

Cloud Point Extraction method for Sensitive determination of Bisphenol A

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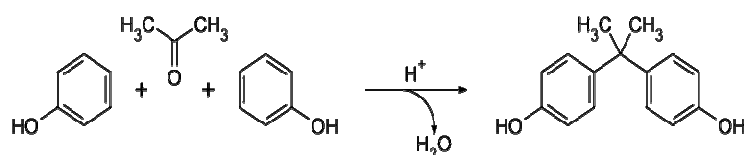
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Abstract : Cloud point extraction has been used for sensitive pre-concentration and determination of Bisphenol A. The analyte is quantitatively extracted to the phase rich in the nonionic Surfactant Triton X-114. The parameters which affecting the separation phase and detection process, were optimized. Calibration graph showed linear trend in rang of 0.5-7.5 mg l⁻¹ with detection limit 0.1 mg l⁻¹ of bisohenol in waste water samples, which gathered from petrochemical factory, has been measured and gave satisfactory results.

Key words: Bisphenol A, Preconcentration, Spectrophotometer.

Introduction

World production capacity of bisphenol compound was 1 million tons in the 80s¹, and more than 2.2 million tons in 2009². In 2003, U.S. consumption was 856,000 tons, 72% of which was used to make polycarbonate plastic and 21% going into epoxy resins³. In the U.S., less than 5% of the BPA produced is used in food contact applications⁴, but remains in the canned food industry and printing applications such as sales receipts^{5,6}.



Bisphenol A was first synthesized by the Russian chemist A.P. Dianin in 1891^{7,8}. This compound is synthesized by the condensation of acetone (hence the suffix A in the name)⁹ with two equivalents of phenol. The reaction is catalyzed by a strong acid, such as hydrochloric acid (HCl) or a sulfonated polystyrene resin. Industrially, a large excess of phenol is used to ensure full condensation; the product mixture of the cumene process (acetone and phenol) may also be used as starting material¹.

A large number of ketones undergo analogous condensation reactions. Commercial production of BPA requires distillation—either extraction of BPA from many resinous byproducts under high vacuum, or solvent-based extraction using additional phenol followed by distillation⁵.

In the present work, a study of the CPE for simple and selective preconcentration of bisphenol after extraction in surfactant reach phase and later analysis by visible spectrophotometric method. The proposed method is also applied to the determination of the bisphenol in some environmental samples such as petrochemical waste water, which shown satisfactory results.

Material And Method

Reagents and solutions

All solutions were prepared with ultra pure water.

BisPhenol A, $K_3Fe(CN)_6$, 4- aminoantipyrine , ammonia solution (25%), ammonium chloride, were prepared from Merck company.

A buffer pH=10 was prepared by ammonia/ammonium chloride (0.1 M) in 500 mL volumetric flask.

The stock phenol solution (300 mg l^{-1}) were prepared by Merck standard solutions.

The nonionic surfactant Triton X-114, 5.0% (W/V) prepared by dissolving 5.0 gr surfactant Triton X-114 made up to 100 ml with distilled water.

A solution of 8.0 g L^{-1} of $K_3Fe(CN)_6$ was prepared by dissolving 8.0 gr of this reagent in 100 ml water.

A solution of 2.0 g L^{-1} of 4- aminoantipyrine was prepared by dissolving 2.0 gr of this reagent in 100 ml water.

Apparatus

All spectral measurements and treatment of data were carried out in 1cm quartz cells using a Perkin-Elmer Lambda 25 double beam spectrophotometer. Measurements of pH were made using a Jenway Model 3510 pH-meter equipped with a glass-saturated calomel combined electrode.

A balance (Sartorius, BL 210S, $d=0.1\text{mg}$), an oven (memmert) were used. A centrifuge (Hettich) was used to accelerate the phase separation process. A thermostated water bath (Memert) was employed to maintain the experimental temperature.

Procedure

In this test method bisphenol form a reddish complex with 4-aminoantipyrine and $K_3Fe(CN)_6$ in the presence of ammonia/ammonium chloride buffer solution (ASTM D1783-01 at $\lambda_{\text{max}}=510\text{ nm}$ [9]). For the cloud point extraction, an aliquots of 10 ml of a solution containing bisphenol, and 2 ml of buffer solution pH=10, 2 ml Triton X-114 5.0% (W/V), 0.2 ml of $K_3Fe(CN)_6$, 8.0 g l^{-1} and 0.2 mL of 2.0 g mL^{-1} 4- aminoantipyrine were placed in a centrifuge tube and heated in a thermostat water bath at 50°C for 20 min. After heated, the resultant solution was subjected to centrifugation at 4000 rpm for 15 min for phase separation, and then cooled in an ice-water for 10 min in order to increase the viscosity of the surfactant-rich phase. The supernatant aqueous phase was easily decanted by simply inverting the tube. A blank solution was also run without adding the analyte.

Preparation Of Real Samples

Waste water samples

Waste waters were collected from some Mahshar petrochemical industry. They were filtered through Watman No. 42 and stored in glass bottles at 4°C . Then the samples were ready for purposed procedure.

Results and Discussion

Effect of Triton X-114 concentration

Triton X-114 was chosen for the formation of the surfactant rich phase due to its low cloud point temperature and commercial availability in a high purified homogeneous form, low toxicological properties, cost and high density of the surfactant rich phase, which facilitates phase separation by centrifugation.

Fig. 1 has shown the effect of TritonX-114 concentration on the CPE pre-concentration of bisphenol. The signals of bisphenol increased as the Triton X-114 concentration increased from 0.5- 3.0% (W/V) and approximately constant when, Triton X-114 concentration was increased larger than 2.0% (W/V). Hence a concentration of Triton X-114, 2.0% (W/V), was employed for the rest of this work.

Selection of the dilution agent for the surfactant – rich phase:

An organic solvent should have characteristics such as low viscosity, low surface tension and combustible for use in atomic absorption [10]. Different solvents for the surfactant-rich phase were tested so as to select the one producing the optimal results regarding sensitivity. Acetone, methanol, ethanol and DMF were tested for this purpose. Methanol dissolved completely the surfactants which in its extracted bisphenol and the best recovery were obtained and an optimum volume is 3 ml.

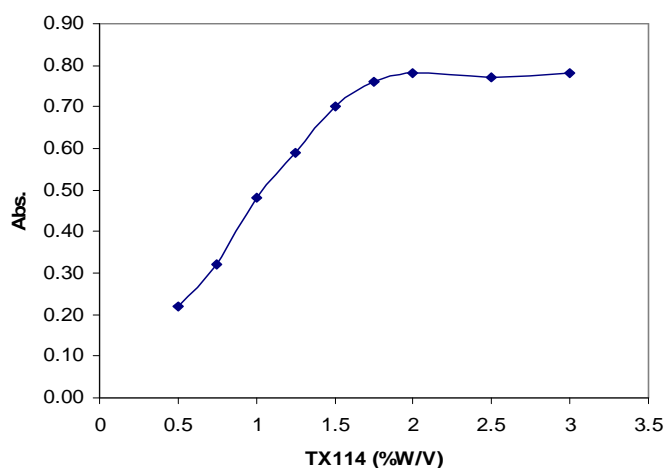


Fig. 1. Effect of the Triton X-114 concentrations on the on the extraction recovery of bisphenol

Practical parameter

The dependence of extraction efficiency on equilibration temperature and time were studied within a range of 30 – 70 °C and 5–25 min, respectively. The results showed that an equilibration temperature of 45 °C and an equilibration time of 20 min are enough to get quantitative extraction of the bisphenol. The effect of the centrifugation time on the extraction efficiency was also studied within a range of 5–25 min. A centrifugation time of 20 min at 4000 rpm was selected for the entire procedure, since analyte extraction in this time is almost quantitative.

Figures of merit

Calibration graph was obtained in optimum conditions and for bisphenol was linear from 0.5-7.5 mg l⁻¹ with a correlation coefficients of 0.9988. The detection limit which obtained by the equation of $DL=3S_b/m$ is 0.10 mg L⁻¹. The relative standard deviation (RSD, n=5) for 1.0 mg l⁻¹ concentration of phenol was 1.8%.

Table 1. Determination of bisphenol in petrochemical waste water samples.

Sample	BisPhenol (mg L ⁻¹) ^a		% Recovery
	Added	Found	
Waste water 1	-	ND	-
	1.00	1.10	110
	3.00	2.90	97
Waste water 2	-	ND	-
	1.00	1.05	105
	3.00	3.20	107
Waste water 3	-	ND	-
	1.00	0.95	95
	3.00	3.20	107

a) After appropriate dilution

Determination of bisphenol in real sample

In order to test the reliability of the proposed methodology suitable for the assaying of bisphenol in waste water samples a series of petrochemical waste water sample were used. For this purpose, 5 ml of each of the samples were pre-concentrated with 2.0% (w/v) Triton X- 114 and, following the proposed procedure. The results are shown in Table 1.

Conclusion

This paper proposes a simple and effective method for the preconcentration and determination of trace levels of bisphenol by CPE in waste water samples for their determination by spectrophotometric method. The methodology offers a reliable method for determination of bisphenol in petrochemical industries.

Acknowledgements

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