Bifunctional magnesium oxide crystal successively as adsorbent and matrix modifier for preconcentration and determination of arsenic by graphite furnace atomic absorption spectrometry

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ABSTRACT

A novel method for determination of total inorganic arsenic in water samples, based on magnesium oxide crystals quantitatively preconcentration and graphite furnace atomic absorption spectrometry (GFAAS) detection has been developed. As the MgO crystals could successively act as the adsorbent and matrix modifier, the method presents great potential in practical routine analysis of inorganic arsenic. With optimization of the experimental conditions, 1.5 mg of MgO was added into 4.0 mL water sample and ultrasonic dispersing 15 min for adsorbing the arsenic at first. Then, the mixture was centrifuged 5 min for separating the adsorbents and the water solution; the deposits were collected and dissolved with HNO₃ for arsenic determination. The enrichment factor of 13, limit of detection (LOD) of 0.087 $\mu\text{g L}^{-1}$, relative standard deviation (RSD) of 4.5% ($n = 7$, $c = 2.0 \mu\text{g L}^{-1}$) were achieved under the optimized conditions. The procedure was validated by analysis of certified water sample (GBW08605), which results in good agreement between the certified and the found values. The method was further demonstrated for analysis of lake water, snow water and tap water, and satisfactory spiked recoveries of 98.5% to 103.0% were achieved for these samples. These preliminary results indicated the present method was practical and accurate for analysis of trace-arsenic in natural water samples.

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1. Introduction

Arsenic in drinking water has caused severe health problems in many areas of the world, including South Asia, Middle of China, West of the USA, Mexico and Argentina, and even worse in developing countries and areas with low level of medical treatment and cognitive ability [1–3]. Millions of people are suffering the chronic poisoning and carcinogenic effects of arsenic. Melanosis, keratosis peripheral neuropathy, diabetes, ischemic heart disease, and impairment of liver function are commonly occurred with long-term exposing to the polluted drinking water [4–7]. Although the arsenic in drinking water has aroused the world wide attentions, and WHO (World Health Organization) has pointed out the maximum arsenic concentration of $10 \mu\text{g L}^{-1}$ as the provisional guideline value in the guidelines for drinking-water quality [8], the drink water arsenic problems especially in the developing countries/areas are still unsolved because of insufficient understanding of the arsenic pollution levels [3,4,9]. At present, the detection and notification of the arsenic levels in these polluted areas are even more urgent than other remedial measurements. Consequently, the economic and practical arsenic detection methods are highly necessitated [10–13].

In natural waters, the arsenic is mostly inorganic, i.e., arsenate and arsenite ions, denoted as As(V) and As(III) [1,14]. However, the As(III) is unstable and rapidly converted to As(V) under ambient conditions [15]. The common methods for As(V) detection are atomic spectrometry methods, such as graphite furnace/electrothermal atomic absorption spectrometry (GFAAS/ETAAS) [16–18], hydride generation atomic fluorescence spectrometry (HGAAS) [19–23] and inductively coupled plasma mass spectrometry (ICPMS) [24–26]. The ICPMS provides the best sensitivity and accuracy among all the commercial detectors, but its high price and maintenance cost is still unaffordable for routine analysis in the developing countries and areas [10,11,27,28]. The GFAAS and HGAAS are more economic and would also provide accurate results while detecting clean samples with no/low level of interference ions [10,29]. The GFAAS and HGAAS methods require adding matrix modifier and hydride generation reagents for each sample detection, respectively. Because the limits of quantitation of arsenic by GFAAS and HGAAS are close to the suggested values of WHO ($10 \mu\text{g L}^{-1}$) for the real water samples, the AAS and AFS cannot be directly used for arsenic determination in real drink water. The preconcentration and separation of arsenic in the water samples are necessary for the GFAAS and HGAAS methods [16,19,23,30].

To date, solid-phase extraction (SPE) [23,31,32], liquid-liquid extraction [33–35], cloud point extraction [30,36,37], co-precipitation [38] and atom/hydride trapping [39–41] have been established for arsenic

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Fig. 1. SEM image (a) and the XRD pattern (b) of the MgO crystal particles.

preconcentration and determination. Recently, Chen et al. has invented a series of SPE methods for arsenic enriching and analytical performance improving of GFAAS and HGAAS, the adsorbents including akaganeite decorated graphene oxide composite [22], branch-polyethyleneimine modified carbon nanotubes [42] and esterified egg-shell membrane [43] were investigated for arsenic preconcentration, respectively. As a result, the limits of detection of HGAAS and GFAAS were significantly improved to tens nanogram per liter. Arsenic in snow, rain, pond water, spring water and certified reference materials could be accurately analyzed by these methods. Zhou et al. also reported a magnetic SPE method by using Fe@polyethyleneimine in combination with hydride generation atomic fluorescence spectrometry (HGAAS) for arsenic adsorption and detection, which enabled HGAAS to accurately analyze the arsenic in river water, reservoir water and cosmetic samples [23].

According to our knowledge, bifunctional materials as adsorbents and also as GFAAS matrix modifiers for preconcentration and determination

of arsenic have not been reported. Herein, MgO crystals were synthesized and used for arsenic adsorption, the MgO adsorbed with arsenic were then eluted and dissolved by nitric acid, and consequently the dissolved Mg^{2+} was functioned as matrix modifier for As detection by GFAAS. The primary results showed MgO crystals were practical for the arsenic preconcentration in real waters, and the analytical procedure were also simplified by Mg^{2+} performing as matrix modifier.

2. Experimental

2.1. Reagents and instrumentations

All chemicals used were at least analytical grade. De-ionized water (18.2 MΩ cm, Milli-Q water purification system) was used for standard reagents and sample dilutions. The standard stock solutions (1000 mg L^{-1}) of As(V) were prepared by $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ (Sigma). The As(V) standard

Fig. 2. The influences of the amount of MgO (a), ultrasonic time (b) and sample pH (c) on arsenic preconcentration and determination by GFAAS. Other experimental conditions are given in Table 1.

solutions used for the experimental condition optimization and calibration were prepared with appropriate dilution. Other reagents (such as HNO_3 , $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$, $(\text{C}_6\text{H}_5\text{NO})_n$ (K90), $\text{C}_2\text{H}_5\text{OH}$, NaCl , KNO_3 , FeCl_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, AlCl_3 , ZnSO_4 , KH_2PO_4 , $\text{Pb}(\text{CH}_3\text{COO})_2$, BaCl_2 , CaCl_2 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and AgNO_3) used in this study were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

The quantification of As(V) was facilitated by a HITACHI Z-5700 atomic absorption spectrophotometer (Hitachi High-Technologies, Japan). A single computer was used to control the atomic absorption spectrometer. The temperature program was set as same as references [44,45]. A KQ-50DE ultrasonic cleaner (Kunshan Ultrasonic Instruments Co. Ltd., China, www.ks-csyq.com/cn/index.aspx) was employed for adsorbents dispersal, and a Universal 320R centrifuge (Huayue Co. Ltd., China, www.huayueco.com) was used for separation of the adsorbents and the water in this study. A PHS-3C pH meter (Shanghai INESA Scientific Instrument Co. Ltd., China, www.lei-ci.com/products) was used to measure pH values. A FA2204B analytical balance (readability 0.1 mg, Shenzhen Right Era Industry Co. Ltd., China, www.yoyitime.com) was used for weighing of standard reagents and correcting of the pipets. The SXL-1216 Muffle furnace (Shenzhen Right Era Industry Co. Ltd., China, www.yoyitime.com) was used to roast the MgO precursor. The microstructure details of MgO crystals were investigated by scanning electron microscopy (SEM; model SU8000, Tokyo, Japan) at an acceleration voltage of 50 kV. The obtained MgO was also characterized by X-ray diffraction (XRD) (a Siemens D5000 X-ray powder diffractometer) with $\text{Cu K}\alpha$ radiation and scanned from 3° and 90° ($\lambda = 0.1542 \text{ nm}$). The scan speed was $5^\circ/\text{min}$. The X-ray tube was set at 100 mA and 40 kV at room temperature. The obtained product was identified by comparing with the Joint Committee of the Powder Diffraction Standard (JPDFS) cards.

2.2. Synthesis of MgO crystal

MgO crystals were synthesized following the polymer template method [46,47]. Briefly, 50 mL of 0.4 mol L^{-1} $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 50 mL of 0.6 mol L^{-1} $\text{CO}(\text{NH}_2)_2$ were prepared in de-ionized water, respectively. The $\text{CO}(\text{NH}_2)_2$ was added into the $\text{Mg}(\text{CH}_3\text{COO})_2$ solution by droplets in 5 min, then the PVP (0.20 g) polymer as template was added into the solution while stirring at room temperature for another 5 min. The mixed solution was transferred to the Teflon-lined autoclave in equal phase reactor at 150°C for 12 h. After being cooled down to room temperature, the crude products were collected by vacuum filter and washed with de-ionized water and ethanol. The obtained products were put in vacuum drying oven at 55°C for 12 h, followed by calcination for 1 h at 600°C to produce MgO crystals.

2.3. Arsenic preconcentration and determination

Before the preconcentration, the water samples were filtrated through $0.22 \mu\text{m}$ membrane filters and the filtrates were diluted appropriately when needed. 4.0 mL of the diluted water sample was pipetted into a 5 mL of centrifuge tube and mixed with 1.5 mg of MgO crystals. The mixtures were placed in the ultrasonic bath for 15 min, and then the mixtures were separated by the high speed centrifuge at 10,000 rpm for 5 min. The supernatants were poured away carefully, and the deposits were dissolved in $100 \mu\text{L}$ of HNO_3 (1 mol L^{-1}). The final solutions were transferred into the sharp-bottomed vessel of GFAAS auto sampler for arsenic detection.

3. Results and discussion

3.1. Characterization of the synthesized MgO particles

The microstructure of the MgO crystal was characterized by the scanning electron microscopy (SEM). The SEM image is shown in Fig. 1a. The MgO crystals were well-distributed, with the length was about 500 nm, and diameter ranged from 100 to 200 nm. The particle size of

Table 1

The optimized experimental conditions for arsenic preconcentration by MgO crystals.

Experimental conditions	Parameter (unit)	Value
Sample	Volume (mL)	4.0
	pH	5.0
MgO	Amount (mg)	1.5
	Concentration (mol L^{-1})	1.0
Nitric acid	Volume (μL)	100
	Time (min)	15
Ultrasonic dispersing	Time (min)	15
	Rotation rate (rpm)	10,000
Centrifuge	Time (min)	5

the MgO crystal particle indicates it could be easily separated by the centrifuge after adsorbing the arsenic in water samples.

The crystal structure of the MgO crystal was investigated by X-ray powder diffraction (Fig. 1b). A wide-angle XRD pattern of the particle was attributed to the cubic symmetry of MgO (JCPDS card no. 74-1225). As illustrated in Fig. 1b, this XRD pattern confirmed that the MgO crystals were highly crystalline. All the obtained Bragg reflection peaks are same as the pure cubic phase of MgO crystal (JCPDS Card No. 71-1176, MgO). The five reflection peaks shown in Fig. 1b were indexed to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) diffraction planes and no obvious impure peaks were observed. These results confirmed the high purity of MgO was synthesized.

3.2. Optimization of the experimental conditions

The experimental conditions for arsenic preconcentration, including amount of MgO crystals, ultrasonic dispersing time and sample pH, were investigated in detail. The results of these parametric influences are summarized in Fig. 2.

Because of the adsorption efficiency of the target analytes directly relates to the amount of the adsorbents, the amount of MgO crystals for the arsenic adsorption was tested. The results are shown in Fig. 2a, by gradually increasing the amount of MgO from 0 to 1 mg, the received absorbance values of GFAAS for arsenic detections are significantly raised, which indicates less than 1 mg of MgO is insufficient for arsenic adsorption in 4 mL of water samples. While, more than 1 mg of MgO is used, the absorbance values are keeping around the highest level. Therefore, in order to ensure the adsorption efficiency, 1.5 mg of MgO was selected for the following experiments.

The ultrasonic time of MgO crystals dispersing in the water samples for adsorbing the arsenic also influences the final preconcentration

Fig. 3. The recorded GFAAS signals for $5 \mu\text{g L}^{-1}$ of As with preconcentration by the MgO crystals and detected directly. The experimental parameters are given in Table 1.

Table 2

The determination of As in certified reference water (GBW08605), lake water, snow water and tap water sample.

Samples	Certified ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Spiked ($\mu\text{g L}^{-1}$)	Spiked found ($\mu\text{g L}^{-1}$)	Recovery (%)
GBW08605	500 $\pm$ 8	494 $\pm$ 15			
Lake water		0.31 $\pm$ 0.10	2.0	2.28 $\pm$ 0.15	98.5
Snow water		0.26 $\pm$ 0.12	2.0	2.32 $\pm$ 0.15	103.0
Tap water		n.d.*	2.0	2.01 $\pm$ 0.07	100.5

n.d.*: not detected.

results. Therefore, the ultrasonic time from 2 to 40 min were tested in this study. The results of the ultrasonic time effecting the absorbance values for arsenic detection by GFAAS are shown in Fig. 2b. It is obvious that the arsenic absorbance improved along with the ultrasonic time extended, especially in 2–15 min. In 15–40 min, the detected arsenic signals increase slightly. As combining the analytical time costs and the method sensitivity, 15 min of ultrasonic time for MgO dispersing in water samples was chosen for the further experiments.

The high acidity of the water sample might cause the MgO dissolving when adding the MgO for adsorption, which would result in arsenic running away and insufficient arsenic adsorption. However, the high alkalinity of the water sample might result in co-precipitating. As a result, the sample pHs from 2 to 6 were investigated in this work. The influence of the pH values on the arsenic preconcentration are shown in Fig. 2c. It clearly indicates that the arsenic absorbance signals obtained at the pH of 5.0 and 6.0 are higher than the signals at other pHs. This phenomenon could be attributed to the electrostatic attractions between MgO and the arsenic species. Because of the hydrolysis of As(V) follows the Eqs. (1)–(3), at the sample pH of around 5.0 and 6.0, the aqueous As(V) dominated as H_2AsO_4^- and HAsO_4^{2-} , which are easier adsorbed by the MgO than H_3AsO_4 . Considering the pH values of the real water samples in nature, pH of 5.0 was selected for the arsenic adsorption.

Other experimental conditions, such as sample volume, centrifuge rotation rate, centrifugal time, nitric acid concentration and volume were also studied. The optimized experimental conditions are summarized in Table 1.

3.3. Interference of coexisting inorganic ions

Considering the potential coexisting ions in nature water, the interference of ions such as alkali metal ions, alkaline earth metal ions, transition metal ions and common anions, were tested by gradually increasing their amount into arsenic standard solution for preconcentration and detection. The experimental results showed that 3000 mg L^{-1} of Na^+ and Cl^- ; 1500 mg L^{-1} of K^+ , PO_4^{3-} , NO_3^- and SO_4^{2-} ; 500 mg L^{-1} of Ca^{2+} ; 100 mg L^{-1} of Zn^{2+} , Ni^{2+} , Al^{3+} and Ba^{2+} ; 50 mg L^{-1} of Cu^{2+} , Pb^{2+} and Ag^+ ; 30 mg L^{-1} of Fe^{3+} did not interfere with 5 $\mu\text{g L}^{-1}$ of As(V) detection (within a 5% error range). For environmental water samples, especially the drinking water samples, the contents of the above species will not exceed the tolerant concentration levels, therefore, the present procedure can be directly employed, and no further treatment or masking reagents are needed for arsenic detection.

3.4. Analytical performance

Under the optimized experimental conditions, the MgO crystals for arsenic preconcentration achieved an enrichment factor of 13.0, and the limit of detection of GFAAS for arsenic detection was

improved to 0.087 $\mu\text{g L}^{-1}$, and the linear range was extended to 20 $\mu\text{g L}^{-1}$ of As. The relative standard deviation (RSD) for seven successive preconcentration and determinations of 2 $\mu\text{g L}^{-1}$ aqueous arsenic was 4.5%.

As obviously shown in Fig. 3, the signal to noise ratio of GFAAS is significantly improved. The detected signals for 5 $\mu\text{g L}^{-1}$ of arsenic with MgO crystals preconcentration were much higher than the signals detected directly by GFAAS. Comparing with the previous SPE methods in combination with GFAAS for arsenic detection, e.g. LOD of 15 [43], 20 [36,48], 4.6 [49], 5 [18], and 1.97 [32] ng L^{-1} , RSD of 3.5% [43,48], 3.9% [49], 3.2% [18], 4.4% [32] and 2.3% [36], the sensitivity of this method is slightly lower than the reported methods, but the reproducibility is at the same level of the reported methods. As the WHO guideline for arsenic concentration in drinking water is 10 $\mu\text{g L}^{-1}$, the present method is confidently appropriate for the arsenic detection in the drinking waters.

3.5. Method validation and application

The present method was validated by analyzing the arsenic content in a certificated water sample (GBW08605). The certified concentration and the analytical result are summarized in Table 2. It is obvious that the found values of As in GBW08605 were in favorable agreement with the corresponding certified values. The method was also applied to analyze the arsenic concentration in three real water samples, i.e. lake water, snow water and tap water. The results are also shown in Table 2. It shows that the arsenic concentration in tap water is below the LOD of the present method, the lake and snow water contains 0.31 $\pm$ 0.10 and 0.26 $\pm$ 0.12 $\mu\text{g L}^{-1}$ of arsenic, respectively. The spiking recoveries for these water samples spiked with 2 $\mu\text{g L}^{-1}$ are in range of 98.5%–103.0%, which further indicates the method could be accurate for arsenic analysis in real water samples.

4. Conclusions

The MgO crystal particles were successfully synthesized and performed as the bifunctional adsorbents for arsenic preconcentration and determination. With the primary investigation, the MgO crystals were appropriate for trace arsenic preconcentration in various real water samples. Sequentially with the nitric acid elution, the concentrated arsenic and the Mg^{2+} were transferred into GFAAS for arsenic determination without other matrix modifiers needed. The method proposed a new strategy for preconcentration and determination of arsenic by SPE in combination with GFAAS, which might have great usage in drinking water analysis in developing countries.

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