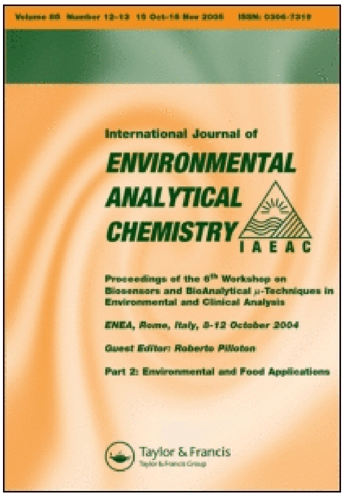

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Inorganic arsenic speciation in various water samples with GFAAS using coprecipitation

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A simple, economic and sensitive method for selective determination of As(III) and As(V) in water samples is described. The method is based on selective coprecipitation of As(III) with Ce(IV) hydroxide in presence of an ammonia/ammonium buffer at pH 9. The coprecipitant was collected on a 0.45 μm membrane filter, dissolved with 0.5 mL of conc. nitric acid and the solution was completed to 2 or 5 mL with distilled water. As(III) in the final solutions was determined by graphite furnace atomic absorption spectrometry (GFAAS). Under the working condition, As(V) was not coprecipitated. Total inorganic arsenic was determined after the reduction of As(V) to As(III) with NaI. The concentration of As(V) was calculated by the difference of the concentrations obtained by the above determinations. Both the determination of arsenic with GF-AAS in presence of cerium and the coprecipitation of arsenic with Ce(IV) hydroxide were optimised. The suitability of the method for determining inorganic arsenic species was checked by analysis of water samples spiked with 4–20 $\mu g\,L^{-1}$ each of As(III) and As(V). The preconcentration factor was found to be 75 with quantitative recovery ($\geq$95%). The accuracy of the present method was controlled with a reference method based on TXRF. The relative error was under 5%. The relative standard deviations for the replicate analysis ($n = 5$) ranged from 4.3 to 8.0% for both As(III) and As(V) in the water samples. The limit of detection (3σ) for both As (III) and As(V) were 0.05 $\mu g\,L^{-1}$. The proposed method produced satisfactory results for the analysis of inorganic arsenic species in drinking water, wastewater and hot spring water samples.

Keywords: speciation; arsenic; coprecipitation; GF-AAS

1. Introduction

Inorganic arsenic species, i.e. arsenite As(III) and arsenate As(V), are generally found in natural waters, while the organic arsenic species, such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA), are present in marine and other biological samples. Inorganic arsenic compounds are known to be more toxic than organic ones, and As(III) is appreciably more toxic than As(V) [1]. Arsenic is a multi-site carcinogen in humans, causing tumours in a variety of tissues including lung, skin and bladder. Arsenic in direct skin contact may cause redness and swelling.

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The WHO recommends a guideline level of $10\,\mu g\,L^{-1}$ for inorganic arsenic in drinking water. Recently, the Environmental Protection Agency lowered the maximum contaminant level for total arsenic in drinking water from 50 (set 70 years ago) to $10\,\mu g\,L^{-1}$ [2]. The current maximum limit for arsenic in natural waters is $10\,\mu g\,L^{-1}$ [3]. Hot water is able to dissolve minerals over time, so that elevated levels of metals and metalloids are often associated with hot springs. Arsenic concentrations of hot spring waters in USA and Japan have been reported as $1.6\,mg\,L^{-1}$ and $25\,mg\,L^{-1}$, respectively [4,5]. The presence of arsenic in geothermal waters is due to the dissolution of arsenic containing minerals such as arsenopyrite, niccolite, enargite, orpiment, realgar, proustite and other pyrites and the most probable form of arsenic in hydrothermal solutions is thought to be arsenite [6,7]. In many cases, inorganic arsenic accounts for over 90% of the arsenic species, with more arsenite present than arsenate [8].

The knowledge given above indicates that the determination and speciation of arsenic species are very important and necessary for natural water samples such as drinking, stream and hot spring waters. There are many analytical instruments available, which have sufficient sensitivity and selectivity to determine the species of arsenic directly at the $\mu g\,L^{-1}$ level in natural waters. The most commonly used are hyphenated techniques based on a combination of chromatographic and highly sensitive detection techniques, such as HPLC-ICP, HPLC-HGAFS, HPLC-HG-ICP-MS, HPLC-ICP-MS and GC-ICP-MS [9–12]. These instruments exhibit superior detection limits and selectivity, but they are relatively expensive to purchase or operate, especially for routine application. On the other hand, graphite furnace atomic absorption spectrometry (GFAAS) is a highly sensitive technique and has been commonly used for the determination of trace arsenic in a variety of matrices [13,14]. However, most of the reported methods for arsenic detection based on GFAAS require preconcentration in order to increase sensitivity. GFAAS as an element selective technique also requires highly selective preconcentration methods for speciation of arsenic [15,16].

Preconcentration and speciation methods for inorganic arsenic are primarily based on solvent extraction [17,18], solid phase extraction [19,20], coprecipitation [21,22], ion-exchange separation [23,24] and cloud point extraction [25].

Among these preconcentration methods, the combination of coprecipitation with filtration has been widely used for preconcentration–separation studies for heavy metals, due to its several advantages: simple, fast, high preconcentration factor, sufficient separation factor, etc. In order to obtain these analytical advantages, the selection of applicable, pure, readily available and easily filterable coprecipitant substance is very important. Metal hydroxides as coprecipitants are often chosen because of the minimal contamination risk and their good properties for coprecipitation indicated above. A number of metal hydroxides such as iron(III) [26,27], Ce(IV) [28], lanthanum [29,30], magnesium [31,32], hafnium, scandium, dysprosium [33], aluminium [34,35] and zirconium [36] have been widely used and successfully applied for the preconcentration of trace metal ions from different media. From our literature search, however, there appears to have been no significant study on the application of hydroxide coprecipitation for inorganic arsenic preconcentration and speciation.

Recently, we reported a sensitive and accurate method for the determination of trace amounts of Cu, Co, Pb, Cd, Ni in aqueous solutions, water and sediment samples, and total chromium at trace levels in natural water by flame atomic absorption spectrometry after their coprecipitations with Ce(IV) hydroxide [28,37]. It is well known that cerium is used as an efficient matrix modifier for some elements in electrothermal atomic absorption spectrometry [38]. The important reason for using cerium as the carrier metal in the coprecipitation of arsenic is that cerium is a suitable modifier for the direct determination of arsenic by GFAAS [39]. In this work, therefore, a simple and efficient method using a combination of Ce(IV) hydroxide coprecipitation method with GFAAS was proposed for the speciation and determination for As(III) and As(V). The method was applied to drinking water, wastewater and hot spring water samples.

2. Experimental

2.1 *Instruments*

The absorbance measurements were performed using a Perkin-Elmer AAnalyst 3110 atomic absorption spectrometer (Norwalk, USA) equipped with graphite furnace atomiser HGA-600. Deuterium-arc background correction was employed to correct non-specific absorbance. All measurements were performed using integrated absorbance signals in the form of peak area and/or peak height at 193.7 nm with a spectral bandwidth of 0.7 nm. The recommended operating conditions for arsenic determination are given in Table 1. The sample solutions were injected as 20 µL. The pH adjustment was controlled using WTW pH 340-A/SET 2 pH meter.

2.2 *Reagents and solutions*

All reagents were of analytical grade (Merck, Darmstadt, Germany) and all solutions were prepared in deionised doubly distilled water (18 MΩ cm^{-1}). The presence of arsenic in the reagents was not detected in the working range (close to 0.1–100 µg L^{-1}). The arsenite stock standard solution (1000 mg L^{-1}) was prepared by dissolving 0.0330 g As_2O_3 in minimum volume of 1.0 mol L^{-1} NaOH, followed by dilution with 1.0 mol L^{-1} HNO_3 to 25 mL. The arsenate stock standard solution (1000 mg L^{-1}) was prepared by dissolving 0.0383 g As_2O_5 in minimum volume of 1.0 mol L^{-1} NaOH, followed by dilution with 1.0 mol L^{-1} HNO_3 to 25 mL. Before use, the arsenic stock solutions were kept at 4°C. Working standard solutions were obtained by appropriate dilution of the stock standard solution. 1.0 mol L^{-1} NaI solution was prepared by dissolution of 0.0749 g of solid NaI in 5 mL of the water.

A Ce(IV) solution (1 mg mL^{-1}) was freshly prepared by dissolving the requisite amounts of $Ce(SO_4)_2 \cdot 4\,H_2O$ in small amounts of nitric acid and diluting to 100 mL with water.

The cellulose nitrate membrane filters were purchased from Sartorius (0.45 µm pore size, 47 mm diameter).

Table 1. Graphite furnace program used for arsenic determination.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar, Flow Rate (mL min^{-1})
Drying	120	10	25	250
Pyrolysis	1200	1	20	250
Cooling	20	1	10	250
Atomisation	2400	10	10	0
Cleaning	2600	1	5	250

2.3 *Sampling*

The drinking water sample was taken from the campus of University of Erciyes-Kayseri. It was freshly taken after running the tap for a few minutes. The fresh tap water was analysed without further treatment.

The wastewater samples were taken in pre-washed-cleaned polyethylene bottles from the stream carrying the Yeni Mahalle (New Quarter)-Kayseri domestic wastewaters and from Karasu stream (out of Kayseri) carrying the wastewaters of Kayseri Organized Industrial region and the houses in Kayseri city. The hot spring water sample was taken from Kozakli thermal spring (spa, 90°C) in Kozaklı town. The collected water samples were filtered through 0.45 µm pore size cellulose nitrate membrane filters immediately after sampling. Then, these samples were acidified with 0.1% of conc. HCl which provided a pH lower than 2 [40]. The samples were stored in a polyethylene (PE) bottle at 4°C in a refrigerator, prior to use and analysed in a few days.

2.4 *Coprecipitation of As(III)*

An aliquot of a model solution (50–150 mL) containing 0.1 µg As(III) and 0.1 µg As(V) was placed in a borosilicate glass beaker, to which of 9 mL of 1 mg $\mathrm{mL^{-1}}$ Ce(IV) solution prepared with nitric acid and 6 mol $\mathrm{L^{-1}}$ NH_3 to adjust pH 9 (optimum) were added successively. The sample solution was allowed to stand for 20 minutes at room temperature for quantitative formation of the coprecipitate, and filtered through the cellulose nitrate membrane filter and then washed with the blank solution. The membrane loaded with the precipitate was dissolved with 0.5 mL of concentrated HNO_3 and the solution was diluted to 2 mL or 5 mL with the water. In order to determine As(III) ions, 20 µL of the final solution containing trivalent species of arsenic was introduced into the GFAAS by manual injection, because As(V) was hardly coprecipitated in the working conditions. The recovery values were calculated as a ratio of amount of analyte in the sample solution to amount of analyte in the final solution obtained after the coprecipitation.

2.5 *Coprecipitation of total inorganic arsenic*

In order to coprecipitate total inorganic arsenic in the sample solution, a second aliquot of the model solution (50–150 mL) containing As(III) and As(V) at the different ratios was placed in a borosilicate glass beaker, to which 200 µL of 1×10^{-2} mol $\mathrm{L^{-1}}$ sodium iodide was added. The beaker and contents were heated on a hot plate adjusted to 80°C for 5 minutes for the prereduction of As(V) to As(III) before the procedure of coprecipitation [41]. The coprecipitation procedure above was applied to the cooled solution.

Arsenic(V) concentration in the sample solution was calculated by the difference in concentration between As(III) and total arsenic in the sample solution.

2.6 *Analysis of water samples*

To apply the method under discussion, 9 mg of Ce(IV) as a carrier element was added to 150 mL of the water samples and the pH of the solution was adjusted to 9 for coprecipitation of As(III) and total arsenic after reducing the As(V). The procedures given above were then followed.

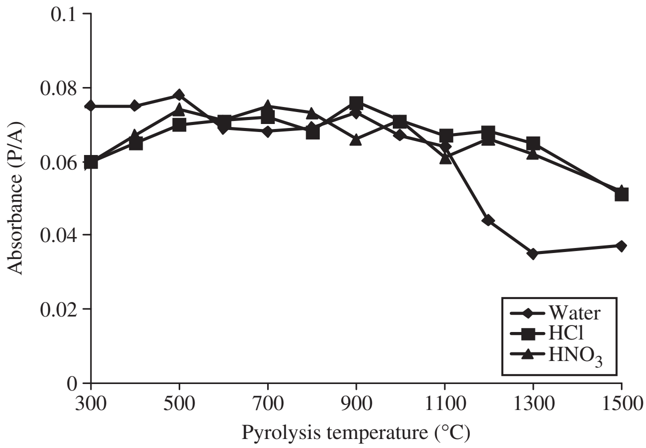

Figure 1. Optimisation of the pyrolysis temperature for 20.0 μg L^{-1} of arsenic in water, 1 mol L^{-1} HCl and 1 mol L^{-1} HNO_3 at atomisation temperature: 2500°C.

3. Results and discussion

3.1 *Effect of pyrolysis and atomisation temperatures on the absorbance of arsenic*

Obtaining sensitive and reproducible analytical results in the determination of elements by GFAAS depends on optimising the temperatures of pyrolysis and atomisation of the analyte. The optimisation of the furnace program was therefore focused on the temperature of the pyrolysis and atomisation steps. Figure 1 shows the effect of the pyrolysis temperature on the peak area (P/A) absorbance of 20.0 μg L^{-1} As(III). For studying the pyrolysis curves, the atomisation temperature was set to 2500°C. The highest tolerable pyrolysis temperatures for arsenic in water, 1 mol L^{-1} HCl and 1 mol L^{-1} HNO_3 solutions were found to be 1000°C, 1300°C and 1300°C, respectively. 1200°C was selected as the optimal pyrolysis temperature for arsenic in 1 mol L^{-1} HCl and 1 mol L^{-1} HNO_3, because, as Figure 1 indicates, the absorbance signals obtained for the arsenic remained almost constant from 500°C up, declining quickly after reaching 1300°C.

Figure 2 illustrates the influence of atomisation temperatures on the peak area absorbance of 20.0 μg L^{-1} As(III). The absorbance signals obtained for the arsenic in water and 1 mol L^{-1} HNO_3 are almost constant from 2300°C to 2700°C, while the signals of arsenic in 1 mol L^{-1} HCl increase continuously in the range of working temperature. The absorbance signals of arsenic obtained with 1 mol L^{-1} HNO_3 were about 1.5- and 2-fold higher than the one with the water (Figures 1 and 2). Therefore, the pyrolysis and atomisation temperatures throughout this study were kept at 1200°C and 2400°C, respectively, to obtain high sensivity and prevent the loss of analyte, and also to prolong the tube life. The use of 1 mol L^{-1} HNO_3 was considered to prepare the final solution obtained after the coprecipitation procedures given above.

3.2 *Effect of cerium concentration on absorbance of arsenic*

In the combination of coprecipitation with metal compounds and GFAAS measurement, the effect of coprecipitant metal ion concentration, cerium in this study, on the absorbance of analyte must be checked because of possible interference or matrix modifier effect.

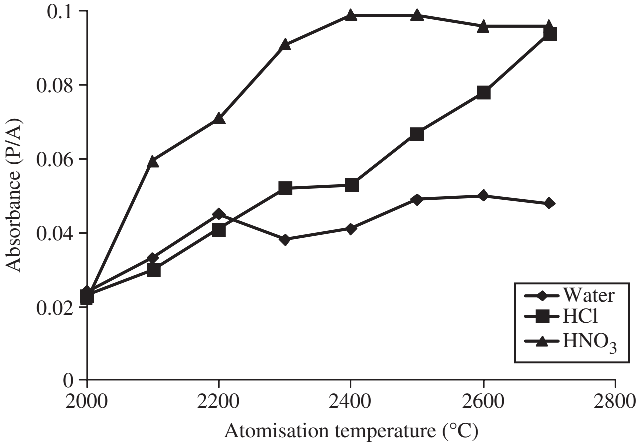

Figure 2. Optimisation of the atomisation temperature for 20.0 μg L^{-1} of arsenic in water, 1 mol L^{-1} HCl and 1 mol L^{-1} HNO_3 at pyrolysis temperature: 1200°C.

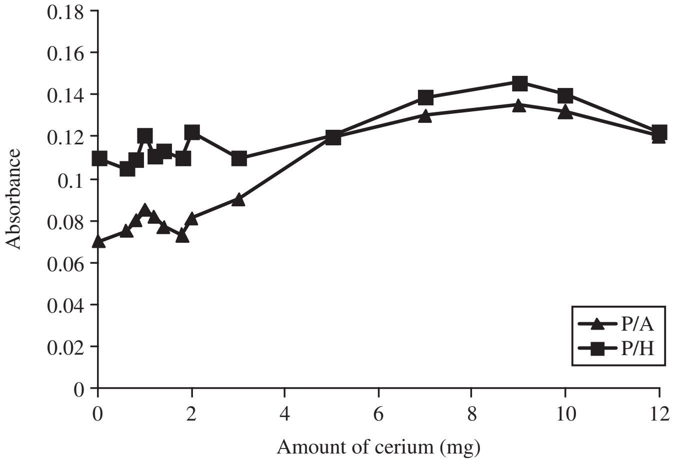

Figure 3. Effect of amount of cerium on determination for 20.0 μg L^{-1} of As(III).
Notes: Atomisation temp.: 2400°C; Pyrolysis temp.: 1200°C; Injected vol.: 20 μL.

To evaluate this probability, Ce(IV) sulphate between 0–12 mg cerium was added to 1 mol L^{-1} HNO_3 solutions containing As(III) at 20 μg L^{-1}. These solutions were directly analysed by GFAAS under optimal conditions. Figure 3 shows that for arsenic determination, 9 mg of Ce(IV) was sufficient to get very good sensitivity. The absorbances remained almost constant in the range of 8–10 mg Ce(IV), while above and below these cerium values the absorbances obtained were slightly lower.

3.3 *Effect of sodium iodide concentration on the absorbance of arsenic*

In order to coprecipitate the total inorganic arsenic (arsenite plus arsenate), the reduction of As(V) to As(III) using a sodium iodide solution was proposed. To test whether there is

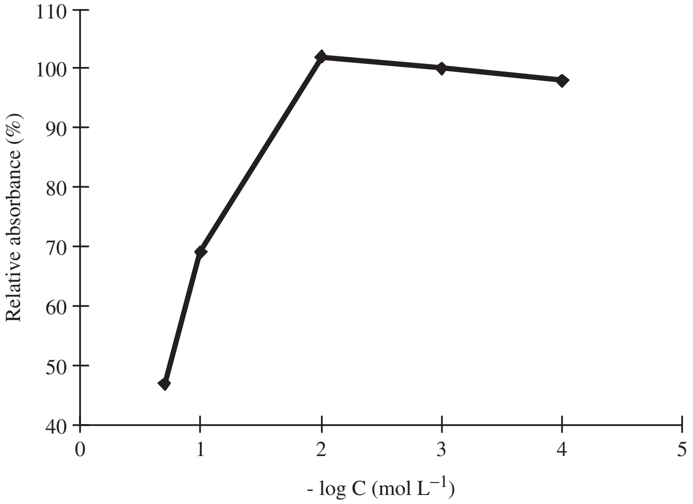

Figure 4. Influence of NaI on determination of arsenic in presence of 1 mol L^{-1} HNO_3 by GFAAS. Notes: $n = 3$; Pyrolysis temperature 1200°C; Atomisation temperature 2400°C.

an interference of NaI on the the arsenic absorbance, the influence of sodium iodide on the absorbance of 4 µg L^{-1} arsenic was examined in concentrations ranging between 1×10^{-4} and 2×10^{-1} mol L^{-1} NaI. Figure 4 shows that absorbance of arsenic slightly decreases beyond 1×10^{-2} mol L^{-1} NaI. With the increase of NaI concentration, the background absorbance also increases and becomes incorrect after that point. However, the use of a sample solution containing 200 µL of 1×10^{-2} mol L^{-1} sodium iodide in the coprecipitation of total arsenic, gives a final concentration much lower than 1×10^{-2} mol L^{-1}.

3.4 *Effect of pH on coprecipitation of As(III) and As(V)*

Since the quantitative differentiation of As(III) from As(V) is to be accomplished, the selection of pH is critical in the coprecipitation with metal hydroxides. The chemical forms of analyte and the quality of coprecipitation depend on the pH of the sample solution. Both arsenate and arsenite can be easily separated by controlling the pH of the sample solution, which should be below the first pKa value of As(III), $pK_{a1} = 9.2$. Under such conditions, As(III) is present as a nonionic species and can be coprecipitated with Ce(IV) hydroxide, whereas As(V) having $pK_{a1} = 2.3$ is present as anionic species and cannot be coprecipitated. Therefore, the coprecipitations of As(III) and As(V) with Ce(IV) hydroxide were separately investigated in the pH range of 2 to 11, according to the coprecipitation procedures given in the experimental section. Figure 5 shows that As(III) was coprecipitated quantitatively within an optimum pH range between 8.0 and 9.2. Arsenic(V) was hardly coprecipitated with a recovery less than 10% when the pH of the sample solution was buffered to 9.0. Considering these results, the selected pH was 9.0. However, using the pH to distinguish As(III) from As(V) is extremely critical in this procedure. Thus, the adjustment of pH must be checked with the aid of a pH metre. Our findings were similiar to those reported by Gil et al. [30].

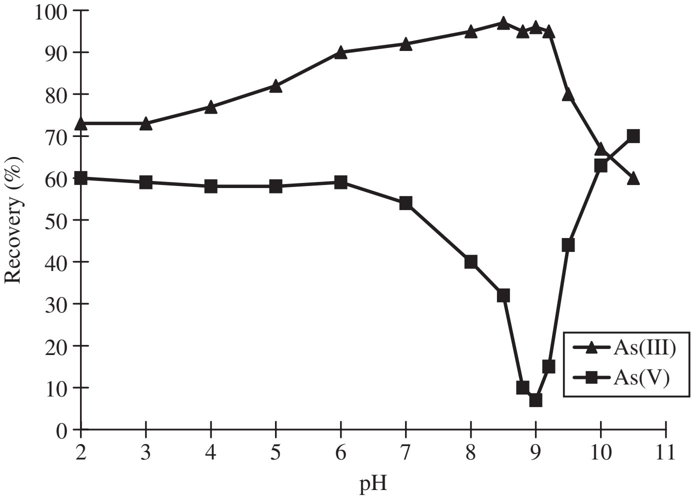

Figure 5. Effect of pH on the coprecipititation of As(III) and As(V) species.
Note: $n = 3$.

3.5 *Effect of reducing agent type*

As shown in Figure 5, the proposed coprecipitation procedure was able to coprecipitate As(V) only slightly. Because of this, the procedure requires a pre-reduction of As(V) to determine total inorganic arsenic content in sample solutions. Several methods have been reported for the reduction of As(V) to As(III). In our experiments, hydrazinium sulphate, hydroxyl amine hydrochloride, sodium nitrite and sodium iodide were evaluated for the reduction of As(V) to As(III) at 80°C. The experiments showed that hydrazinium sulphate ($1.2 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$), hydroxyl amine hydrochloride ($1.0 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$) and sodium nitrite ($1.5 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$) have negative effects on the coprecipitation of $4\,\mu\mathrm{g\,L^{-1}}$ As(III) and do not reduce As(V) to As(III), quantitatively. Thus, the recovery values of As(III) and As(V) in the presence of hydrazinium sulphate, hydroxyl amine hydrochloride and sodium nitrite were under 80%. On the other hand, it was found that $200\,\mu\mathrm{L}$ of $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ sodium iodide could completely reduce As(V) to As(III) in sample solution, which was then quantitatively ($\geq$95%) coprecipitated with the Ce(IV) hydroxide. Therefore, sodium iodide was preferred for the prereduction of As(V) to As(III) before the coprecipitation procedure for total arsenic.

The effect of sodium iodide concentration on the coprecipitation was also tested. It was found that there was no important effect on the coprecipitation of As(III) and As(V) within an NaI concentration range of 1×10^{-5} to $1 \times 10^{-1}\,\mathrm{mol\,L^{-1}}$ and the recoveries were higher than 95%. Considering these results, the concentration of sodium iodide was selected as $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$.

3.6 *Amount of cerium as coprecipitant element*

In order to examine the effect of amounts of Ce(IV) on recoveries of As(III) and total inorganic arsenic obtained by coprecipitation with Ce(IV) hydroxide, various amounts of cerium were added into sample solution, which contained $0.2\,\mu\mathrm{g}$ of As(III) and $0.2\,\mu\mathrm{g}$ of

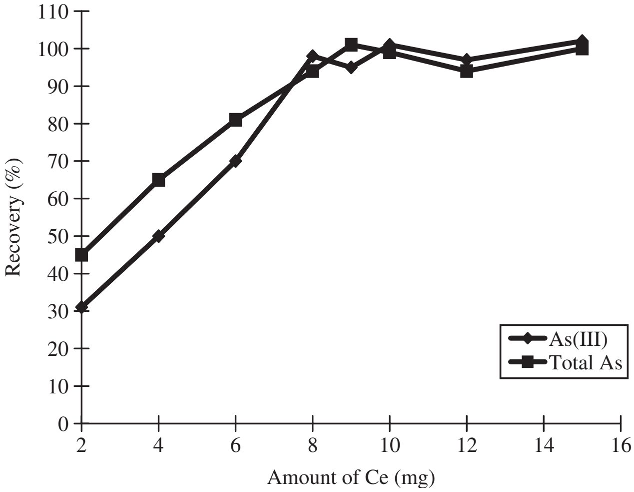

Figure 6. Effects of amounts of Ce(IV) on coprecipitation of As(III) and total arsenic.
Notes: As(III): 0.2 µg; Total As: 0.2 µg As(III) + 0.2 µg As(V); sample vol.: 50 mL.

As(V), according to the analytical procedures recommended above. As shown in Figure 6, it was found that recoveries of arsenic species by coprecipitation became almost constant when 8–15 mg of Ce(IV) was used. Under 8 mg Ce(IV), the recoveries were not quantitative. Depending on these results and the data given in Figure 3, the use of 9 mg Ce(IV) was recommended in this work.

3.7 *Effect of sample volume*

In order to demonstrate the relationship between recoveries of arsenic by coprecipitation and sample volumes, which contained 0.2 µg of As(III) or 0.2 µg of As(V), the effect of sample volume was examined according to the analytical procedures mentioned above. It was found that recoveries of As(III) and As(V) sharply decreased after 150 mL of sample solutions, as shown in Figure 7.

The preconcentration factor (PF) is defined as the volume ratio of the aqueous sample to the final solution obtained after the coprecipitation and it is 75 in this work.

3.8 *Interference studies*

The effects of matrix ions in water samples on the coprecipitation of As(III) and total inorganic arsenic were investigated using a solution containing 4 µg L^{-1} of arsenic in the selected conditions (Table 2). The tolerable limit was taken as a relative error $\leq \pm 5\%$. Fe^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, Cr^{6+} (as $Cr_2O_7^{2-}$), Cu^{2+}, Zn^{2+} and Co^{2+} could be tolerated up to at least 250 mg L^{-1}. Fe^{3+} and Ni^{2+} up to at least 100 mg L^{-1} could be tolerated. Commonly encountered matrix components, such as Na^+, K^+, Ca^{2+} and Mg^{2+}, did not show any interferences on the coprecipitation. The anions investigated, PO_4^{3-}, HPO_4^{2-}, HCO_3^- and CO_3^{2-} did not possess any adverse effects on the coprecipitation of As(III) and total arsenic at concentration levels studied. Thus, it could be concluded

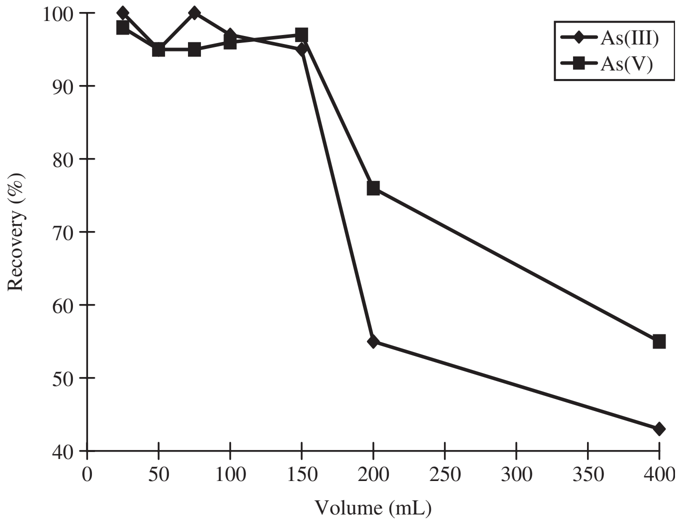

Figure 7. Effect of sample volume on coprecipitation.
Notes: $n = 3$; 0.2 µg As(III); 0.2 µg As(V).

Table 2. Effect of matrix ions on the coprecipitation of As(III) and total arsenic.

Ion	Added as	Tolerable concentration ($mg\,L^{-1}$)
Na^+	NaCl	20,000
K^+	KCl	2500
Mg^{2+}	$MgCl_2$	5000
Ca^{2+}	$CaCl_2$	2500
HCO_3^-, CO_3^{2-}	Sodium salt	1000
PO_4^{3-}	Na_3PO_4	5000
HPO_4^{2-}	Na_2HPO4	250
Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, Cr^{3+}, $Cr_2O_7^{2-}$(potassium salt), Fe^{2+}	Nitrate salt	250
Ni^{2+}, Fe^{3+}	Nitrate salt	100

Notes: $n = 3$; sample volume: 50 mL; final solution volume: 2 mL.

that the proposed coprecipitation system tolerates the presence of ions at the concentration levels that may be found in natural water samples.

3.9 *Analytical performance of the method and analysis of real samples*

In this work, water samples with certified arsenic contents with respect to the oxidation states were not available. Therefore, to validate the method for accuracy, we chose to study the recoveries of spiked As(III) and As(V) to drinking water and wastewater samples. The recoveries of As(III) and total arsenic from the synthetic mixtures prepared by the varying amounts of As(III) and As(V) in pure water were quantitative in the range 95–104% (Table 3). In addition, it can be seen from Table 4 that As(III) and As(V) spiked to the drinking and wastewater samples were quantitatively recovered.

Table 3. Analysis of the synthetic mixtures of As(III) and As(V).

		As(III), ($\bar{x} \pm$ s)		Total arsenic, ($\bar{x} \pm$ s)	
As(III), Added (μg)	As(V), Added (μg)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
0.50	0.00	0.49 ± 0.01	98 ± 2	0.48 ± 0.01	96 ± 1
0.40	0.10	0.38 ± 0.02	95 ± 4	0.49 ± 0.02	98 ± 3
0.25	0.25	0.24 ± 0.01	96 ± 2	0.52 ± 0.01	104 ± 2
0.10	0.40	0.10 ± 0.01	100 ± 1	0.48 ± 0.01	96 ± 2
0.00	0.50	–	–	0.51 ± 0.01	101 ± 2

Notes: $n = 5$; sample vol.: 50 mL.

Table 4. Determination of As(III) and As(V) in spiked drinking water and wastewater samples.

	Added (μg)		Found (μg), ($\bar{x} \pm$ s)		Recovery (%), ($\bar{x} \pm$ s)	
Samples	As (III)	As(V)	As(III)	As(V)	As(III)	As(V)
Drinking water	0.00	0.00	0.00	0.00	–	–
	0.20	0.20	0.19 ± 0.01	0.21 ± 0.02	95 ± 5	105 ± 10
	0.50	0.50	0.47 ± 0.06	0.49 ± 0.03	94 ± 5	98 ± 5
	1.00	1.00	0.96 ± 0.06	1.01 ± 0.02	96 ± 1	101 ± 3
Wastewater (Yeni Mahalle)	0.00	0.00	0.12 ± 0.02	0.19 ± 0.04	–	–
	0.20	0.20	0.31 ± 0.01	0.41 ± 0.02	95 ± 5	105 ± 10
	0.50	0.50	0.59 ± 0.03	0.68 ± 0.01	94 ± 5	98 ± 3
	1.00	1.00	1.12 ± 0.02	1.25 ± 0.03	100 ± 2	106 ± 3

Notes: $n = 3$; sample vol.: 50 mL.

Additionally, we compared the total arsenic concentration ($200.0 \pm 20.0\,\mu g\,L^{-1}$) in the hot spring water with a reference value ($210\,\mu g\,L^{-1}$) found by TXRF method [42]. Good agreement was obtained between the estimated contents by the proposed method and TXRF. The relative error was −5.0%.

The reproducibility of the coprecipitation method was evaluated by repeating this procedure 10 times with 50 mL of synthetic mixture solution of As(III) and As(V). The relative standard deviation (RSD) was found to be 2–10% for concentration range of 0.2 to $4.0\,\mu g\,L^{-1}$. The detection limit (DL) was calculated as the concentration of As(III) and total arsenic that was equal to three times the standard deviation of the background signal (3σ). The value of DL obtained for the coprecipitation of 50 mL of aqueous solutions of As(III) and total arsenic was $0.05\,\mu g\,L^{-1}$. The preconcentration factor was 75 in this work.

Finally, the method was applied to the analysis of drinking water, hot spring water and wastewater samples, taken from Yeni Mahalle Stream and Karasu Stream, collecting the household wastewaters and industrial plus household wastewaters, respectively. The concentrations of As(III) and As(V) species in the drinking water sample were not measured because of their very low concentrations. The results for the other samples are given in Table 5. The relative standard deviations for As(III) and total arsenic determinations in the real samples ranged from 4.3 to 9.1%.

Table 5. Differential determination of speciation of inorganic arsenic in water samples.

Samples	Concentration ($\mu g\,L^{-1}$, ($\bar{x} \pm ts/\sqrt{N}$, P: 0.95)) As(III)	Total As
Yeni Mahalle Stream	2.34 ± 0.14	3.86 ± 0.35
Karasu Stream	19.00 ± 1.30	32.00 ± 1.70
Kozaklı Hot Spring Water	160.0 ± 15.0	200.0 ± 20.0

Notes: $n = 5$; sample vol.: 150 mL.

4. Conclusions

The coprecipitative speciation and preconcentration procedure described above facilitates a selective preconcentration of As(III) in the presence of As(V) from very dilute solutions. Furthermore, the iodine reduction of As(III) to As(V) allows the determination of total inorganic arsenic. The concentration of As(V) in the samples could be calculated by the difference in concentration between As(III) and the total arsenic. The proposed method has advantages of low detection limit, high selectivity, good reproducibility, adequate accuracy, quantitative recovery, relatively high preconcentration factor. With 150 mL sample volume, one sample can be analysed in 30 minutes. The recommended procedure can be successfully applied to speciation, preconcentration and determination of inorganic arsenic in a wide range of natural water samples.

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