of the 7500 ICPMS was performed daily. Collision mode using He as collision gas was selected to resolve polyatomic interferences on m/z 75 arising from the seawater samples. Typical operating conditions are summarized in Table 1. A solution of 5% HNO_3 was used to efficiently rinse the system between samples to eliminate any carry-over between samples. Samples were introduced in the following sequence: unspiked sample – spiked 1x – spiked 2x – spiked 4x – unspiked sample, and quantitated using online PVG ICPMS. The intensity of As obtained from the prepared blank solution was subtracted from the intensities measured in all samples.

2.4. Statistical treatment of data

Minitab 16 software (Minitab Inc., USA) was used to perform experimental design and statistical treatment of the results.

3. Results and discussion

3.1. Optimization of UV-PVG

PVG efficiencies are highly dependent on the type and concentrations of organic reductants used [20]. Volatile species of As have been generated in formic, acetic and propionic acid media [24]. In

Table 1
Typical ICPMS operating conditions.

Instrument settings	ICPMS
Rf power	1300 W
Rf matching	1.83 V
Plasma Ar gas flow rate	15.0 L min^{-1}
Auxiliary Ar gas flow rate	1.00 L min^{-1}
Sampler cone orifice	1.00 mm
Skimmer cone orifice	0.88 mm
Sample depth	5.3 mm
Torch-H	0.3 mm
Torch-V	-0.2 mm
Extract 1	-199.9 V
Extract 2	0 V
Omega Bias-ce	-18 V
Omega Lens-ce	4.2 V
Cell Entrance	-30 V
QP Focus	2 V
Cell Exit	-30 V
OctP RF	131 V
OctP Bias	-4.6V
He gas	2.1 mL min^{-1}
Discriminator	9.7 Mv
Dwell time	0.10 s
Total measurement time	90 s
	UV-PVG
Ar carrier gas flow rate for GLS	1.04 L min^{-1}
Sample flow rate	0.7 mL min^{-1}

the presence of formic acid (FA), generation of volatile arsenic from arsenite was rapid but the efficiency was low [20,23]. Acetic (AA) and propionic acids (PA) were found to be much more efficient for photochemical reduction of arsenate. Interestingly, use of a mixture of low molecular weight organic acids efficiently facilitated the photochemical reduction of As [22]. Since PA has an unpleasant odor and typically causes frothing in the GLS, FA and AA were selected for further study. The Ar carrier gas flow rate (F_{Ar}) to the GLS determines the liquid–gas separation efficiency of the volatile As species as well as influences the sampling depth in the ICP. The sample uptake rate (F_{sample}) determines both the sample irradiation time and the rate of delivery of As to the PVG reactor. Therefore, the concentrations of FA and AA, the flow rate of Ar and the sample uptake flow rate were considered for further investigation of their effects on the response. Based on a preliminary study, PVG efficiency of As was greatly enhanced when a mixture of AA and FA was used. The optimum concentrations of AA and FA for the PVG of As in standard solution were 15% (v/v) and 5% (v/v), respectively. As in the case of Sb [31], response of As in seawater was less than 35% of that from the same concentration of matrix-free standard solution due to the effect of sample matrix. Since the sample matrix have a significant influence on the PVG of As, NASS-6 seawater spiked with 1 ng g^{-1} As was used to optimize the experimental conditions. However, it was difficult to obtain the optimum concentrations of AA and FA when traditional univariate optimization approach was used as a result of the influence of sample matrix and both acids had correlated effects. The intensity of As increased with the increased concentrations of both acetic acid and formic acid up to 50% (v/v) (the highest level available in order to maintain less than 2-fold dilution of the seawater for a better sensitivity, as the photo-assisted reductant in this system) in seawater. Therefore, multivariate optimization technique was selected in this study.

3.2. Plackett–Burman experimental design

A Plackett–Burman (PB) design (in duplicate) was developed to identify the statistically significant parameters impacting optimization of the procedure by use of a few simple experiments [32].

Four factors, consisting of 12 randomized runs and 3 replicates of center points (mean value between the low and high values) were investigated for the optimization. Minimum and maximum levels of each factor, chosen in accordance to previous reports [22,24] and our preliminary experiments are presented in Table 2. Table 1S (Supplementary Information) summarizes the PB experimental design matrix together with the analytical response (expressed as intensity) for each run.

Statistical evaluation of the results produced a minimum t-value of 2.26 at a confidence level of 95%. The standardized Pareto chart is shown in Fig. 1 wherein bar lengths are proportional to the absolute values of the estimated effects, and assist in evaluating the relative importance of variables. The critical t-value is included as a vertical reference line. When exceeding the reference line, variables were considered as statistically significant factors. As shown in Fig. 1, the concentrations of FA, AA and the carrier gas flow rate are statistically significant parameters. The effects of these three variables are positive, leading to enhanced analytical signals at their higher values. Therefore, the higher concentrations of FA and AA as well as carrier gas flow rate were selected for system operation. Interestingly, varying the sample uptake rate in the studied range did not show a significantly positive effect on response. Based on preliminary experiments, response increased with sample flow rates from 0.1 to 0.4 ml min⁻¹, reaching a state-steady between 0.4 and 0.85 ml min⁻¹ and thereafter decreasing. Low sample uptake rates lead to a smaller rate of delivery of As to the PVG reactor along with generation of many gas bubbles, leading to poor precision. Conversely, high flow rates yield short irradiation times and potentially inefficient reduction of As [22]. A sample uptake rate of 0.8 mL min⁻¹ was selected for further experiments in consideration of both effects.

3.3. Central composite design

After screening out the parameter which has insignificant effect on the response, the remaining three factors affecting the PVG and ICPMS detection for As were simultaneously optimized using a central composite design (CCD). Their effects as well as their mutual interactions were investigated. The CCD comprised a 2³ full factorial design, augmented with 2 × 3 axial points ($\alpha = 1.682$) and 6 replicates of the center point, resulting in 20 non-randomized runs. Table 2S (Supplementary Information) summarizes the experimental field definition used for the CCD. The complete design matrix and the corresponding analytical response of each run are shown in Table 3S (Supplementary Information).

A second-order polynomial quadratic model was developed to analyze and interpret the relation between experimental responses and the selected factors by means of a multiple linear regression, including the linear terms, the quadratic terms and the first order interaction terms. The general equation is:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (1)$$

where Y is the intensity of signal response, X_i is the factors or

Table 2
Experimental Placett-Burman design.

Parameter	Symbol	Low (-)	High(+)
Concentration of formic acid (% v/v)	C _{FA}	5	25
Concentration of acetic acid (% v/v)	C _{AA}	5	25
Carrier gas flow rate (L min ⁻¹)	F _{Ar}	0.94	1.0
Sample uptake rate (mL min ⁻¹)	F _{sam}	0.5	1.0

Pareto Chart of the Standardized Effects
(response is intensity, Alpha=0.05)

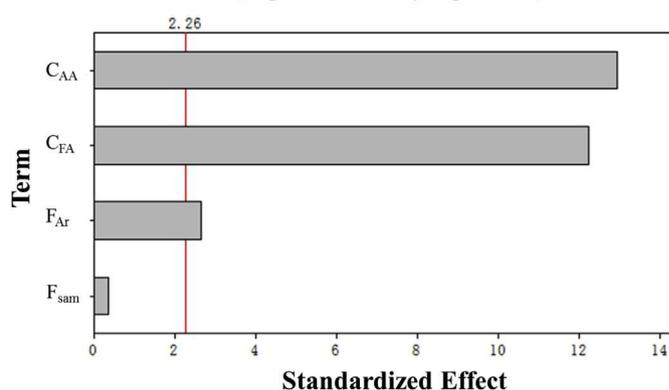


Fig. 1. Standardized Pareto chart for Plackett–Burman design. Vertical line is critical t-value for 95% confidence.

variables, β_i is the linear coefficient, β_{ii} is the quadratic response, β_{ij} is the first-order interaction coefficient, and β_0 is the random error of this method. Based on the experimental results, the following second-order polynomial equation was established:

$$y = -216904 + 322[C_{FA}] + 308[C_{AA}] + 410777[F_{Ar}] - 7[C_{FA}]^2 - 7[C_{AA}]^2 - 197546[F_{Ar}]^2 \quad (2)$$

The significance and adequacy of the model were tested using ANOVA and P-value significance levels. Accordingly, the F-value of the model (92.53) was much greater than the tabulated F-value with the same number of degrees of freedom of three sources of variance, confirming the adequacy of the model. A maximum p-value for lack-of-fit (LOF) of 0.351 (>0.05) was obtained for the above equation, suggesting the significance of the quadratic model. However, the interaction terms between the three parameters were found to be insignificant. The correlation coefficient (R^2), quantitatively evaluating the correlation between the experimental data and the predicted response, was 97.7%. Adjusted R^2 (Adj- R^2) was also used to measure the goodness of fit and found to be 96.7%, close to the corresponding R^2 and further confirming that the model is well-fitted to the experimental data.

As shown in Fig. 2, high concentrations of FA and AA are beneficial to response. Obviously, to achieve highest sensitivity, the concentration of FA must be higher than that used in earlier studies (7.5%, v/v) [22], and higher than that suggested by the initial univariate optimization experiments with standard solutions of As (5%, v/v). This confirms that the optimum conditions for PVG of As in matrix-free solutions and seawater are different due to the influence of the sample matrix. The results obtained in this study show that multivariate optimization approach is more efficient to find optimum conditions over the traditional univariate optimization approach. Reductive radicals arising from photo-decomposition of FA may not only participate in the generation of AsH₃ [22], but also are consumed by any oxidizing radicals arising from the sample matrix. Similarly, signal intensity increases with the Ar flow rate, as low flows result in inefficient phase separation of the As species.

The response contour described by equation (2) exhibits a maximum point that can be calculated using the following equations:

$$\frac{\partial y}{\partial C_{FA}} = 322 - 14[C_{FA}] = 0 \quad (3)$$

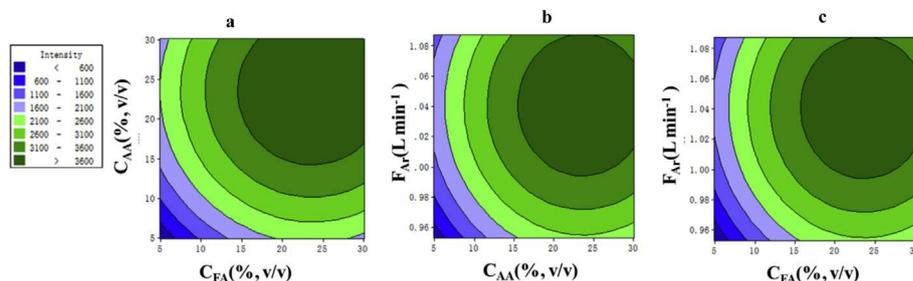


Fig. 2. Estimated contour plots of signal intensity as functions of (a) C_{FA} and C_{AA} (F_{Ar} : 1.06 L min⁻¹); (b) C_{AA} and F_{Ar} (C_{FA} : 25%, v/v); (c) C_{FA} and F_{Ar} (C_{AA} : 25%, v/v).

$$\frac{\partial y}{\partial C_{AA}} = 308 - 14[C_{AA}] = 0 \quad (4)$$

$$\frac{\partial y}{\partial F_{Ar}} = 410777 - 395092[F_{Ar}] = 0 \quad (5)$$

By solving these equations, optimum values were found to be $C_{FA} = 23\%$ (v/v), $C_{AA} = 22\%$ (v/v) and $F_{Ar} = 1.04$ L min⁻¹, similar to the range 15–25% (v/v) evident from Fig. 2a. Taking into consideration reagent consumption and the small impact on deviation from these optimal values, a concentration of 20% (v/v) for both FA and AA was conveniently selected for all subsequent work.

3.4. Figures of merit

Using optimized experimental conditions, a 13-fold enhancement in sensitivity is realized using PVG compared to that of direct solution nebulization. Precision of 5.0% RSD was obtained from replicate measurements of a 1 ng g⁻¹ spike of As in 1.75% NaCl (matching the sample matrix prepared for seawater analysis). A method detection limit of 3 pg g⁻¹ for As is estimated based on three times the standard deviation of the concentration of As in the method blank determined from the linear calibration and is 15-fold lower than that available using direct sample introduction solution nebulization (45 pg g⁻¹ in this study), and is comparable to hydride generation ICPMS (6 pg g⁻¹) [33]. Linear response is obtained in the range 0.01–200 ng g⁻¹ ($r^2 = 0.9999$). Since steady-state signals were generated, sample throughput with the current PVG ICPMS system is 12/h, not significantly different from that of direct liquid nebulization. After each sample, a solution of 5% HNO₃ was introduced to the PVG reactor for 45 s, efficiently eliminating any carryover.

3.5. Determination of As in seawater

In surface water, inorganic As (III and V), MMA(V) and DMA(V) are commonly found to be present [3,34,35]. Other organic arsenic species have also been reported but at much lower levels. Inorganic As(V) is the major form in surface water; As(III), MMA, DMA, and the other arsenic species exist at lower levels [34,35]. As reported in previous studies [18,36,37], hydride generation efficiencies may be or may not be different for different As species. Thus, PVG of individual As species was investigated. No significant difference in sensitivity (less than 5%) was evident amongst As (III), As(V), MMA and DMAs as 2 ng g⁻¹ (as inorganic As) standard solutions containing 1.75% NaCl, making determination of total As in seawater directly feasible. This conclusion contrasts that from a previous report [24] wherein a two-fold difference in response was noted for As(III) and As(V) using PVG. The current use of a high-efficiency thin-film photoreactor with a source of 185 nm vacuum ultraviolet light provides sufficient energy to completely oxidize any organoarsenic species to As(V) within 3.5 s in the absence of any

additional chemical oxidants [38]. The extremely high efficiency arises from the powerful hydroxyl radical (redox potential of 2.8 V), efficiently produced from water molecules under the influence of 185 nm UV irradiation [38]. It is likely that As(III) and other organometallic species are initially rapidly oxidized to As(V) and then reduced to their volatile forms, similar to the reactions occurring in such a photoreactor reported by Suzuki et al. [39] for the various organometallic forms of Se. Furthermore, elevation of the temperature of the sample solution occurs on passage through the PVG reactor and may facilitate these reduction processes of As(V), as in the case of Se(VI) [26].

Although isotope dilution (ID) is capable of compensating for matrix effects, instrument drift and any losses of analyte during subsequent sample treatment [40], As is not amenable to this, being monoisotopic. Consequently, matrix effects were compensated for by use of the method of standard additions along with an internal standard (IS). For this purpose, ⁸²Se (as Se(IV)) was selected (at 10 ng g⁻¹), based on the premise that PVG of Se is highly efficient and it behaves in an identical manner to As regarding the impact of any changes in plasma conditions, presence of matrix or variations in other experimental conditions. Initially, a set of CASS-5 seawater solutions with gravimetric additions of approximately 1-, 2- and 4-fold the endogenous As content were prepared, yielding a calibration curve having a correlation coefficient greater than 0.999. Noteworthy was that no significant difference in As concentration was obtained using either multiple additions or a single point addition corresponding to a doubling of the endogenous concentration. Thus, one point standard addition calibration with internal standardization was adopted for the determination of As in seawater samples in order to achieve higher sample throughput. Under such conditions, equation (6) was used for the calculation of the mass fraction of As:

$$w_x = \frac{w_{std} \cdot m_{std}}{m_0} \cdot \frac{R_{un}}{R_{sp} - R_{un}} \cdot \frac{m_{xf}}{m_x} \quad (6)$$

where w_x is the mass fraction of the analyte in the sample (ng/g); w_{std} is the mass fraction of the analyte in the primary standard solution (ng/g); R_{un} is the measured intensity ratio of analyte to internal standard in the unspiked sample; R_{sp} is the measured intensity ratio of analyte to internal standard in the spiked sample; m_{std} is the mass of the standard solution added to the spiked sample (g); m_0 is the mass of sub-sample used to prepared the spiked sample (g); m_x is the mass (g) of the original sample; m_{xf} is the mass of the original sample after addition of the internal standard. For comparison purposes, equation (7) is used for calculation of the mass fraction of As in seawater based on a one point gravimetric standard addition calibration and the absence of the IS:

$$w_x = \frac{I_{un} \cdot w_{std} \cdot m_{std}}{I_{sp} \cdot m_{of} - I_{un} \cdot m_0} \quad (7)$$

Table 3
Analysis of seawater.

Sample and method	As, ng g ⁻¹
CASS-5 (Std. Add., SD, n = 4)	1.204 ± 0.074
CASS-5 (Std. Add. with IS, SD, n = 4)	1.209 ± 0.042
CASS-5 certified (U, k = 2)	1.21 ± 0.09
NASS-6 (Std. Add., SD, n = 3)	1.374 ± 0.091
NASS-6 (Std. Add. with IS, SD, n = 3)	1.415 ± 0.045
NASS-6 certified (U, k = 2)	1.40 ± 0.12

where I_{un} is the measured intensity of analyte in the unspiked sample; I_{sp} is the measured intensity of analyte in the spiked sample; m_{of} is the mass of the spiked sample after addition of standard solution (g).

Results are summarized in Table 3 showing that As concentrations in both seawater CRMs are in agreement with certified values, confirming the accuracy of the methodology. Precisions of 3.5% and 3.2% for As in CASS-5 and NASS-6 (n = 4 and 3, respectively), obtained using one point gravimetric standard addition with IS are superior to the values of 6.2% and 6.7% for these respective samples in the absence of the added IS.

4. Conclusion

A sensitive and accurate approach is demonstrated for direct determination of total As in seawater based on thin-film PVG for sample introduction and ICPMS detection. A 13-fold enhancement in sensitivity for As is realized with this approach compared to solution nebulization. The method provides a detection limit of 3 pg g⁻¹ for As, 15-fold superior to that achieved using direct solution nebulization, and comparable to that for conventional chemical HG-ICPMS. A 2-fold improvement in precision of determination is realized based on use of one point gravimetric standard addition with internal standardization for calibration. Multivariate optimization approach is more efficient to find optimum conditions for PVG ICPMS over the traditional univariate optimization approach.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.aca.2015.10.020>.

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