INTRODUCTION

Arsenic occurs naturally in the Earth’s crust in its inorganic form, trivalent (arsenite) or pentavalent (arsenate). Erosion of arsenic containing surface rocks probably accounts for a significant amount of arsenic in water supplies. It is a ubiquitous element in water, soil and sediments. The occurrence of arsenic in plants and animals generally reflects its accumulation from the environment. The presence of arsenic in drinking water has reached calamitous proportions in many parts of the world. There are numerous reports in the literature based on past and ongoing experience in various countries in Asia and South America concerning the higher risks of skin, bladder, lung, liver, and kidney cancer that result from continued consumption of elevated levels of arsenic in drinking water [1]. Consumption of even low levels of arsenic over a long period can cause a multitude of diseases. The maximum permissible limit for arsenic in drinking water is 0.05 mg/L as recommended by WHO [2]. In certain areas in India, Bangladesh, China, and Mongolia [3], arsenic levels in groundwater exceed 1 mg/L. Regarding inorganic arsenic, arsenic(III) is appreciably more toxic than arsenic(V). Usually these species of arsenic in natural water are found at the trace levels [10]. There are only a few analytical techniques available, which have sufficient sensitivity and selectivity to directly determine these species of arsenic, at the trace levels in natural water. Therefore, the development of sensitive and accurate methods for speciation and preconcentration of trace amounts of arsenic(III) and arsenic(V) is necessary. Recently, many kinds of conventional analytical techniques, such as hydride generation—inductively coupled plasma atomic emission spectrometry (HG-ICP-AES) [5], capillary electrophoresis inductively coupled plasma-mass spectrometry (CE-ICP-MS) [4], high performance liquid chromatography—inductively coupled plasma mass spectroscopy [5], electrothermal atomic absorption spectrometry (ETAAS) [6], hydride generation — atomic absorption spectrometry [7], hydride generation — atomic fluorescence spectrometry [8], cathodic stripping voltammetry [9], anodic stripping voltammetry [10], neutron activation analysis [11], photometric analysis [12], ion selective electrodes [13] and energy-dispersive X-ray fluorescence spectrometry [14], have been used for the determination of low concentrations of arsenic. But all these techniques are costly and require trained staff. Recently, most of the spectrophotometric methods have been developed as an alternative for the determination of arsenic instead of conventional techniques.

The N-substituted dithiocarbamates are widely used as chelating agents for the separation of trace heavy metals from matrix species as well as their preconcentration prior to determination. Among the N-substituted dithiocarbamates, ammonium pyrrolidine-dithiocarbamate (APDC) and sodium diethyldithiocarbamate (NaDDC) are chelating agents which have found widespread application in the extraction of metal ions. However, hexamethylene ammonium — hexamethylenedithiocarbamate (HMA-HMDTC) has been used recently in various preconcentration and separation techniques [15]. Metal-dithiocarbamate complexes are usually measured by UV-Visible spectrophotometry and flame atomic absorption spectrometry after extraction with nonpolar organic solvents. Solvent extraction techniques are time-consuming, tedious and usually involve harmful solvents.

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Abstract—We have developed a cost-effective and sensitive spectrophotometric method for the determination of arsenic at trace level using a new reagent, hexamethylene ammonium-hexamethylenedithiocarbamate (HMA-HMDTC). Here we show that arsenic reacts with HMA-HMDTC in acidic conditions to yield the As(HMDTC)₃ complex. We studied the Beer’s law at 256 nm, which showed linearity over the concentration range 0.2–1.0 µg/mL of arsenic. We have shown that molar absorptivity, Sandell’s sensitivity and the detection limit of the method are 6.06×10⁴ L/mol cm, 0.0012 µg/cm² and 0.060 µg/mL, respectively. We have applied this new method to the determination of arsenic in drinking water.

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However, micellar systems have been conveniently used in UV-Vis spectrophotometry because they are stable in aqueous solution and transparent optically, enhance sensitivity, and are readily available.

When the concentration of surfactant exceeds the critical micelle concentration, micelles are formed in aqueous solution. Micelles appear to be homogeneous in aqueous solution. In the nonpolar core of micellar media, nonpolar compounds, such as organic molecules or nonionic complexes, are highly soluble. The anionic or nonionic surfactants have been used more than cationic surfactants to determine metal ions by UV-Vis spectrophotometry. Since a metal ion is a cation and there is no electrostatic attractive interaction between a metal ion and cationic surfactant, the complex forming process is not affected.

The present work aims at developing a rapid, low cost, accurate and simple analytical method for the determination of arsenic(III) at sub milligram per liter levels. In the proposed method arsenic reacts with HMA-HMDTC in acidic conditions to form the As(HMDTC)₃ complex. The liberated complex is measured at the maximum absorbance wavelength of 256 nm. HMA-HMDTC was firstly used for the determination of As(III). This method has been compared with some of the common spectrophotometric methods reported for arsenic and found to be more sensitive.

**EXPERIMENTAL**

A Shimadzu UV-1601 PC spectrophotometer was used for all spectral measurements. To adjust the pH values and prepare the buffer solutions, a Hanna pH 211 model digital pH meter equipped with a combined glass and calomel electrode, was used. All the reagents used were of analytical grade, and de-ionized water was used for preparation of solutions. Standard arsenic solutions were made from 1000 mg/L stock solutions; 0.1% (w/v) solution of hexamethylene-dithiocarbamate (HMDTC) was prepared daily by dissolving appropriate amounts of home-synthesised crystalline hexamethyleneammonium HMDTC in 96% ethanol [7]. The solutions of surfactant were made as 1% (w/v) in 96% ethanol and 10% KOH (Merck); 2.5% KOH and 0.1 M HNO₃ (Merck) solutions were used to adjust the pH. To prepare KI-ascorbic acid (5%, m/v each) reducing solution, 5 g of KI and 5 g of ascorbic acid (p.a., Merck), were dissolved in 100 mL of water.

### Analytical Procedure for the Determination of Arsenic(III)

For the spectrophotometric examination of arsenic with HMDTC in Triton X-100 media, 1 mL of 10 mg/L of arsenic was placed into a 10 mL volumetric flask then 1 mL of 1.0% Triton X-100 and 0.5 mL of 0.1% HMDTC were added into this flask. The mixture was diluted with pH 3 solution to 10 mL. To obtain the absorption spectrum of this mixture, it was transferred to a quartz cuvette. The absorbance was measured at 256 nm against a reagent blank which was prepared in the same way as described above. Standard arsenic solutions were prepared in the range of 0.2–1.0 mg/L. The calibration graph was constructed by UV-Vis spectrophotometry; the calibration graph is linear up to 1.0 mg/L of arsenic. The analytical parameters of the calibration curve are shown in Table 1.

### Table 1. Optical characteristics, precision and accuracy of the proposed method

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.0</td>
</tr>
<tr>
<td>λ&lt;sub&gt;max&lt;/sub&gt;, nm</td>
<td>256</td>
</tr>
<tr>
<td>Beer’s law limits, µg/mL</td>
<td>0.2–1.0</td>
</tr>
<tr>
<td>Limit of detection, µg/mL</td>
<td>0.060</td>
</tr>
<tr>
<td>Molar absorptivity, L/mol cm²</td>
<td>6.06 × 10⁴</td>
</tr>
<tr>
<td>Sandell’s sensitivity, µg/cm² per 0.001 absorbance unit</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

### Sample Preparation and Measurement Conditions

Generally, total inorganic arsenic is determined after prereducing As(V) to As(III) using KI-ascorbic acid or L-cysteine in HCl medium. In this work, we used KI-ascorbic acid as reducing reagent. To use KI and ascorbic acid as reducing reagent 5 mL aliquot of sample were transferred to a 10 mL test tube and then 1 mL of 5% KI-Ascorbic acid solution was added. The solution was mixed and left for 1 h at room temperature to complete the reduction. Tap water samples were taken from Kocaeli and Istanbul regions in Turkey. Water samples were collected in polyethylene containers and the samples were conserved with 1 ml of conc. HNO₃ (68%) added to 1 L until pH 2–3. The recovery investigation of arsenic in tap water was performed with a solution of 5 mL of the water, 1 mL of 1.0% Triton X-100, and 0.5 mL 0.1% HMDTC and 0.0 mL, 0.5 mL, and 1.0 mL of 1 mg/L of arsenic standard solution added to each 10 mL volumetric flask and filled to 10 mL with pH 3.0 solution.

### RESULTS AND DISCUSSION

**Absorption spectra of As (HMDTC)₃ in Triton X-100**

A large number of surfactants is available for scientific use. These are usually categorized according to the type of hydrophilic group. As stated above, the anionic or nonionic surfactants have been used more frequently than cationic surfactants to determine metal ions by UV-Vis spectrophotometry. Hence, we preferred non-ionic Triton X-100 as the surfactant reagent. In this method, the surfactant may play the...
role of a stabilizer. Here we show that it stabilizes the formed complex up to 15 min. One mL of 1.0% Triton X-100 and 0.5 mL of 0.1% HMDTC were added to this volumetric flask. This mixture was diluted with pH 3 solution to 10 mL. The absorption spectra of the formed complex, Triton X-100 and HMDTC are shown in Fig. 1. All spectral measurements were performed at 256 nm.

**The effect of pH on the absorbance of As(HMDTC)₃.** The effect of pH on the absorbance of As(HMDTC)₃ in 1% (v/v) Triton X-100 and 0.1% (w/v) HMDTC was investigated (Fig. 2). This result proves that the complex is formed in acidic media at pH 3, too. Based on this result, pH 3 was chosen for the further experiments. It was observed that there was no variation of the absorbance between pH 6 and 7.

**The effect of amount of HMDTC.** The stoichiometry of As-hexamethylenedithiocarbamate using the isomolar continuous variation method was reported by Dapaah et al. [16]. It is known that arsenic is stoichiometrically combined with HMDTC to form 1 : 3 complexes. For metal complexes to be formed quantitatively, however, one must add an excess of the chelating agent to the sample solution. Figure 3 shows how the absorbance of As(HMDTC)₃ complex changes with the amount of HMDTC in 1% (v/v) Triton X-100 in pH 3 medium. An optimum volume of 0.5 mL of 0.1% (w/v) HMDTC was fixed for further studies.

**The effect of concentration of Triton X-100.** As the concentration of surfactant increases, more micelles are formed so more nonpolar complexes will be contained in the micelles. Triton X-100 is a nonionic surfactant and its critical micelle concentration is 0.021% (w/v). The micelles were formed as the concentration of surfactant in the present experiment was above the critical micelle concentration. With the concentration of Triton X-100 varying from 0.5 to 2.0 mL, the absorbance of As³⁺ complex was investigated (Fig. 4).

**Stability of As (HMDTC).** The temporal stability of the As (HMDTC)₃ complex was investigated at pH 3.0 in the presence of Triton X-100. The arsenic complex was observed to be stable in Triton X-100 for up to 15 min. However, the arsenic complex was formed in 5 min and remained stable for up to 15 min. It seems that HMDTC combines with the metal ion to form a nonpolar complex, and the complex is extracted instantaneously into the local nonpolar environment of the micelle.

**Interference studies.** Although hexamethylene-dithiocarbamate does not form complexes with alkali and alkaline earth metals, high concentrations of them were tested, due to their presence in natural water. K and Na were tolerable up to 1 g/L while Mg and Ca up to 100 mg/L. Chloride anions do not cause any significant interference even in concentrations (5 g/L). On the other hand it is well known that transition metals form strong complexes with HMDTC, so the recovery

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**Fig. 1.** a) Absorption spectra of As (HMDTC)₃ (1.0 µg/mL) in nonionic Triton X-100; 1 mL of 1% Triton X-100 + 0.5 mL of 0.1% HMDTC + pH 3; b) under the same conditions, only Triton X-100 without HMDTC; c) only HMDTC without Triton X-100.

**Fig. 2.** Effect of pH on absorption spectra of As(HMDTC)₃ (1.0 µg/mL); 1 mL of 1% Triton X-100 + 0.5 mL of 0.1% HMDTC.

**Fig. 3.** Effect of the amount of HMDTC on absorption spectra of As(HMDTC)₃ (1.0 µg/mL); 1 mL of 1% Triton X-100, pH 3.

**Fig. 4.** Effect of pH on absorption spectra of As(HMDTC)₃ (1.0 µg/mL); 1 mL of 1% Triton X-100 + 0.5 mL of 0.1% HMDTC.
of 0.1 mg/L of arsenic was tested in the presence of these metals under the optimum conditions described above. The elements Mn(II), Fe(III), and Cr(III) were found not to interfere at concentrations up to 50 mg/L, while Cu(II), Co(II), Cd(II), and Sn(II) were tolerable up to 5 mg/L.

Accuracy and Application of the Proposed Method

The calibration graph was linear in the concentration range 0.2–1.0 mg/L of As(III). We show that molar absorptivity, Sandell’s sensitivity and the detection limit of the method are $6.06 \times 10^4$ L/mol cm, 0.0012 µg/cm² and 0.060 µg/mL, respectively. The calibration graph of arsenic constructed by a UV-Vis spectrophotometer is linear up to 1.0 mg/L of arsenic. The calibration curve for As$^{3+}$ constructed under optimum conditions show good linearity. The results obtained by using these techniques are given in Table 2. This method has been compared with some of the common spectrophotometric methods reported for arsenic and found to be more sensitive (Table 3).

CONCLUSION

The proposed procedure provides a selective, accurate and precise method for the determination of

Table 2. Analytical data of the determination of arsenic(III) in real samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spiked, µg/mL</th>
<th>Measured*, µg/mL</th>
<th>CV</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water (Izmit)</td>
<td>0.000</td>
<td>n.d.</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tap water (Izmit)</td>
<td>0.500</td>
<td>0.495 ± 0.017</td>
<td>2.3</td>
<td>99</td>
</tr>
<tr>
<td>Tap water (Izmit)</td>
<td>1.000</td>
<td>0.990 ± 0.016</td>
<td>2.2</td>
<td>99</td>
</tr>
<tr>
<td>Tap water (Istanbul)</td>
<td>0.000</td>
<td>n.d.</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tap water (Istanbul)</td>
<td>0.500</td>
<td>0.524 ± 0.021</td>
<td>2.7</td>
<td>105</td>
</tr>
<tr>
<td>Tap water (Istanbul)</td>
<td>1.000</td>
<td>1.022 ± 0.022</td>
<td>1.9</td>
<td>102</td>
</tr>
</tbody>
</table>

* Mean ±ts/√n (95% confidence level), n = 3.

Table 3. Comparison with other methods

<table>
<thead>
<tr>
<th>no.</th>
<th>Reagents/reference</th>
<th>Wavelength max, nm</th>
<th>Range of determination, mg/L</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ammonium molybdate + sodium metavanadate [17]</td>
<td>460</td>
<td>1–30</td>
<td>Phosphorus, silicon, interfere; less sensitive</td>
</tr>
<tr>
<td>2</td>
<td>Silver diethylidithiocarbamate + piperidine [18]</td>
<td>500</td>
<td>0.03–0.24</td>
<td>A toxic reagent used</td>
</tr>
<tr>
<td>3</td>
<td>Ammonium molybdate + SDHA [19]</td>
<td>780</td>
<td>0.02–0.14</td>
<td>Extraction required; time consuming</td>
</tr>
<tr>
<td>4</td>
<td>HMDTC (proposed method)</td>
<td>256</td>
<td>0.2–1.0</td>
<td>Sensitive, simple, rapid; free from common interference</td>
</tr>
</tbody>
</table>
arsenic in environmental samples. This suggested method could be used for rapid and simple determination of As(III) in drinking water. The results of analysis of samples are very close to those obtained by the other common methods. Our method has enormous practical potential for simple detection of arsenic, including field conditions which require no complex equipment or skilled laboratory support. As seen in Figs. 2 and 3, this method based on using HMDTC and Triton X-100 is very suitable for the analysis of natural samples. This chelating agent has been used before to determine other metals with different methods but this is its first application to the determination of arsenic.

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REFERENCES