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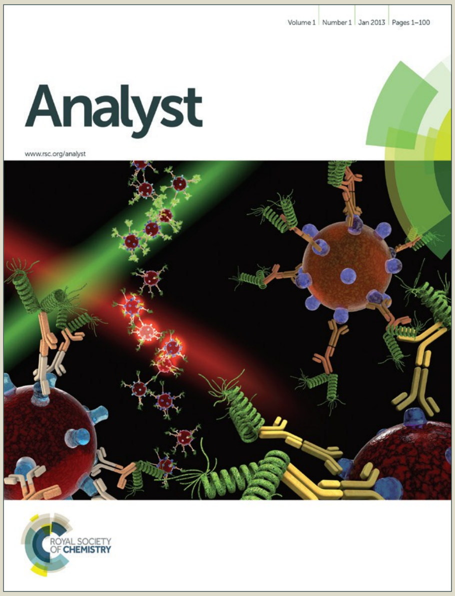

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Ferric Ion Enhancement Ultraviolet Vapour Generation Atomic Fluorescence Spectrometry for the Determination of Ultratrace Inorganic Arsenic in Surface Water

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Abstract: A novel method of ultraviolet vapour generation (UVG) coupled with atomic fluorescence spectrometry (AFS) was developed for the determination of ultratrace inorganic arsenic (iAs) in surface water. In this work, different ferric species were utilised for the first time as an enhancement reagent for the ultraviolet vapour generation of As(III), and their UVG efficiencies for volatile species of arsenic were investigated. 15 mg/L of ferric chloride provided the greatest enhancement of approximately 10-fold, using 20% acetic acid combined with 4% formic acid with 30 s ultraviolet irradiation at a 200 mL/min Ar/H_2 flow rate. Under the optimised conditions, the linear range was 1.0 μg/L - 100.0 μg/L, and the spiked recoveries were 92% - 98%. The limit of detection was 0.05 μg/L for iAs, and the relative standard deviation (RSD) value of repeated measurements was 2.0% (n = 11). This method was successfully applied to the determination of ultratrace iAs in tap water, river water, and lake water samples using 0.2% H_2SO_4 (v:v) as the sample preserver. The obtained values for the water samples of certified reference materials (CRMs) including GSB-Z50004-200431, GBW08605 and GBW(E)080390 were all within the certified ranges.

1. Introduction

Arsenic (As) is a toxic element and widely distributed in the nature. In addition to As discharge from natural activities,[1,2] manmade causes such as uncontrolled industrial discharge, mineral exploration, and agricultural inputs including arsenical pesticides, fertilizers, and veterinary drugs are the main contributions to arsenic contamination of environmental water.[3] Arsenic exists in various forms with different toxicities, including As(Ⅲ), As(Ⅴ), MMA, DMA, arsenosugars, AsC and AsB, in which inorganic As (iAs) is the most toxic species.[4] It was reported that iAs is the predominant species in surface water,[5] and contaminated drinking water has been considered as one of the most important iAs exposure sources to humans.[6] Because of ultratrace As levels in surface water, it is necessary to develop a highly sensitive analytical method for monitoring iAs in water samples to protect the health of humans and animals.

In recent years, many spectrometric instrumental methods have been employed to determine the presence of As, such as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry / mass spectrometry (ICP-OES/MS), and so on. Among these methods, ICP-MS is the most commonly used because of its high analytical sensitivity and wide dynamic linear range. However, the direct nebulizer of the ICP-MS instrument leads to possibly serious interferences from high levels of chloride due to the formation of argon chloride ($^{40}Ar^{35}Cl$) in the plasma.[7,8] Furthermore, the ICP-MS technique is not suitable for some low-input analytical laboratories because of the high cost and extensive training requirements for instrument operation.

With the development of chemical vapour generation (CVG) techniques, particularlythe tetrahydroborate (Ⅲ) (THB) reaction, hydride generation - atomic fluorescence spectrometry (HG-AFS) is also a powerful approach for ultratrace As analysis, considering the advantages of its high vapour generation efficiency, efficient matrix separation, and low analytical cost.[9] However, the conventional HG-AFS method is also limited by the instability of the THB reagent and the matrix interference caused by transition metals.[10]

From 2004, the Sturgeon team employed ultraviolet vapour generation (UVG) to improve the conventional HG-AFS method,[11-16] utilising free radicals generated by photoredox reactions in a low molecular weight organic acid (LMWOA). It not only retains the primary advantages of conventional CVG techniques but also shows simpler control, easier miniaturization, and safer operation and is more environmentally friendly.

At present, the UVG-AFS instrumental methods have been applied to many elemental analysis, including conventional hydride-forming elements such as Hg,[17-19] Se,[20-22] Sn,[23] As, Bi, Sb, Te,[24] Pb,[25] as well as several non-hydride-forming elements, including Fe, Co, Ni, I, and Br.[15,26-32] Among them, Gao et al [25] firstly employed inorganic elements (Ni^{2+} and Co^{2+}) to enhance the sensitivity of UVG of Pb. For arsenic, Zheng et al employed an UVG reaction of As (Ⅲ) in acetic acid to obtain the limit of detection (LOD) of 0.5 ng/mL.[24] Unfortunately, it is still not sensitive enough for ultratrace As analysis in surface water samples. Moreover, few UVG-AFS methods in previous studies can be employed in the real analysis of surface water samples, likely due to poor conversion efficiency and analytical sensitivity.

In this work, a new method is developed to determine ultratrace iAs in surface water samples using ferric chloride as an enhancement reagent for UVG-AFS. To optimise the working conditions, different LMWOAs, ultraviolet irradiation times, ferric chloride concentrations, and Ar/H_2 carrier gas flow rates were investigated. Subsequently, the UVG enhancement mechanism of ferric chloride and potential interferences from other ions were also studied. Furthermore, the recommended method was used to determine ultratrace iAs in real samples including tap water, river water, lake water samples, and certified reference materials (CRMs).

2. Experimental

2.1 Instrumentation

A commercial atomic fluorescence spectrometer (AFS-8220, Beijing Titan Instrumental Co., Ltd., Beijing, China) fitted with an arsenic high intensity hollow cathode lamp (HCL, Beijing Research Institute of Nonferrous Metals, Beijing, China) was used. The operational parameters were in accordance with the manufacturer. A flow injection system with an AFS detector was assembled in this work comprising a peristaltic pump (PP), a photo chemical reactor (PCR), a primary gas-liquid separator (PGLS), a secondary gas-liquid separator (SGLS), and so on. A schematic diagram of the system is shown in Fig. 1.

In addition, a commercial instrument of high performance liquid chromatography atomic fluorescence spectrometry (HPLC-AFS) for elemental speciation analysis (AFS-SA-20, Beijing Titan Instrumental Co., Ltd., Beijing, China) coupled with a C_8 chromolith (100×4.6 mm(i.d.), 5 μm) purchased from Merck Millipore (Billerica, MA, USA) was used to measure the reduction of As(V).

2.2 UV reactor

For high-efficiency ultraviolet irradiation, a 19 W low pressure mercury discharge lamp (LPML) (Beijing Titan Instrumental Co., Ltd., Beijing, China) was employed as the PCR, which was different to conventional ultraviolet lamps in terms of structure.[33] A synthetic quartz tube (0.8 mm i.d. × 1.0 mm o.d., 880 mm length) was sintered into the body of a LPML, and the sample solution could be irradiated around 360° by 185 nm UV-light.

The working procedure of the UVG system is as follows: Step 1, the sample solution was introduced into the PCR by the PP via a polytetrafluoroethylene (PTFE) tube in 7 s and irradiated by UV-light for different time periods; Step 2, the solution was pumped into a PGLS, and the volatile As species was separated from the solution at the distribution plate (DP) by a carrier gas (CG); Step 3, the volatile As species were passed through a SGLS and mixed with a drying gas (DP) to remove water vapour; Step 4, the volatile As species was transported into the AF detector to be determined. The optimal instrumental parameters for UVG-AFS are listed in Table 1.

2.3 Reagents and samples

All chemicals were guarantee reagent and purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China) unless otherwise stated in this work. Standard stock solutions (100 mg/L) of arsenic (III) and arsenic (V) were purchased from the National Research Center for Certified Reference Materials (NRCCRM) (Beijing, China), and diluted as required. Simulated natural water samples of CRMs containing arsenic including GSB-Z50004-200431, GBW08605 and GBW(E)080390 were also purchased from NRCCRM. Mixed solutions of acetic acid and formic acid was diluted with deionized (DI) water (Milli-Q Integral Water Purification System, Millipore, Billerica, MA, USA). Tap water, river water, and lake water samples were collected from Beijing, and preserved using 0.2% H_2SO_4 (v:v). The cation exchange column (Cleanert SCX SPE) was obtained from Bonna-Agela Technologies (Tianjin, China), and activated using a 10% NaCl solution to remove transition metals, including Cu(II), Co(II), and Ni(II), prior to use.

2.4 Sample preparation

The recommended method for the determination of iAs was verified by using CRMs (GSB-Z50004-200431, GBW08605 and GBW(E)080390), in comparison to real surface water samples including tap water, river water, and lake water. Real water samples were filtered through a 0.22 μm membrane, and then treated using a cation exchange column (Cleanert SCX SPE). Due to that the response of As(V) was largely less than that of As(III) at the same condition of UVG-AFS, the pre-reduction of As(V) to As(III) was performed to avoid the under-estimation of iAs concentration. Approximately 50 mL of a treated water sample was mixed with 20 mL of acetic acid, 4 mL of formic acid, and 0.5 mL of a 1.0 g/L sodium thiosulfate solution stepwise into a 100 mL volumetric flask, and diluted to 100 mL with DI water. Subsequently, the flask was kept in a water bath at 70 ^{o}C for 2 h to obtain a sufficient reduction reaction. After cooling to ambient temperature, 2.5 mL of the solution from the flask was diluted to 10 mL using the mixed acid, and then subjected to the UVG-AFS technique.

3. Results and discussion

3.1 Selection of the UVG reagent

The UVG was strongly dependent on the LMWOA reagents. To obtain the highest UVG efficiency, acetic acid, formic acid, and their mixture were tested using a 100 μg/L As (III) solution and irradiated with UV for 30 s. The results are shown in Fig. 2-A. It was found that the AF intensities using formic acid were higher than those using acetic acid, which differed significantly from a previous report.[24] These findings likely result from the co-generation of Fe and As, and this is discussed in detail in Section 3.3 of this paper. However, the responses using formic acid or acetic acid alone were both too weak to measure ultratrace iAs in environmental water samples. In comparison, the UVG efficiencies were significantly enhanced by mixing the organic acids when compared with using formic acid or acetic acid alone. As shown in Fig. 2-B, the relative intensity was significantly increased at higher formic acid concentrations in solutions containing 20% - 40% acetic acid, irrespective of the acetic acid concentration. The maximum response was obtained when the volume fraction of formic acid in the mixed acid was 3% - 4%; while concentrations exceeding 4% formic acid resulted in a decreased intensity. As a result, the optimum concentration of the UVG reagent for this system was 20% acetic acid combined with 4% formic acid.

To investigate the reaction mechanism of LMWOA with arsenic, the UV absorption signals of different mixtures of As(III), formic acid and acetic acid were measured by the UV spectrophotometer, and the result was shown in Fig. 3. In the Fig. 3, the UV absorption peaks of every LMWOA with 50 μg/L As(III) were obviously higher at ~185 nm and ~210 nm than those of only LMWOA medium without arsenic, except formic acid. However, the UV absorption intensity of As(III) was very weak compared to the solutions containing LMWOA. Hence, the increase of UV absorption intensities of acetic acid and mixed acid with arsenic was not due to free arsenic ions but possible complexes of LMWOA with arsenic. On the other hand, the UV absorption peaks of the mixed acid with arsenic at ~185 nm and ~210 nm were greatly higher than those of acetic acid with arsenic or arithmetic sum of formic acid with arsenic and acetic acid with arsenic, which was probably the reason of the strongest UVG capability in the mixed acid for arsenic.

3.2 Effects of irradiation time

The irradiation time is one of the crucial factors that impact the UVG efficiency of arsenic. To optimise the irradiation time, 100 μg/L of As(III) was measured using the UVG-AFS system. As shown in Fig. 4, the UVG efficiency rose sharply with increasing irradiation time in the range from 5 to 20 s; a response plateau was obtained from 20 to 35 s; however, exceeding an irradiation of 35 s may lead to the decomposition of the volatile arsenic species, which is indicated by the observed decrease of the AFS response with increasing irradiation time. Considering the efficiency and stability of the UVG reaction, an optimal UV irradiation time of 30 s was ultimately chosen for the following experiments.

3.3 Effect of ferric ions on UVG efficiency

In this work, the effects of ferric ions including Fe^{3+}, Fe^{2+}, and $Fe(CN)_6^{3-}$ as enhancement reagents on the UVG efficiency were investigated using a 100 μg/L As (III) solution. As shown in Fig. 5, in absence of ferric ions in the reaction system, a weak AFS response was obtained, which was less than one tenth of the highest response at the optimal Fe^{3+} and Fe^{2+} concentrations. On increasing the ferric ion concentration from 0 to 9 mg/L, the UVG efficiencies went up rapidly. Increasing the concentration of ferric ions further from 9 to 18 mg/L resulted in a plateau in the AFS response for each ferric ion examined; the optimal concentration of Fe^{3+} and Fe^{2+} were 12 to 15 mg/L, and 9 to 12 mg/L, respectively. However, the optimal UVG efficiency of $Fe(CN)_6^{3-}$ was significantly lower than that of the ferric cations, which may be attributed to a lower free ferric ion concentration due to the very high stability of the $Fe(CN_6)_3^-$ complex. These results imply that free ferric ions or unstable ferric complexes, rather than elemental iron, are the real crucial factors for UVG enhancement. Ferric ions concentrations exceeding 15 mg/L resulted in a decreased UVG efficiency as expected. Because the UV absorption of Fe was greatly stronger than that of the LMWOAs, when ferric existed in the LMWOA medium, the UV absorption intensity from Fe could take an absolute predomination. Furthermore, the more ferric in the medium, the more UV irradiation they consumed. Hence, when the ferric concentration was more than 15 mg/L, the excessive UV irradiation consumption from ferric might lead to a decrease of UVG efficiency for arsenic. This was probably the reason that more than 15 mg/L of ferric resulted in the decrease of AFS signals for arsenic. Therefore, a 15 mg/L Fe^{3+} solution was chosen as the optimal enhancement reagent in this work due to the instability of reagents containing Fe^{2+} in common use.

According to a previous study,[24] the UVG efficiency of As (III) in acetic acid systems in the absence of ferric cations was higher than that in formic acid. However, the opposite result (in Fig. 2 - A) was obtained in this work in presence of ferric cations in this UVG reaction system. This behavior may be owed to the formation of iron pentacarbonyl in the presence of formic acid, which was the main volatile iron species generated by UV photolysis.[14] Furthermore, in the interference studies in Table 2, more than 30 mg/L Cu^{2+} caused severe interferences in the presence of ferric cations, where the UVG of arsenic was severely weakened even to zero. To investigate the effects of Cu^{2+} on the UVG enhancement of arsenic, a trial was performed to measure the arsenic AFS signals after UVG using 10 and 30 mg/L of copper without ferric, respectively. The arsenic recovery was 93% using 10 mg/L copper without ferric, while the recovery was only 72% using 30 mg/L copper. It was showed that the UVG of arsenic was not severely interfered by copper in the absence of ferric. However, it was proved by experiments that Cu^{2+} had a severe decrease on the UVG of ferric. Therefore, the above mentioned findings were both likely due to the co-generation of iron and As (III) in a formic acid medium.

3.4 Effect of the carrier gas flow rate

The efficiency of the gas liquid separation, vapour transportation, and duration of the volatile arsenic species in the AFS atomiser were significantly influenced by the carrier gas flow rate. In this work, the effect of the flow rate of the argon and hydrogen mixture (v:v = 9:1) was investigated using 100 μg/L As(III) in a 15 mg/L Fe^{3+} acidic medium. In Fig. 6, prior to 100 mL/min, the AFS response increased significantly as the carrier gas flow rate increased. Furthermore, a flow rate of more than 150 mL/min caused the dilution of the analyte in the carrier gas and shorter durations in the atomiser, resulting in decreasing AFS responses with an increasing carrier gas flow rate. Although a carrier gas flow rate of 50 mL/min to 150 mL/min demonstrated the highest AFS responses, their spectrograms showed severe tailed peaks leading to poor quantification of the peak areas. The AFS responses obtained using a flow rate from 200 mL/min to 300 mL/min reached a plateau, and the relative standard deviations (RSD) were kept at a minimum. Consequently, a flow rate of 200 mL/min was chosen as the optimum Ar/H_2 flow rate in this work.

3.5 Pre-reduction of As(V)

In the UVG reaction system, only As(III) volatile species could be enhanced by the presence of ferric ions, rather than As(V). In Table 3, the response of As(V) was less than 7% of that of As(III) at the same condition of UVG-AFS. As such, the pre-reduction of As(V) was inevitable to measure the total iAs. The UVG of As(III) was attributed to the free radicals generated by photoredox reactions in the LMWOA medium, which differed significantly compared with the

HG reaction. As a result, the frequently used reductants for As(V) in the HG system, such as potassium iodide, thiourea, ascorbic acid, and L-cysteine, were infeasible because of severe interference. In this work, 5 mg/L to 10 mg/L sodium thiosulfate was attempted to reduce 500 μg/L As(V) to As(III) at 70 °C for 100 min. The reduction efficiency was approximately 95% as confirmed by HPLC-AFS analysis, which could satisfy the demands for iAs analysis. At the same time, there was no obvious conversion of As(III) to As(V) for this UVG reaction system, which was also proved by HPLC-AFS analysis of arsenic species after the UVG reaction of As(III). The As(III) recovery is more than 93%, while As(V) is little. Therefore, As(V) was reduced to As(III) in the presence of 5 mg/L sodium thiosulfate in 20% acetic acid and 4% formic acid at 70 °C for 100 min.

3.6 Interference study

In this work, the interference from potential coexisting elements were investigated using 50 μg/L As(III) under the recommended conditions. As shown in Table 2, most of the ions and substances examined had no significant impact on the As(III) volatile species in the UVG system, other than some transition metals including Cu^{2+}, Co^{2+}, and Ni^{2+}. To remove the Cu^{2+}, Co^{2+}, and Ni^{2+}, a cation exchange column (Cleanert SCX SPE) was employed before introducing the water samples into the UVG system. As a result, there was no significant interference from potential coexisting ions and substances in most of surface water samples for UVG-AFS by the recommended method, in consideration of a quite low concentration of organic arsenic species, NO_3^-, NO_2^-, Br^- or H_2O_2 in most of real samples. Whereas, the recommended method is not fit for the determination of inorganic arsenic in water samples rich in organic arsenic species, such as water samples contaminated by animal manure. On the other hand, to avoid the interferences from high levels of NO_3^- and NO_2^-, we employed the 0.2% (v/v) H_2SO_4 to preserve the water samples for this method, due to no interference of SO_4^{2-} on the UVG of arsenic in this system. Otherwise, the water samples with a high level of NO_3^- or other interferences should be measured after diluting to an appropriate concentration.

3.7 Analytical figures of merit and real sample analysis

Under the optimised conditions, the analytical figures of merit were evaluated. The linearity of the calibration curve was investigated by measuring a series of standard solutions ranging from 0.5 μg/L to 100 μg/L, and the linear regression coefficient (R^2) was 0.999. The LOD of iAs for this method was 0.05 μg/L, calculated by taking 3 times the standard deviation of the blank solution divided by the sensitivity (i.e., the slope) from 11 measurements. The RSD of the 25 μg/L iAs standard solution from 11 measurements was within 2.0%, demonstrating a good analytical precision. In addition, to compare the recommended method with others reported in previous studies, the analytical figures of merit of the flow injection HG-AFS (FI-HG-AFS), conventional HG-AFS, and other UVG-AFS methods are also listed in Table 4. Among these four methods, besides a good precision, the recommended UVG-AFS method possessed the lowest LOD, which was only one tenth that of the previous UVG-AFS method.[24]

To verify the recommended method, some real samples including tap water, river water, lake water, and CRMs of GSB-Z50004-200431, GBW08605 and GBW(E)080390 were determined for iAs. As shown in Table 5, the spiked recoveries of tap water, river water, and lake water were 92% to 98%, and the measured value of the GSB-Z50004-200431, GBW08605 and GBW(E)080390 samples were in good agreement with the certified values. In summary, the established UVG-AFS method in this work could be used to determine ultratrace iAs sensitively, accurately, and precisely in surface water samples without organic arsenic, NO_3^-, NO_2^-, Br^- or H_2O_2 at high levels.

4. Conclusion

A novel and sensitive method was developed for the accurate and precise determination of inorganic arsenic in surface water samples using Fe^{3+} ion-assisted UVG in a 20% acetic acid and 4% formic acid medium coupled with an AFS detector. The established method provided a method LOD of 0.5 μg/L for inorganic arsenic, and a 10-fold enhancement in the method LOD was realized compared with the previous UVG-AFS method.[24] In contrast with the conventional HG-AFS method, the recommended method is simpler, with a smaller blank, and lower reagent consumption. Although only some indirect evidence has been obtained, the mechanism of the UVG using ferric cations is not fully understood, and further investigations should be performed in the future. On the other hand, the method may be to some extent interfered by organic arsenic species and NO_3^- at high levels. Despite all that, due to the simplicity, safety and portability of the UVG coupled with a miniaturised AFS compared to HG-AFS, the established method has great potential for the analysis of ultratrace inorganic arsenic in a variety of real surface water samples, especially for on-site analysis.

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Table 1 Optimal instrumental parameters for UVG-AFS.

Parameters of UVG-AFS	Values
Lamp current (total/main) / mA	80/40
Voltage of PMT / V	-300
Concentration of formic / acetic acid / %	20/4
Irradiation time / s	30
The concentration of Fe^{3+} / mg/L	15
Pre-reduction temperature / ^{o}C	70
Pre-reduction time / min	100
Flow rate of carrier gas / mL/min	200
Flow rate of shield gas / mL/min	700
Flow rate of drying gas / mL/min	200

Table 2 The effect of coexisting substances.

Interfering ions	Concentration / mg/L	Recovery / %	Recovery using SPE / %
Na^+	800	96	—
Mg^{2+}	200	98	—
K^+	400	98	—
Ca^{2+}	200	98	—
Zn^{2+}	300	100	—
Cu^{2+}	30	-10, 72[a], 93[b]	103
Co^{2+}	30	8	98
Ni^{2+}	30	14	97
Cl^-	400	97	—
SO_4^{2-}	1600	96	—
NO_3^-	30	95	—
	50	89	—
	100	82	—
NO_2^-	30	98	—
	50	76	—
PO_4^{3-}	100	104	—
Br^-	10	97	—
	50	54	—
H_2O_2	10	99	—
	50	52	—
$Na_2S_2O_3$	2.5	98	—

[a & b] means the arsenic recoveries using 10 mg/L and 30 mg/L of Cu^{2+} in absence of ferric, respectively.

Table 3 The relative responses of all arsenic species by UVG-AFS

Species [a]	As(III)	As(V)	MMA	DMA
Relative response (%)	100	6.6	12.2	73.1

[a] The concentrations of arsenic species are all 100μg/L, respectively, of which the response of As(III) is set as 100%.

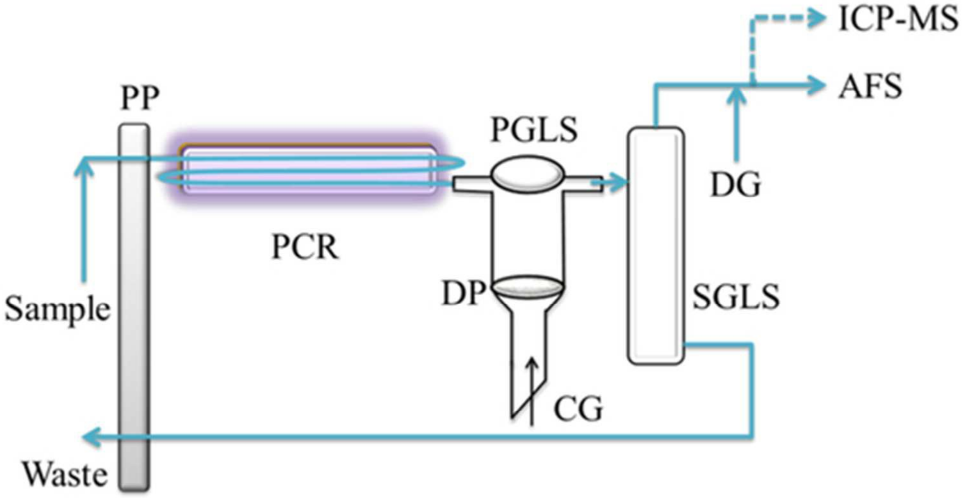
Table 4 Analytical figures of merit of the UVG-AFS methods in comparison with those for similar CVG-AFS methods.

	FI-HG-AAS	HG-AFS	UVG-AFS	
LOD / μg/L	0.5 (As(III))	0.1	0.5	0.05
R^2	0.9878	0.9991	0.9991	0.9994
RSD / %	<2	0.8	1.2	2.0
Reference	[34]	[24]	[24]	This work

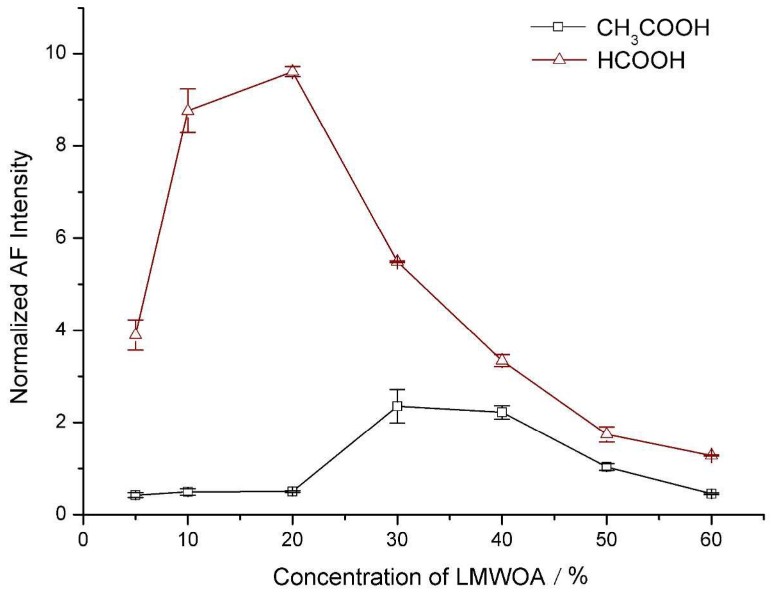
Table 5 Spiked recoveries of total inorganic arsenic in water samples.

Samples	Measured[a], μg/L	Added, μg/L	Found[a], μg/L	Recovery, %
Tap water	ND[b]	10.0	9.2 ± 0.4	92
River water	8.1 ± 0.3	10.0	17.5 ± 0.6	94
Laker water	15.1 ± 0.2	10.0	24.9 ± 0.3	98
GSB-Z50004-200431[c]	58.9 ± 2.5	—		
GBW08605[d]	502 ± 6	—		
GBW(E)080390[e]	491 ± 8	—		

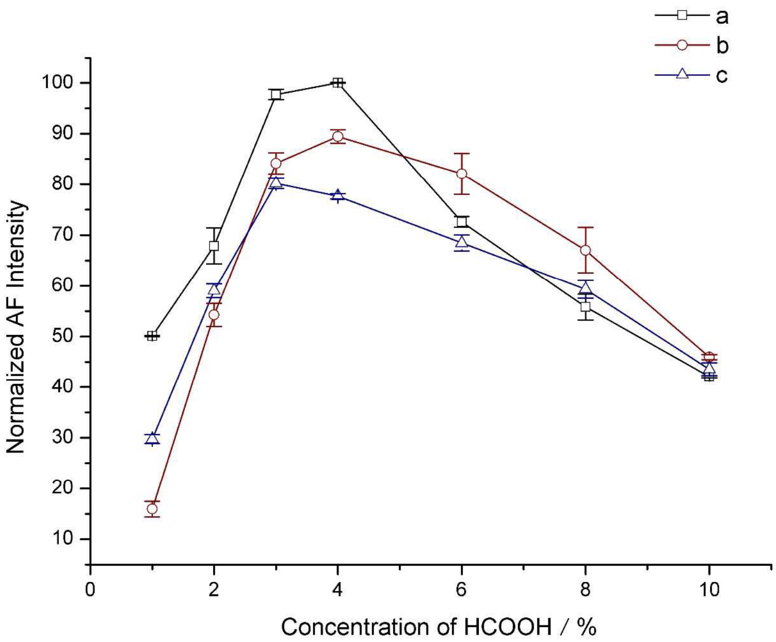
[a] Mean value and standard deviation (n = 3). [b] ND, not detected. [c] Certified value: 60.6 ± 4.2 μg/L. [d] Certified value: 0.500 ± 0.008 μg/g. [e] Certified value: 0.50 ± 0.02 mg/L.



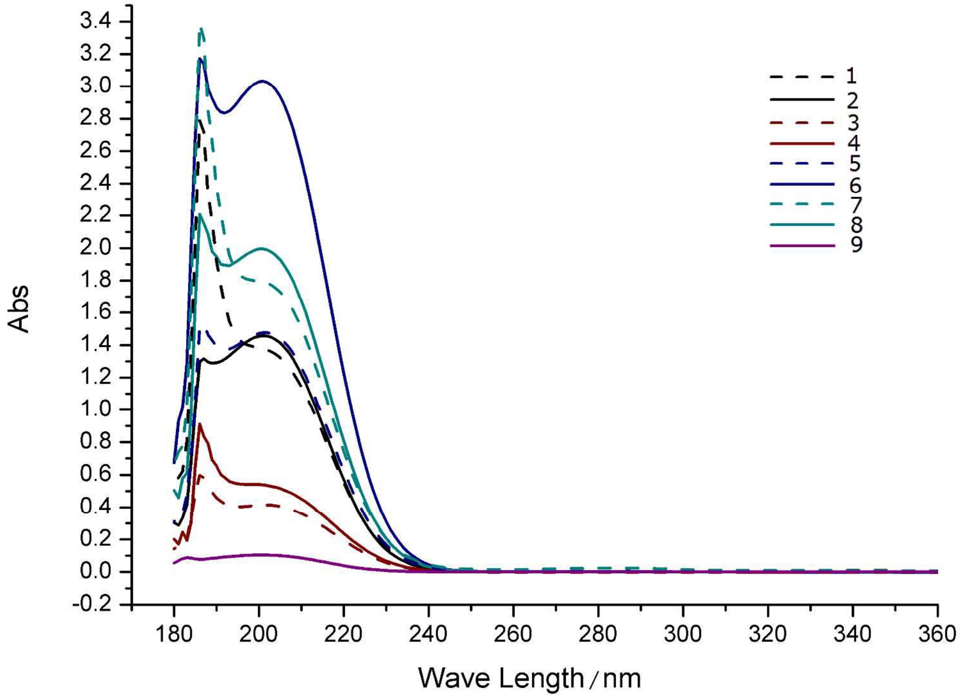
47x25mm (300 x 300 DPI)



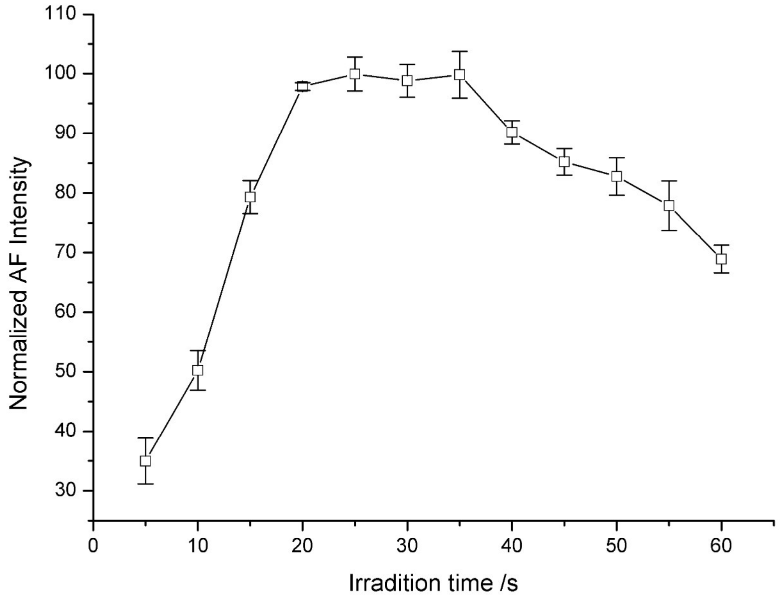
297x210mm (300 x 300 DPI)



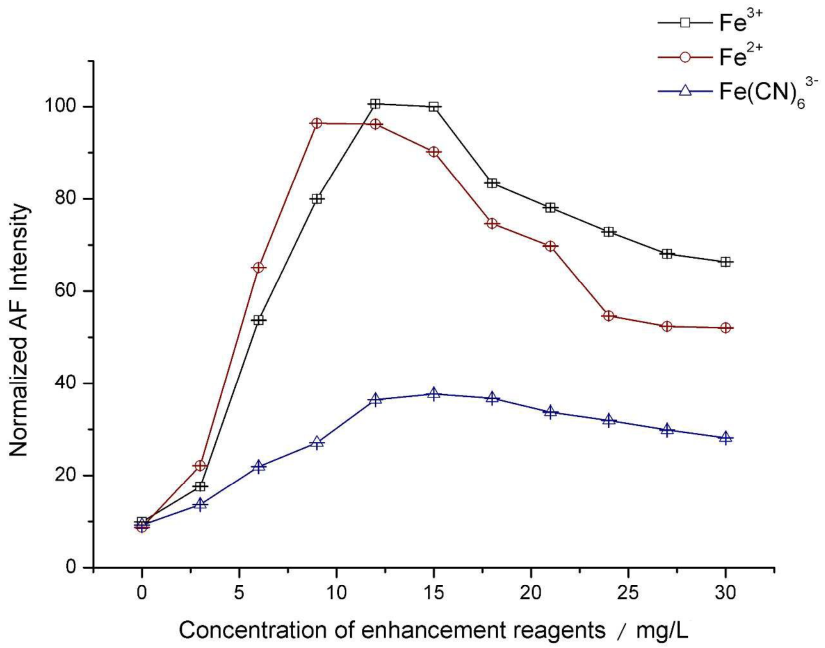
297x210mm (300 x 300 DPI)



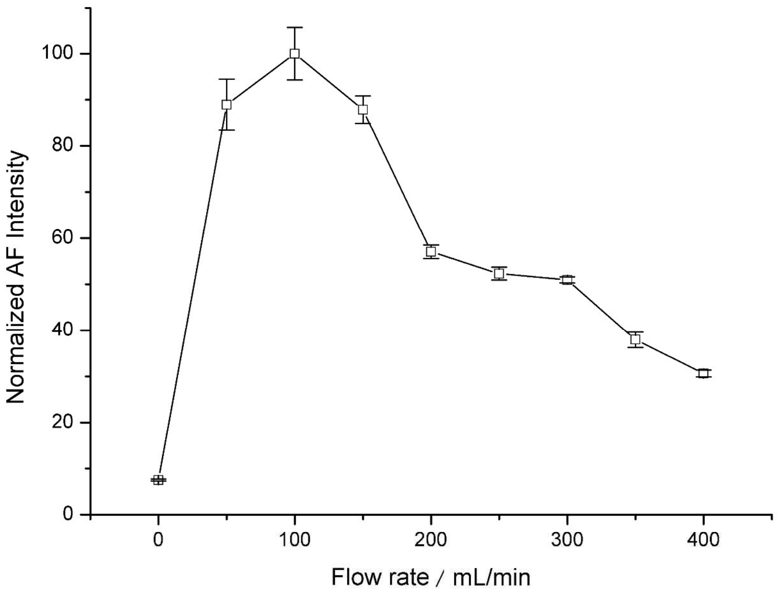
251x187mm (300 x 300 DPI)



297x210mm (300 x 300 DPI)



297x210mm (300 x 300 DPI)



297x210mm (300 x 300 DPI)