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Spectrophotometric Method Combined with HPLC for Bisphenol F Determination in Plastic Bottled Water and Thermal Paper

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Abstract:

Based on the diazotization-coupling reaction, a new, simple, and sensitive spectrophotometric method for determining of a trace amount of (BPF) is presented in this paper. Diazotized metoclopramide reagent react with bisphenol F produces an orange azo-compound with a maximum absorbance at 461 nm in alkaline solution. The experimental parameters were optimized such as type of alkaline medium, concentration of NaOH, diazotized metoclopramide amount, order additions, reaction time, temperature, and effect of organic solvents to achieve the optimal performance for the proposed method. The absorbance increased linearly with increasing bisphenol F concentration in the range of 0.5-10 µg mL^{-1} under ideal conditions, with a correlation coefficient of 0.9931 and a detection limit of 0.15 µg mL^{-1}. The effect of different temperatures and different extraction time was studied on the leaching out and the data indicates that as time and temperature rising, the concentration of BPF leached out of all thermal papers increased. To confirm that extracts from thermal papers contained BPF, samples containing the analytic were subjected to high-performance liquid chromatography (HPLC-UV detector) analysis. The analysis was carried out on a C18 column with a mobile phase of acetonitrile/water (55/45v:v), and the detection was conducted spectrophotometrically at 230 nm. The retention time of standard BPF was determined to be 5.649 min and the peak eluting time for most thermal papers extract was at 5.6 minutes, demonstrating that BPF was present in the thermal papers. The method was applied to quantify the proposed analyses in a variety of samples with excellent results.

Keywords: Bisphenol F; Diazotization-Coupling Reaction; HPLC; Metoclopramide; Spectrophotometric Technique.

Introduction:

Exogenous chemicals that interact with the endocrine system and impair hormone physiology are known as endocrine disrupting compounds (EDCs). Natural and manufactured EDCs have been associated to a decrease in sperm count in males and an increased risk of breast cancer and reproductive disorders in females when detected in the environment. Endocrine disrupting chemicals' ability to (a) mimic natural hormones, (b) inhibit their action, (c) change their synthesis and metabolism pattern, or (d) alter the expressions of certain receptors may be the origin of their endocrine and reproductive impacts [1,2].

Bisphenols are endocrine disruptor chemicals, possess two hydroxyphenyl groups that are widely utilized and found in a variety of home products, including food packaging, drink containers, cosmetics, toys, plastic PVC flooring, water pipes epoxy resins, thermal print paper, and dental sealants [3-7]. Human exposed to these substances has been linked to significant diseases such cardiovascular disease, diabetes, obesity, asthma, early puberty, and altered sperm morphology/sperm count. Damage to DNA [8,9]. Bisphenol A (BPA) is the most prevalent of these compounds, which was first studied as a synthetic estrogen but eventually found usage in the manufacture of plastics and is now one of the most widely used chemicals on the planet [3].

Due to health and environmental concerns, bisphenol analogues that have similar physicochemical properties to BPA have been substituted in some industrial applications, such as bisphenol F (BPF) in products often advertised as "BPA free," resulting in an increase in BPF production in recent years [10,11].

BPF is utilized in pipe and tank linings because of its ability to increase the durability and thickness of materials [12,13]. It may also be found in food packaging products and beverage containers, as well as in paper products. Because of the physiochemical similarity to BPA, it has similar endocrine properties.

Furthermore, because it is poorly biodegradable and has a rather high polarity, it spreads easily in the environment. Castroetal obtained in vivo evidence of the possible detrimental effects of BPF in the developing brain of mammals in 2015 [14], and Rosenmaietal discovered that endocrine interference was the predominant effect of bisphenol exposure [15]. Thermal sheets are harmful to humans not just directly, but also indirectly through recycling and trash discharge. Bisphenol A (BPA) is utilized as a color developer in thermal paper, where it reacts with a leuco dye and converts it into a colored form that is present as a free, unreacted monomer and is thus predicted to be easily released into the environment following a heating procedure [16].

When handling certain types of papers, particularly thermal papers, dermal absorption is a probable pathway for human exposure to BPA and bisphenol analogues [17, 18]. Other bisphenols, such as bisphenols (F, S, AF, E, and B), which have been proposed as potential BPA substitutes, were only discovered at trace quantities in thermal paper items [16-20].

Liquid chromatography or gas chromatography with mass spectrometry (LC-MS and GC-MS) or tandem-mass spectrometry (LC-MS/MS and GC-MS/MS) are used to determine bisphenol F in various matrices, as well as high-performance liquid chromatography with FID detector. [13, 21-26].

The aim of this study was to develop, a low-cost, simple and sensitive spectrophotometric method based on the diazotization-coupling reaction with the diazotized metoclopramide for the quantification of BPF in plastic bottled water and thermal paper with excellent results. In Fig 1, the chemical structure of bisphenol F is shown.

Figure 1. The chemical structure of Bisphenol F

Materials and Methods:

Instruments

All of the absorption spectra were recorded using a Shimadzu (UV-1800 (Kyoto, Japan)) double-beam spectrophotometer with a 5-mm optical path cell. Experts on the WNB7-45 Thermostatic Water Bath (England). Electric Balance Sartorius (0.0000) made in Germany. A RP-HPLC Shimadzu system with (LC-20A) pump was used, C18 column with dimensions (250 mm Å~4.6 mm) and particle size5μm, using acetonitrile/water (55/45v:v) at a flow rate of 1 mL/min as the mobile phase and the absorbance of the eluent was monitored at 230 nm.

Chemicals

All of the reagents were analytical grade, Fluorochem provided the bisphenol F. (UK). Sigma Aldrich provided (95.5%) metoclopramide HCL (MCP) and sodium nitrite (USA). Sodium hydroxide, hydrochloric acid (BDH, UK). Potassium hydroxide, potassium carbonate, Ammonia, Sodium carbonate(anhydrous)(BDH), Sodium bicarbonate, 1-propanol, Ethanol, Acetonitrile, and Acetone were all obtained from (BDH), whereas Methanol, Carbon tetrachloride, and Methylene chloride were obtained from GCC (BDH, UK). In all of the studies, double distilled water was used.

Preparation of Solutions

The following substances are the solutions that have been prepared: Bisphenol F standard stock solution was prepared by dissolving 0.1gm in 10 mL ethanol, diluting with water to a final concentration of 1000 mg/mL, and keeping in brown bottles at 4 °C. The working solutions were prepared by further diluting to the stock solution by distilled water. To make 0.1M of potassium hydroxide, potassium carbonate, sodium bicarbonate, sodium carbonate(anhydrous), and sodium hydroxide, dissolving 0.2805, 0.6910, 0.4200, 0.5299, and 0.2 gm respectively in 50 ml volumetric flask with distilled water. To prepare 0.1M ammonia hydroxide, dilute 0.37 mL concentrated ammonia in a 50 mL volumetric flask with distilled water. To prepare 1M hydrochloric acid, dilute 8.62 ml of the concentrated solution (11.6M-HCl) to 100 ml with distilled water.

Diazotized metoclopramide reagent solution (5mM) [27-29]

After 0.1772 gram of MCP was dissolved in a small volume of distilled water, 3 mL of Hydrochloric acid (1M) was added in ice at 5°C with stirring for 5 minutes, then 0.0345 g sodium nitrite was added and thoroughly mixed into the mixture. The solution was made up with distilled water in a 100 mL volumetric flask. In a brown bottle, the solution is kept in the refrigerator for at least three days.

Sampling

Thermal receipt paper samples were collected from a variety of locations across town. All receipts were individually wrapped in aluminum foil and stored in BPA-free paper envelopes (to avoid contamination) until they were analyzed. Water bottle samples (Pearl and Aquafina bottled water 500 ml) were obtained and analyzed from various workplaces.

Procedure for extracting BPF from plastic water bottle samples

After properly washing the samples with double distilled water, the 1:1 methanol: water solution was produced, heated to 70°C in a beaker, and put into the plastic item, which was then placed in a water bath and heated to 60°C for one hour before cooling to room temperature. Finally, a portion of the sample was diluted with distilled water or supplemented with bisphenol F to assess the method's recovery under optimal conditions for the development of the colored product[30].

Procedure for extracting BPF from thermal paper samples

BPF was extracted from the paper samples using a modified version of a previously published method [31]. Briefly, 200 mg of thermal papers were weighted and placed in different dry and sterilized clean test tubes and kept in an oven at two different temperatures (40 and 60°C, respectively, (the highest temperatures expected in Iraq) for one hour. Thermal paper samples were then transferred into a clean 200 ml beaker and immersed 100 ml of methanol and water (1:1, v:v) for one and five hours. An aliquot of extract was obtained and the absorption spectra of the product solution were measured under optimal parameters for the formation of the colored product.

Results and Discussion:

Selecting the Wavelength of Maximum Absorption

The first attempt of this research is to find the reaction of bisphenol F with diazotized MCP reagent in basic medium (sodium hydroxide), which produced colorful orange products with a maximum absorbance of 461 nm. The colored products' absorbance was compared to a reagent blank(yellow). The initial research focused on optimizing the experimental variables in order to determine the ideal conditions for the fast and quantitative formation of the product with the greatest stability and sensitivity.

Optimizing Experimental Variables for BPF Detection

In order to optimize the spectrophotometric method sensitivity and precision, a number of experiments were conducted. It was possible to optimize factors such as types of alkaline medium, the amount of metoclopramide, order additions, reaction time, temperature and organic solvent effect.

Influences alkaline mediums of different types

This experiment was carried out in a 10 ml volumetric flask with 0.3ml diazotized metoclopramide, 0.1ml (100 mg.ml^{-1}) BPF, and 0.3ml (0.1 M) from each base [NaOH, KOH, NH_4OH, Na_2CO_3, K_2CO_3, and $NaHCO_3$]. At 461nm, the absorbance was measured. As shown in Fig.2a, sodium hydroxide has a higher absorbance because in an alkaline media, the phenol ion is converted to the more effective phenoxide ion by combining diazonium salts with phenols. This base will be fixed in future studies.

Influences various volume of alkaline medium

0.3 ml diazotized metoclopramide, 0.1ml (100mg.ml-1) BPF, and various volumes of 0.1M NaOH (0.1-1ml) were added to a 10 ml volumetric flask, and the absorbance was measured at 461nm. Fig 2b, illustrates the data. The absorbance increases as the volume of NaOH increases, but the signals suddenly diminish because the breakdown occurs as basicity increases and the creation of (Diazotate ions) cannot be coupled These findings agree with those of earlier research[32]. (The optimum volume of 0.1M NaOH was found to be 0.3ml, resulting in greater absorbance levels. This volume will be fixed in future experiments as well.

Influences various amount of diazotized metoclopramide

To avoid the effects of sodium nitrite excesses, a 1:1 mole ratio of MCP to sodium nitrite

(5mM) was chosen. Various concentrations of diazotized MCP (5mM) were used to determine the influence of the reagent on the intensity of the produced color at the indicated wavelengths. The optimum volume of diazotized MCP (5mM) was found to be 0.8mL Fig.2c, which was adequate to provide maximal and repeatable color intensity. Under the conditions of phenolic compound identification, MCP is quickly diazotized and produces water soluble azo dyes.

Influences various order additions

This influence on absorption colored product is investigated using four alternative sequence additions. Order(R+BPF+B) where diazonium salts with phenols occurs in alkaline medium where the phenol ion turns into the more effective phenoxide ion is recommended in the next tests based on the results below because it has the best effect on the colored system's stability. Fig.2d.

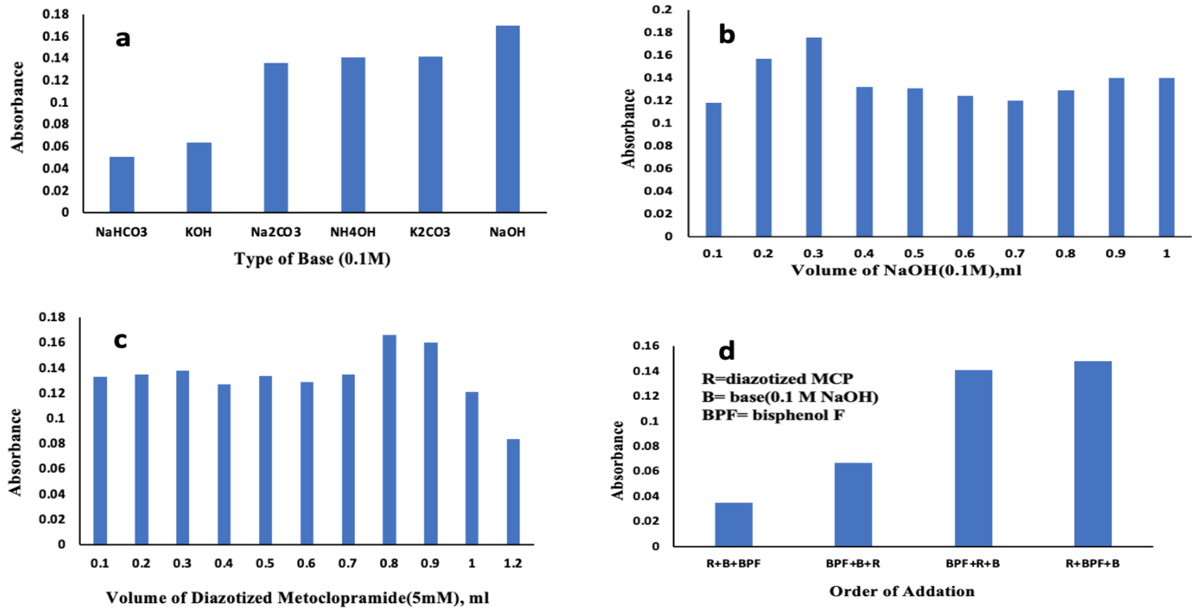


Figure 2. Optimum conditions for determination of BPF

Influences Various of Reaction Time on Stability of the Product

Diazotization and coupling reaction time are two of the most essential aspects affecting the colored product's stability. The required time is (0-60) minutes. The absorbance is then measured at 461 nm. The dye color develops completely in 15 minutes and remains stable for at least 25 minutes, according to the data in the Fig 3.

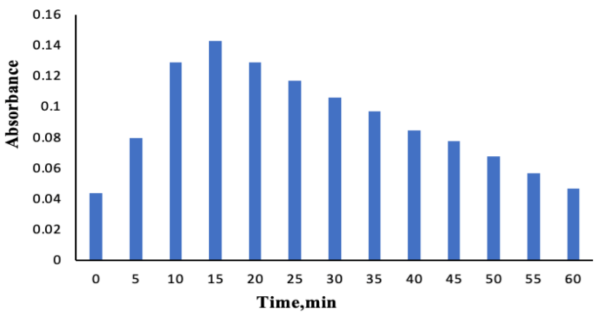


Figure 3. Influences various of reaction time on stability color product

Influences Various Temperature in the Formation of Color Product and Stabilization.

The effect of different temperatures on the color product has been investigated from (5-45)°C, and the rest of the addition has been optimized before being diluted with distilled water in a 10ml volumetric flask. The absorbance is measured, and the results are displayed in the Fig.4 The absorbance at temperature (15°C) has recorded the highest value, but when the temperature rises, the absorbance remains stable.

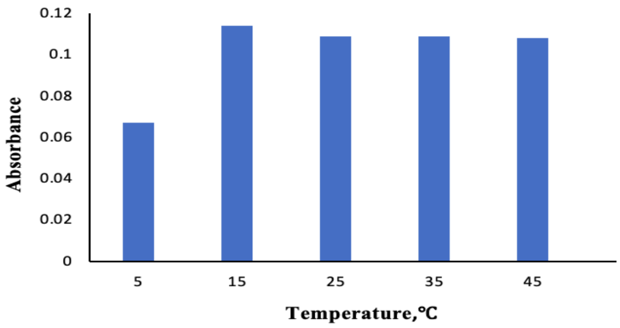


Figure 4. Influences various temperatures on absorbance of color product

Influences Various Organic Solvents

The spectral characteristics of the solution are influenced by the solvent. Depending on the polarity of the solvent, solvatochromism refers to the effect of the solvent on the position, intensity, or form of the spectral peak. The polarity of the solvent is affected by intermolecular charge transfer between the solute and the solvent. The charge transfers peak combines with the aromatic ring in very aqueous media, making it impossible to locate. Various organic compounds' solvatochromism is used to define π^*, which refers to polarity, α and β, which represent their ability to behave as hydrogen bond donor or acceptor. The physical intramolecular solute-solvent interaction forces tend to affect the energy difference between ground and excited states of the absorbing species containing the chromophore, resulting in a shift in spectra and absorption when using organic solvents compared to water[33]. Table 1 illustrates the effect of different organic solvents on the spectrum of the dye formed. The above data show that the nature of the solvent affects, to a large extent, the absorption spectrum of the dyes. Water is still being the choice because of its availability, nontoxic and low cost as well as the sensitive reaction.

Table 1. Influences various solvents on the spectral properties of color product

Type of solvent	λmax, **nm**	**ε × 10 ^{4} l.mol $^{-1}$ .cm $^{-1}$**
1-propanol	481	1.46
Ethanol	478	1.76
Acetonitrile	471	2.00
Water	462	2.34
Methanol	461	2.81
Acetone	499	3.99
Carbon tetrachloride	Two layers	---
Methylene chloride	two layers	---

Final Absorption Spectra

Absorption spectra were obtained for the colored products under ideal conditions (Table 2). The absorption spectra of the product solution versus reagent blank, as well as the reagent blank versus pure water are shown in Fig. 5. Absorption maxima were recorded at 461nm. As a result, the maximum absorption wavelength of 461 nm was selected for the following experiments.

Table 2. The optimum conditions for the determination of BPF

Parameters studied	Optimum
Volume of NaOH	0.3ml
Volume of diazotized MCP	0.8 ml
Time of reaction	15 min
Temp	15℃

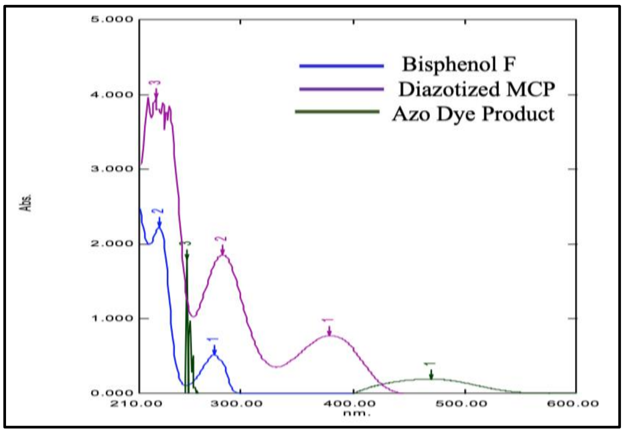


Figure 5. Absorption Spectra of Bisphenol F versus distilled water, Diazotized metoclopramide reagent versus distilled water, and Azo dye product against reagent blank.

Stoichiometry of the Formed Colored Product

The formed product's stoichiometry was studied using the mole ratio and continuous variation (Job's method) methods. An increased volume of 8× 10^{-4} M diazotized metoclopramide was added to a series of 10 ml volumetric flasks, followed by 1 mL (8× 10^{-4} M) bisphenol F, and 0.3 mL of 0.1M sodium hydroxide solution in the mole ratio technique. The volumes were made up with distilled water and allowed to stand for 15 minutes and measuring the absorbance versus reagent blank at maximum wavelength of 461 nm. The data were plotted and shown in Fig. 6a, indicating the presence of a 1:1 ratio (MCP: BPF). The job's method involved putting 0.1 to 0.9 mL of 8× 10^{-4} M diazotized Metoclopramide solution into a series of 10 mL volumetric flasks, then adding 0.9 to 0.1 mL of 8× 10^{-4} M bisphenol F, then 0.3 mL of 0. M NaOH solution, diluting to the mark with distilled water, allowing the solutions to stand for 15 minutes, and measuring the absorbance versus reagent blank at 461 nm. The findings were plotted and shown in Fig. 6 b, indicating the existence of a 1:1 ratio (MCP: BPF). The proposed reaction path for the production of azo dye can be anticipated as indicated in the scheme 1 below based on the mole ratio and continuous variation results.

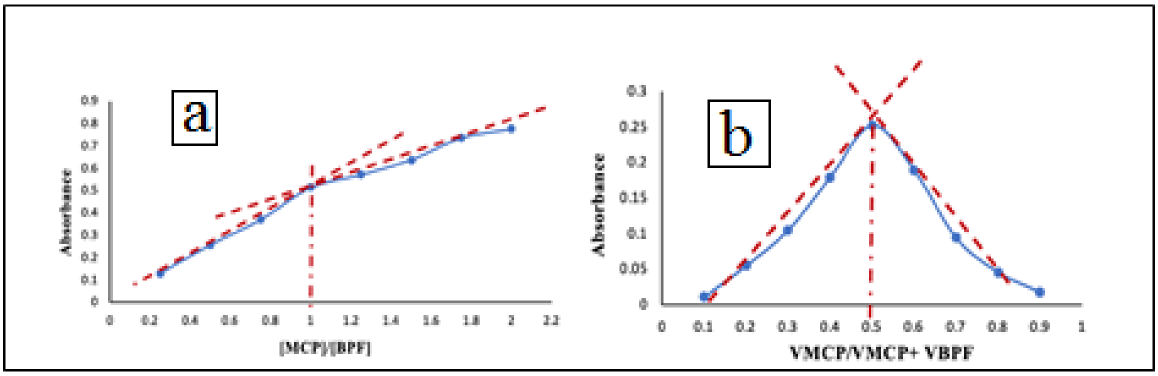
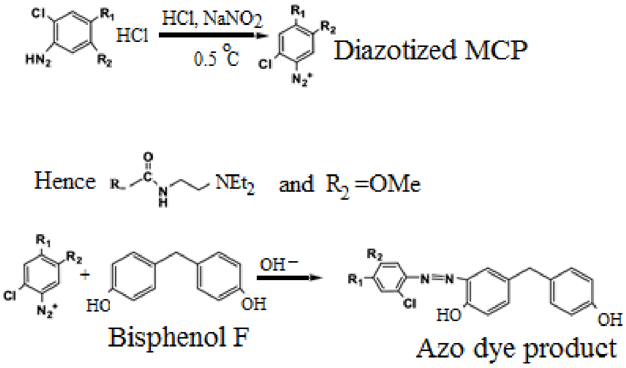


Figure 6. Stoichiometric determination of product (a)Mole ratio plot, (b) Continuous variation plot

The proposed reaction path for the production of azo dye can be anticipated as indicated in the scheme below based on the mole ratio and continuous variation results



Scheme 1. The possible reaction mechanism of BPF with diazotized MCP in basic medium

Stability constant of Colored Product

The interaction between BPF and the diazotized metoclopramide reagent in the rate 1:1then the stability constant of formed dye is estimated with ratio 1:1, based on both the way, mole ratio, and continuous variations methods previously described. Table 3 shows the average stability constant is high, indicating that the dye formed has a high stability, as seen in the table below.

Table 3. Stability constant of the product for BPF with diazotized metoclopramide

Volume of 8×10^{-4} M of BPF/ml	Final Conc. of BPF /ml $\times10^{5}$	$^{*}A_S$	$^{*}A_m$	α	K (Liter.mol^{-1}) $\times10^{4}$	Mean of K (Liter.mol^{-1})
0.3	2.4	0.144	0.310	0.5354	6.83	4.44×10^{4}
0.5	4	0.231	0.474	0.5126	6.64	
0.7	5.6	0.332	0.585	0.6130	1.84	

[*] = Standard deviation for n=3 measurements

The Analytical Method's Validation

The analytical aspects of the optimized method are summarized in Table 4, which includes the regression equation, linear range, molar absorptivity, correlation coefficient, and detection limits. As shown in Fig.7.b, a calibration curve for the analysis of BPF by reaction with diazotized metoclopramide reagent was constructed by plotting the absorbance (at a maximum of 461nm) as a function of the relevant quantities (1-10 mg mL^{-1}). The average intensities(n=3) of 10 BPF concentrations were used to calculate all linear dynamic ranges. Limits of detection (LOD) and limits of quantitation (LOQ) were calculated using the formulas LOD=3 SB /m and LOQ=10 SB /m, respectively, where SB represents the standard deviation of the average blank signal and m represents the slope of the calibration curve. At middle linear concentrations, the (RSD) value was excellent.

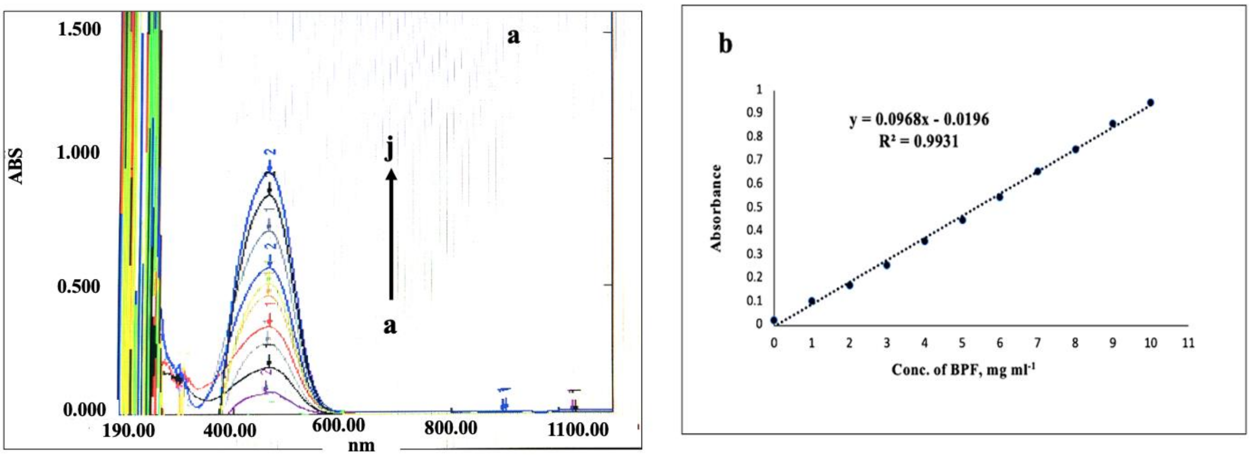


Figure 7. (a) MCP-BPF azo adduct absorbance spectra as BPF concentrations increase. BPF concentrations in samples a-j were 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 mg mL^{-1}, respectively. (b) Typical standard curve for the relationship between absorbance intensity and BPF concentration.

Table 4. Analytical characteristics of the proposed method

Parameter	**Proposed method**
Product colour	Orange
Wavelength (nm)	461
Linear Regression equation	y=0.0968x-0.0196
coefficient of determination (r^2)	0.9931
LDR (mg mL^{-1})	0.5-10
Reproducibility (RSD %)	0.128
Molar absorptivity (L.mol-1.cm^{-1})	1.94× 10^4
LOD (μg mL^{-1})	0.15
LOQ (μg mL^{-1})	0.52
Sandell's sensitivity (µg cm^{-2})	0.0103
Mole ratio	1:1

Accuracy and Precision

The accuracy and precision of the suggested method for determining bisphenol F were assessed under ideal conditions by measuring five independent samples at three different concentration levels of standards BPF. The measured E%, Rec%, and RSD% are acceptable for BPF determination, indicating that the proposed approach is accurate and precise for BPF analysis Table 5.

Table 5. Accuracy and Precision data for the proposed method

Conc. mg.ml^{-1}		E_{rel} %*	Rec % *	Average recovery %	Relative standard deviation RSD %
Present	*Found				
2	2.03	+1.5	101.5		5.37
4	3.92	-2	97.95	100.01	2.65
6	6.03	+0.5	100.5		2.16

[*] = Standard deviation of five determinations
Rec% = (Found / Taken) X 100
RSD%=(S/X^-) ×100
Erel% = [(Found- Taken) / Taken] X 100

The Effect of Excipients

The interfering effect of several excipient substances were investigated under ideal experimental conditions to evaluate the selectivity of the proposed approach for the determination of BPF. Table 6 summarizes the results collected2,6-dimethylphenol and Cumylphenol in a 100-flod concentration interfere. When a 100-flod concentration of para nitrophenol and a 50-fold concentration of 4,4-dihydroxybenzophenone and ions coexisted in the solution, there was no interference, and the concentration of added excipients caused less than a 5% relative error for determining BPF in the solution under optimum conditions. These observations indicate that the proposed method might be applied to determine BPF in an aqueous sample in a selective and efficient method.

Table 6. The Effect of excipients on the recovery of BPF (2µg mL^{-1})

Excipient	Concentration mg/l	Absorbance at λmax =461 nm for BPF	Recovery%
Para nitrophenol	20	0.177	101.54
2,6-dimethylphenol	5	0.176	100.03
Cumylphenol	2	0.174	100
4,4-dihydroxybenzophenone	10	0.156	90.87
Zn^{+2}	10	0.175	100.68
Co^{+2}	10	0.195	98.45
Ni^{+2}	10	0.167	96.72
Cr^{+3}	10	0.170	98.45
K^{+1}	10	0.169	96.90
Mn^{+2}	10	0.173	99.48

Application of the method in real samples

Concentration of the BPF in plastic of water samples

BPF migration from plastic packaging can be determined using the proposed method. The samples were prepared and treated in accordance with the experimental section. Because BPF was not detected in the plastic leaching aqueous samples, the recoveries were investigated using three different concentrations of BPF standard solution. S Spectrophotometric analysis was used to determine the amount of BPF in the samples, with the results presented in Table 7.

Table 7. BPF content in plastic of water bottle samples

Sample of bottled water	Standard Added (mg/ml)	Found*(mg/ml)	Recovery* (%)	RSD (%)
Pearl	2	1.82	91.04	0.78
	4	4.42	109.57	1.04
	6	6.51	108.51	0.198
Aquafina	2	1.45	72.62	0.51
	4	4.30	107.50	0.39
	6	5.2	88.65	0.94

[*] = Standard deviation for n=3 measurements.

Concentration of the BPF in thermal papers at different temperatures and different extraction time

The thermal paper samples were exposed to temperatures ranging from 40 to 60℃ (highest temperatures expected in Iraq). The extraction process detailed in the experimental section was used to extract BPF from the pre-heated paper samples concentration of BPF was leached out at two different temperatures 40, 60°C and two different extraction times 1, 5 hours, as shown in Table 8 below. The data indicates that as time and temperature rising, the concentration of BPF leached out of all thermal papers increased, showing that higher temperature enhanced desorption of BPF from the paper, making it more available for extraction. It was also chosen to use a 1:1 methanol: water solution as the extract solvent to increase in solubility. Because of their polarity, availability, and simplicity, they were chosen especially. These compounds can dissolve BPF since they are polar solvents [30]. The results are consistent with those of a recent study that looked at the effects of extraction time and temperature on phthalate metabolites and BPA levels in urine [34-37].

Table 8. The UV-Vis concentration of the BPF in thermal papers at different temperatures (40, 60°C) and different extraction times (1,5 h)

Store name	Concentration of BPF at 40℃ (mg/10 ml $\pm$ SD)*	Concentration of BPF at 60℃ (mg/10 ml $\pm$ SD)*
Mall	1.7$\pm$0.0119	3$\pm$0.0178
Market	2.08$\pm$0.0059	2.42$\pm$0.010
	Concentration of BPF at 1 hour (mg/10 ml $\pm$ SD)*	**Concentration of BPF at 5 hours (mg/10 ml $\pm$ SD)***
Mall	2.5$\pm$0.0059	3$\pm$0.0178
Market	1.80$\pm$0.119	2.08.$\pm$0.010

[*] = Standard deviation for n=3 measurements.

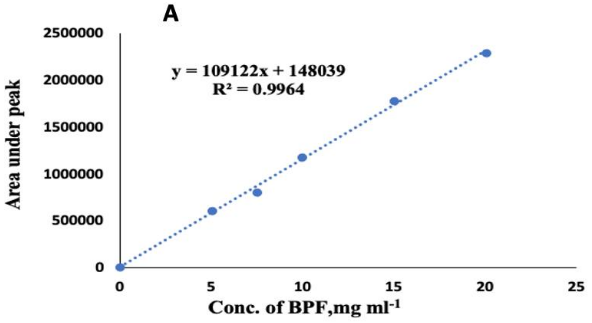
Table 9 displays the results of thermal paper samples where BPF concentration was evaluated. BPF was detected in all of the analyzed thermal paper receipts. The highest BPF concentrations were found in mall samples No. 2, 3, and the restaurant sample. In consideration of these results and excessive customer circulation, mall cashiers may be the people most at risk of being exposed to BPF. In comparison to other samples, however, low values were seen in market #3 and bank account receipt.

Table 9. BPF concentration in thermal paper receipts according to the type of store

Store name	BPF (mg/g paper±SD)*
Mall #1	30.10 ± .17
Mall #2	58.70 ±0.631
Mall #3	55.91±0.157
Market #1	24.25±0.103
Market #2	27.92±0.119
Market #3	3.78±0.103
Restaurant	56.05±0.103
Bank	3.12 ±0.059

High Performance Liquid Chromatography (HPLC-UV) Method

This section of the study aimed to confirm that extracts from thermal papers contained BPF, and further analysis using an HPLC-UV detector was required. The retention time of standard BPF was determined to be 5.649 min. There was a linear relationship between the area under the peak and the concentration of BPF range (5-20 mg/ml) is illustrated in Fig. 8A. Standard BPF was found to elute with a retention time of 5.649 min as shown in Fig. 8B. In Figs. 8C, D, E, and F, the peak eluting time for most thermal papers extract was at 5.6 minutes (similar peak eluting with retention time for standard BPF demonstrating that BPF was present in the thermal papers). In comparison to previous published methods, the method demonstrated improved reliability, low detection limit, and sensitivity as shown in Table 11.



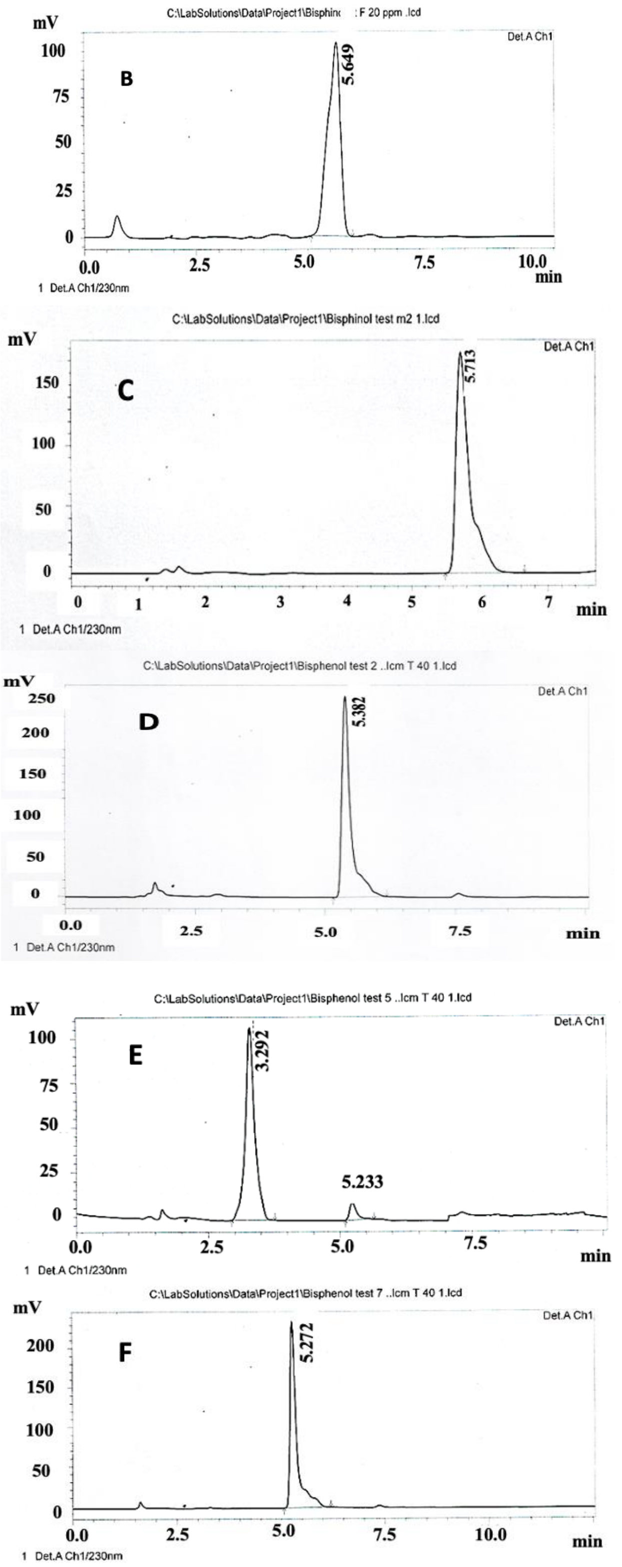


Figure 8. Typical RP-HPLC chromatograms of (A) Standard curve of BPF analyzed by using RP-HPLC coupled with UV detection, (B) Standard BPF 20 ppm, [market(C), mall(D), bank(E), and restaurant(F)] extracts of a representative cash receipt analyzed using RP-HPLC coupled with UV detection.

Table 10. Retention time and peak area of BPF in thermal paper extract

Store name	Retention time(min)	Peak area
Mall #1	5.639	3367259
Mall #2	5.382	2934741
Mall #3	5.345	2653358
Market #1	5.737	1555838
Market #2	5.713	2553419
Market #3	5.223	52731
Restaurant	5.272	2610474
Bank	5.233	96778

Table 11. The proposed method is compared to those that are currently in use

Analyte	Sample	Analytical Technique	LOD mg/ml	Remarks	Ref
BPA, BPAF, BPB, BPE, BPF BPS	**Paper products**	GC-MS/MS	0.23-2.70	Needs a derivatization step prior to analysis.	20
BPA, BPAF, BPB, BPE, BPF,BPS	**Paper products**	LC-MS/MS	0.29- 0.40	Expansive instrument	25
BPS, BPA, BPF, BPAF, BPM and BPTMC	Bottles and sippy cups	UPLC-MS/MS	-----	Expansive instrument Higher maintenance Matrix effect	26
BPF	Thermal paper and water bottle	Uv-vis	0.15	Low cost, short time analysis	This work

Conclusions:

Bisphenol F is determined using a simple, and sensitive spectrophotometric approach based on the diazotization-coupling reaction metoclopramide produces an orange azo-compound with a maximum absorbance at 461 nm in alkaline solution. The HPLC method was used to determine the presence of bisphenol F in samples. In addition, the method's validation revealed adequate recoveries, good linearity and precision, as well as quantifiable LODs and LOQs. The approach worked well for analyzing BPF in water bottle and thermal receipt paper samples gathered from Iraqi markets. All of the samples examined contained the desired BPF.

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Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors' contributions statement:

M. A. presented the idea, analysis, discussion of the results and writing of the manuscript. N. M. H. contributed to the design and implementation of the esearch, laboratory work, M. L. T., N. K. S., H. M. A. verified the analytical methods and discussed the results and contributed to the final manuscript

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طريقة قياس مطيافية الاشعة الفوق البنفسجية والمرئية مع تقنية كروماتوغرافيا السائل عالي الأداء HPLC لتقدير البسفينول F في بلاستك قناني الماء والأوراق الحرارية

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الخلاصة:

بناء على تفاعل الازوتة والاقتران تم اقتراح طريقة جديدة وبسيطة لتحديد كمية البسفسنول Fفي هذا البحث. تفاعل محلول الميتاكلوروبرمايد مع البسفسنول F لتكوين مركب لونه برتقالي مع اقصى امتصاص عند الطول الموجي 461 نانوميتر. تم دراسة الظروف المثلى للتفاعل مثل نوع الوسط القاعدي، تركيز الوسط القاعدي، كميه الميتاكلوروبومايد، تسلسل الإضافة، زمن التفاعل، درجه الحرارة، تأثير المذيبات العضوية لتحقيق الأداء الأمثل للطريقة المقترحة. زاد الامتصاص بصوره خطيه مع في نطاق 0.5-10 ميكروغرام مل -1 في ظل الظروف المثالية مع معامل ارتباط 0.9931 وحد كشف يبلغ 0.15 ميكروغرام مل $^{-1}$. تم دراسة تأثير درجه الحرارة ووقت الاستخلاص على تركيز البسفينولF من الأوراق الحرارية اثبتت النتائج عند زيادة درجة الحرارة ووقت الاستخلاص يزداد تركيز البسفينولF. لأثبات ان المستخلص من الأوراق الحرارية يحتوي على البسفينول F تم استخدام تقنية السائل عالي الأداء بوجود عمود الفصل C18 واستخدام كاشف الأشعة الفوق البنفسجية عند الطول الموجي 230نانوميتر مع طور متحرك يتكون من الماء والاسيتونيترايل ,(55/45v:v) وكان وقت الاستبقاء للمحلول القياسي لبسفينول F 5.649 دقيقة ووقت الاستبقاء لمعظم مستخلصات الأوراق الحرارية عند 5.6 دقيقة مما يدل على وجودBPF في الأوراق الحرارية . في هذا البحث تم تطبيق الطريقة المقترحة على نوعين من عينات زجاجات الماء البلاستيك Pearl وAquafinaو الأوراق الحرارية (السوق، المول، المطعم، والبنك) والتي تم جمعها من أماكن متنوعة.

الكلمات المفتاحية: بسفينول F، تفاعل الازوته والاقتران، تقنية الطيف الضوئي، ميتاكلوروبومايد، كرموتوغرافيا السائل عالي الأداء.