Highly sensitive procedure for the determination of ultra-trace amounts of bromate ions in water by dispersive liquid-liquid microextraction combined with UV-Vis spectrophotometry

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ABSTRACT
In the present work, a novel, simple, and green procedure is presented for the determination of bromate ions in water. The method is based upon using tetraphenylphosphonium iodide (TPP 1) as an ion pairing reagent and a source of iodide ions that react with bromate to produce triiodide ion (I3-) in the presence of chlorate. The complex ion associate formed between I3- and TPP was extracted by dispersive liquid-liquid microextraction. Under the optimum conditions, Beer’s-Lambert law and Ringbom’s plot of the colored complex ion associate were obeyed in the range of 0.01-0.5 and 0.02-0.2 µg/mL of BrO3- at 365 nm, respectively, with a relative standard deviation in the range of 2.1 ± 1.3%. The proposed method offers 0.003 and 0.012 µg/mL lower limits of detection (LOD) and quantification (LOQ) of the bromate ion, respectively. Moreover, the chemical composition and the stability constant of the developed ion associate were found to be [TPP+ I3-] and 4.43 × 104, respectively. The proposed method was free from most interferences present in many chlororganic, spectrofluorometric and spectrophotometric methods. The developed method did not need a special treatment of sample for eliminating the interferences prior to the application of DLLME and was successfully used to the analysis of bromate ion in both drinking water treated by ozone and tap water.

1. Introduction
As a result of the processes used to disinfect drinking water, important inorganic oxyhalide disinfection by-products (DBPs) have been reported. Chlorite (ClO2-) and chlorate (ClO3-) are formed when chlorine dioxide (ClO2) is used as a disinfectant, and the presence of chlorine in waters treated with hypochlorite has also been described [1]. Additionally, the ozonation of water containing bromide induces the formation of several by-products such as bromine, hypobromite ion (OHBr), hypobromous acid (HOBr), bromoform (CHBr3), and bromate (BrO3-) [2]. Bromate has been classified in Group 2B by the International Agency of Research on Cancer (IARC) as a primary causative agent of cancer, and therefore, the US Environmental Protection Agency (EPA) and World Health Organization (WHO) established a maximum contaminant level (MCL) of 10 µg/L for bromate in drinking water [3]. In fact, this guideline value is provisional because of limitations in analytical techniques available for monitoring bromate levels in different samples. Thus, sensitive and selective analytical techniques and predominantly routine methods are necessary for the determination of ultra trace and trace levels of bromate. The literature provides a wide range of methods to analyze bromate in variety of samples from sub-µg/L level to mg/L concentration, e.g., ion chromatography with conductivity detection (IC-CD) [4], high performance liquid chromatography combined with inductively coupled plasma mass spectrometry (HPLC/ICP-MS) [5], ion chromatography with atmospheric pressure ionization mass spectrometry (IC/API-MS) and with inductively coupled plasma mass spectrometry (IC/ICP-MS) [6], and GC-MS with negative chemical ionization [7]. Among these techniques, (IC-CD) is documented as an official method by EPA and International Organization for Standardization (ISO) for monitoring bromate concentration [4]. In fact, ion chromatography with both conductivity and UV detectors is widely used for the direct determination of bromate at detection limit of 7 and 10 µg/L, respectively [8]. Lower detection limit in the range of 0.5-1.0 µg/L can only be achieved by preconcentration step or evaporating of bromate-containing solution. On the other hand, IC-CD suffers from severe interferences of chloride, sulphate, and some metal ions [1,9]. Although many improvements were carried out to increase the selectivity and sensitivity of method, such improvements made this method time-consuming and highly cost. However, on the other hand, the main other disadvantages of this technique are the complexity and the need of some degree of expertise for their proper operation. Therefore, such techniques are not suited for routine analysis. The development of low cost method, easy to operate, highly sensitive and reliable for routine analysis, e.g., spectrophotometry is still of great concern. A series of spectrophotometric methods has been reported for bromate determination in different samples [2,9-13]. However, most of these methods are not suitable for monitoring the ultra trace and trace concentrations of bromate in drinking water due to their low sensitivity and selectivity.

Although, there are many kinds of instruments with high selectivity and sensitivity, the direct determination of analytes at extremely low concentrations is still problematic. In this
case, the preconcentration step is necessary. Liquid-liquid extraction (LLE) is widely used as a pre-treatment technique for separation and preconcentration of both organic and inorganic analytes from aqueous samples. Nevertheless, it has several drawbacks, such as emulsion formation or the use of large volumes of toxic organic solvents, which makes LLE tedious, and environmentally unfriendly. The search for alternatives to the conventional LLE using negligible volumes of extractant and in minimum number of steps has driven the development of some new miniaturized methodologies like single-drop microextraction (SDME), hollow fiber liquid-phase microextraction (HF-LPME), cloud point extraction (CPE), and dispersive liquid-liquid microextraction (DLLME) [14]. DLLME developed by Assadi et al. in 2006 has been widely applied to the analysis of heavy metals, pesticide residues and so on [15-18] due to its excellent analytical performance compared to other microextraction techniques.

It is well known that, the ion pairing reagents tetraphenylphosphonium halide (TPP+X−) can form stable complex ion associates with several of oxoanions in organic media. One of these complexes, formed between tetraphenyl phosphonium bromide (TPP–Br-) and halochromate (CrO3Cl−), has been employed for developing a simple, convenient, and low cost spectrofluorimetric and spectrophotometric methods for the determination and speciation of chromium (III, VI) in water samples [19,20]. Therefore, the aim of the present study was to develop a novel environmentally friendly procedure for the determination of bromate ions in water using the ion pairing reagent tetraphenylphosphonium iodide (TPP+I−), followed by DLLME of the formed ion associate into organic phase and subsequent UV-Vis spectrophotometric detection.

2. Experimental

2.1. Apparatus

The UV-visible (190 - 1100 nm) spectra were recorded on a Perkin-Elmer (model Lambda 25, USA) spectrophotometer using a quartz micro cell (45 mm high, internal width 4 mm and path length 10 mm) with 800 µL internal capacity. A digital micropipette (Volac) and an Orion pH meter (model EA 940) were used for the preparation of more diluted bromate ion solutions and pH measurements, respectively. Deionized water was obtained from Milli-Q Plus system (Millipore, Bedford, MA, USA) and used for preparation of solutions.

2.2. Reagents

All chemicals and solvents used were analytical reagent grade and used without further purification. Stock solutions (1000 µg/mL) of Br2, Cr(VI), Cr(III), As(V), MnO4−, NO2−, ClO4−, I2− and H2O2 were prepared from the BDH chemicals (Poole, England) KBrO3, K2CrO4, Cr(NO3)3, Na2S2O3, KMnO4, NaNO2, KClO3, KIO3 and H2O2 (30% w/v) in water (100.0 mL), respectively. Solutions of other metal ions were prepared from their nitrate or chloride salts in deionized water. A stock solution (0.1%, w/v) of the reagent TPP+I− (Merck, Darmstadt, Germany) was prepared by dissolving the required weight in ethanol (3.0 mL) and the solution was then completed to the mark with deionized water.

2.3. Recommended procedure for bromate determination

Various concentrations (0.01-0.50 µg/mL) of bromate ion were put into centrifugal tubes. Next, 0.3 mL of 5 mol/L HCl and 0.2 mL of 0.1 %TPP+I− were added, and the volume was filled up to 1 mL with deionized water. After that, 0.5 mL of methanol (as a disperser solvent) containing 70 µL of chloroform (as extraction solvent) was rapidly injected using a 2.0 mL syringe. A cloudy solution was rapidly produced due to the formation of fine droplets of extraction solvent, and the complex ion associate formed was extracted into these fine droplets. The mixture was gently shaken and then centrifuged at 3000 rpm for 2 min. After this process, the dispersed fine droplets of CHCl3 were sedimented at the bottom of conical test tube, and the remaining organic layer was then removed using a Hamilton syringe and diluted to 500 µL by methanol. The absorbance of diluted organic phase was measured at 365 ± 3 nm.

2.4. Determination of bromate in tap and bottled water

Tap water collected from the laboratories of Chemistry Department, King Abdul Aziz University, Jeddah city, KSA, and bottled water, commercially available in Saudi market, were filtered through 0.45 µm cellulose membrane filter prior to analysis and stored in LDPE sample bottles (250 mL). Aliquots of 1.0 mL of each sample were adjusted to the required acidity and analyzed following the recommended procedure of bromate determination.

3. Results and discussion

Preliminary study has shown that, on mixing bromate ion with the ion pairing reagent TPP+I− (Figure 1) in aqueous HCl solution, yellow-colored species was developed. The electronic absorption spectrum of the mixture in water showed two well-defined peaks at 290 and 352 nm against reagent blank (Figure 2b) confirming the formation of triiodide ion (I3−) [21]. In the absence of BrO3−, the absorption spectrum of the reagent TPP+I− in aqueous HCl solution showed no absorption band in the range of 300-500 nm (Figure 2a). Similar trend was also observed on shaking the reagent or bromate ion individually with chloroform. However, bathochromic shift of the above mentioned two peaks has occurred at 295 and 365 nm (Figure 2c) after shaking the aqueous HCl solution containing the reagent TPP+I− and bromate ion with chloroform confirming the formation of complex ion associate. The composition of the produced ion associate was determined by Job’s continuous variation and molar ratio methods at 365 nm [22]. The results revealed that, the ratio of I3−, equivalent to bromate ions, to TPP+I− was 1:1 molar ratio. Thus, the most probable composition of the extracted species is [TPP+I−]. The stability constant of the produced complex ion associate calculated from the Job’s plot from the ratio of the true absorbance (A) to the extrapolated (A∞) absorbance was found equal to 4.43 × 105 [22].

![Figure 1](https://example.com/figure1.png)  
**Figure 1.** The chemical structure of reagent TPP+I−.

Based on these results in chloroform and the data reported earlier for the complex ion associate of the ion pairing reagent TPP+Br− with chloro bromate (CrO3Cl−) in HCl media [20], and the reaction of bromate with iodide ion in acidic medium [10], the overall reaction of bromate with TPP+I− in HCl (1.5 mol/L) is most likely proceeded as follows:

\[ \text{TPP}^+ + \text{I}^- \rightarrow \text{TPP}^+ \text{I}^- \]  

(1)

\[ \text{BrO}_3^- + 9\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_3^- + \text{Br}^- + 3\text{H}_2\text{O} \]  

(2)

\[ \text{TPP}^+ + \text{I}_3^- \rightarrow [\text{TPP}\text{I}_3^-] \]  

(3)
...concentration (2.0 mol/L). 3.1.1. Extraction of bromate ions

On the other hand, the value of the molar absorptivity (ε) at 365 nm of the complex ion associate developed in chloroform was found to be 2.5×10^4 L/mol·cm suggesting the possible use of the title reagent for the spectrophotometric determination of bromate ions. With taking into account the characteristics of DLLME technique compared to normal LLE, the further work will be focused on the use of this technique to develop sensitive extractive spectrophotometric method for the determination of bromate ion in water.

3.1. Optimization of DLLME

3.1.1. Influence of acidity

Because the ion pairing reagents tetraphenylphosphonium halides (TPP+·X) have strong trend for the formation of ion associates in strong acidic media [19,20], the effect of acidity on DLLME efficiency was tested in H2SO3, HCl, HNO3 or CH3COOH (2.0 mol/L). The maximum and stable absorbance was achieved using HCl. This behavior is most likely attributed to the influence of chloride ion on the oxidative properties of bromate explained in detail in [23]. Therefore, the effect of HCl concentration (0.5-2.0 mol/L) was critically studied. The results shown in Figure 3 indicate that, the maximum analytical signal (absorbance) was achieved above 1.0 mol/L. Thus, HCl concentration of 1.5 mol/L was employed in further work.

![Figure 3](image)

Figure 3. Influence of HCl concentration (0.5 - 2.0 mol/L) on absorbance of the ion associate in organic phase.

3.1.2. Effect of the extraction and disperser solvent type

The type of extraction solvents used in DLLME is an important factor for efficient extraction. The extraction solvents used in normal DLLME should have a higher density than water, high efficiency for the extraction of target analyte and low solubility in water. Moreover, in the case of UV-vis detection, there is one more requirement, namely minimum extraction of the blank test [24]. On the other hand, when ion pairs are extracted, the dielectric constant of extraction solvent must be taken into account. Thus, a series of organic solvents with low dielectric constant, and higher density than water, e.g. dichloromethane (dielectric constant, 9.1, density, 1.33 g/mL), carbon tetrachloride (dielectric constant, 2.2, density, 1.59 g/mL) and chloroform (dielectric constant, 4.81, density, 1.48 g/mL) was tested. On the other hand, the selection of a dispersive solvent is limited to solvents that are miscible with both water and extraction solvents such as methanol, acetonitrile, ethanol and acetone. In this study, all combinations of chloroform, dichloromethane, carbon tetrachloride as extraction solvents with methanol, acetonitrile, ethanol and acetone as dispersive solvents were performed, and the value of analytical response as well as signal-to-noise ratio were then investigated. The results presented in Figure 4 revealed that, the extraction recovery decreased in the order CHCl3 = CCl4 > CH2Cl2 in all used disperser solvents. On the other hand, the blank response in CCl4 was higher than that in CHCl3 (Figure 4). Moreover, mixture of chloroform and methanol formed more stable two-phase system. Therefore, chloroform and methanol were selected as extraction and disperser solvents, respectively in further work.

![Figure 4](image)

Figure 4. Effect of the extraction solvent on the analytical signal. DLLME conditions: water sample, 1.00 mL; disperser solvent (methanol), 0.50 mL; acidity (HCl), 1.5 mol/L; the ion pairing reagent (TPP+·Br), 0.2 mL (0.1% w/v); BrO3−, 0.2 µg/mL; dilution solvent (methanol), = 500 µL.

3.1.3. Effect of the extraction and disperser solvent volume

To examine the effect of the extraction solvent volume, the experimental conditions were fixed and included the use of 0.50 mL methanol plus different volumes of chloroform. Figure 5 indicates that the absorbance increased by increasing the volume of chloroform to 70 µL and then remained approximately constant by further increasing of its volume between 70 and 90 µL. Therefore, 70 µL was selected as the optimum volume of extraction solvent. In order to examine the effect of the disperser solvent volume, solutions containing different volumes of methanol (in the range of 0.2 - 0.8 mL) and 70 µL of chloroform were subjected to the same DLLME procedure. The obtained results showed that, the absorbance reached to its maximum value at 0.5 mL of the methanol and then gradually decreased by further increasing of its volume, probably due to increasing of the dissolution of the extraction solvent in water and thus lower extraction efficiency of the ion associate.

3.1.4. Effect of the concentration of ion-pair reagent

The variation of the absorbance as a function of the reagent TPP+· concentration was evaluated by increasing volumes of the reagent (0.1%, w/v) from 0.1 to 0.5 mL at the optimum
Table 1. Tolerance limits of interfering species in the analysis of 20.0 μg/Lbromate ion.

<table>
<thead>
<tr>
<th>Interfering species</th>
<th>Interfering to analyte ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>As²⁺, Ni²⁺, Bi³⁺, Li⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺, Ag⁺, CO₃²⁻, SO₄²⁻, NO₂⁻, CN⁻, Fe³⁺, Fe²⁺, H⁺, Pb²⁺, Mn²⁺, Co²⁺, Cr³⁺, Cl⁻, Br⁻, NO₂⁻, H₂O₂, ClO₂⁻, BrO⁻, MnO₂⁻, Cr⁺⁶, I⁺⁻, I⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000:1</td>
</tr>
<tr>
<td></td>
<td>100:1</td>
</tr>
<tr>
<td></td>
<td>70:1</td>
</tr>
<tr>
<td></td>
<td>5:1</td>
</tr>
<tr>
<td></td>
<td>0.5:1</td>
</tr>
</tbody>
</table>

experimental conditions. The results showed that, 0.2 mL of 0.1% (w/v) of TPP⁺·I⁻ was sufficient to extract up to 0.5 μg/mL. A large excess of the reagent concentration tends to decrease the absorbance possibly owing to the increased absorbance of the reagent blank. Amounts of the reagents smaller than the recommended value gave incomplete extraction. Thus, the volume of 0.2 mL, corresponding to its maximum value, was used in further experiments.

3.1.5. Effect of the extraction time

Extraction time is one of the most key factors in the most of extraction procedures. In DLLME, extraction time is defined as the time between injection mixture of disperser solvent and extractant and starting to centrifuge. The effect of extraction time was examined in the range of less than 1 to 15 min with constant experimental conditions. The results showed the extraction accomplished in a very short time after the formation of cloudy solution and the equilibrium state was achieved quickly, which was one of the main advantages of DLLME. In fact that, the complex ion associate formed diffuses quickly into the extraction solvent due to the infinitely large surface area between extraction solvent and aqueous phase after the formation of cloudy solution. In this method, the only time-consuming step, that required about 2 min, was centrifugation of sample solution performed for collecting the fine droplets of extraction solvent dispersed in aqueous phase.

3.2. Selectivity

To test the selectivity of the proposed method, the influence of various ions involving common inorganic oxohalide disinfection by-products, e.g., ClO₃⁻, ClO₄⁻, and OBr⁻ on the determination of a concentration of 0.20 μg/mL of bromate was investigated under the optimum conditions. The tolerance limit was defined as the concentration of added species causing less than ±5% relative error. As demonstrated in Table 1, most metal ions, and inorganic anions were tolerated even at a high concentration level. The only ions interfering seriously with bromate determination are I⁺⁻, Cr⁺⁶, and MnO₂⁻. However, the interference of MnO₂⁻ was eliminated by the addition of few drops 0.1%, m/v NaN₃ to reduce manganese(VII) to manganese(II). After this modification, the tolerance of the interfering ions was improved to acceptable limit (98±2%).

3.3. Figure of merits

Under the optimized experimental conditions, the plot of bromate ion concentration vs. absorbance of [TPP⁺·I⁻] in CHCl₃ was linear in the concentration range 0.01-0.5 μg/mL (7.94×10⁻⁸ to 3.97×10⁻⁴ mol/L) with the regression equation:

\[ A = 1.912 C (\mu g/mL) + 0.0037 \]

with correlation coefficient of 0.997 (n = 8), which indicates good linearity in the mentioned concentration range. UV-visible absorption spectra of [TPP⁺·I⁻] in chloroform upon addition of selected concentrations of bromate ion are shown in Figure 6. The effective concentration range of bromate ions evaluated by the Ringbom’s plot was in the range of 0.02-0.2 μg/mL. Based on the IUPAC [22], the values of LOD and LOQ of bromate ions were 0.003 and 0.012 μg/mL, respectively, using 1.00 mL of sample. The relative standard deviation at concentration 0.25 μg/mL of bromate ions was in the range of 2.1±1.3% (n = 6). A comparison of the main analytical features of the proposed method made with many of the previously published fluorimetric, and spectrophotometric methods [2,10,23,25,26] is summarized in Table 2. Some of these method exhibits high detection limit [11], and serious interferences of NO₂⁻, ClO₃⁻, ClO₄⁻, Cd²⁺, Br⁻, and Cl⁻ [2,10,23,25,26]. Moreover, the developed method was also compared to conventional LLE based on the same reaction (the formation of ion associate of [TPP⁺·I⁻]). The main characteristics of both procedures are given in Table 3. The novel DLLME procedure has the following significant advantages in comparison to normal LLE: (a) lower consumption of extraction solvent and consequent production of a lower amount of organic waste, thus making the procedure environmentally friendly; (b) shorter extraction and analysis times; (c) better sensitivity.

3.4. Application

The accuracy of the developed method was checked by the analysis of bromate ions in bottled water, available in local market of Saudi Arabia, and Tap water, collected from the laboratories of Chemistry Department, King Abdul Aziz
Table 2. Figure of merits of the developed and some of the reported fluorimetric and spectrophotometric methods for bromate determination in water.

<table>
<thead>
<tr>
<th>Method, Ref.</th>
<th>Reagent</th>
<th>Linear Rang, (µg/mL)</th>
<th>LOD, (µg/mL)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>FL - Spectrophotometry, [23]</td>
<td>Prochlorperazine (PCP)</td>
<td>0.01 - 0.13</td>
<td>0.002</td>
<td>Very sensitivity, the interferences of NO₂⁻, ClO₃⁻, ClO₄⁻.</td>
</tr>
<tr>
<td>Direct - spectrophotometry, [4]</td>
<td>KI</td>
<td>0.05 - 5.00</td>
<td>0.014</td>
<td>Low sensitivity, the interferences of MoO₄²⁻, WO₄³⁻, NO₂⁻</td>
</tr>
<tr>
<td>FL - Fluorimetry, [26]</td>
<td>Sulphite - steroid hydrocortisone</td>
<td>0.045 - 63.00</td>
<td>0.010</td>
<td>Low sensitivity, the interferences of Br₃⁻, Cl⁻.</td>
</tr>
<tr>
<td>Kinetic - Spectrophotometry, [10]</td>
<td>KI</td>
<td>0.05 - 1.50</td>
<td>0.01</td>
<td>Low sensitivity, the interferences of MoO₄²⁻, WO₄³⁻, NO₂⁻</td>
</tr>
<tr>
<td>FL - Spectrophotometry, [25]</td>
<td>Chlorpromazine</td>
<td>0.025 - 0.750</td>
<td>0.006</td>
<td>Moderate sensitivity, the interferences of NO₂⁻, ClO₂⁻, hypochlorite.</td>
</tr>
<tr>
<td>SIA - Spectrophotometry, [13]</td>
<td>5-bromo(PADAD) - SCN⁻ - TPP-1-</td>
<td>0.18 - 3.00</td>
<td>0.15</td>
<td>Very low sensitivity, the interferences of ClO₂⁻, IO₃⁻, Cr⁶⁺.</td>
</tr>
</tbody>
</table>

Spectrophotometry, [Present work] The method is very sensitivity, and free from the interferences of inorganic exhalide disinfection by-products e.g., ClO₂⁻, ClO₃⁻ and Br⁻, the only interferences are IO₃⁻, Cr⁶⁺, MoO₄²⁻.

Table 3. Comparison of conventional LLE, and DLLME procedures for determination of bromate ions in water.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Procedure</th>
<th>LLE*</th>
<th>DLLME</th>
</tr>
</thead>
<tbody>
<tr>
<td>λmax, nm</td>
<td>365</td>
<td>365</td>
<td></td>
</tr>
<tr>
<td>Regression equation</td>
<td>A = 0.001 + 0.186 × C</td>
<td>A = 0.0037 + 1.912 × C</td>
<td></td>
</tr>
<tr>
<td>Linear range, µg/mL</td>
<td>0.05 - 1.2</td>
<td>0.01 - 5.00</td>
<td></td>
</tr>
<tr>
<td>LOD, µg/mL</td>
<td>0.017</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Volume of organic phase used for absorbance measurement, µL</td>
<td>4000</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>*Condition of LLE HCl and reagent concentrations = 1.5 mol/L, 0.008% (w/v), respectively; volume of extraction solvent = shaking twice with chloroform (2x2 mL); shaking time = 3 min.</td>
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</tr>
</tbody>
</table>

Table 4. Analysis of bromate ions by the developed spectrofluorimetric method in water samples (mean ± standard deviation, n = 5).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bromate ion, Added (µg/mL)</th>
<th>Bromate ion, Found (µg/mL)</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottled water</td>
<td>-</td>
<td>0.036 ± 0.0012</td>
<td>102.1 ± 1.2</td>
</tr>
<tr>
<td>Ozonated bottles water (1)</td>
<td>-</td>
<td>0.015 ± 0.0018</td>
<td>-</td>
</tr>
<tr>
<td>Ozonated bottles water (2)</td>
<td>-</td>
<td>0.062 ± 0.0013</td>
<td>95.5 ± 2.3</td>
</tr>
<tr>
<td>Tap water</td>
<td>-</td>
<td>0.062 ± 0.0013</td>
<td>95 ± 2.3</td>
</tr>
</tbody>
</table>

ND = Not detected.

University, Jeddah City, KSA. The results are summarized in Table 4, the percentage recoveries of the method were always higher than 95% confirming the accuracy of the developed method and its independence from the matrix interference.

4. Conclusions

This work describes a new sensitive and selective spectrofluorometric procedure for the determination of bromate ions in water samples without pre-treatment step prior to the application of DLLME. The proposed method has the following advantages: high selectivity, good reproducibility, stable absorbance up to 4 h. On the other hand, the developed method is free from the interferences of SO₄²⁻, Cl⁻, NO₂⁻ and ClO₄⁻ that can be considered common interferences in many-chromatographic, spectrofluorimetric and spectrophotometric methods. The method provides LOD much lower than the maximum allowable level (1.0 µg/L) of bromate ion in drinking water recommended by the US Environmental Protection Agency and World Health Organization (WHO).

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