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A micellar sensitized kinetic method for quantification of low levels of bisphenol A in foodstuffs by spectrophotometry

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In the current study, because of its potential to leach out into foodstuffs as a result of food contact uses, a new kinetic method for the monitoring and determination of bisphenol A in foods by spectrophotometry for a fixed-time method of 5.0 min at 447 nm was established without a prior preconcentration step. The method is based on selective and rapid reduction of oxalate stabilized-Mn(III) with trace amounts of bisphenol A in the presence of cationic surfactants, CPC and CTAB, as both counter ion and sensitivity enhancer at pH 5.5 and 6.0, respectively. The effects of pH, concentration of reactants, reaction time, reaction temperature, and matrix components on the analytical signal were evaluated in detail, and the optimal conditions were established. There was a good linear relationship in the ranges of 2–120 μg L^{-1} and 5–200 μg L^{-1} with detection limits of 0.58 μg L^{-1} and 1.46 μg L^{-1} for CPC and CTAB, respectively. The method was validated by using two spiked quality control samples in linear working range. The samples were analyzed with a minimum 3-point calibration around the method quantification limit to minimize matrix effect. The kinetic method was successfully applied to the quantification of trace bisphenol A in the selected food samples, the intra-day and inter-day precisions as a result of stabilization of PVA were lower than 6.0% (as RSD%, *n*: 5), and the recoveries were quantitatively higher than 93.5% for the two quality control samples spiked with 10, 30 and 50 μg L^{-1} with satisfactory results.

1. Introduction

Bisphenol A (BPA) is an acidic endocrine disrupter and can induce adverse effects on human beings and the ecosystem.[1] BPA is a common monomer for producing polycarbonate plastics and resins that are used as linings for food and beverage packaging, as dental sealants, and as additives in other widely used consumer products. BPA can migrate from containers into a variety of foods and beverages, and is thus considered to be a potential toxic food contaminant.[2–6]

In light of some dispute about the actual levels of bisphenol A that are able to cause toxic effects on humans; in fact, recent reports[7,8] indicate that health risks can result from exposure to doses much lower than the limit of 50 μg per (kg body weight) per day that was previously reported by chemical corporations and regulatory agencies.[9] Therefore, to assess actual human health risks caused by BPA exposure, it is essential to achieve accurate and reliable data on its levels in foodstuffs, even at very low concentrations.

So far, many methods based on chromatography, such as micellar LC,[10] LC-FL,[11,12] LC-UV,[13] LC-MS,[14] GC-MS,[15] CE,[16] and GC-MS,[17] electrochemical sensors[18–20] and molecular absorption/emission, such as spectrofluorimetry[21,22] and spectrophotometry,[23–25] have been reported to quantify bisphenol A in different sample matrices. However, the main drawbacks of chromatographic methods, which are often used in analysis of bisphenol A in the literature, are related to the process of pre- or post-column derivatisation leading to long analysis times, low reproducibility, interference and problems connected to the stability of derivatisation products. To get rid of the matrix effect, they also require tedious and time-consuming extraction or preconcentration steps in the hands of well-trained technicians. To reduce the most frequent problems, such as poor precision, selectivity and detection limits, further separation/preconcentration techniques with their own advantages and disadvantages were used in the analysis of trace bisphenol A in complex matrices.[26,27]

Unlike all the above-mentioned analytical methods, catalytic and/or inhibitory spectrophotometry, which is based on measurement of an analyte at trace or ultra-trace amounts, in which an indicator substance, a chromophore absorbing in the UV-Vis region, reacts with only a reductant or oxidant, is often a preferred kinetic method in trace analysis. To further improve their low sensitivity and selectivity, these methods only require the use of masking agents and ion-exchange resins to suppress the matrix effect, and surfactants and activators to improve their sensitivity and reproducibility without a prior separation/preconcentration step.

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The use of surfactants is one of the most effective ways of improving the analytical features of chemical reactions.[28] The use of a surfactant in the catalyzed and unanalyzed reactions is usually intended to increase sensitivity, and hence to reduce the detection limit for the catalyst/inhibitor to the lower limits, and to improve the selectivity and precision of the determination. Surfactant aggregates often accelerate or catalyze chemical reactions in premicellar and micellar regions, but they also inhibit reactions. Surfactant micelles also can enhance the sensitivity and can bring about changes in the solubility, pK_a, chemical equilibrium, reaction rates mechanisms, spectral properties (peak maximums and wavelengths) and selectivity of some chemical processes. In this sense, UV-Vis spectrophotometry is one of the preferred detection tools for the analysis of organic and inorganic analytes owing to its simplicity, rapidity, low cost, availability in almost every analytical research laboratory and wide applicability.

Manganese (Mn) is a key element in environmental processes, catalytic materials, and biological systems owing to its rich redox chemistry and ability to form Mn(III) and MnO_2 species with a high oxidizing potential. Mn(III) is a necessary intermediate in the reduction of Mn(IV) to Mn(II)[29] and an important component of environmental systems.[30] Soluble Mn(III) has been thought to disproportionate to soluble Mn(II) and particulate MnO_2 in natural waters, although it persists as complexes in laboratory solutions.[31] Metal reduction is a key step in water oxidation using Mn oxide catalysts[32–35] with evidence that Mn(III) plays an important role in O_2 generation.[36] In this sense, soluble Mn(III), likely stabilized by organic or inorganic ligands, can potentially serve as both the oxidant and the reductant in one-electron-transfer reactions with different redox species. Because of its instability, the dissolved Mn(III) must be complexed by a high affinity chelating agent to prevent reduction or disproportionation. Surfactants in the micellar and/or premicellar regions can significantly enhance the cycling of Mn among the +4, +3, and +2 valence states and control the stability of the binary and/or ternary complexes formed in reactions with stabilizing organic acids such as oxalate, malonate, lactate and tartrate[37–42] in order to monitor bisphenol A that occurs as a serious contaminant in environmental, food and beverage matrices.

The main aim of the existing study is to develop a highly selective and sensitive kinetic method for the determination of BPA in food and beverages. Since most interferents in the samples are water soluble, for detection with a spectrophotometer, which is simple, easy to use, fast and accessible almost in every research laboratory, it is desirable to increase the hydrophobicity of the target compound(s) and distinguish them from hydrophilic matrices. Therefore, charged and uncharged surfactants such as CPC, CTAB and PVA with high hydrophobic properties were chosen as both a counter ion and sensitivity enhancer to increase the hydrophobicity of the target compound and to protect from the matrix components. The sensitivity and selectivity of the method was also greatly enhanced by the introduction of micellar systems above the CMC with excellent absorption properties into the target anionic complex chosen as a chromophore at 447 nm for monitoring the degradation of bisphenol A.

2. Materials and methods

2.1. Instrumentation

Absorbance measurements at 447 nm were made on a double beam UV-Vis spectrophotometer (Shimadzu UV-1800 PC, Kyoto, Japan) equipped with a 1.0 cm quartz cells. A centrifuge (Universal Hettich, London, England) was used to extract molybdenum in milk-based samples. A pH meter (pH-2005 model, JP Selecta, Spain) was used to adjust the pH of the solutions. Eppendorf variable pipettes (10–100 and 200–1000 μL) were used to deliver accurate volumes. An ultrasonic bath (UCS-10, Jeiotech, Seoul, Korea) with ultrasound frequency of 40 kHz at 300 watt was used to assist the fast and efficient extraction of the analyte from milk samples. A vortex mixer with a frequency of 50 Hz at 12 watt (VM-96B, Jeiotech, Seoul, Korea) was also used in the sample preparation step. A refrigerator was used to keep the samples fresh and cool until the analysis. A stopwatch was used to record the reaction time.

2.2. Reagents and standard solutions

All chemicals and reagents used were of analytical-reagent grade or higher purity. Ultra-pure water with a resistivity of 18.2 MΩ cm was prepared using a Labconco (Kansas City, USA) water purification system. A stock solution of bisphenol A (1000 mg L^{-1}) was prepared by dissolving the required amount (≥98%, Sigma-Aldrich) in methanol and it was then stored under dark conditions at 4 °C. The standard working solutions were obtained daily by appropriate dilution of the stock solution with methanol. The oxidant solution, Mn(III)-oxalate at 16.5 mg L^{-1}, was prepared by mixing 3.0×10^{-4} mol L^{-1} MnO_4^- solution with 1.2×10^{-3} mol L^{-1} of Mn(II)-acetate solution in the presence of excess oxalate solution at pH 5.0, so as to be a minimum 16-fold excess according to the concentration of Mn(III). The solution was freshly prepared daily before kinetic analysis. From the mixtures prepared in the range of 5–50 mg L^{-1} in a similar way, the molar absorption coefficient, ε_{max}, of the oxidant solution was found to be 911.26 mol^{-1} L^{-1} cm^{-1} at the wavelength of 447 nm. For the cationic surfactants, cetylpyridinium chloride (CPC) and cetyltrimethylammonium bromide (CTAB), solutions of 1.0×10^{-3} mol L^{-1} were also prepared by dissolving and diluting suitable amounts of pure solid surfactants (≥95%, Sigma-Aldrich) in water. Acetate buffers at pH 5.5 and 6.0 were used to keep the pH of the solutions. The buffers at pH 5.5 or 6.0 were prepared by dissolving 27.2 g NaAc or 20 g NH_4Ac (≥98%, Sigma-Aldrich), respectively, in 50 mL of water by heating to 35 °C, cooling and adding slowly 5.0 or 0.8 mL, respectively, of glacial HAc and sufficient water to 100 mL, adjusting the pH if necessary. The vessels and pipettes used for trace analysis were kept in 10% (w/v) HNO_3 for at least 24 h and were subsequently washed five times with water.

2.3. Sampling and sample preparation

Milk samples in PET containers were purchased from local open-markets and a Turkish store in Sivas, Turkey. To obtain accurate and reliable analytical results and for stabilizing the BPA signal or improving the precision of the results in especially

low concentrations during analysis, and in order to observe whether or not there is a great variation between the BPA contents of the pretreated samples, an extraction approach based on ultrasonic effect was adopted in the digestion step with a slight modification of procedures reported in the literature. In order to provide more complete dissolution of the samples, they were independently subjected to the extraction procedure under ultrasonic effect prior to analysis.

5 mL samples of milk, buttermilk and other liquid beverage samples in contact with PC or PVC containers, which were homogenized by vortexing for 2 min at 1200 rpm, were placed in 50 mL centrifuge tubes and 20 mL of acetonitrile containing 0.05 g mL^{-1} NaCl was added. The samples were then kept at 40 °C for 20 min in an ultrasonic bath until a clear solution was obtained, and were then centrifuged for 5 min at 4000 rpm. After centrifugation, the supernatant was withdrawn and 2 mL of ethanol was added to this liquid and then made up to a total volume of 25 mL with water. After adding three different standard concentrations of BPA under optimal conditions to 3 mL of this sample, so as to fall into the calibration range, the BPA contents of the samples were determined by the fixed-time kinetic method. An analyte blank including two quality control samples spiked before pretreatment was also submitted to the procedure in a similar way. After that, the pretreated and extracted samples were analyzed by spectrophotometry at 447 nm according to the present micellar sensitized method for CPC and CTAB at pH 5.5 and 6.0 under the optimized conditions. The three point calibration curve approach for spiked samples was preferably adopted in order to calculate recovery values and check the accuracy of the results.

2.4. The kinetic procedure

In each set of different 10 mL volumetric flasks, 3.0 mL of acetate buffer solution (pH 5.5 or 6.0), 2.0 mL of 16.5 mg L^{-1} oxidant, $Mn(Ox)_3^{3-}$, 2.5 mL of 3.0×10^{-3} mol L^{-1} of CPC and/or CTAB, 1.0 mL of 2.0% (v/v) PVA, and various concentrations of bisphenol A in the ranges of 2–120 and 5–200 μg L^{-1} were taken and made up to the mark with water. Afterwards, the mixture was kept in an ultrasonic bath (40 kHz, 300 watt) for of 5 min at 35 °C and/or 40 °C for CPC and CTAB, respectively. The absorbance was measured at 447 nm against the reagent blank for a fixed time of 5 min, in which there is a linear relationship, so as to give a decreasing slope with increasing bisphenol A concentration.

3. Results and discussion

In the absence of bisphenol A, the degradation of the ternary complex by disproportionation is very slow owing to stabilization by cationic surfactants, including PVA, as a viscosity enhancer. However, when trace amounts of bisphenol A as a contaminant are present, degradation of $HMn(Ox)_3^{2-}$ or $Mn(Ox)_3^{3-}$ in the presence of cationic surfactants CPC and CTAB, which act as protective/stabilizing agents above the critical micelle concentration (CMC), will occur with a significant absorbance difference in the first 5 min and the color of ternary complex will gradually fade as a function of time. Fig. 1(a) shows the decrease in absorbance at 447 nm for a fixed time of 5 min as a function of bisphenol A concentration at levels of 25, 50 and 100 μg L^{-1} in the presence of CTAB at pH 6.0, in which the analytical curves under optimal conditions in Fig. 1(b) are structured for bisphenol A AT 2–120 and 5–200 μg L^{-1} for CPC and CTAB, respectively. Mn(III), which is a highly reactive metal ion and powerful oxidant, can undergo reduction or disproportionation according to the following reactions:[38,43,44]

$$Mn^{3+} + e^- \rightarrow Mn^{2+}, E^0 = +1.51 \text{ V or}$$

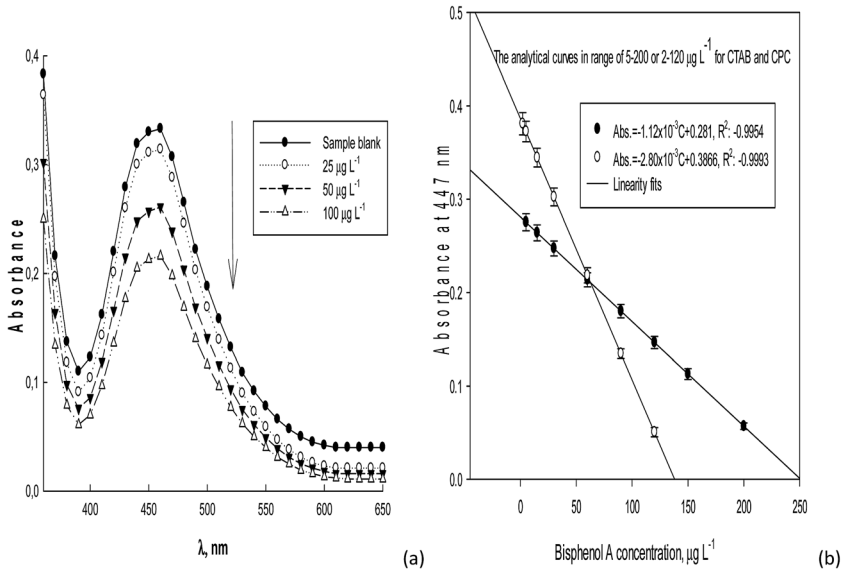

Fig. 1 (a) The spectral absorbance changes against sample blank for three different concentrations of bisphenol A in the presence of CTAB (b) the analytical calibration curves obtained from the aqueous standard solutions in range of 5–200 or 2–120 μg L^{-1} for CTAB and CPE under optimal conditions.

$$MnOOH + 3H^+ + e^- \rightarrow Mn^{2+} + 2H_2O,\ E^0 = +1.50\ V$$

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_{2(s)} + 4H^+,\ E^0 = +0.53\ V.$$

In the context of development of a new analytical method, the following mechanism is suggested for the micellar sensitized kinetic spectrophotometric method at pH 5.5 and 6.0 in the presence of CPC and CTAB as both counter ion and sensitivity enhancer. Mn(III) as a transition metal ion with d^4-electronic configuration is a stronger Lewis acid and powerful oxidant with a pK_h value of 0.43 and/or 0.88 to bind hydroxyl ions compared to other transition metal ions with charge of +3, such as Fe^{3+} and Cr^{3+}, due to Jahn–Teller distortion.[45]

$$Mn^{3+} + H_2O \leftrightarrow MnOH^{2+} + H^+,\ pK_h\text{: } 0.43 \quad (1a)$$

Mn(III) complexes are known to be relatively unstable, although chelating with an organic acid can partially stabilize them.[45,46] At pH 5.5 and 6.0, it is expected that Mn(III) as a Lewis acid with six coordination sites kinetically forms the more stable oxalate complexes with oxalate in the presence of CPC and CTAB as follows:

$$Mn^{3+} + \text{oxalate} \rightarrow Mn(Ox)^+,\ \log K\text{: } 9.98 \quad (2a)$$

$$Mn^{3+} + 2\text{oxalate} \rightarrow Mn(Ox)_2^-,\ \log K\text{: } 16.57 \quad (2b)$$

$$Mn^{3+} + 3\text{oxalate} \rightarrow Mn(Ox)_3^{3-},\ \log K\text{: } 19.42 \quad (2c)$$

Here, CPC and CTAB act as either a counter ion or sensitivity enhancer in the micellar region at pH 5.5 and/or 6.0, so as to cause a concentration-dependent controllable signal increase for the determination of bisphenol A at low levels.

$$Mn(Ox)_3^{3-} + \text{cationic surfactant, } 3CPC \rightarrow Mn(Ox)_3(CPC)_3 \quad (3)$$

$$Mn(Ox)_3^{3-} + \text{cationic surfactant, } 3CTAB \rightarrow Mn(Ox)_3(CTAB)_3 \quad (4)$$

At pH 5.5 or 6.0, the formed stable ternary complex is subject to reduction reaction depending on an increase in the concentration of bisphenol A. Furthermore, due to dissociation of the ternary complex at 5.0, a gradual decrease in analytical signal is observed.

$$Mn(Ox)_3^{3-2n} \leftrightarrow Mn^{2+} + (n-1)Ox^{2-} + CO_2 + CO_2^{\bullet -},\ \text{carbonate radical, } n\text{: } 1, 2, 3 \quad (5a)$$

$$2CO_2^{\bullet -} \rightarrow Ox^{2-} \text{ by recombination in absence of bisphenol A} \quad (5b)$$

$$CO_2^{\bullet -} + H_2O \rightarrow HCOO^- + {}^{\bullet}OH \quad (6a)$$

$$2CO_2^{\bullet -} + 2H^+ \rightarrow H_2O_2 + 2CO_2 \quad (6b)$$

$$Mn^{2+} + H_2O_2 \rightarrow Mn^{3+}\ (\text{or } MnOH^{2+}) + OH^- + {}^{\bullet}OH \quad (6c)$$

$${}^{\bullet}OH + \text{bisphenol A} \rightarrow \text{bisphenoxy radical} + H_2O \quad (7a)$$

$$\text{Bisphenoxy radical} + H_2O \rightarrow \textit{ortho}\text{-hydroxylated bisphenoxy radical} + \text{bisphenol A} \quad (7b)$$

It is believed that the reaction mechanism proceeds by hydroxyl radical generation in the presence of bisphenol A, disproportionation and then proton/charge transfer of the instable *ortho*-hydroxylated bisphenoxy radical produced by eqn (5a)–(7b), so as to give semi-quinone and quinone products. Furthermore, the proposed mechanism has been individually supported by means of two studies, which are based on the effect of pH and oxalate on hydroquinone-derived hydroxyl radical formation (2,5-DMHQ) from 2,5-dimethoxybenzoquinone (2,5-DMBQ) with Fe(II) in the pH range of 2.0–4.0 and the decolorization rate of indigo carmine in the pH range of 3.0–5.5 at 609 nm with Mn(III)-tartrate as the oxidant in the literature.[47,48] In order to detect hydroxyl radical formation with and without bisphenol A, the possible mechanism is also supported and confirmed by other studies in literature.[37,38,49,50] For detection of bisphenol A based on degradation of the ternary complex for a fixed time of 5.0 min at incubation temperatures of 35 and 40 °C at pH 5.5 and 6.0 for CPC and CTAB, respectively, in light of all this information, the general oxidation reaction can be expressed as follows:

$$Mn(Ox)_3(\text{CPC or CTAB})_3 + \text{bisphenol A} \leftrightarrow \text{degradation products at 447 nm} \quad (8)$$

Accordingly, in order to control the possible fluctuations in analytical signal at low concentration levels, PVA as a stabilizer was successfully used.

3.1. Optimization step

The effect of the analytical variables (pH, buffer, oxidant, ionic surfactant and PVA concentration, including reaction time and temperature) on the absorbance change for a fixed time of 5.0 min at 447 nm were investigated by the univariate method, varying each parameter one-by-one and keeping the remaining parameters fixed, in order to take into account the sensitivity and precision of the analytical measurements. Owing to familiarity and ease of use, the univariate method is widely used in optimization of analytical methods to obtain maximum efficiency. The standard concentration of bisphenol A, so as to fall into the linear working range, was fixed at a level of 50 μg L^{-1} during the optimization.

3.1.1. Effect of pH and 0.5 mol L^{-1} acetate buffer volume. The effect of pH on the absorbance of the ternary complex, $Mn(Ox)_3$(CPC or CTAB)$_3$ as the oxidant at 50 μg L^{-1} at 447 nm was investigated in the pH range 3.5–8.0 in Fig. 2(a). From the results obtained, it is clear that the ternary complex is a pH-sensitive oxidant, so that the absorbance linearly increases with increasing pH in the range of 3.0–6.0. In the presence of CPC and CTAB, the ternary complex gives a higher absorbance value at pH 5.5 as a result of micellar catalysis of CPC in the micellar region while it shows a maximum absorbance in the presence of CTAB at pH 6.0. At higher pHs, the absorbance gradually decreases owing to precipitation of Mn^{3+} ions as MnO(OH).

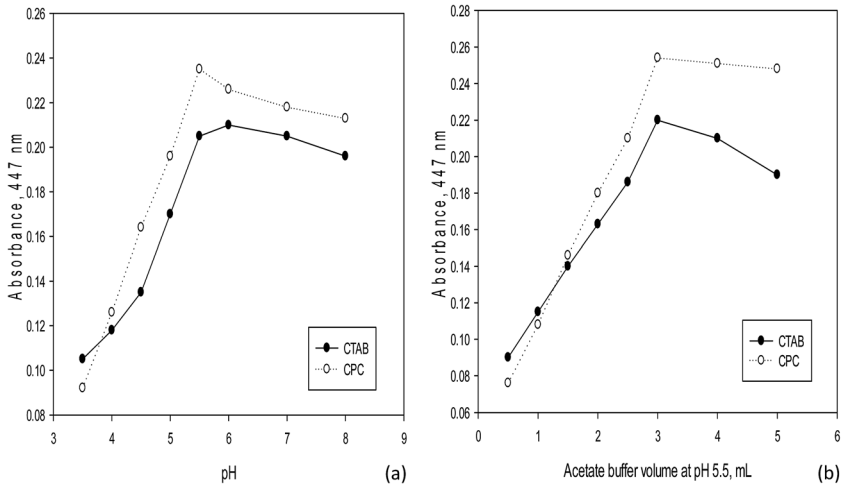

Fig. 2 The effect of (a) pH and (b) buffer volume on analytical signal.

Therefore, a pH value of 5.5 for CPC and 6.0 for CTAB was adopted and chosen as optimal for further studies.

In addition, the effect of acetate buffer volume at pH 5.5 and pH 6.0 was investigated in the range of 0.5–5.0 mL in Fig. 2(b), and a buffer volume of 3.0 mL for each surfactant was chosen as optimal to give maximum absorbance.

3.1.2. Effect of 16.5 mg L^{-1} of oxidant solution volume on analytical signal. The effect of oxidant volume with $HMn(Ox)_3^{2-}$ or $Mn(Ox)_3^{3-}$ at 16.5 mg L^{-1} was investigated in the volume range of 0.5–5.0 mL in presence of 50 μg L^{-1} bisphenol A at optimal pHs. As can be seen in Fig. 3, the best analytical signal was obtained at a volume of 2.0 mL for each surfactant. At volumes higher than 2.0 mL, the absorbance was gradually decreased. This decrease in absorbance may be owing to the concentration-dependent degradation of the ternary complex by intra-molecular charge transfer. Therefore, an oxidant volume of 2.0 mL at 16.5 mg L^{-1} was considered to be sufficient for further studies.

3.1.3. Effect of volume of 3.0×10^{-3} mol L^{-1} ionic surfactant on analytical signal. The effect of 3.0×10^{-3} mol L^{-1} ionic surfactant volume was investigated in the range of 0–4.0 mL in the presence of 50 μg L^{-1} bisphenol A at pH 5.5 and 6.0. As can be seen in Fig. 4, the best analytical signal was obtained at a volume of 2.5 mL. At concentrations higher than 2.5 mL, the absorbance was gradually decreased depending on the surfactant volume. Therefore, a surfactant volume of 2.5 mL of 3.0×10^{-3} mmol L^{-1} was considered to be sufficient for further studies. In fact, this maximum value, equal to a concentration of 0.75 mmol L^{-1}, is either comparable to or greater than the CMC of each surfactant, in which their CMC values for CPC and CTAB are determined as 0.8 and 0.6 mmol L^{-1} by cyclic voltammetry.[51] In this sense, for accurate and reliable measurement of bisphenol A, it is clear that each ionic

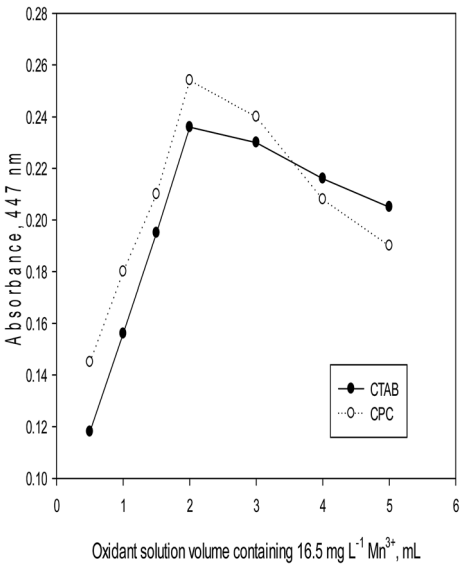

Fig. 3 The effect of 16.5 mg L^{-1} oxidant solution volume on analytical signal.

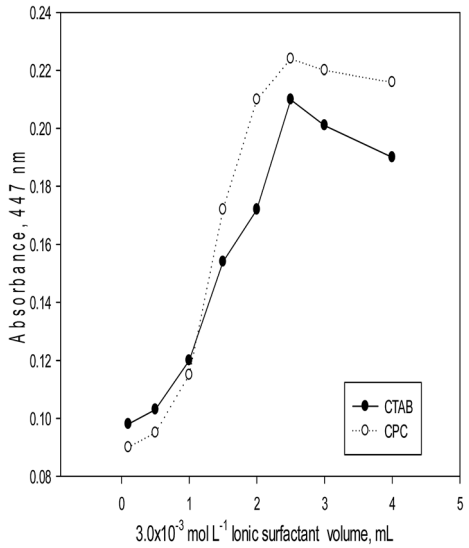

Fig. 4 The effect of 3.0×10^{-3} mol L^{-1} ionic surfactant volume on analytical signal.

surfactant above the CMC acts as a protector and stabilizer to prevent possible fluctuations in absorbance, especially at low concentrations.

3.1.4. Effect of volume of 2.0% (v/v) PVA as stabilizer on analytical signal. The effect of the volume of 2.0% (v/v) PVA as a stabilizer on the analytical signal was investigated in range of 0.1–2.5 mL for the measurement of 50 μg L^{-1} bisphenol A at optimal pHs. As can be seen in Fig. 5, the best analytical signal was obtained at a volume of 1.0 mL. At volumes higher than 1.0 mL, the absorbance was gradually decreased and kept constant depending on the PVA volume. This decrease in signal may arise from the suppressing effect of PVA on micellization of CPC or CTAB owing to the increase in viscosity of the micellar solution.[52] Therefore, a PVA volume of 1.0 was considered to be sufficient for further studies.

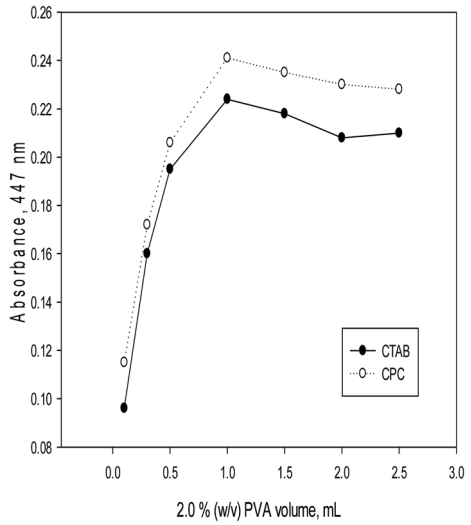

Fig. 5 The effect of 2.0% (v/v) PVA volume as stabilizer on analytical signal.

3.1.5. Effect of reaction time and temperature on analytical signal. The effect of temperature on the reaction rate was examined in the range of 25–50 °C under optimized conditions. As can be seen in Fig. 6(a), the results show that the reaction rate increases with increasing temperature to 35 °C for CPC and 40 °C for CTAB. It can be seen that it gradually decreased with temperatures higher than 40 °C and reached a plateau. This is an indication that the reaction has been kinetically completed and reached thermal equilibrium. Therefore, a reaction temperature of 35 °C for CPC and 40 °C for CTAB was chosen as optimal for further studies.

The time to measure the change in absorbance for each surfactant was also optimized. The effect of time on the reaction rate was studied for times of 0.5–20 min under optimized conditions without adding an inert salt like KCl to the reaction media. As can be seen in Fig. 6(b), the maximum signal difference occurred and completed within the first 5 min after the initiation of the reaction. At longer reaction times, there was a gradual decrease in the analytical signal. This decrease may perhaps be owing to disproportionation of Mn(III)-oxalate, so as to cause an increase in the bank signal. For this reason, a fixed time measurement of 5 min was adopted as the most suitable reaction time.

4.1. Analytical figures of merit

Under the optimized conditions, as can be seen in Table 1, a good linear relationship was obtained in the concentration ranges of 2–120 μg L^{-1} and 5–200 μg L^{-1} of bisphenol A with a correlation coefficient of −0.99993 and −0.9943 in the presence of CPC and CTAB, respectively, at 447 nm and regression equations of Abs = $-2.80 \times 10^{-3} C_{BPA} + 0.3866$ for CPC and Abs = $-1.12 \times 10^{-3} C_{BPA} + 0.281$ for CTAB, where C is in μg L^{-1} of bisphenol A. The limits of detection and quantification of the method (LOD = $3s_{blank}/m$, LOQ = $10s_{blank}/m$, where s_{blank} and m are the standard deviation of twelve blank replicate measurements and the slope of the calibration curve, respectively, $n = 10$) were calculated to be 0.58

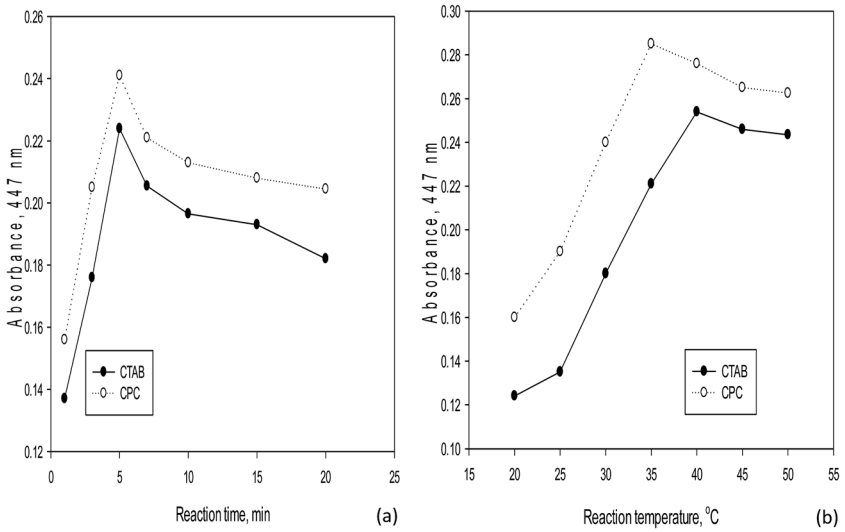

Fig. 6 The effect of (a) reaction time and (b) reaction temperature on analytical signal.

Table 1 The analytical features of the proposed micellar enhanced kinetic method

	By fixed-time method[a] for time interval of 5 min at 447 nm	
Analytical parameters	With CPC at 35 °C	With CTAB at 40 °C
Linear working range, μg L^{-1}	2–120	5–200
Slope, *m*	-2.80×10^{-3}	-1.12×10^{-3}
Intercept, *b*	0.3866	0.281
Correlation coefficient, r^2	−0.9993	−0.9941
LOD and LOQ, μg L^{-1}	0.58, 1.93	1.46, 4.87
RSD% (25 and 100 μg L^{-1}, *n*: 5)	2.85–4.35	3.20–4.70
Recovery% (25 and 100 μg L^{-1}, *n*: 5)	97.2–101.3	96.8–99.5
Optimal pH	5.5	6.0

[a] In presence of 1.0 mL of 2.0% (w/v) PVA as stabilizer.

and 1.93 μg L^{-1} for CPC and 1.46 and 4.87 μg L^{-1} for CTAB, respectively. The intra-day precision as RSD% from five replicate measurements of bisphenol A for two quality control samples spiked at levels of 10, 25 and 50 μg L^{-1} was found to be in range of 2.9–5.2% for the same day whereas the inter-day precision as RSD% from five replicate measurements of bisphenol A for two quality control samples spiked at levels of 10, 30 and 50 μg L^{-1} was found to be in range of 2.9–5.9% for period of three consecutive days.

4.2. Matrix effect

To study the selectivity of the proposed method, the effect of potential interfering inorganic and organic species on the determination of 50 μg L^{-1} BPA was tested under the optimum conditions. The results are summarized in Table 2. It is shown that within the tolerance limit ranging from 50 to 1500, the studied common ions and organic substances do not interfere with the determination in the recovery range of 93.5–105.7% with an RSD lower than 3.7%. However, the interfering effect of ions, in the state of mineral-rich sample matrices, can be completely minimized by using a strong anion exchange resin, IRA-400, and a strong cation exchange resin, Amberlite IR 120 Plus, before analysis. At the same time, the interference from other phenolic compounds, such as octylphenol and nonylphenol including ascorbic acid, which can be potentially available in many food and beverage samples, can be significantly minimized by Amberlite XAD-4, a polystyrene-divinylbenzene resin without functional groups. In our experiment, solutions with different concentrations of BPA with maximum 250-fold excess of each interfering ion were passed through this resin at pH 3.0, and the recoveries were 95.2–103.5%. Therefore, the proposed kinetic method has good selectivity. Moreover, it is implied in the literature[20] that bisphenol A can be accurately and reliably detected in the range of 0.1×10^{-5} to 1.0×10^{-5} mol L^{-1} in the presence of CTAB at pH 8.0 by SWV without any

Table 2 The effect of possible matrix components on the determination of bisphenol A at level of 50 μg L^{-1} (*n*: 3)

Coexisting ions	Interferent/BPA ratio	Mean recovery ± SD[a] (%)
Ca^{2+}, Mg^{2+}	1500 : 1	98.0 ± 2.5
Zn^{2+}	1250 : 1	102.5 ± 3.0
Fe^{2+}	1000 : 1	101.1 ± 2.0
Cl^-, Br^-	1000 : 1	98.2 ± 2.5
HCO_3^-	750 : 1	97.5 ± 3.0
Pb^{2+}, Cd^{2+}, Ag^+	600 : 1	(96.0–97.5) ± 2.5
Bromobenzaldehyde	500 : 1	96.0 ± 2.5
Ni^{2+}	500 : 1	103.9 ± 35
Cu^{2+}	400 : 1	96.8 ± 3.0
2-Chlorobenzaldehyde, phenol, 2-aminophenol	350 : 1	(94.0–95.4) ± 2.0
F^-, ethanol	300 : 1	98.1 ± 3.0
Co^{2+}, Cr^{3+}	250 : 1	(100.5–103.5) ± 2.6
NO_3^-, 2-nitrophenol, 4-nitrophenol	200 : 1	(95.0–97.3) ± 2.0
HSO_3^-, NO_2^-	150 : 1	(94.5–96.0) ± 3.0
HPO_4^{2-}	100 : 1	102.4 ± 3.0
Benzaldehyde, 2,4-dinitrophenol	75 : 1	(102.0–105.2) ± 3.0
Formaldehyde, acetaldehyde	50 : 1	95.5 ± 3.0
Fe^{3+}, $V^{4+,5+}$, Mo^{6+}	25 : 1	(92.5–95.5) ± 3.5
Ascorbic acid	10 : 1 (250 : 1[b])	90.2 ± 3.5

[a] The percent recoveries and their standard deviations obtained from three replicate measurements of binary mixtures. [b] The tolerance ratio, which can be improved by using 2.5 mL of 25 mg L^{-1} Pb^{2+} at pH 5.5.

interference arising from the nonylphenol, in which nonylphenol can be monitored by SWV at a more positive potential of 170 mV than bisphenol A at pH 11.0 in the presence of CTAB. Furthermore, owing to the formation of a highly stable chelate complex with $\log \beta_1 = 9.3 \pm 0.2$ and $\log \beta_2 = 18.0 \pm 0.1$,[53] the interference from ascorbic acid was also improved up to a tolerance limit of 250-fold by 2.5 mL of 25 mg L^{-1} Pb^{2+} at pH 5.5 before kinetic determination.

4.3. Method validation and analytical applications

To learn about the accuracy (recovery%) and precision (as RSD%) of the proposed procedure, laboratory reproducibility and repeatability in terms of intra-day and inter-day studies were evaluated by the analysis of two quality control samples spiked with three different concentrations of BPA at levels of 10, 30 and 50 μg L^{-1} before pretreatment so as to represent the sample matrix. In the study, the proposed method was repeated five times on the same day to evaluate intra-day variability and was repeated on five consecutive days to determine inter-day variability. The data of the study performed are given in Table 3. From examining Table 3, the RSDs for both laboratory reproducibility and repeatability were found to be lower than 5.2%. From the analysis results, the intra- and inter-day precisions obtained for BPA were less than 5.0%, which is the normal level in any food quality control measurement and is always acceptable according to Horwitz's formula for intra-laboratory analysis.[54] The results showed that the extraction of the BPA from the selected samples is highly reproducible and selective. Because of the lack of a certified reference material for the BPA, the validity of the method was assessed by recovery studies. Recovery studies for samples spiked at different concentrations were carried out, and the obtained results are given in Table 3 for quality control samples and selected foodstuffs. The results show that the method is highly satisfactory with a recovery rate higher than 93.5%. In terms of analytical parameters, good results were quantitatively obtained for repeatability (<5.0% as RSD) and recovery (≥93.5% or ≤99.0%), so as to fulfill the requirements set out by the European Union (EU).[55]

After evaluating the validation parameters, the applicability of the proposed method to the selected sample matrices was tested by using the standard addition method. Each sample matrix was analyzed in five replicates. The average results of the study are given in detail in Table 4. The results of the study for the samples in terms of recovery% are in the range of 91.3–98.0% with an RSD lower than 5.0%, and good reproducibility and excellent linearity were demonstrated. Furthermore, when the mean values intrinsically obtained by both analytical methods based on the enhancement of the sensitivity and selectivity with CPC and CTAB above their CMCs under the optimized conditions were compared, it is clear that there is no statistically significant difference between the found results, in which the paired *t*-values ranging from 0.53 to 2.10 are lower than the tabulated *t*-value of 2.31. When the results are studied in detail, it can be seen that bisphenol A level in beverage samples is in the range of <MDL – 6.90 μg L^{-1} with an RSD lower than 5.0% while bisphenol A in milk samples is in the range of <MDL – 1.70 μg kg^{-1} with an RSD lower than 4.8%. It is clear that the results are highly in agreement with those of other reported methods in the literature, which are based on determination of bisphenol A levels in non-canned drinks (0.1–3.4 μg L^{-1})[4] and canned soft drinks (0.032–4.5 μg L^{-1}).[11,12] It is clear that the results found for all foodstuffs are much lower than the EU migration limits of 3 mg per (kg food) and are reasonably unable to produce a daily intake exceeding the limit of 50 μg per (kg body weight) established by EFSA.[9] Nevertheless, when it is used as a marker for the quality control of especially acidic foods and beverages with a tolerable daily intake of 5 μg per (kg body weight) per day for BPA in terms of food safety,[9] there is still a need to control residual bisphenol A levels in complex matrices even with low levels in terms of food safety if it will be taken on an iterative basis in the long term.

When considering other analytical detection techniques without preconcentration, such as inhibitory fluorescence,[22] spectrophotometry after separation with HPLC,[23] ratio derivative spectrophotometry,[24] cysteamine-modified colorimetric method,[25] CE-UV,[16] micellar LC,[10] LC-MS[13] HPLC-FD,[14] GC-MS,[15] and LSV,[18,19] it can be seen that the detection limit of the method is either comparable or better than those of the other analytical methods reported in the literature. The lower detection limits of the analytical methods based on electrochemical

Table 3 The reproducibility and repeatability for the replicate measurements of bisphenol A in quality control samples spiked with 10, 30 and 50 μg kg^{-1} (*n*: 5)

Samples	Spiked concentration μg kg^{-1}	Inter-day precision			Intra-day precision		
		Found	Recovery%	RSD%	Found	Recovery%	RSD%
Whole milk	—	ND[a]	—	—	ND[a]	—	—
	10	9.6 ± 0.5	96.0	5.2	9.7 ± 0.5	97.0	5.2
	30	29.2 ± 1.2	97.3	4.1	29.5 ± 1.2	98.3	4.1
	50	49.0 ± 1.5	98.0	3.1	49.5 ± 1.5	99.0	3.0
Apple vinegar	—	3.40 ± 0.16	—	4.7	3.35 ± 0.15	—	4.5
	10	12.8 ± 0.5	94.0	3.9	12.7 ± 0.5	93.5	3.9
	30	32.0 ± 1.1	95.3	3.4	31.6 ± 1.1	94.2	3.5
	50	52.0 ± 1.5	97.2	2.9	51.7 ± 1.5	96.7	2.9

[a] Under the method detection limit.

Table 4 The analysis results of bisphenol A in some beverage samples in contact with PC and/or PVC plastic products (n: 5)

	In presence of CPC at pH 5.5 and 35 °C				In presence of CTAB at pH 6.0 and 40 °C				
Samples	Added, μg L^{-1}	Found, μg L^{-1}	RSD%	Recovery%	Added, μg L^{-1}	Found, μg L^{-1}	RSD%	Recovery%	The Student's paired t-test[b]
Whole milk	15	ND[a]	—	—	15	ND[a]	—	—	—
		14.7 ± 0.6	4.1	98.0		14.5 ± 0.7	4.8	96.7	—
Mixed fruit juice	10	5.20 ± 0.20	3.8	—	10	5.10 ± 0.20	3.9	—	0.79
		14.8 ± 0.5	3.4	96.0		14.6 ± 0.5	3.4	95.0	—
Orange $juice_1$	10	6.30 ± 0.30	4.8	—	10	6.40 ± 0.30	4.7	—	0.53
		15.8 ± 0.6	3.8	95.0		15.6 ± 0.6	3.8	92.0	—
Cold tea	20	ND[a]	—	—	20	ND[a]	—	—	—
		19.2 ± 0.7	3.6	96.0		18.8 ± 0.7	3.7	94.0	—
Energy drink	15	1.80 ± 0.08	4.4	—	15	1.90 ± 0.09	4.7	—	1.86
		15.8 ± 0.6	3.8	93.0		15.6 ± 0.6	3.8	91.3	—
Orange $juice_2$	10	5.30 ± 0.20	3.8	—	10	5.10 ± 0.20	3.9	—	1.58
		14.8 ± 0.5	3.4	95.0		14.7 ± 0.6	4.1	96.0	—
Cola	15	3.40 ± 0.15	4.4	—	15	3.50 ± 0.15	4.3	—	1.05
		18.1 ± 0.6	3.3	98.0		18.2 ± 0.7	3.8	98.0	—
Soda	15	1.40 ± 0.05	3.6	—	15	1.35 ± 0.05	3.7	—	1.58
		15.8 ± 0.6	3.8	96.0		15.6 ± 0.6	3.8	93.0	—
Grape $vinegar_1$	10	2.10 ± 0.10	4.8	—	10	2.00 ± 0.1	5.0	—	1.58
		11.8 ± 0.50	4.2			11.6 ± 0.50	4.3	96.0	—
Grape $vinegar_2$	15	1.50 ± 0.06	4.0	—	15	1.55 ± 0.06	3.9	—	1.32
		16.1 ± 0.6	3.7	97.3		15.8 ± 0.6	3.8	95.0	—
Apple $vinegar_1$	15	3.30 ± 0.15	4.5	—	15	3.40 ± 0.15	4.4	—	1.05
		17.8 ± 0.7	3.9	96.7		17.6 ± 0.7	4.0	94.7	—
Apple $vinegar_2$	10	6.90 ± 0.30	4.3	—	10	6.80 ± 0.30	4.4	—	0.53
		16.5 ± 0.6	3.6	96.0		16.4 ± 0.7	4.3	96.0	—
Pomegranate	15	1.75 ± 0.06	3.4	—	15	1.80 ± 0.07	3.9	—	1.22
		16.3 ± 0.5	3.1	97.0		16.2 ± 0.6	3.7	96.0	—
Fruit flavored yoghurt	15	1.35 ± 0.05	3.7	—	15	1.40 ± 0.06	4.3	—	1.44
		15.7 ± 0.5	3.2	95.7		15.5 ± 0.5	3.2	94.0	—
Fruit flavored milk	15	1.60 ± 0.07	4.4	—	15	1.70 ± 0.08	4.7	—	2.10
		15.8 ± 0.5	3.2	94.7		15.5 ± 0.5	3.2	92.0	—

[a] Under the method detection limit. [b] Based on statistical comparison of the mean values obtained by two analytical methods, in which the tabulated t-value is 2.31 for degree of freedom of 8 at 95% confidence level.

stripping and fluorescence detection, which firstly depend on the radiant power of the exciting source, are related to the use of HPLC-FL with detection limit of[14] 0.02 μg L^{-1} and LSV on the CTAB modified electrode above CMC with a detection limit of[18] 0.205 μg L^{-1}, but these sensitive techniques suffer from a narrow working range, low recovery rates, and poor precision, especially at low concentrations, owing to time-consuming and tedious solvent and/or pH gradient procedures in HPLC. In this sense, the proposed micellar sensitized kinetic method for accurate and reliable monitoring of BPA in sample matrices is simpler, safer, easier to use, relatively faster, low cost and eco-friendly with minimal damage to samples, unlike from electrochemical techniques such as LSV and electrophoretic/chromatographic techniques such as CE, CZE, LC, micellar LC and/or HPLC with UV, fluorometric and MS detection. Moreover, compounds containing functional groups with active hydrogen atoms, such as phenol and phenol derivatives like bisphenol A, are difficult to analyze directly by GC or GC-MS because of their insufficient volatility and thermal instability. Those compounds are generally derivatized prior to GC analysis to increase their volatility, reduce thermal degradation and increase detector response. When a comparison is made with the laborious, time consuming, expensive but more sensitive fluorometric techniques with preconcentration, such as first-derivative fluorescence following MLLE[26] and excitation fluorescence following MLLE using a chemometric tool[27] for monitoring and determination of low levels of bisphenol A in complex matrices, the micellar sensitized kinetic method shows a comparable capacity level, good accuracy and precision, comparable sensitivity and selectivity enhancement, and a wide working range, and is a simple, safe, easy to use, rapid and low-cost method for the monitoring of BPA in the selected sample matrices with satisfactory results.

5. Conclusions

When considering the analytical results achieved in the current study, the surfactant sensitized kinetic method shows some advantages, especially over the other spectrophotometric methods in the UV-Vis region, including further detection techniques: (1) it is simple, easy to use, low-cost, sufficiently rapid, accurate, selective and sensitive; (2) satisfactory recoveries, intra- and inter-day precision were obtained; (3) kinetic method, using standard addition approach around the method

quantification limit, allows an accurate and reliable quantification of the analyte without signal suppression from matrix effects; (4) the short analysis time of 30 min, including sample pretreatment, allows the method to be applied in routine analysis; and, finally, (5) it can be considered as a suitable detection tool for use in the quality control of foodstuffs thanks to the low detection limit reached in comparison with the specific migration limit, which was reduced from 3 to 0.6 mg kg^{-1} for BPA in food or food simulants.

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References

1 F. S. Vom Saal and C. Hughes, *Environ. Health Perspect.*, 2005, **113**, 926–933.
2 S. Sungur, M. Köroglu and A. Özkan, *Food Chem.*, 2014, **142**, 87–91.
3 E. Ferrer, E. Santoni, S. Vittori, G. Font, J. Manes and G. Sagratini, *Food Chem.*, 2011, **126**, 360–367.
4 X. L. Cao, J. Corriveau and S. Popovic, *J. Agric. Food Chem.*, 2009, **57**, 1307–1311.
5 L. Grumetto, D. Montesano, S. Seccia, S. Albrizio and F. Barbato, *J. Agric. Food Chem.*, 2008, **56**, 10633–10637.
6 B. M. Thomson and P. R. Grounds, *Food Addit. Contam.*, 2005, **22**, 65–72.
7 F. S. Vom Saal and W. V. Welshons, *Environ. Res.*, 2006, **100**, 50–76.
8 N. Rajapakse, E. Silva and A. Kortenkamp, *Environ. Health Perspect.*, 2002, **110**, 917–921.
9 Opinion of the Scientific Panel on Food Additives, *Flavourings, Processing Aids and Materials in Contact with Food on a request from the Commission related to 2,2-bis(4-hydroxyphenyl)propane (bisphenol A)*, EFSA J, 2006, vol. 428, pp. 1–75.
10 A. Szymański, I. Rykowska and W. Wasiak, *Acta Chromatogr.*, 2006, **17**, 161–171.
11 R. Braunrath, D. Podlipna, S. Padlesak and M. Cichna-Markl, *J. Agric. Food Chem.*, 2005, **53**, 8911–8917.
12 D. Podlipna and M. Cichna-Markl, *Eur. Food Res. Technol.*, 2007, **224**, 629–634.
13 Y. Watabe, T. Kondo, M. Morita, N. Tanaka, J. Haginaka and K. Hosoya, *J. Chromatogr. A*, 2004, **1032**, 45–49.
14 Y. Watabe, K. Hosoya, N. Tanaka, T. Kondo, M. Morita and T. Kubo, *Anal. Bioanal. Chem.*, 2005, **381**, 1193–1198.
15 M. Del Olmo, A. Gonzalez-Casado, N. A. Navas and J. L. Vilchez, *Anal. Chim. Acta*, 1997, **346**, 87–92.
16 S. Alsudir, Z. Iqbal and E. P. C. Lai, *Electrophoresis*, 2012, **33**, 1255–1262.
17 F. Canale, C. Cordero, C. Baggiani, P. Baravalle, C. Giovannoli and C. Bicchi, *J. Sep. Sci.*, 2010, **33**, 1644–1651.
18 W. Huang, *Bull. Korean Chem. Soc.*, 2005, **26**, 1560–1565.
19 B. K. Kim, J. Y. Kim, D. H. Kim, H. N. Choi and W. Y. Lee, *Bull. Korean Chem. Soc.*, 2013, **34**, 1065–1069.
20 M. F. Brugnera, M. A. G. Trindade and M. V. B. Zanoni, *Anal. Lett.*, 2010, **43**, 2823–2836.
21 A. Maroto, P. Kissingou, A. Diascorn, B. Benmansour, L. Deschamps, L. Stephan, J. Y. Cabon and P. Giamarchi, *Anal. Bioanal. Chem.*, 2011, **401**, 3011–3017.
22 J. Fan, H. Guo, G. Liu and P. Peng, *Anal. Chim. Acta*, 2007, **585**, 134–138.
23 Y. Zhuang, M. Zhou, J. Jia Gu and X. Li, *Spectrochim. Acta, Part A*, 2014, **122**, 153–157.
24 G. Cao, Y. Zhuang and B. Liu, *S. Afr. J. Chem.*, 2014, **67**, 99–103.
25 J. Xu, Y. Li, J. Bie, W. Jiang, J. Guo, Y. Luo, F. Shen and C. Sun, *Microchim. Acta*, 2015, **182**, 2131–2138.
26 M. del Olmo, A. Zafra, A. B. Jurado and J. L. Vilchez, *Talanta*, 2000, **50**, 1141–1148.
27 M. del Olmo, A. Zafra, N. A. Navas and J. L. Vilchez, *Analyst*, 1999, **124**, 385–390.
28 A. Stoyanova and A. Alexiev, *Trakia Journal of Sciences*, 2005, **3**, 1–9.
29 G. W. Luther, *Geomicrobiol. J.*, 2005, **22**, 195–203.
30 A. S. Madison, B. M. Tebo, A. Mucci, B. Sundby and G. W. Luther, *Science*, 2013, **341**, 875–878.
31 R. E. Trouwborst, B. G. Clement, B. M. Tebo, B. T. Glazer and G. W. Luther, *Science*, 2006, **313**, 1955–1957.
32 R. K. Hocking, R. Brimblecombe, L.-Y. Chang, A. Singh, M. H. Cheah, C. Glover, W. H. Casey and L. Spiccia, *Nat. Chem.*, 2011, **3**, 461–466.
33 M. Wiechen, I. Zaharieva, H. Dau and P. Kurz, *Chem. Sci.*, 2012, **3**, 2330–2339.
34 D. M. Robinson, Y. B. Go, M. Mui, G. Gardner, Z. Zhang, D. Mastrogiovanni, E. Garfunkel, J. Li, M. Greenblatt and G. C. Dismukes, *J. Am. Chem. Soc.*, 2013, **135**, 3494–3501.
35 N. Birkner, S. Nayeri, B. Pashaei, M. M. Najafpour, W. H. Casey and A. Navrotsky, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 8801–8806.
36 T. Takashima, K. Hashimoto and R. Nakamura, *J. Am. Chem. Soc.*, 2012, **134**, 1519–1527.
37 M. Kimura, M. Ohota and K. Tsukahara, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 151–155.
38 J. E. Kostka, G. W. Luther and K. H. Nealson, *Geochim. Cosmochim. Acta*, 1995, **S9**, 885–894.
39 U. Urzúa, P. J. Kersten and R. Vicuña, *Arch. Biochem. Biophys.*, 1998, **360**, 215–222.
40 Y. Wang and A. T. Stone, *Geochim. Cosmochim. Acta*, 2006, **70**, 4477–4490.
41 H. Wariishi, K. Valli and M. H. Gold, *J. Biol. Chem.*, 1992, **267**, 23688–23695.
42 H. Podgornik, M. Stegu, A. Podgornik and A. Perdih, *FEMS Microbiol. Lett.*, 2001, **201**, 265–269.
43 A. T. Stone, K. L. Gottfredsen and B. Deng, Sources and reactivity of reductants encountered in aquatic environments, in *Chemistry of Aquatic Systems: Local and Global Perspectives*, ed. G. Bidoglio and W. Stumm, Kluwer, 1994, pp. 337–374.

44 A. E. Martell, R. M. Smith and R. J. Motekaitis, *NIST Critically Selected Stability Constants of Metal Complexes Database*, US Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD, 2004.
45 M. J. Sisley and R. B. Jordan, *Inorg. Chem.*, 2006, **45**, 10758–10763.
46 H. Wariishi, K. Valli and M. H. Gold, *J. Biol. Chem.*, 1992, **267**, 23688–23695.
47 E. Varela and M. Tien, *Appl. Environ. Microbiol.*, 2003, **69**, 6025–6031.
48 H. Podgornik, M. Stegu, A. Podgornik and A. Fems, *FEMS Microbiol. Lett.*, 2001, **201**, 265–269.
49 L. Jiang, C. Huang, J. Chen and X. Chen, *Arch. Environ. Contam. Toxicol.*, 2009, **57**, 221–229.
50 U. T. Twahir, A. Ozarowski and A. Angerhofer, *Biochemistry*, 2016, **55**, 6505–6516.
51 A. B. Mandal and B. U. Nair, *J. Phys. Chem.*, 1991, **95**, 9008–9013.
52 A. A. Rafati, H. Gharibib and H. Iloukhani, *Phys. Chem. Liq.*, 2001, **39**, 521–532.
53 G. Branica, M. Metikos-Hukovic and D. Omanovic, *Croat. Chem. Acta*, 2006, **79**, 77–83.
54 W. Horwitz, P. Britton and J. C. Stuart, *J. AOAC Int.*, 1998, **81**, 1257–1265.
55 *Directive, 2002/657/EC of 12 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and interpretation of results. OJ L 221*, European Commission, Brussels, Belgium, 17.8.2002, p. 8.