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CONTENTS

A novel colorimetric method for field arsenic speciation analysis

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Abstract

Accurate on-site determination of arsenic (As) concentration as well as its speciation presents a great environmental challenge especially to developing countries. To meet the need of routine field monitoring, we developed a rapid colorimetric method with a wide dynamic detection range and high precision. The novel application of $KMnO_4$ and CH_4N_2S as effective As(III) oxidant and As(V) reductant, respectively, in the formation of molybdenum blue complexes enabled the differentiation of As(III) and As(V). The detection limit of the method was 8 μg/L with a linear range ($R^2 = 0.998$) of four orders of magnitude in total As concentrations. The As speciation in groundwater samples determined with the colorimetric method in the field were consistent with the results using the high performance liquid chromatography atomic fluorescence spectrometry, as evidenced by a linear correlation in paired analysis with a slope of 0.9990–0.9997 ($p < 0.0001$, $n = 28$). The recovery of 96%–116% for total As, 85%–122% for As(III), and 88%–127% for As(V) were achieved for groundwater samples with a total As concentration range 100–800 μg/L. The colorimetric result showed that 3.61 g/L As(III) existed as the only As species in a real industrial wastewater, which was in good agreement with the HPLC-AFS result of 3.56 g/L As(III). No interference with the color development was observed in the presence of sulfate, phosphate, silicate, humic acid, and heavy metals from complex water matrix. This accurate, sensitive, and easy-to-use method is especially suitable for field As determination.

Key words: arsenic speciation; colorimetric method; groundwater; field analysis

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Introduction

Naturally occurring arsenic (As) has been promulgated with the greatest exposure in developing countries including Bangladesh, India, Vietnam, and China where groundwater As concentrations are at as high as several mg/L level (Nordstrom, 2002). Until 2010, over 100 million people are still drinking untreated groundwater with As concentrations far exceeding the World Health Organization (WHO) guideline of 0.13 μmol/L (10 μg/L) (Fendorf et al., 2010) . The toxicity and mobility of As depend on its oxidation state where arsenite (As(III)) is 50-100 times more toxic than arsenate (As(V)). Nevertheless, As(III) is the dominant As species in most groundwater samples and can be readily oxidized to As(V) upon exposure to air (Meng et al., 2003). Thus, the As(III) oxidation reactions may happen during the sample collection, storage, and transferring to the laboratory, and could lead to biased conclusions about the toxicity. Therefore, accurate rapid *in situ* speciation analysis is of great importance.

Powerful methods of detecting low concentrations of As(III/V) are generally established with sophisticated laboratory instrumentation. The most popular speciation analysis combines an effective separation using high per-

formance liquid chromatography (HPLC) with an adequate element-specific detector such as mass spectrometry (MS) and atomic fluorescence spectrometry (AFS). However, these instruments are not designed for field application. It is an urgent need to develop effective *in situ* speciation method with affordable equipments for routine environmental monitoring (Liao and Deng, 2006).

The colorimetric As analysis has become the most practical technique for field application. One of the widely used colorimetric As analyses is based on the Gutzeit's method. A recent development of the Gutzeit's method is the As field testing kits. However, the kits failed in a high fraction (up to 68%) when analyzing groundwater samples (Arora et al., 2009; Rahman et al., 2002). In addition, the Gutzeit's method generates highly toxic arsine gas that requires specific protective equipments to practice this assay.

The As molybdenum blue method, another commonly used field As analysis technique, is based on the fact that As(V) can form molybdenum blue complexes with reduced molybdate while As(III) could not (Johnson, 1971; Johnson and Pilson, 1972). Researchers optimized the method to reach a detection limit of 7 μg/L with a mean recovery of total As of 97% ± 5% in a total As range 10–1000 μg/L (Dhar et al., 2004). However, the reducing

reagent used in previous studies (14% $Na_2S_2O_5$ + 1.4% $Na_2S_2O_3$ + 10% H_2SO_4) generates highly toxic SO_2 gas (Johnson, 1971; Johnson and Pilson, 1972; Dhar et al., 2004). Tsang et al. (2007) attempted to modify the reducing reagent and used sodium dithionite to reduce 7–75 μg/L As(V) in neutral samples. Nevertheless, this narrow linear range and complication in operation limit its field application. The other limitation in previous molybdenum blue method is the usage of KIO_3 as oxidant which could inhibit molybdate reduction (Dhar et al., 2004).

The objective of this study was to develop a rapid colorimetric method for routine analysis of As speciation in environmental samples. In the present report, we compared and proposed the oxidants and reductants based on the molybdenum blue complexes to differentiate As species. To explore the possible interference from the complex matrix of environmental samples to the colorimetric method, natural groundwater and industrial wastewater samples were analyzed and the results were compared with the high-performance liquid chromatography coupled with atomic fluorescence spectrometry (HPLC-AFS). The proposed method with a portable spectrophotometer provides a reliable and affordable approach for *in situ* determination of As concentration and speciation.

1 Materials and methods

1.1 Materials

All reagents were of analytical reagent grade and used without further purification. Potassium iodate (KIO_3, >99.0%), potassium permanganate ($KMnO_4$, >99.5%), sodium hypochlorite (NaClO, >9%), monopotassium phosphate (KH_2PO_4, >99.5%), sodium thiosulfate (Na_2SO_3, >97.0%), sodium pyrosulfite ($Na_2S_2O_5$, >96.0%), hydrochloric acid (HCl, >36%), and sulphuric acid (H_2SO_4, >95.0%) were obtained from Beijing Chemicals Corporation (China); sodium arsenate ($Na_3AsO_4 \cdot 12H_2O$, >99.0%), sodium arsenite ($NaAsO_2$, >99.8%), ascorbic acid ($C_6H_8O_6$, >99.7%), ammonium molybdate ((NH_4)$_6Mo_7O_{24} \cdot 4H_2O$, >99.0%), antimony potassium tartrate ($C_4H_4O_6KSbO \cdot 1/2H_2O$, >99.0%), potassium iodide (KI, >99.0%), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, >98.5%), hydrazine hydrate ($N_2H_4 \cdot H_2O$, 50%), thiourea (CH_4N_2S, >99.0%), stannous chloride ($SnCl_2$, >98.0%), sodium sulfide (Na_2S, >98.0%), and sodium citrate ($C_6H_5O_7Na_3 \cdot 2H_2O$, >99.0%) were from Beijing Chemical Reagents Company (China). Milli-Q water was used in all experiments.

Groundwater samples were collected in Shanxi, China. The samples were passed through a 0.45-μm syringe filter for soluble As analysis. Subsamples were acidified with HCl for As speciation analysis using HPLC-AFS (Jitian, China) in the laboratory. Soluble metals (Al, Ca, Mg, Na, K, Si, total Fe, and Mn) and anions (F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$) were determined using an inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer, USA) and an ion chromatography DX-1100 (Dionex, USA), respectively. All samples were stored at

4°C until analysis.

The industrial wastewater sample was obtained from a copper smelting company in China. The wastewater was highly contaminated with 3.56 g/L As(III), 24 mg/L Cu, 5 mg/L Pb, 369 mg/L Cd, and 0.28 mol/L SO$_4^{2-}$ at pH 1.4 (Luo et al., 2010).

1.2 Procedure of As colorimetric method

Briefly, 30 mL samples were acidified with 1% HCl and 10 μmol/L phosphate. Three parallel 10 mL sub-samples were treated with 1 mL of an oxidizing reagent (Oxidized sub-sample), a reducing reagent (Reduced sub-sample), and deionized (DI) water (Untreated sub-sample), respectively. After 30 min, 1 mL color reagent was added which is a mixture of 10.8% $C_6H_8O_6$, 3% (NH_4)$_6Mo_7O_{24} \cdot 4H_2O$, 0.56% $C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$, and 13.98% H_2SO_4 in a volume ratio 2:2:1:5. The absorbance was measured after 5 min using a portable single-beam Hach DR2800 spectrophotometer at 880 nm. The As(III) and As(V) concentrations were calculated using following equations:

Total As = As$_{oxidized}$ − As$_{reduced}$

As(III) = As$_{oxidized}$ − As$_{untreated}$

As(V) = As$_{untreated}$ − As$_{reduced}$

1.3 Selection of oxidant

Three oxidizing reagents (NaClO, $KMnO_4$ and KIO_3) were selected as potential oxidant because they do not interfere the process of formation of molybdenum blue complexes (Lenoble et al., 2003). To compare the oxidation kinetics using $KMnO_4$, NaClO, and KIO_3, experiments were carried out by reacting 1 L of 500 μg/L As(III) with 0.3 mmol/L oxidant. The solution was mixed vigorously and samples were taken at designated time intervals for As speciation analysis. As(III) and As(V) were separated immediately after collection using As speciation cartridges as described in our previous report (Jing et al., 2003). The cartridges selectively removed As(V) but did not adsorb As(III). The As concentration was then determined using a graphite furnace atomic absorption spectrometer (AAS-800, Perkin Elmer, USA).

1.4 Selection of reductant

In order to optimize the reducing reagent, 11 reductants including Johnson's reducing agent (14% $Na_2S_2O_5$ + 1.4% $Na_2S_2O_3$ + 10% H_2SO_4) (Johnson and Pilson, 1972), $C_6H_8O_6$, KI, $NH_2OH \cdot HCl$, $N_2H_4 \cdot H_2O$, CH_4N_2S, $SnCl_2$, Na_2SO_3, $Na_2S_2O_5$, Na_2S, and $C_6H_5O_7Na_3 \cdot 2H_2O$ were tested and compared. Experiments were carried out by reacting 10 mL 1000 μg/L As(V) sample with 1 mL different concentrations of reducing reagent. Then, one group of the mixtures was incubated at room temperature for an hour to facilitate As(V) reduction, the other group was placed in a water bath at 80°C for 30 min. After samples were cooled to room temperature, 1 mL color reagent was added and the absorbance was measured.

1.5 Accuracy comparison between colorimetric method and HPLC-AFS

The As speciation results obtained with the proposed colorimetric method was compared with those using HPLC-AFS. Separation of As compounds was carried out in a Hamilton PRP-X100 anion exchange column, using 15 mmol/L phosphate buffer at pH 6 as mobile phase at 1.0 mL/min flow rate. Following the separation of different As species, online hydride generation was achieved by reacting with 1.5 wt.% KBH$_4$ and 7 wt.% HCl. The hydride was atomized in a hydrogen flame and the fluorescence signal for each of the As species was recorded using an AFS-8130 spectrometry (Jitian, China).

2 Results and discussion

2.1 Optimization of oxidizing reagent

Figure 1a shows the change of absorbance as a function of KIO$_3$, KMnO$_4$, and NaClO concentrations. When concentrations of KMnO$_4$ and KIO$_3$ were increased to higher than 0.1 mmol/L, the absorbance reached a plateau at approximately 0.22 and remained unchanged with further increasing concentrations up to 5 mmol/L. The results indicate that 0.1 mmol/L KMnO$_4$ and KIO$_3$ could completely oxidize 1000 μg/L (0.013 mmol/L) As(III) to As(V). However, NaClO resulted in a significantly lower absorbance than that of KMnO$_4$ and KIO$_3$ (Fig. 1a), which could be attributed to the lower standard potential of NaClO ($E^° = 0.89$ eV) comparing to KMnO$_4$ (1.51 eV) and KIO$_3$ (1.14 eV) (Speight, 2005). Therefore, KMnO$_4$ and KIO$_3$ were selected for further kinetic studies at a 0.3 mmol/L concentration level to compensate for possible interferences from reducing materials such as sulfide in groundwater.

Figure 1b shows the kinetics of 500 μg/L As(III) oxidation by 0.3 mmol/L KMnO$_4$ and KIO$_3$. KIO$_3$ exhibited a great pH dependence as evidenced by a complete As(III)

oxidation in 5 min for acidified samples and an incomplete oxidation in 30 min without acidification (Fig. 1b). In stark contrast, KMnO$_4$ required no acidification, and As(III) was completely oxidized to As(V) in 2 min. The results suggest that KMnO$_4$ is a more efficient oxidant comparing to KIO$_3$. Furthermore, KMnO$_4$ has been used as an As(III) oxidant in groundwater treatment for its high efficiency and no dependence on pH values (Li et al., 2007). In addition, no interference to colorimetric As analysis was observed using KMnO$_4$, which is in agreement with a previous study (Lenoble et al., 2003). Therefore, 0.3 mmol/L KMnO$_4$ was used as oxidant regent in the proposed method.

2.2 Optimization of reducing reagent

Among the eleven tested reducing agents, N$_2$H$_4$·H$_2$O, Na$_2$SO$_3$, SnCl$_2$, Na$_2$S, and C$_6$H$_5$O$_7$Na$_3$·2H$_2$O interfered with the molybdenum blue color formation. Therefore, these five agents were excluded for further considerations.

Figure 2 shows the change of As(V) species as a function of concentrations of NH$_2$OH·HCl, KI, CH$_4$N$_2$S, C$_6$H$_8$O$_6$, and Na$_2$S$_2$O$_5$. None of the reagents could completely reduce As(V) to As(III) at room temperature (Fig. 2a), even though the concentrations of these reducing agents were increased up to 30% (mass ratio). Although Na$_2$S$_2$O$_5$ resulted in a slightly higher reducing capacity than other agents, it was excluded for further consideration because toxic SO$_2$ gas was generated as a byproduct. When the mixed solution was heated with an alcohol burner for 1 min and then cured at room temperature for 1 hr, none of the reagents could completely reduce 1000 μg/L As(V) to As(III) (Fig. 2b).

Because high temperature may be required for some reagents to fulfill their reducing abilities, the reducing step was incubated in a water bath at 80°C for 30 min. NH$_4$N$_2$S could completely reduce 1000 μg/L As(V) when its concentration was higher than 10% (Fig. 2c). Therefore, 10% NH$_4$N$_2$S was used as reducing reagent in the present method.
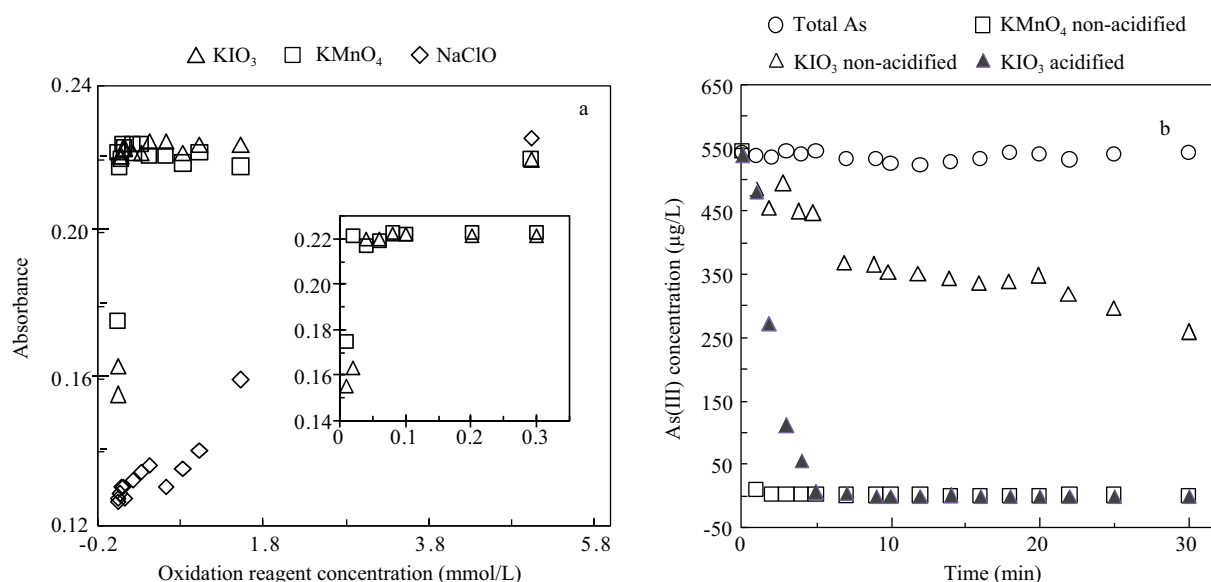

Fig. 1 Absorbance of 1000 μg/L As(III) as a function of KIO$_3$, KMnO$_4$, and NaClO concentration. Inset shows the absorbance with oxidation concentrations less than 0.3 mmol/L (a). Changes of As(III) concentration as a function of time when oxidized by KIO$_3$ and KMnO$_4$ (b).
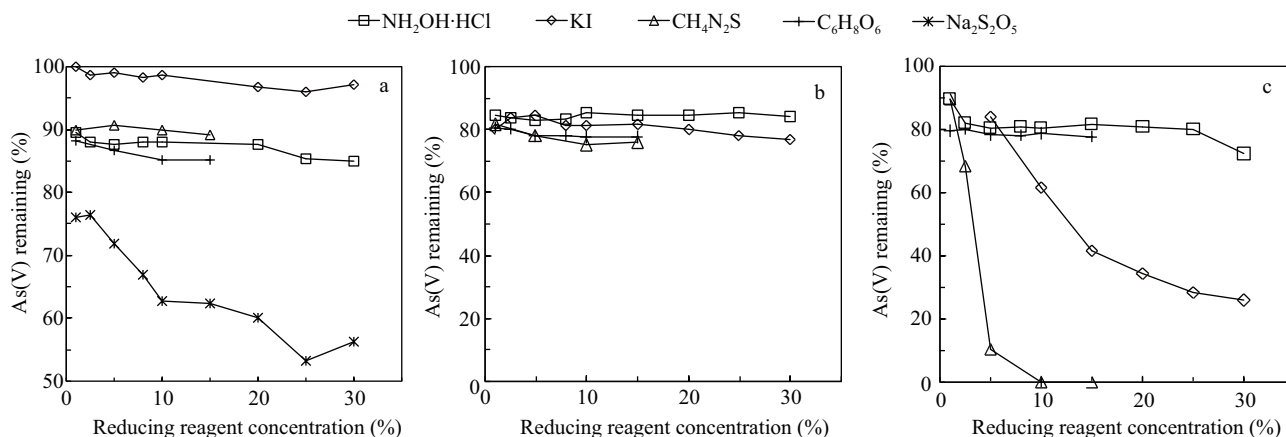
Fig. 2 Percentage of remaining As(V) concentrations in an initial 1000 μg/L As(V) sample as a function of reducing reagents under three conditions: at room temperature in an hour (a); heated with an alcohol burner for 1 min before color development at room temperature in an hour (b); and reacting in a water bath at 80°C for 30 min (c).
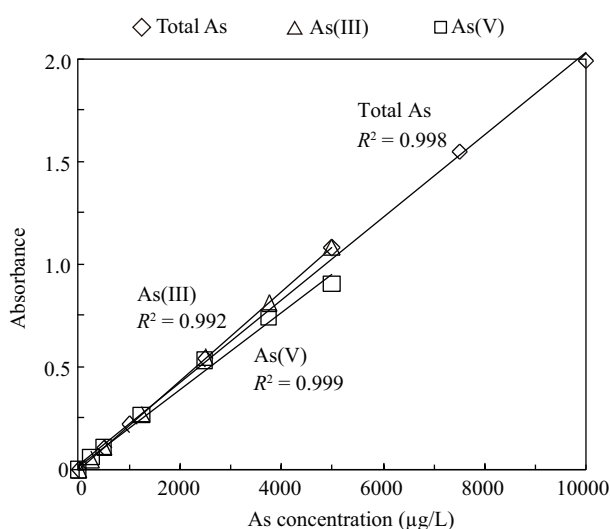
Fig. 3 Absorbance of total As, As(III), and As(V) as a function of As concentration.

2.3 Dynamic detection range

Figure 3 shows the linear dynamic detection range of total As, As(III), and As(V) using the present colorimetric method. A linear regression ($R^2 = 0.9979$) was achieved in four orders of magnitude concentration range (total As, 0.01–10 mg/L). The wider linear range increased from 2–220 (Johnson and Pilson, 1972) and 10–1000 μg/L (Dhar et al., 2004) to 10 mg/L enabled direct measurements of groundwater As concentrations in several mg/L level (Nordstrom, 2002) without sample dilution.

The method detection limit was estimated to be 0.1 μmol/L (8 μg/L) with seven repeated measurements of reagent blank containing 10 μmol/L phosphate, which is comparable to previous reported value of 0.09 μmol/L (7 μg/L) (Dhar et al., 2004).

2.4 Interferences of sulfate and humic acid (HA)

Because sulfate and dissolved organic matter (DOM) are commonly found in elevated concentrations in industrial and natural water samples, their possible interference to the color formation is critical to develop an effective colorimetric method. To study their effects, increasing amount of sulfate and HA, a representative DOM, were

added in the sample, and the absorbance of the three sub-samples in reduced, acidified, and oxidized forms were monitored as shown in Fig. 4. The absorbance in all three treatment samples proportionally increased with the increase of SO_4^{2-} concentrations (Fig. 4a), indicating the addition of SO_4^{2-} would lead to an increase in absorbance. However, the interference of SO_4^{2-} was eliminated by the subsequent subtraction calculations as shown in the experimental section. Furthermore, the absorbance difference remained unchanged for various As concentrations when SO_4^{2-} concentrations increased to 0.3 mol/L (Fig. 4b). In addition, no interference was observed with HA concentrations up to 10 mg/L (Fig. 4c). The results suggest that the novel colorimetric method is applicable for As analysis in high sulfate and DOM waters.

2.5 As determination in natural waters

Figure 5 shows the comparison of total As, As(III), and As(V) concentrations measured using the colorimetric method and HPLC-AFS for 28 groundwater samples collected from Shanxi Province, China. The soluble metals in the groundwater samples are Al (0.1–0.2 mg/L), Ca (3.6–219.8 mg/L), Na (40.0–946.4 mg/L), K (0.4–10.9 mg/L), Si (7.2–11.8 mg/L), Fe (0–0.35 mg/L), and Mn (0–1.2 mg/L). The soluble anions in the groundwater samples are F$^-$ (0.3–5.6 mg/L), Cl$^-$ (39.0–1644.5 mg/L), NO_3^- (0–20.0 mg/L), SO_4^{2-} (0.4–973.3 mg/L), and PO_4^{3-} (0.075–1.589 mg/L). The colorimetric results obtained in the field were consistent with the HPLC-AFS results with a slope in the range 0.998–1.026 ($p < 0.0001$).

Table 1 shows the recovery of total As, As(III), and As(V) in six groundwater samples spiked with 50 μg/L As(III) and As(V). A recovery of 96%–115% (total As), 85%–122% (As(III)), and 88%–127% (As(V)) was achieved for samples with total As concentration between 100–800 μg/L.

Some common constituents such as Fe, SiO_3^{2-}, PO_4^{3-}, and SO_4^{2-} may inhibit the application of molybdenum blue analysis (Geng and Zhu, 2006; Melamed, 2005). The substration procedure could eliminate the interference from complex groundwater matrix as evidenced by the good agreement with results of HPLC-AFS (Fig. 5). In

Table 1   Recovery analysis of total As, As(III), and As(V) in groundwater samples[a]

Sample	Total As			As(V)			As(III)		
	Raw (μg/L)	Spiked (μg/L)	Recovery (%)[b]	Raw (μg/L)	Spiked (μg/L)	Recovery (%)	Raw (μg/L)	Spiked (μg/L)	Recovery (%)
1	24	125	101	10	63	107	14	61	94
2	326	432	106	44	93	98	277	329	113
3	370	485	115	59	122	127	305	357	103
4	384	490	106	107	151	88	272	333	122
5	0	96	96	0	54	107	0	42	85
6	648	758	110	73	132	117	563	615	103

[a] All the samples was spiked with 50 μg/L As(III) and As(V); [b] Recovery = ((Spiked-Raw)/Spiked) ×100%.
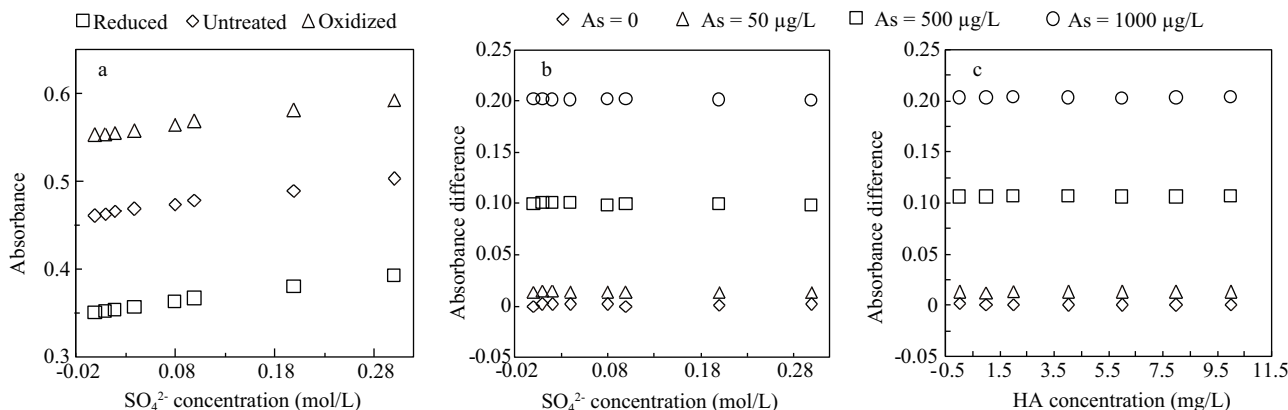
Fig. 4   Absorbance of reduced, untreated, and oxidized samples of 1000 μg/L total As (As(III):As(V) = 1:1) as a function of SO_4^{2-} concentration (a). Absorbance difference (oxidized-reduced) of total As (As(III):As(V) = 1:1) as a function of SO_4^{2-} (b), and HA (c) concentration.
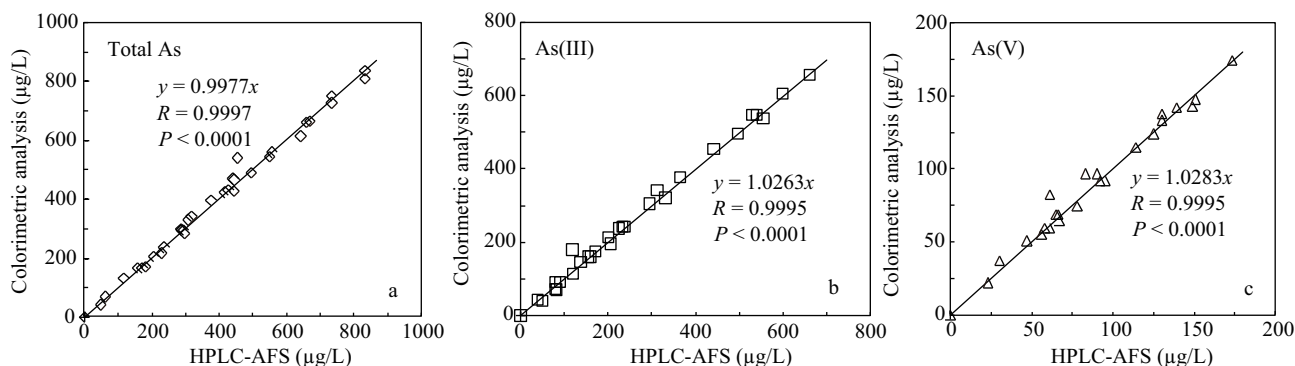
Fig. 5   Comparison of total As (a), As(III) (b), and As(V) (c) concentrations in groundwater samples determined by the present colorimetric method and HPLC-AFS.

addition, the great recovery further confirmed that no interference occurred with high concentrations of Si, Fe, and PO_4^{3-} in our groundwater samples.

To extend the usage of the colorimetric method, it was employed to determine As concentration and speciation in an industrial wastewater containing 0.28 mol/L SO_4^{2-} at pH 1.4. The colorimetric analysis showed that 3.61 g/L As(III) existed as the only As species in the sample, which was in good agreement with the HPLC-AFS result of 3.56 g/L As(III). The highly complex matrix of this copper smelting wastewater (Luo et al., 2010) further proved the versatile application and consistency of our method.

3 Conclusions

The As concentration and speciation determined using the colorimetic method are in line with the HPLC-AFS results

for the analysis of groundwater and industrial wastewater samples. Furthermore, the presence of phosphate, silicate, sulfate, humic acid, and other heavy metals in the water matrix could not interfere with the colorimetric analysis. In addition, the portable spectrophotometer used in the study is an inexpensive and versatile instrument which is suitable for a broad spectrum of analytical applications. Therefore, the present method offers an excellent choice in field As determination.

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