Kinetic-spectrophotometric determination of trace amounts of As(III) based on its inhibitory effect on the redox reaction between bromate and hydrochloric acid

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Abstract

A simple, sensitive, rapid and reliable method has been developed for spectrophotometric determinations of As(III) in the presence of As(V) based on its inhibition effect on the redox reaction between bromate and hydrochloric acid. The decolorization of methyl orange by the reaction products was used to monitor the reaction spectrophotometrically at 525 nm. The method allows the determination of arsenic in the range of 6–1000 μg l⁻¹. The relative standard deviation for 10 determinations of 40 μg l⁻¹ of As(III) was 1.43% and the limit of detection, corresponding to a signal to noise ratio of three, was 3.4 μg l⁻¹. The proposed method was applied to the determination of As(III) in water samples with satisfactory results. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Arsenic (III) determination; Kinetic-spectrophotometric; Bromate; Water

1. Introduction

Arsenic (As) occurs in the earth’s crust at an average level of 2–5 ppm. The primary anthropogenic source of arsenic is fossil fuel combustion. Mining provides a secondary source, especially as a by-product of copper, gold, and lead refining. Dissolved arsenic can occur in natural waters in both inorganic and organic forms. Arsenic is a toxic element. Its biochemical effects include protein coagulation, enzyme inhibition, and uncoupling of phosphorylation. Acute poisoning results from the ingestion of ca. 100 mg of the element, and much lower levels cause chronic poisoning. There is some evidence that arsenic is also carcinogenic [1]. For potable water, the United States Public Health Service recommended 10 μg l⁻¹, with a maximum permissible concentration of 50 μg l⁻¹ [2]. Therefore, simple, rapid, highly sensitive, and accurate methods are required for the determination of trace amounts of arsenic in samples.

Different methods were used for arsenic determination. These include titrimetry [3,4], chemiluminescence [5,6], polarography [7], hydride generation atomic absorption spectrometry [8,9], inductively coupled plasma atomic emission spec-
trometry (ICP-AES) [10,11], inductively coupled plasma mass spectrometry (ICP-MS) [12], chromatography [13,14], and spectrophotometry [15–18]. Some of these methods are either not sensitive enough or require complicated and expensive instruments or only allow us to determine directly the total amount of arsenic, that is, the distinction between As(III) and As(V) requires ancillary manipulation.

Kinetic methods of analysis are attractive alternatives for the determination of trace amounts of arsenic. Such methods have the general advantage of combining high sensitivity with relatively simple procedures and apparatus [19–21]. Alekseeva and Kurtova determined As(III) in the range of 0.03–0.15 µg ml⁻¹ based on its effect on the induction period of the oxidation reaction of Br⁻ by periodate [22]. Garcia et al. determined As(III) in the range of 6.2–62.6 µg l⁻¹ based on its inhibition effect on the Pd(II)-catalyzed reaction between pyronine G and hypophosphite [23]. Sicilia et al. determined As(III) in the range of 7–320 µg l⁻¹ based on its accelerating effect on the Os(VIII)-catalyzed reaction between iodide and bromate in micellar media [24]. Stoytcheva et al. determined As(III) based on its inhibition action on the enzyme acetylcholinesterase [25].

Burgess and Ottaway reported a method for the determination of As(III) based on its effect on the redox reaction of bromate with bromide ion in sulfuric acid media [26]. The bleaching of methyl orange with liberated bromine was used to measure the reaction time. They used different working conditions for the determination of different concentrations of As(III). In some conditions, As(III) showed inhibitory effect at high concentrations and catalytic effect at low concentrations. Any calibration equation or other analytical parameters were not reported.

In this paper, we describe the development of a new method for the determination of As(III) based on its inhibition effect on the reaction of bromate with hydrochloric acid. The method is very rapid, simple, sensitive, and accurate. As(III) as low as 6 µg l⁻¹ could be determined by this method.

2. Experimental

2.1. Reagents

All solutions were prepared using reagent grade substances and triply distilled water. A standard solution (1000 mg l⁻¹) of As(III) was prepared by dissolving 0.3301 g As₂O₃ (Merck) in 25 ml 0.10 N NaOH solution followed by the addition of 25 ml 0.10 N H₂SO₄ solution and diluting to the mark in a 250-ml volumetric flask. Working solutions were prepared by appropriate dilution of stock solutions as required. A 0.10 M potassium bromate solution was prepared by dissolving 1.770 g of KBrO₃ (Merck) in water and diluting to 100 ml in a volumetric flask. A solution of 100 mg l⁻¹ methyl orange was prepared by dissolving 0.01 g of methyl orange (Merck) in water and diluting to 100 ml with water. Hydrochloric acid solution was prepared by appropriate dilution of concentrated hydrochloric acid (Merck).

2.2. Apparatus

Absorbance–time graphs at fixed wavelength were recorded on a Shimadzu model UV-265-UV–Visible recording spectrophotometer.

2.3. Procedure

All the solutions were equilibrated at 23 ± 0.1°C before the beginning of the reaction. The inhibited reaction was followed spectrophotometrically by monitoring the change in absorbance at 525 nm. A suitable aliquot of sample solution containing 60–10,000 ng As(III) was transferred into a 10-ml volumetric flask, then 1.4 ml of 2.50 M HCl solution was added, followed by 1.0 ml of 100 mg l⁻¹ methyl orange solution. The solution was diluted to ca. 9 ml with water and then 1.0 ml of 4.2 × 10⁻⁴ M bromate solution was added. The stopclock was started just after the addition of bromate solution. The solution was diluted to the mark with water and a portion was transferred to a glass cell within 20 s for measurement of the variation in absorbance with time at 525 nm.
3. Results and discussion

Bromate is reduced by chloride ion in acidic media to produce Br\(_2\) and Cl\(_2\).

\[2\text{BrO}_3^- + 10\text{Cl}^- + 12\text{H}^+ \leftrightarrow \text{Br}_2 + 5\text{Cl}_2 + 6\text{H}_2\text{O}\]

The produced Br\(_2\) and Cl\(_2\) react with methyl orange and decolorize it.

Therefore, this reaction could be monitored spectrophotometrically by measuring the decrease in absorbance versus time at 525 nm.

The presence of As(III) in the medium slows the reaction, which is fairly fast in its absence or when the medium is very acidic. As(III) reacts with the liberated Br\(_2\) and Cl\(_2\) according to the following reaction and causes an induction period [26,27]:

\[\text{As(III)} + \text{X}_2 \rightarrow \text{As(V)} + \text{X}^- \quad (\text{X} = \text{Cl or Br})\]

Fig. 1 shows the graph of absorbance change versus time for different concentrations of As(III). As Fig. 1 shows, an increase in As(III) concentration caused an increase in the induction period of the reaction.

A graph of the induction period versus As(III) concentration was linear within a range of As(III) concentration. The induction period was measured mathematically from the regression equations of the linear parts of the absorbance–time graph. The regression equation for the first linear part of the graph is:

\[A = a_1 + b_1t\]

For the second linear part, it is:

\[A = a_2 + b_2t\]

By equating these equations, the induction period is calculated as:

\[t_{ip} = (a_1 - a_2)/(b_2 - b_1)\]

3.1. Effect of variables

To take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimized. Various experimental parameters were studied in order to obtain the optimized system. These parameters were optimized by setting all parameters to be constant and optimizing one each time.

The effect of hydrochloric acid concentration was studied in the range of 0.05–0.45 M. As Fig. 2 shows, an increase in HCl concentration caused a decrease in induction period and an increase in the slope of the absorbance change after initiation of the reaction. In order to find the optimum concentration of hydrochloric acid, the absorbance change for the uninhibited reaction (the reaction in the absence of arsenic) and inhibited

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Fig. 1. Change in absorbance of 10 mg l\(^{-1}\) methyl orange with time in the presence of \(4.2 \times 10^{-5}\) M bromate, 0.35 M HCl and (a) 0.00, (b)100, (c) 300, (d) 500, and (e) 1000 \(\mu\)g l\(^{-1}\) As(III).
Fig. 2. Change in absorbance of 10 mg l\(^{-1}\) methyl orange with time in the presence of 4.2 \(\times\) 10\(^{-5}\) M bromate, 350 \(\mu\)g l\(^{-1}\) As(III) and (a) 0.20, (b) 0.25, (c) 0.30 and (d) 0.35 M HCl.

Fig. 3. Absorbance change for (■) uninhibited and (▲) inhibited reactions and (△) their difference as a function of HCl concentration. Conditions: BrO\(_3^−\), 8.4 \(\times\) 10\(^{-5}\) M; As(III), 350 \(\mu\)g l\(^{-1}\); methyl orange, 10 mg l\(^{-1}\); \(\Delta t = 80\) s.

Fig. 4. Change in absorbance of 10 mg l\(^{-1}\) methyl orange with time in the presence of 0.35 M HCl, 350 \(\mu\)g l\(^{-1}\) As(III) and (a) 2.0 \(\times\) 10\(^{-5}\), (b) 4.0 \(\times\) 10\(^{-5}\), (c) 6.0 \(\times\) 10\(^{-5}\), (d) 1.0 \(\times\) 10\(^{-4}\) and (e) 2.0 \(\times\) 10\(^{-4}\) M bromate.

Table 1

<table>
<thead>
<tr>
<th>As(III) taken (µg l(^{-1}))</th>
<th>Relative error (%)</th>
<th>RSD (n = 8) (%)</th>
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<tr>
<td>20.0</td>
<td>1.80</td>
<td>2.11</td>
</tr>
<tr>
<td>40.0</td>
<td>−1.20</td>
<td>1.60</td>
</tr>
<tr>
<td>150.0</td>
<td>0.87</td>
<td>1.43</td>
</tr>
<tr>
<td>250.0</td>
<td>0.90</td>
<td>1.27</td>
</tr>
<tr>
<td>600.0</td>
<td>−0.40</td>
<td>0.89</td>
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</table>

reaction (the reaction in the presence of arsenic) at a fixed time of 80 s as a function of HCl concentration was measured. The results are shown in Fig. 3. As Fig. 3 shows, the difference between absorbance change for uninhibited and inhibited reactions is maximum at 0.35 M HCl. Therefore, a final concentration of 0.35 M acid was selected as optimum.

The effect of bromate concentration in the range of 2.0 \(\times\) 10\(^{-5}\) – 2.0 \(\times\) 10\(^{-4}\) M was investigated. As Fig. 4 shows, an increase in bromate concentration caused a decrease in the induction period and an increase in the slope of the absorbance change after initiation of the reaction. It was also observed that the calibration range differed according to the concentration of bromate and hence the concentration of bromate must be selected on this basis.
3.2. Analytical parameters

The calibration graph was obtained under the following conditions: BrO$_3^-$, $4.2 \times 10^{-5}$ M; HCl, 0.35 M; methyl orange, 10 mg l$^{-1}$ and temperature, 23$^\circ$C. The calibration graph was linear in the range of 6–1000 μg l$^{-1}$. The regression equation is $t_{ip} = 17.83 + 0.33301C$, with a correlation coefficient of 0.9998, where $t_{ip}$ is the induction period in seconds and $C$ is As(III) concentration in micrograms per liter.

To evaluate the precision and accuracy of the method, a series of independent standard samples was used. The results are given in Table 1.

The limit of detection, which can be calculated on the basis of $Y_{LOD} = Y_B + 3S_B$, in which $Y_{LOD}$, $Y_B$ and $S_B$ are the signal of limit of detection, signal of blank, and standard deviation of blank [21], respectively, was 3.4 μg l$^{-1}$.

3.3. Selectivity

To study the selectivity of the proposed method, the effect of various cations and anions on the determination of 100 μg l$^{-1}$ of As(III) was studied. An error of ±3% was considered tolerable. The results are given in Table 2. As Table 2 shows, As(V) and most of the investigated cations and anions did not interfere even when present in 100-fold excess over As(III). This shows that the method is suitable for distinction between As(III) and As(V) species.

3.4. Application

To evaluate the analytical applicability of the

<table>
<thead>
<tr>
<th>Sample</th>
<th>As(III) added (μg l$^{-1}$)</th>
<th>As(III) found* (μg l$^{-1}$)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drinking water</td>
<td>30.0</td>
<td>31.0</td>
<td>103</td>
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<tr>
<td></td>
<td>50.0</td>
<td>48.0</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>200.0</td>
<td>198.0</td>
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<tr>
<td>Spring water</td>
<td>20.0</td>
<td>19.0</td>
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</tr>
<tr>
<td></td>
<td>60.0</td>
<td>62.0</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>500.0</td>
<td>505.0</td>
<td>101</td>
</tr>
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</table>

* Average of five determinations.
proposed methods, As(III) was determined after addition to water samples. Table 3 shows the results. The recoveries being close to 100% indicates that there is no serious interference in such water samples.

References