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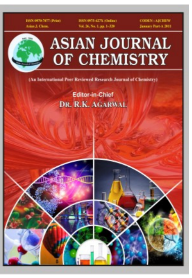

Fluorimetric Determination of Trace Bisphenol-A Based on its Oxidative Reaction with Fenton-Like Reagent as Oxidant

JIANTING WANG, JIAN ZHANG, JUN ZHU and RENMIN GONG*

College of Life Science, Anhui Normal University, Wuhu, 241000, P.R. China

*Corresponding author: Tel: +86 553 5991085; E-mail: rmgong.nju@163.com

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Bisphenol-A (BPA) is an exogenous substance that acts like hormones in the endocrine system and disrupts the physiologic function of endogenous hormones. Due to the widespread human exposure to bisphenol-A and its potential adverse effects on human health, special attention has been paid to the determination of bisphenol-A in the environment. In this paper, a simple, sensitive and selective fluorimetric method for the determination of bisphenol-A, based on the oxidative reaction of bisphenol-A in the presence of hydrochloric acid by Fenton-like reagent (Fe^{3+}+H_2O_2), had been developed. The fluorescence came from the oxidation product of bisphenol-A at $\lambda_{excitation}$ 315 and $\lambda_{emission}$ 415 nm in pH 8.90 Tris-HCl buffer solution. Under the optimum conditions, a linear relationship had been obtained between the fluorescence intensity and the concentration of bisphenol-A in the range of 0.01-0.5 μg/mL, with detection limit and correlation coefficient being 0.64 ng/mL and 0.9995, respectively. The proposed method had been successfully applied for the determination of trace bisphenol-A in water, beverage bottle and cling wrap film.

Keywords: Fluorimetric determination, Bisphenol-A, Fenton-like reagent and oxidative reaction.

INTRODUCTION

Endocrine disrupting compounds (EDCs) are exogenous substances that act like hormones in the endocrine system and disrupt the physiological function of endogenous hormones. Among various problems caused by endocrine disrupting compounds, the pollution of phenolic endocrine disrupting compounds in environmental water has aroused the public concerns as these contaminants were frequently detected in different water sources in recent years[1,2]. Bisphenol-A (BPA), a phenolic endocrine disrupting compound, has been widely used as the monomeric substance for the production of polycarbonate and epoxyphenolic resins and as the stabilizer or antioxidant for many types of plastics[3]. Due to the widespread human exposure to BPA and its potential adverse effects on human health, special attention has been paid to the determination of BPA in the environment. Various methods such as high-performance liquid chromatography (HPLC)[4-6], liquid chromatography-mass spectrometry (LC-MS)[7-9], gas chromatography-mass spectrometry (GC-MS)[10-12], fluorimetry[13,14] and electrochemical analysis[15,16], have been reported for the determination of BPA. However, some of these methods are expensive, time consuming and need skilful technicians and sometimes require enrichment[17,18] and extraction steps[19,20] that increase the risk of sample loss.

Bisphenol-A shows intrinsic fluorescence in different organic solvents but its fluorescence intensity in aqueous solution is too low to be directly determined[21]. Our studies showed that BPA could be oxidized by Fenton-like reagent in the medium of dilute hydrochloric acid, the oxidation product of BPA emitted strong natural fluorescence in pH 8.90 Tris-HCl buffer solution and the fluorescence intensity was linearly related to the concentration of BPA. Based on this new discovery, an inexpensive, sensitive and selective method of fluorimetry had been proposed for the determination of BPA. To our best knowledge, no literatures are available concerning the determination of trace BPA based on the fluorescence signal of its oxidation product. The proposed method had been successfully applied to the determination of BPA in real samples.

EXPERIMENTAL

All chemicals were of analytical reagent grade or the best grade commercially available and double distilled water was used throughout. Standard stock solution of bisphenol-A (0.200 mg/mL) was prepared by dissolving 0.100 g of solid BPA in 0.5 mL of 0.1 g/mL (w/v) sodium hydroxide solution, then diluting in 500 mL volumetric flask with water and stored in the dark at 4 °C. Working BPA solutions were obtained by diluting the stock solution to the required concentration.

Standard Fe(III) stock solution (0.10 mg/mL) was obtained by dissolving 0.2420 g of solid $FeCl_3{\cdot}6H_2O$ in water and diluting to 500 mL in a volumetric flask. Working Fe(III) solutions were freshly prepared by appropriate dilution of the stock solution. Other chemical solutions used during the study include: 0.005 % hydrogen peroxide solution, 0.008 mol/L hydrochloric acid and 0.1 mol/L Tris-HCl buffer solution (pH 8.9).

The fluorescence spectra and fluorescence intensities were recorded on a Shimadzu RF-5301 spectrofluorometer equipped with a xenon lamp and 1 cm quartz cells. Slit widths of both monochromator were set at 10 nm, unless otherwise noted. A Model 501 thermostat bath (Chongqing, China) was used to control reaction temperatures.

Sample processing: The environmental water samples were filtrated and the filtrates were passed through the anion exchange resin (Strong-base OH form, Xi'an, China), cation exchange resin (Strong-acid H form, Xi'an, China) and XDA-1 adsorption resin (Xi'an, China) orderly in the pH 3.0, then the leachates were adjust to pH 7 for analysis.

The beverage bottle were washed with water, solarized and cut into pieces of 0.5 cm^2. An appropriate amount of sample was put in a conical flask and 100 mL of water was added. A given amount of the cling wrap film was cut into pieces and put in a conical flask and 100 mL of water was added. The solutions were heated in a water bath (90.0 ± 0.2 ºC) for 2 h and then cooled to room temperature.

Procedure: An appropriate amount of standard or sample solution containing 0.25-12.5 µg BPA was transferred to a 25 mL colorimetric tube and then the following reagents were added successively: 0.5 mL of 0.4 µg/mL Fe(III), 1 mL of 0.005 % hydrogen peroxide, 1 mL of 0.008 mol/L hydrochloric acid. The mixture was diluted to 10 mL with water and mixed completely. The colorimetric tube was heated in a thermostatted water bath (90 ± 0.2 ºC) for 8 min and cooled to room temperature by running water. Then the mixture was diluted to the mark with 0.1 mol/L Tris-HCl buffer solution (pH 8.90) and mixed thoroughly. After 10 min, the fluorescence intensity of the mixture solution was measured at excitation and emission wavelengths of 315 and 415 nm, respectively. The fluorescence intensity of a reagent blank solution without BPA was similarly measured under the same conditions.

RESULTS AND DISCUSSION

Spectral characteristics: According to the proposed procedure, the excitation and emission spectra of BPA oxidation product were measured. Fig. 1 showed that the maximum emission wavelength of BPA oxidation product was 415 nm with the excitation wavelength at 315 nm. Furthermore, it was observed that there was a linear relationship between the fluorescence intensity ($F - F_0$) and the concentration of BPA in the system.

Effects of the medium and concentration: The following media had been tried in the present experiments: sulfuric acid, phosphoric acid, nitric acid and hydrochloric acid. It was found that in sulfuric acid and phosphoric acid, the sensitivity of the reaction was very low, but in nitric acid, the sensitivity of the reaction was high but with poor stability. In hydrochloric acid, the sensitivity and stability of the reaction were both satisfactory.

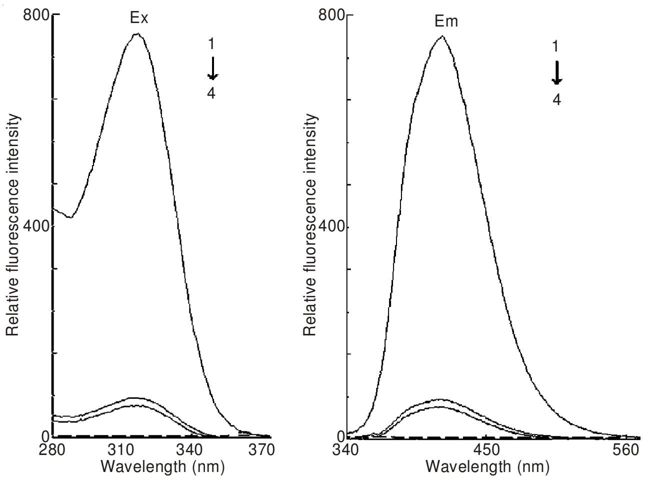

Fig. 1. Excitation (Ex) and emission (Em) spectra of BPA oxidation product: (1) BPA-H_2O_2-Fe(III)-HCl/Tris-HCl buffer, (2) BPA-H_2O_2-HCl/Tris-HCl buffer, (3) BPA-Fe(III)-HCl/Tris-HCl buffer, (4)BPA-HCl/Tris-HCl buffer systems. [BPA]: 0.4 µg/mL, [H_2O_2]: 2×10^{-4} %, [Fe(III)]: 8 ng/mL, [HCl]: 0.32 mmol/L, buffer pH value: 8.9, temperature: 90 ºC, time: 8 min

The influence of hydrochloric acid concentration was studied in the range of 0.08-0.56 mmol/L. As could be seen from Fig. 2, the fluorescence intensity increased by increasing the hydrochloric acid concentration to 0.32 mmol/L and then decreased. Because Fe(III) can only remain stable in acidic solution, the oxidative reaction of BPA must be carried out in acidic medium. However, when the pH value is very low, the excess H^+ quenches the produced peroxyl radicals. It causes a decrease in the fluorescence intensity. Therefore, a final concentration of 0.32 mmol/L hydrochloric acid was selected as optimum condition.

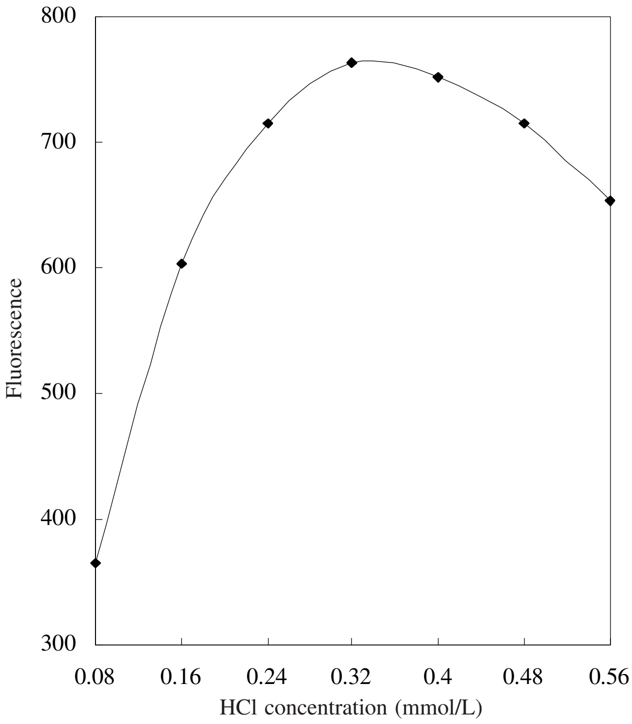

Fig. 2. Effect of HCl concentration on fluorescence signal ([BPA]: 0.4 µg/mL, [H_2O_2]: 2×10^{-4} %, [Fe(III)]: 8 ng/mL, buffer pH value: 8.9, temperature: 90 ºC, time: 8 min)

Effects of pH and buffers: It is observed that the fluorescence intensity of BPA oxidation product increased significantly by changing acidic medium to basic medium. So the following buffer solutions had been tested in the present experiments: phosphate buffer solution, carbonate buffer solution, borate buffer solution and Tris-HCl buffer solution. The Tris-HCl buffer solution was found to be best among the above buffer solutions. It could be seen from Fig. 3 that the highest fluorescence signal was obtained in pH 8.90 Tris-HCl buffer solution. The similar result was reported in literature[22].

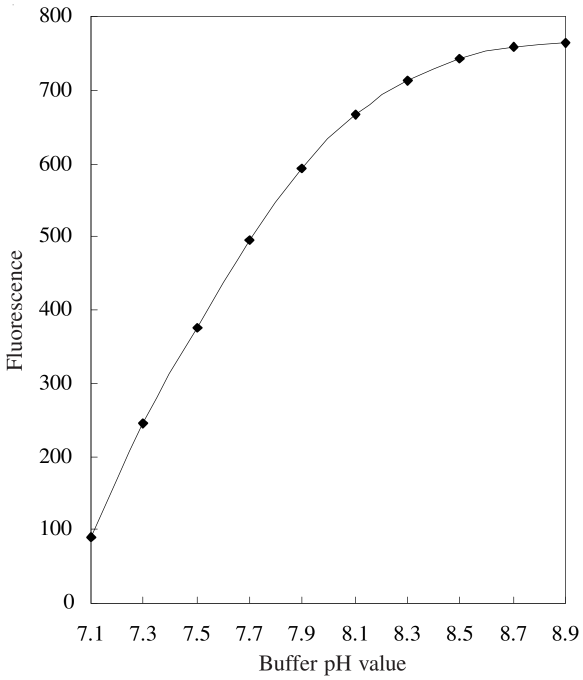

Fig. 3. Effect of buffer pH value on fluorescence signal ([BPA]: 0.4 μg/mL, [H_2O_2]: 2 × 10^{-4} %, [Fe(III)]: 8 ng/mL, [HCl]: 0.32 mmol/L, temperature: 90 ºC, time: 8 min)

Effects of H_2O_2 and Fe(III) concentration: As the precursor of the hydroxyl radicals, the concentration of H_2O_2 affects the oxidation of BPA. The effect of the H_2O_2 concentration on the oxidation of BPA was investigated in the range of 0.4-3.2 × 10^{-4} % H_2O_2 and the result was shown in Fig. 4. It was found that when the H_2O_2 concentration was lower than 2 × 10^{-4} %, the fluorescence intensity increased rapidly with the increase of H_2O_2 concentration, then the fluorescence intensity had a slight decrease with the further increase of the H_2O_2 concentration.

The effect of Fe(III) concentration on the oxidation of BPA was shown Fig. 5. It was observed that the fluorescence intensity increased with the increase of Fe(III) concentration up to 8 ng/mL and then decreased with the further increase of the Fe(III) concentration. Because Fe(III) is used as the initial oxidant in the redox system, its concentration greatly influences peroxyl radicals generated. So final concentrations of 2 × 10^{-4} % H_2O_2 and 8 ng/mL Fe(III) were selected as optimum condition.

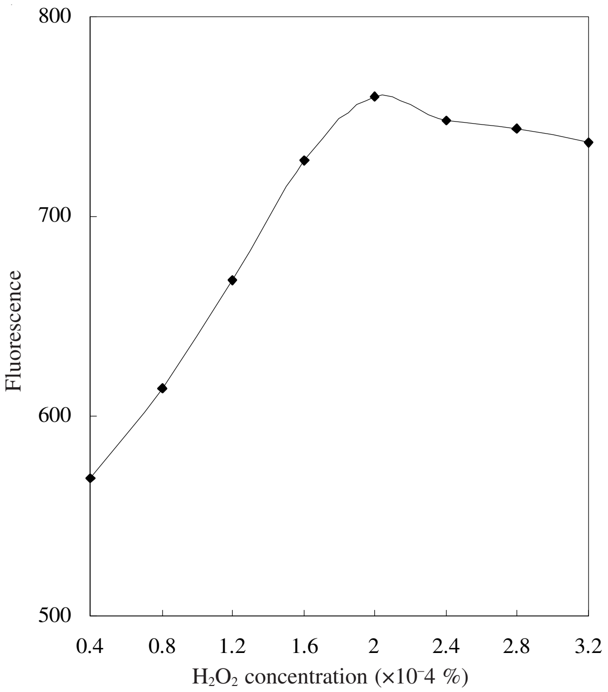

Fig. 4. Effect of H_2O_2 concentration on fluorescence signal ([BPA]: 0.4 μg/mL, [Fe(III)]: 8 ng/mL, [HCl]: 0.32 mmol/L, buffer pH value: 8.9, temperature: 90 ºC, time: 8 min)

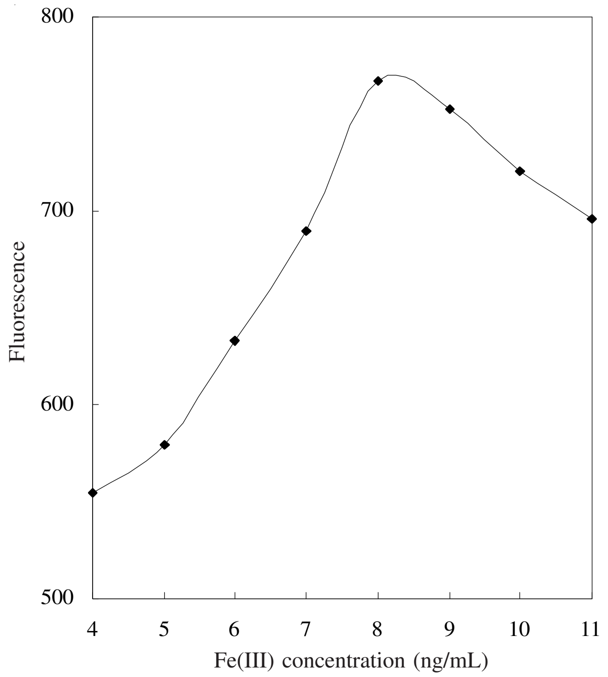

Fig. 5. Effect of Fe(III) concentration on fluorescence signal ([BPA]: 0.4 μg/mL, [H_2O_2]: 2 × 10^{-4} %, [HCl]: 0.32 mmol/L, buffer pH value: 8.9, temperature: 90 ºC, time: 8 min)

Effects of reaction temperature and time: The effects of the reaction temperature and time on the oxidation of BPA were investigated in the range of 30-100 ºC for 2-14 min, respectively. The effect of temperature on the oxidation of BPA was illustrated in Fig. 6. It could be seen that the fluorescence intensity increased with increasing temperature up to 90 ºC. But the fluorescence intensity decreased at the temperature above 90 ºC.

Fig. 7 showed that the fluorescence intensity increased with prolonging reaction time in the range of 2-8 min, but the fluorescence intensity decreased in longer reaction time. Thus, 90 ºC and 8 min were recommended as the best reaction temperature and time. Because the fluorescence compound may be decomposes in higher temperature and longer time.

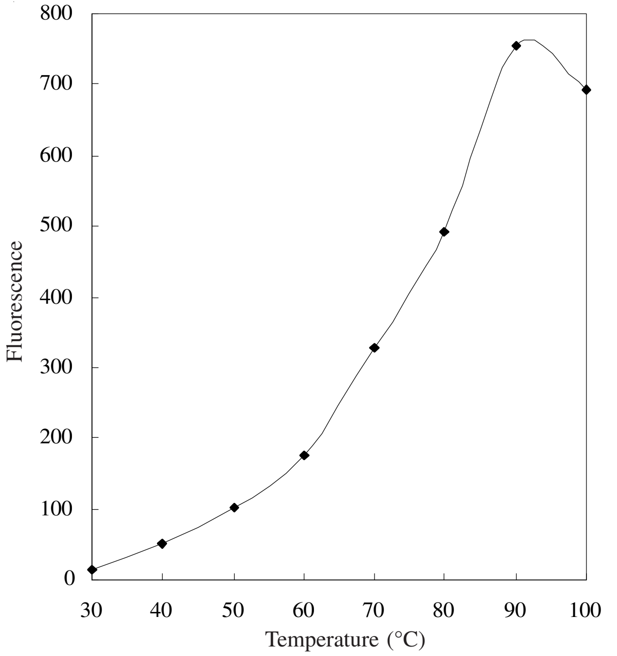

Fig. 6. Effect of temperature on fluorescence signal ([BPA]: 0.4 µg/mL, [H_2O_2]: 2 × 10^{-4} %, [Fe(III)]: 8 ng/mL, [HCl]: 0.32 mmol/L, buffer pH value: 8.9, time: 8 min)

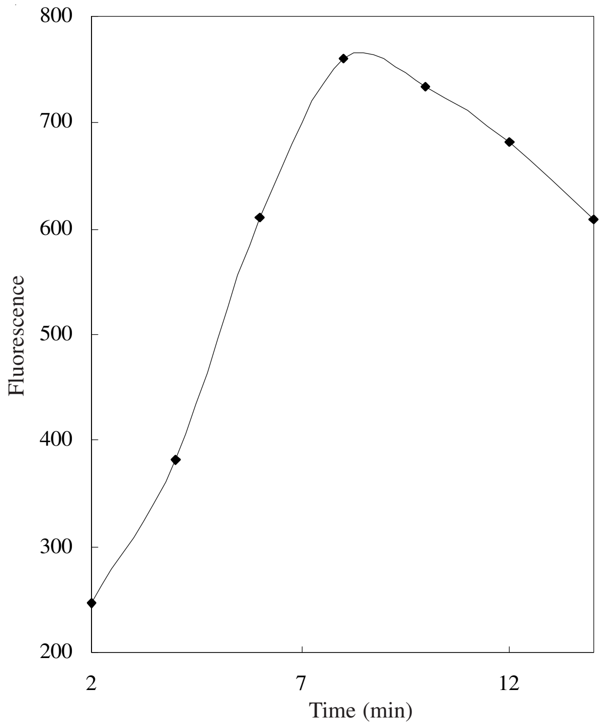

Fig. 7. Effect of time on fluorescence signal ([BPA]: 0.4 µg/mL, [H_2O_2]: 2 × 10^{-4} %, [Fe(III)]: 8 ng/mL, [HCl]: 0.32 mmol/L, buffer pH value: 8.9, temperature: 90 ºC)

Fluorimetric determination of BPA and the calibration curve: Based on the optimum conditions described above for the oxidation of BPA in the presence of hydrochloric acid by Fenton-like reagent, the new fluorimetric method for the determination of BPA was established. Under these optimum conditions, a linear relationship was obtained between the relative fluorescence intensity and the concentration of BPA in the range of 0.01 and 0.5 µg/mL. The linear regression equation of the calibration curve was $\Delta F = 1895.1C_{(\mu g/mL)} + 3.9916$ (ΔF is the difference between relative fluorescence intensity of sample and blank and C is the concentration of BPA), with the correlation coefficient 0.9995. The detection limit of the method ($3S_b/k$, three of the standard deviation blank divided by slope of the calibration curve) was 0.64 ng/mL. It could be found that the proposed method had wider linear range and lower detection limit, compared with the fluorimetric method reported in literature[14].

Effect of foreign substances: To study the selectivity of the proposed method, the interference of a series of foreign substances on the determination of 0.4 µg/mL BPA was investigated under the optimum conditions. The tolerance limit was defined as the concentration at which the species caused an error of less than ± 5 %. The interferences were listed in Table-1. The results demonstrated that except for some metal cations, citric acid, salicylic acid and phenolic compounds, most of the studied inorganic and organic substances did not interfere with the determination. However, the influences of metal cations, citric acid and salicylic acid could be completely removed by using a cation exchange resin of strong-acid H form and an anion exchange resin of strong-base OH form; through the research of synthetic samples, it was found that the interference of the other phenolic compounds could be effectively removed by XDA-1 adsorption resin (Xi'an, China)[14]. Therefore, the proposed method had good selectivity.

Practical application: To evaluate the analytical applicability of the method, the proposed method was applied to the determination of BPA in water and plastics samples. After being pre-separated to remove interferences, BPA in samples was determined directly and the results were given in Table-2. The recoveries for the samples determination were in 97-105 % with relative standard deviation less than 3.2 %, which indicated that there was no serious interference through the proposed sample preparation.

Conclusion

Combined the traditional Fenton oxidation technique with sensitive fluorimetric method, a new spectrofluorimetry had been proposed for the determination of BPA, a phenolic endocrine disrupting compound. By pre-separating with ionic exchange resins and adsorption resin, the BPA in samples could be determined directly at ng/mL levels with the recoveries between 97 and 105 % in all the cases. Compared with the fluorimetric methods reported in literatures[13,14], its operation procedure was simple, fast and convenient. In comparison with the conventional determination method, the proposed method also was rapid, inexpensive, simple for operation and easy of popularization. But for acquiring accurate result, the determination procedure must be controlled under the optimum conditions.

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TABLE-1
EFFECT OF FOREIGN SUBSTANCES ON THE DETERMINATION OF BISPHENOL-A

Foreign substance	Tolerance ratio	Substance	Tolerance ratio
Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-	>1000	CO_3^{2-}, HCO_3^-, HPO_4^{2-}, $H_2PO_4^-$	> 500
SO_4^{2-}, PO_4^{3-}, NO_3^-, Zn^{2+}, Cd^{2+}	>200	Al^{3+}, Ba^{2+}, sucrose, fructose	> 100
SO_3^{2-}, Sn^{2+}, Br^-, dextrose	>50	Cr^{3+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}	> 10
Hg^{2+}, Pb^{2+}, citric acid	>5	Salicylic acid, nitrophenol, phenol	< 1

TABLE-2
RESULTS OF BISPHENOL-A DETERMINATION IN REAL WATER SAMPLES (n = 5)

Sample	BPA				
	Added (μg/mL)	Found (μg/mL)	Recovery (%)	RSD (%)	Found in sample[a]
Tap water	0	0	–	–	0
	0.1	0.098	98	2.25	
Wastewater	0	0.12	–	2.71	0.5
	0.1	0.225	105	3.18	
Beverage bottle	0	0.023	–	1.87	0.958
	0.1	0.125	102	2.69	
Cling wrap film	0	0.012	–	1.44	1.25
	0.1	0.109	97	2.19	

[a] Sample content in μg/ml for water samples and μg/g for plastics samples.

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