Research Article

Separation/Preconcentration and Speciation Analysis of Trace Amounts of Arsenate and Arsenite in Water Samples Using Modified Magnetite Nanoparticles and Molybdenum Blue Method

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A new, simple, and fast method for the separation/preconcentration and speciation analysis of arsenate and arsenite ions using cetyltrimethyl ammonium bromide immobilized on alumina-coated magnetite nanoparticles (CTAB@ACMNPs) followed by molybdenum blue method is proposed. The method is based on the adsorption of arsenate on CTAB@ACMNPs. Total arsenic in different samples was determined as As(V) after oxidation of As(III) to As(V) using potassium permanganate. The arsenic concentration has been determined by UV-Visible spectrometric technique based on molybdenum blue method and amount of As(III) was calculated by subtracting the concentration of As(V) from total arsenic concentration. MNPs and ACMNPs were characterized by VSM, XRD, SEM, and FT-IR spectroscopy. Under the optimal experimental conditions, the preconcentration factor, detection limit, linear range, and relative standard deviation (RSD) of arsenate were 175 (for 350 mL of sample solution), 0.028 µg mL⁻¹, 0.090–4.0 µg mL⁻¹, and 2.8% (for 2.0 µg mL⁻¹, n = 7), respectively. This method avoided the time-consuming column-passing process of loading large volume samples in traditional SPE through the rapid isolation of CTAB@ACMNPs with an adscititious magnet. The proposed method was successfully applied to the determination and speciation of arsenic in different water samples and suitable recoveries were obtained.

1. Introduction

Speciation analysis refers to the process of identification and determination of different physical and/or chemical species in a sample. Arsenic contamination in environmental waters supply is a worldwide problem and despite the analytical advances made in the field of speciation analysis of this element during the last decades, there are still a relatively limited number of studies dealing with the determination of arsenate and arsinite species in real samples such as natural waters [1]. The toxicity of arsenic highly depends on its inorganic and organic chemical forms. In natural waters, arsenic is predominantly present in inorganic forms of As(III) and As(V) [2]. As(III) is several hundred times more toxic than organoarsonic and 25–60 times more toxic than As(V) [3]. Thus, it is important to determine each of arsenic species rather than the total amount of arsenic in water samples. Except for some like electroanalytical methods [4], simultaneous and direct determination of As(III) and As(V) species is difficult by other instrumental techniques such as UV-Visible. molecular absorption spectrometry. In recent years, several methods of simultaneous separation/preconcentration and speciation of As(III) and As(V), such as hydride generation [5, 6],
liquid-liquid extraction (LLE) [7], ion chromatography [8, 9], high-performance liquid chromatography (HPLC) [10], solid phase extraction (SPE) [11–15], solidification of floating drop microextraction (SFDME) [16], and coprecipitation [17, 18], have been developed. Among them, SPE due to faster operation, easier manipulation, reduction of the use of organic solvents, less stringent requirements for separation, higher preconcentration factor, and easier compatibility with analytical instruments have been widely studied. At present, nanosized materials such as SiO$_2$, Al$_2$O$_3$, TiO$_2$, and carbon nanotubes have been more important in SPE due to their special property of high adsorption capacity [19–22]. Among these adsorbents, activated alumina, with its many types of adsorptive sites and high surface area, is the perfect choice for the adsorption of various unwanted minerals such as arsenic in water. But separation of alumina particles from aqueous medium is difficult because of high dispersion and very small dimension. Magnetite nanoparticles (MNPs), as a new kind of NPs, are widely used in many separation fields such as SPE method [23–32]. The surface modification of MNPs is a challenged key for SPE application. SPE with a magnetic core consisting of Fe$_3$O$_4$ with a nonreactive shell made of alumina have been synthesized and as sorbent applied recently [23, 24, 29, 30, 32]. The main advantage of the preparation of alumina-coated magnetite nanoparticles (ACMNPs) compared to only MNPs is higher stability in acidic and basic solutions. Recently, we also reported the methods for separation, preconcentration, and speciation of Ni(II), Ag(I), Pb(II), Hg(II), and Cr(III)/Cr(VI) using ACMNPs [24, 28–30, 32]. These methods were based on the SPE of trace amounts of these ions using dithizone, mercaptobenzothiazole/sodium dodecyl sulfate (SDS), dimethylglyoxime/SDS, and cetyltrimethylammonium bromide (CTAB) immobilized on ACMNPs. To our knowledge, this is the first report of using magnetite nanoparticles for the SPE and speciation analysis of species of arsenic from real samples. In this study, ACMNPs were successfully synthesized and modified by cationic surfactant of CTAB. The sorbent of CTAB@ACMNPs has proved to be suitable for the extraction of arsenate and arsenite ions from different water samples prior to determination by spectrometric technique based on molybdenum blue method.

2. Experimental

2.1. Apparatus. Absorbances were measured at 840 nm using a GBC UV-Visible Cintra 6 Spectrophotometer model, attached to a Pentium (IV) computer, with 10 mm glass cell. A Fourier transform infrared spectrometer (FTIR Prestige-21, Shimadzu), scanning electron microscope (LEO 1455 VP SEM), and vibrating sample magnetometer (VSM 7400 Model Lake-Shore) were used to characterize the structure of the prepared MNPs and ACMNPs.

Other instruments used were ultrasonic bath (S60H Elmasonic, Germany), mechanical stirrer (Heidolph, RZR2020), orbital shaker (Ika, KSI30 Basic), and an electronic analytical balance (Adam, AA220LA) which was used for weighting the solid materials. In addition, for magnetic separations, a strong neodymium-iron-boron (Nd$_2$Fe$_{12}$B) magnet (1.2 T, 2.5 cm × 5 cm × 10 cm) was used. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300°C) was used.

2.2. Chemicals and Solutions. All chemicals used were at least of the analytical reagent grade. Triple distilled water was used throughout. A 1000 µg mL$^{-1}$ stock solution of As(III) was prepared by As$_2$O$_3$ (Merck). Similarly, a 1000 µg mL$^{-1}$ stock solution of As(V) was prepared by dissolving KH$_2$AsO$_4$ (Sigma). Accurately diluted solutions of As(III) and As(V) were prepared daily using standard stock solutions. The calibration curve was established using the standard solutions prepared in 1 mol L$^{-1}$ HNO$_3$ by dilution from stock solutions. The calibration curve solutions were prepared daily. Cetyltrimethylammonium bromide (CTAB), ferrous chloride (FeCl$_2$·4H$_2$O), ferric chloride (FeCl$_3$·6H$_2$O), potassium permanganate, aluminum isopropoxide, ethanol, acetonitrile, hydrochloric acid, and ammonia were used without further purification processes. The stock solution of ascorbic acid was prepared according to Lenoble et al. [33]. It was prepared daily before use. Stock solution of molybdate was prepared by adding 5.2 g ammonium molybdate and 8.8 mg potassium antimony tartrate in 30 mL of 9 mol L$^{-1}$ sulfuric acid and diluted by triple distilled water to a final volume of 50 mL in a volumetric flask and it is stable for one month. To adjust the pH, we used the buffered salts containing low negatively charged ions. The pH adjustments were made with HCl/KCl buffer solution to pH 1-2, CH$_3$COONa/CH$_3$COOH buffer solution to pH 3–5, CH$_3$COONH$_4$/CH$_3$COOH buffer solution to pH 6-7, and NH$_3$/NH$_4$Cl buffer solution to pH 8–10.

2.3. Preparation of CTAB@ACMNPs. ACMNPs were prepared according to our previous works [29, 30, 32]. In order to prepare ACMNPs coated with admicelles, 50 mg of CTAB was added to a beaker containing 100 mg of ACMNPs. The pH of this suspension was adjusted at the range from 8.0 to 9.0 by addition of 5 mL of NH$_3$/NH$_4$Cl buffer solution (0.1 mol L$^{-1}$). The mixed solution was shaken for 5 min and then CTAB@ACMNPs were separated from the reaction medium under the magnetic field and rinsed with 10 mL pure water. This product was used as sorbent for arsenate and arsenite ions.

2.4. General Procedure. The procedure for the magnetic extraction is presented in Figure 1 and details are as follows: 10 mL of As(V) solution (2 µg mL$^{-1}$) was added to CTAB@ACMNPs from the above section; subsequently, the pH value was adjusted to 8.5 with NH$_3$/NH$_4$Cl buffer and the solution was shaken for 2 min to facilitate adsorption of the As(V) ions onto the NPs. Then, the magnetite adsorbents were separated easily and quickly using magnet and decanted directly. Subsequently, 5.0 mL of mixture solution of 0.25 mol L$^{-1}$ H$_2$SO$_4$ and 0.25 mol L$^{-1}$ HNO$_3$ as eluent was added. Finally, the magnet was used again to settle
the magnetic nanoparticles and the eluate was separated for molybdenum blue method analysis. 0.5 mL of 98% H₂SO₄ was added to the eluate; subsequently, the solution was shaken and then 2.0 mL molybdate and 1.0 mL ascorbic acid stock solutions were added to the solution. After 45 s of shaking, the solution diluted by triple distilled water to a final volume of 50 mL in a volumetric flask and after 10 min waiting its absorbance was measured at 880 nm.

2.5. Oxidation of As(III) to As(V) and Determination of Total Arsenic. Oxidation of As(III) to As(V) has been performed under favourable conditions by spectrophotometric method using the procedure given in the literature [33–35]. After adjustment of the pH of the solution (pH 8.5), 1 mL of 10⁻² mol L⁻¹ KMnO₄ was added. After contact time of 5 min and oxidation of As(III) to As(V), the method given in Section 2.4 was applied to the determination of the total arsenic. The level of As(III) is calculated by difference of total arsenic and As(V) concentrations.

2.6. Sample Preparation Procedure for Water and Wastewater. Samples of water (i.e., tap water, river, and spring water) and wastewater were filtered through filter paper (Whatman, no. 4) to remove suspended particulate matter after collection and buffered to a pH of 8.5 with NH₃/NH₄Cl buffer prior to storage in polyethylene container for use. The SPE procedure was carried out as described in general procedure.

3. Results and Discussion

3.1. Characterization of ACMNPs. To enable practical application of ACMNPs, it is the most important that the sorbents should possess superparamagnetic properties. Magnetic properties were characterized by measuring the hysteresis and remanence curves by means of a vibrating sample magnetometer (VSM). SEM images of MNPs and ACMNPs also showing which the uniform size distribution of the nanoparticles [29, 30].

The XRD pattern for the ACMNPs showed eight characteristic peaks for Fe₃O₄ and Al₂O₃ according the software database file. The average crystallite size (D) is calculated to be 18.0 ± 2 nm for ACMNPs using the Debye-Scherrer formula of 

$$D = \frac{K \lambda}{\beta \cos \theta}$$

where K, λ, β, and θ are the Scherrer constant, the X-ray wavelength (λ = 1.5406 Å), the full peak width at half maximum (FWHM), and the Bragg diffraction angle, respectively (Figure 2).

3.2. Effect of Amounts of CTAB and ACMNPs. Hemimicelles and admicelles, which are formed by the adsorption of ionic surfactants on mineral oxides such as MNPs, have recently been used as novel sorbents for SPE of organic compounds with good results. Positively charged surfactants, such as CTAB, can strongly adsorb on negatively charged surfaces of ACMNPs in basic solutions. A concentration of CTAB, below its critical micellar concentration (CMC, 1 × 10⁻³ mol L⁻¹), was used. Above this concentration, the excess of CTAB
would form micelles in the aqueous solution, which were not adsorbed on ACMNPs surfaces. Therefore, influence of various amounts of 5, 10, 20, 30, 40, 50, 60, 80, and 100 mg CTAB on adsorption of As(V) ions through the ACMNPs substrate was investigated. The results showed that maximum adsorption was obtained when 50 mg of CTAB/0.1 g ACMNPs was used (Figure 3). Thus, this amount was selected as the optimum concentration of CTAB for further studies.

The effect of nanoparticles amounts on the quantitative extraction of As(V) was studied by applying various amounts of CTAB@ACMNPs (from 30 to 200 mg). The extraction was found to be quantitative when it is 100 mg or more. Experiments were carried out with 100 mg modified nanoparticles.

3.3. **Effect of pH.** In order to establish the effect of pH on the adsorption of arsenate, the batch equilibrium studies at different pH values were carried out in the range of 2–10 (Figure 4). Results show that the maximum removal of As(V) on the adsorbents was observed at the range from 8.0 to 9.0 by shaking the solution containing CTAB and ACMNPs for 5 min. When solution was basified, CTAB would form hemimicelles on ACMNPs by strong sorption and this micelles could trap As(V) ions. Therefore, the pH value of 8.5 was used as pH optimum for further studies.

3.4. **Effect of Sample Volume and Desorption Conditions.** In order to carry out SPE procedure on water samples leading to high preconcentration factor, the sample volume needs to be optimized. In this case, the effect of sample volume on the adsorption of 5.0 μg of As(V) on CTAB@ACMNPs was investigated. By using different feed volumes of water samples ranging between 50 and 600 mL, each of which containing fixed amounts of CTAB@ACMNPs (0.1 g), the maximum sample volume with high recovery percentage for the process was determined. According to results, the removal of As(V) ions was quantitative up to 350 mL of sample volume (removal >95%). At volumes higher than 350 mL, the analyte was not adsorbed effectively which is probably due to the lower magnetic field strength at higher dilutions (more dilutions cause an increase in height of test solutions in the beaker and so the strength of magnetic field decreases toward far points near the top of the solution), so the preconcentration factor of 175 was obtained.

In order to choose the best eluent for desorption of the adsorbed As(V) ions on ACMNPs, different eluents such as HNO₃, H₂SO₄ and HCl were investigated. Among these reagents, the mixture of H₂SO₄ and HNO₃ provided the maximum recovery. It was found that 5.0 mL of mixture solution of 0.25 mol L⁻¹ H₂SO₄ and 0.25 mol L⁻¹ HNO₃ was sufficient for quantitative recovery of adsorbed As(V).

3.5. **Standing and Magnetic Separating Time.** The effect of time on As(V) adsorption on the CTAB@ACMNPs was studied. In the experiment, CTAB@ACMNPs possessed large saturation magnetization and superparamagnetism properties, which enabled them to be completely isolated at the less than 1 minute by a strong magnet. When the CTAB@ACMNPs were isolated immediately without a standing process, the recovery of As(V) ions was only 65%. But, when the standing time was adjusted to 2, 5, 10, and 15 min, recoveries were improved to 93.0, 97.0, 97.5, and 97.5%, respectively. Standing time of 5 min...
was sufficient to achieve satisfactory adsorption and better recovery of As(V).

3.6. Interference Study. The study of interference ions was performed by binary mixtures containing 2.0 ng mL\(^{-1}\) of As(V) and a certain amount of one of the foreign ions. The following excesses of ions do not interfere (i.e., caused a relative error of less than 5%): less than a 1000-fold (the largest amount tested) amount of Na\(^+\), K\(^+\), NO\(_3^-\), F\(^-\), Cl\(^-\), and Br\(^-\); a 500-fold amount of NH\(_4^+\), Co\(^{2+}\), Zn\(^{2+}\), and Ca\(^{2+}\); a 200-fold amount of Ni\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\), Fe\(^{3+}\), Mn\(^{2+}\), Cd\(^{2+}\), Fe\(^{3+}\), and Al\(^{3+}\); a 100-fold amount of Ca\(^{2+}\), Ba\(^{2+}\), and Mg\(^{2+}\); a 50-fold amount of Pb\(^{2+}\), Hg\(^{2+}\), and Ag\(^+\); and a 1-fold amount of PO\(_4^{3-}\). The results showed that most of the investigated ions do not interfere in the adsorption-desorption and determination of traces of As(V) in real samples; only PO\(_4^{3-}\) appeared to interfere with arsenate for molybdenum blue method [41]. As was to be expected, PO\(_4^{3-}\) has a similar effect as arsenate for the absorbance intensity of this method. The interference of PO\(_4^{3-}\) was eliminated when the sample solution was masked by a certain amount of one of the foreign ions. The interference of PO\(_4^{3-}\) and As(V) and a certain amount of one of the foreign ions. The studied ions interfered with arsenate for molybdenum blue method [41].

3.7. Adsorbent Regeneration and Adsorption Capacity. In this research, it also was found that the adsorbent can be reused up to four times without loss of analytical performance. Considering that 4.0 g of modified ACMNPs could be prepared in one batch and only 100 mg of ACMNPs was used for one extraction operation, this reusability time is acceptable. Adsorption capacity study used here was adapted from the method recommended by Maquielra et al. [42]. The static sorption capacity of CTAB@ACMNPs was found to be 9.4 mg g\(^{-1}\) for As(V) ions.

3.8. Adsorption Isotherm. The equilibrium isotherm of As(V) adsorption by the CTAB@ACMNPs in 0.01 mol L\(^{-1}\) NH\(_4\)/NH\(_4\)Cl buffer solution at pH 8.5 and 25\(^{\circ}\)C is shown in Figure 5. The adsorption behavior could be described by the Langmuir adsorption equation:

\[
\frac{C_e}{Q_e} = \frac{1}{KQ_m} + \frac{C_e}{Q_m},
\]

where \(Q_m\) is the equilibrium adsorption amount of As(V) (mg g\(^{-1}\)), \(C_e\) is the equilibrium As(V) ions concentration in the solution (mg mL\(^{-1}\)), \(Q\) is the maximum adsorption amount of As(V) per gram of adsorbent (mg g\(^{-1}\)), and \(K\) is the Langmuir adsorption equilibrium constant (L mg\(^{-1}\)) [43]. A plot of \(C_e/Q_e\) against \(C_e\) will result in a straight line with slope \(1/Q\) and intercept \(1/KQ\) (Figure 6).

3.9. Analytical Performance and Method Validation. Under the optimal experimental conditions, the analytical features of the method such as limit of detection (LOD), limit of quantitation (LOQ), linear range of the calibration curve and precision were examined. The LOD and LOQ of the proposed method based on three and ten times the standard deviation of the blank (3S\(_b\) and 10S\(_b\)) were 0.028 and 0.093 \(\mu\)g mL\(^{-1}\), respectively. The linear range of calibration curve for As(V) was 0.090–4.0 \(\mu\)g mL\(^{-1}\) with a correlation coefficient of 0.9996. The regression equation was \(A = 0.2390C_{As(V)} + 0.0056\) (n = 10), where \(C_{As(V)}\) is the concentration of As(V) in \(\mu\)g mL\(^{-1}\) and \(A\) is the absorbance. The relative standard deviation (RSD) for 7 replicate measurements of 2.0 \(\mu\)g mL\(^{-1}\) of As(V) was 2.8%.

3.10. Real Sample Analysis. The performance and reliability of the method for the analysis of real samples were checked by determination of As(V), As(III), and total arsenic content in different water samples. In order to determine total arsenic, model solutions that contain different amounts of As(V) and As(III) were prepared. Then, the oxidation of As(III) to As(V) in the test solutions was performed by the procedure explained in Section 2.5. The results show that the proposed method could be successfully applied to the determination and speciation of arsenic (Table 1).
Table 1: Application of the proposed method to the speciation of As in different water samples (sample volume: 50 mL, $n = 7$). The results are mean of seven measurements ± standard deviation.

| Sample                  | Added, As(III) ($\mu$g mL$^{-1}$) | Added, As(V) ($\mu$g mL$^{-1}$) | Found, As(III) ($\mu$g mL$^{-1}$) | Found, As(V) ($\mu$g mL$^{-1}$) | Found, total As ($\mu$g mL$^{-1}$) | As(III) Recovery (%) | As(V) Recovery (%) | Total As Recovery (%) |
|-------------------------|-----------------------------------|---------------------------------|----------------------------------|---------------------------------|-----------------------------------|----------------------|---------------------|----------------------|
| Tap water from Kerman city | 4.0                               | —                               | 4.06 ± 0.18                      | —                               | 4.06 ± 0.18                      | 101.5 ± 2.1          | —                   | 101.5 ± 2.0          |
|                         | —                                 | 4.0                             | 4.15 ± 0.22                      | —                               | 4.15 ± 0.22                      | —                    | 103.7 ± 2.0         | 103.7 ± 2.7          |
|                         | 4.0                               | 4.0                             | 4.10 ± 0.10                      | 4.20 ± 0.24                     | 8.30 ± 0.20                      | 102.5 ± 2.3          | 105.0 ± 2.8         | 103.7 ± 2.4          |
| River water from Hajiabad river | 4.0                               | —                               | 4.24 ± 0.09                      | 0.28 ± 0.05                     | 4.52 ± 0.08                      | 106.0 ± 1.8          | —                   | 105.6 ± 2.2          |
|                         | —                                 | 4.0                             | 4.30 ± 0.18                      | 4.30 ± 0.18                     | —                                | 101.2 ± 2.0          | 101.2 ± 2.0         | 103.4 ± 2.0          |
|                         | 4.0                               | 4.0                             | 4.20 ± 0.12                      | 4.35 ± 0.20                     | 8.55 ± 0.20                      | 105.0 ± 1.8          | 102.5 ± 2.2         | 103.4 ± 2.0          |
| Spring water from Bandar Abbas city | 4.0                               | —                               | 0.36 ± 0.03                      | 0.61 ± 0.03                     | 0.97 ± 0.03                      | —                   | —                   | 102.2 ± 2.0          |
|                         | —                                 | 4.0                             | 4.48 ± 0.11                      | 0.58 ± 0.06                     | 5.06 ± 0.12                      | 103.0 ± 1.8          | —                   | 100.6 ± 2.2          |
|                         | 4.0                               | 4.0                             | 0.34 ± 0.03                      | 4.66 ± 0.20                     | 5.00 ± 0.15                      | —                   | 100.2 ± 2.0         | 101.7 ± 2.7          |
|                         | 4.0                               | 4.0                             | 4.45 ± 0.14                      | 4.66 ± 0.18                     | 9.11 ± 0.22                      | 102.2 ± 2.4          | 101.7 ± 2.7         | 101.5 ± 2.2          |
4. Conclusions

It has been demonstrated that the modified NPs provide a new and fast route for separation/preconcentration and speciation analysis of As(V) and As(III). This method is certainly faster and more convenient than other methods that have been proposed for simultaneous SPE and speciation of arsenic ions. Magnetic separation greatly shortened the analysis time of the method. This sorbent was successfully applied to efficient enrichment of trace amounts of arsenic ions from real samples. Table 2 shows a comparison of the proposed method with other reported methods. It could be seen that some obtained values for the proposed method such as relative standard deviation (RSD), enrichment factor, sorbent capacity, and detection limit are as or better than some of the previously reported methods. Furthermore, it avoids the time-consuming column passing (about 1 h in conventional SPE method) and filtration operation, and no clean-up steps were required. The main benefits of this methodology are simplicity and high capacity of sorbent, preconcentration factor, fast adsorption, and low cost.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Table 2: Comparison of the characteristic data between typical published methods and the proposed method in this work.

| Sorbent      | Species                | Enrichment factor | Sorbent capacity (mg g⁻¹) | RSD (%) | Detection limit (µg mL⁻¹) | Detection method | Reference |
|--------------|------------------------|-------------------|---------------------------|--------|--------------------------|------------------|-----------|
| APDC/C-18    | As(III), As(V)         | 50                | NR                        | NR     | 0.0012¹, 0.09²           | ICP-MS          | [15]      |
| TiO₂         | As(III)                | 20                | NR                        | 2.4    | 0.1³                      | GFAAS           | [36]      |
| APDC/CNTs    | As(III), As(V)         | 250               | 9.1                       | 3.5    | 0.02²                     | GFAAS           | [37]      |
| PVP⁻⁻-impregnated SPE membrane disk | As(III) | NR | NR | NR | 0.01 | Colorimetry | [38] |
| CTAC⁻⁻/CNTs  | As(V)                  | NR                | NR                        | 5.3    | 2.0                       | AF²⁴             | [39]      |
| Hybrid nano ZrO₂/B₂O₃ | As(III), As(V) | 20 | 98.04 | 5.0 | 9.25 | HGAAS| [40] |
| CTAB@ACMNPs  | As(V), As(III)         | 175               | 9.4                       | 2.8    | 0.028                     | Molybdenum blue | This work |

¹Ammonium pyrrolidine dithiocarbamate, ²not reported, ³is in µg L⁻¹, ⁴Inductively coupled plasma-mass spectrometry, ⁵carbon nanotubes, ⁶poly(vinyl-pyrrolidone), ⁷cetyltrimethylammonium chloride, ⁸atomic fluorescence spectrophotometry, ⁹hydride generation atomic absorption spectrometry.
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