



Determination of 4,4-(propane-2,2-diyl) diphenol (Bisphenol A) Concentration in Canned Tomatoes

G.P. Fabusola*, V.O.E Akpambang

Department of Chemistry, School of Science, Federal University of Technology Akure, Ondo State, Nigeria

*Author for corresponding: gbengafabusola@gmail.com

Abstract

Bisphenol A (BPA) is a chemical used in the production of polycarbonate plastics and for lining metal cans, used in canned foods. BPA is a well-known endocrine disrupting chemical, it therefore, is very hazardous to human health. BPA levels were determined in three brands of canned tomatoes (Gino, Super Mama, Deric) as sold in Nigerian markets. The samples were analyzed using solvent extraction, separation and quantitation by gas chromatography- mass spectrometric method. The recovery value for BPA in the method was 89% with the relative standard deviations of 3%. The BPA concentration in the samples ranged from 0.124 to 0.141 (mg/kg), which are higher than the European Food Safety Authority Specific Migration Limit (SML) of 0.05 mg/kg in food sample. The samples analyzed in this work may be, therefore, of a potential health concern to the consumers.

Keywords: Bisphenol A, Canned food, Acetylation, Solvent extraction

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1. Introduction

In the food industry, packaging plays a vital role to the food product. The main motive of food packaging is: [1] (a) to provide containment of the food product; (b) to ensure preservation of the food product from the outer environment; and (c) to give

the consumer detailed nutritional and other information of the food product enclosed in it. metal, glass, paper, wood and plastic are the various materials used for the packaging of food. For the purpose of this research, metal used for canning food will be the focus.

Bisphenol A (BPA), is an organic compound that has two phenol functional groups. It is a monomer for several essential polymers and polymer additives. It is an important monomer that had been used for the synthesis of polycarbonate, epoxy resin used for metal can linings, and it is also used as stabilizer or antioxidant for many types of plastics such as polyvinyl chloride (PVC) [2]. BPA is also known as 2,2-bis(4'-hydroxyphenyl) propane, 4,4'-isopropylidenediphenol, and 2,2'-bis(4-hydroxyphenyl) propane [3]. It also finds application in unsaturated polyester-styrene resins, flame retardants, food and drink packaging, and as antioxidants in plastics [4]. It is worth knowing that even though BPA is not a strong estrogenic compound, it has managed to do harm in the environment and is a potential health risk for humans even at low concentrations [5]. In fact, when a suggested ranking system was done for pharmaceuticals, personal care products and endocrine- disrupting chemicals or EOCs, out of 100 chemicals, the overall priority for BPA was second place [6].

The illustration of the transfer of small molecules in the packaging system is migration, which relates to the release of compounds from the packaging materials [7]. The released components can be residual monomers, oligomers, processing aids and additives. Migration of BPA happens when these packaging materials are in direct contact with the food system [8-13]. Additives, such as plasticizers, stabilizers, UV absorbers and anti-oxidants, make the packaging materials more process able and lasting. When those components go into the food product, they may affect the quality and safety of the food product.

BPA is well known as one of the endocrine disrupting compounds (EDCs), which are chemicals or group of chemicals that interact with steroid hormone receptors of human and animals and disrupt normal endocrine functions [14] Since BPA is widely used in food packaging, in recent years, there is an increasing concern regarding the level of BPA in the food system which could impact the human health. Thus, there is a need to determine the level of BPA that migrate into the food system in order to ensure food safety.

The method used for the extraction of BPA from sample is a very efficient recording a method recovery of 89%. The method is a new and recent technique employed by S. Arar and M. Alawi, 'A New Solvent Extraction Method with Gas Chromatography–Mass

Spectrometry for Bisphenol A Determination in Canned Foods' [15]. The method was applicable in terms of eliminating the use of solvents like acetonitrile for the extraction step, where relatively long evaporation times may have been needed to evaporate acetonitrile. Also, removing lipids and precipitating most of the proteins at acidic conditions (pH = 4) prior to diethyl ether extraction can replace the often used heptane or hexane or solid sorbents.

2. Experimental section

2.1. Materials

All equipment and apparatus used are in good condition which include steel blender, weighing balance, micro pipette, measuring cylinder, suction pump, Buchner flask, glass funnel, pH meter, separatory funnel, fume compound, beaker, standard flask, burette, hot plate, glass fiber, 10 mL reaction vial.

2.2. Reagents

0.1M NaOH, 1.2M HCl, Diethylether, Acetone, Ethanol, Sodium Sulphate, Acetic Anhydride, Distilled water, Hexane, Dichloromethane, Sodium Acetate, BPA standard. All reagent used were provided by the Department of Chemistry, Federal University of Technology Akure, while diethyl ether was gotten from Pascal scientific Limited, Akure, Ondo state.

2.3. Sampling

For the purpose of this study, three (3) different brand of tomatoes in triplicate were employed for the analysis. All products were gotten from NOA supermarket, Akure. Purchased tomatoes cans were stored at laboratory shelves, all the contents of the can were homogenized with a blender.

2.4. Procedure

This technique used eliminates the use of solvents like acetonitrile for the extraction step, where relatively long evaporation times may have been needed to evaporate acetonitrile. Also, removing lipids and precipitating most of the proteins at acidic conditions (pH = 4) prior to diethyl ether extraction can replace the often used heptane or hexane or solid sorbents.

All the glassware were washed, dried and rinsed with acetone before it was heated to 220° to remove any possible contaminate with BPA since the melting point of BPA is 158°C and the boiling point is 220°C.

The sample was test for its pH, 4g of the wet weight of homogenized sample was mixed with 20 mL of 0.1 M NaOH, stirred for 2 minutes and left to stand for 5 minute. For recovery study, the wet weight was spiked with 400 µg of 50 mg/ mL standard BPA.

The mixture was filtered using suction filtration, the solid residue is then wash with 15 mL of 0.1 M NaOH.

The filtrate pH was adjusted to 4 using 1.2 M HCl to precipitate proteins. This ascertain that extract is void of all lipophilic proteins and lipids thereby eliminating the need of solvents like acetonitrile and heptane for the extraction and clean-up steps.

It was transferred into a 250 mL separatory funnel and 20 mL of diethylether was added which lead to the formation of two layers (Organic and Inorganic layer).

The organic layer is then collected and added back to the funnel to re-extract with additional 20 mL of diethylether.

The upper ether layer is then put in a beaker containing sodium sulphate to remove the water that might be present. The dry ether is then transferred into a second beaker and left on a hot plate at 30°C to evaporate to dryness.

The wall of the beaker was then rinsed with 5 mL diethylether and transferred into a 10 mL reaction vial and it was evaporated to dryness.

3 mL of Acetic anhydride and 0.5 g of sodium acetate (excess amounts to make acetylating conditions basic) were added to the reaction vial, sealed tightly and heated at 110°C for 30minutes.

The vial was allowed to cool down then distilled water was added to destroy excess acetic anhydride and remove excess catalyst.

The acetylated BPA was then extracted with two portions of 2 mL (50%:50%) hexane-dichloromethane was added and passed through a burette closely packed with glass fiber and sodium sulfate.

The hexane-dichloromethane was then collected back into the reaction vial for further instrumental analysis.

The blank analysis was done by repeating the above procedure without the sample and the standard.

3. Results and Discussion

The extracts were analyzed to qualify and quantitate the amount of BPA present in them. The GC-MS analysis results are provided for each extract.

Table 1. BPA concentrations in different brand of canned Tomatoes

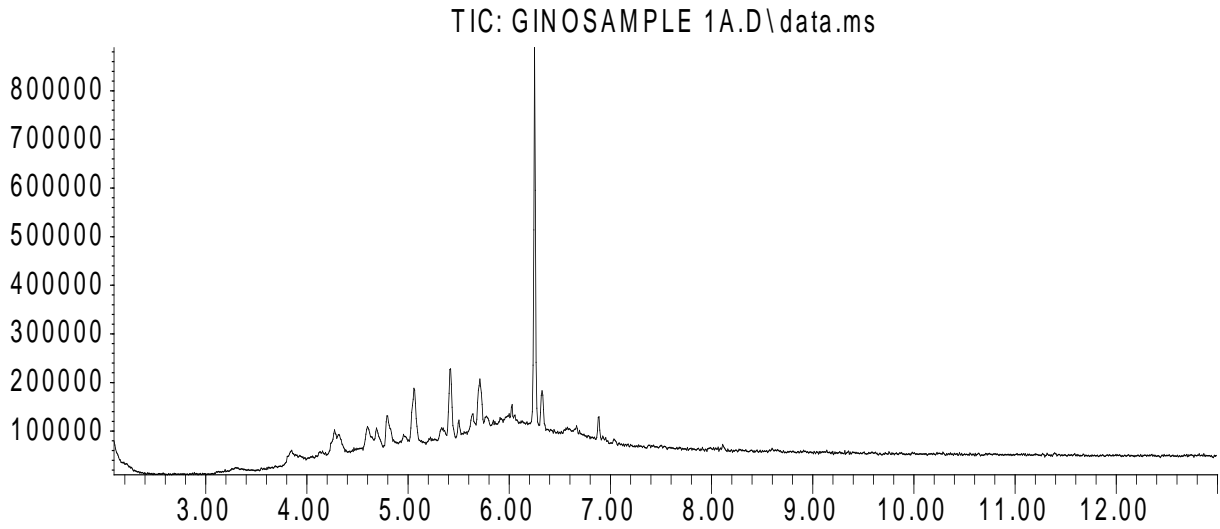
| Brand name (Tomatoes) | Average BPA±(SD) (mg/kg) | pH | 2- or 3- piece/ lacquered part |
|-----------------------|--------------------------|-----|---|
| Gino | 0.124±0.004 | 4.3 | 3-piece/ all pieces coated with grey lining |
| Super Mama | 0.136±0.008 | 4.1 | 3-piece/ all pieces coated with grey lining |
| Derica | 0.141±0.040 | 4.3 | 3-piece/ all pieces coated with grey lining |

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Table 2 percent recoveries of BPA in food matrix

| Product name (Tomatoes) | BPA spiking concentration ($\mu\text{g/mL}$) | Recovered BPA spiked Concentration ($\mu\text{g/kg}$) | Percentage average recovery \pm RSD* |
|----------------------------|---|--|---|
| DERICA | 0.50 | 0.276 | 89 \pm 3 |

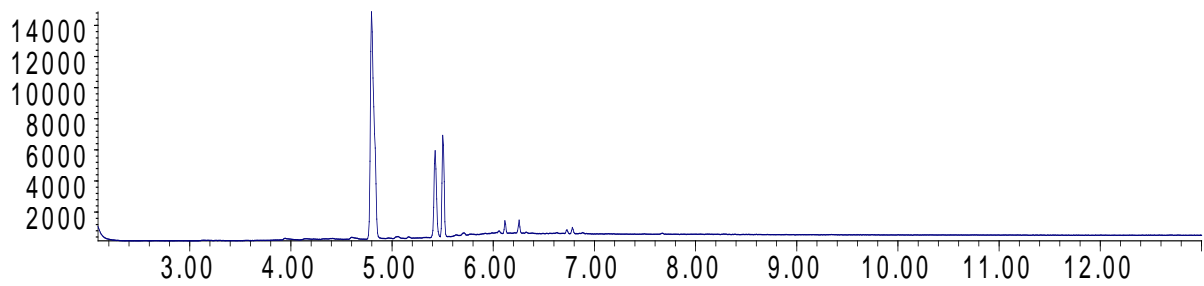
Abundance



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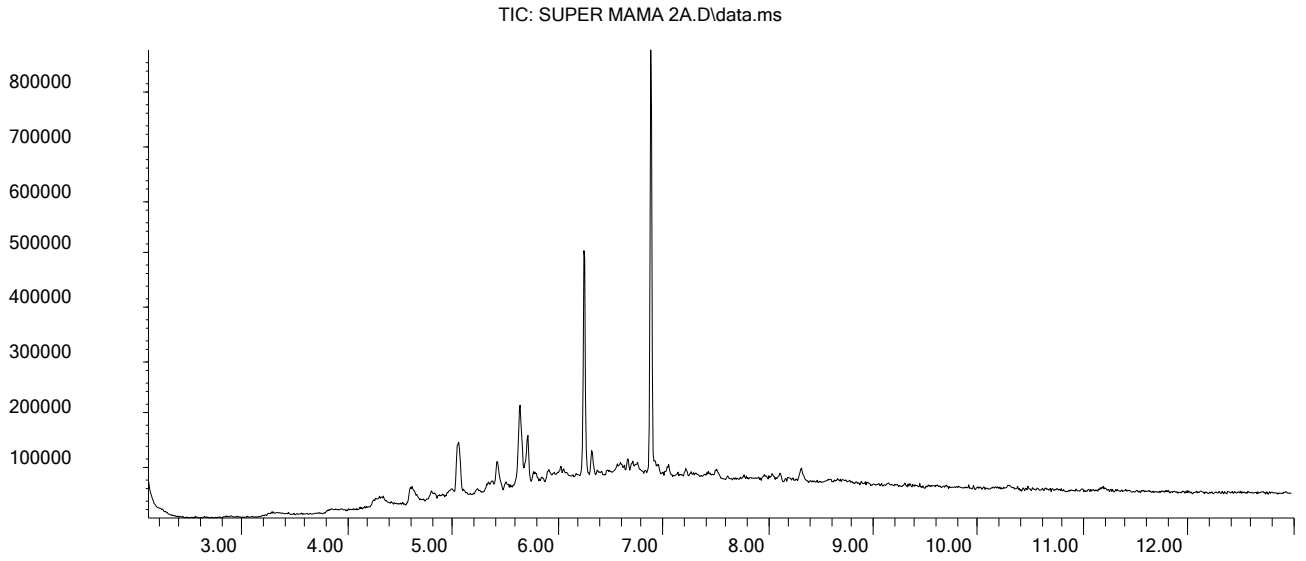


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Figure1. Chromatogram of Gino Sample

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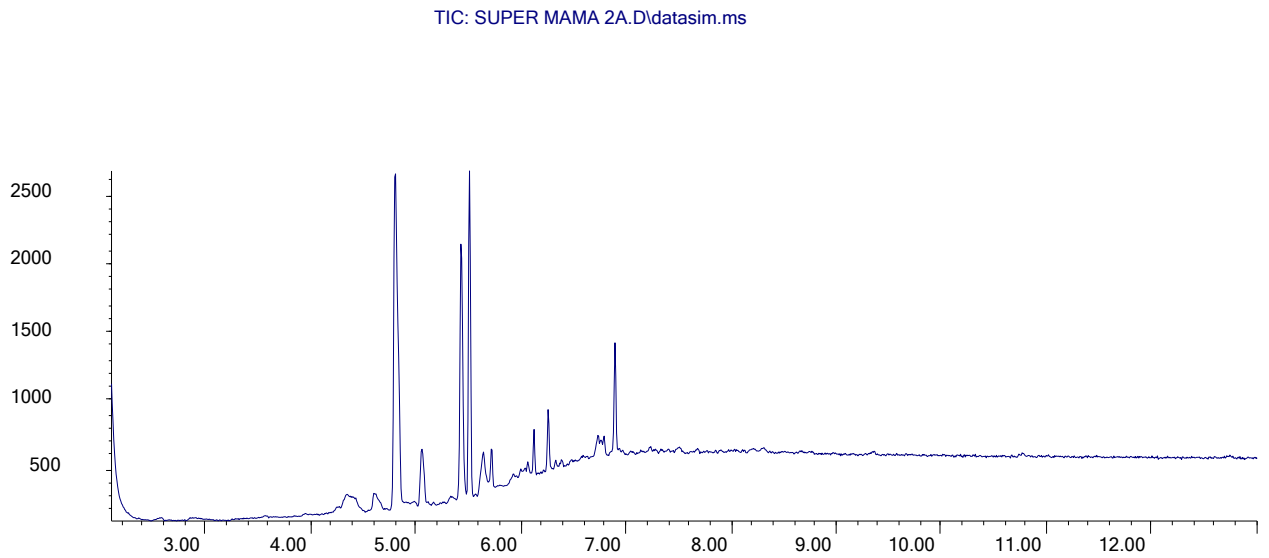
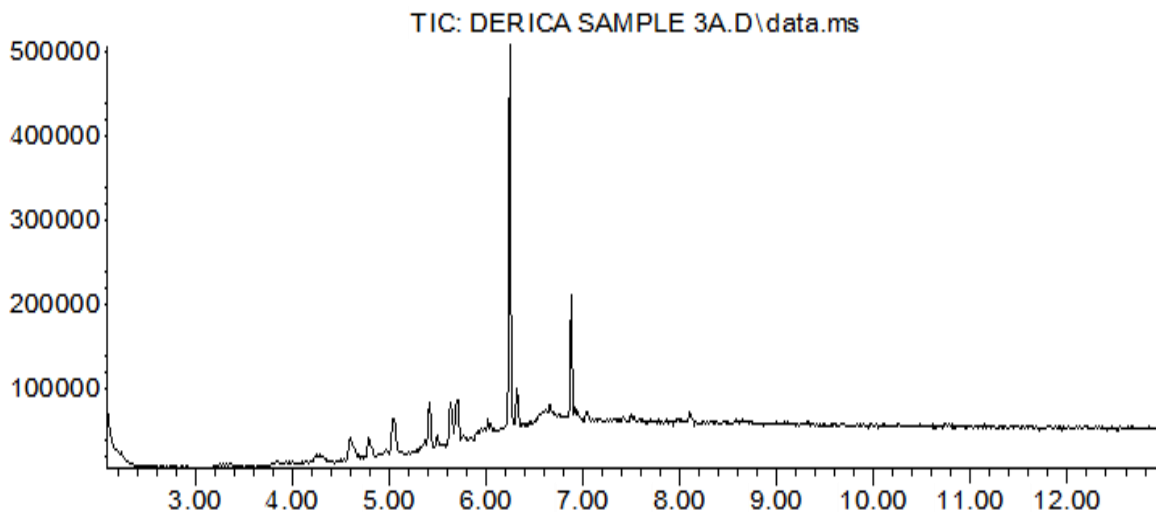


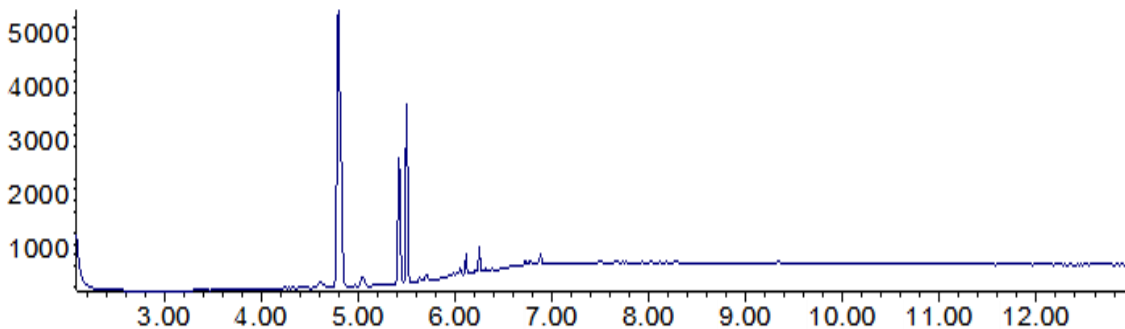
Figure 2. Chromatogram of Super Mama Sample

Abundance



Time→
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Figure3. Chromatogram of Derica Sample

The obtained BPA quantitative GC–EI/MS results for the Tested Canned Tomatoes are summarized in tables 1 and 2 indicated with the food brand with final units in mg/kg. Samples were injected in triplicate in addition to method blanks. The levels of BPA in the samples were ranged from 0.124 to 0.141 ± (0.04) mg/kg. Spiked samples in

table 2 showed recovery value of 89% in De Rica with relative Standard deviations (RSDS) of 3% affirming the validity of the method according to the guidelines for performance criteria and validation procedures of analytical methods used in controls of food contact materials [16]. The obtained recovery values in this study (89 ± 3) were

lower than those reported by Kawamura and co-workers in 2014 (recovery = 97.1 ± 4.4) [17] employing Methanol as extracting solvent and hexane for clean-up step and Fat removal, but higher than reported recoveries by Cunha and co-workers in 2013 (recovery = 77% at 5 $\mu\text{g}/\text{kg}$ spiking level) [18] employing heptane for fat removal, acetonitrile, and solid sorbent for BPA extraction. Samples ranged from $0.124 \pm (0.004)$ mg/kg (GINO) to $0.136 \pm (0.008)$ mg/kg (SUPER MAMA) where all of these canned foods had in common; the 3-piece can with white colour lacquered heavily from inside (most of them produced in China, Nigeria). De Rica are those with the highest BPA concentrations Reaching maximum value of 0.43mg/kg and minimum Value of 0.38mg/kg with an average value of 0.141mg/kg. These relatively high results were not surprising since these food cans were totally lacquered from inside with the white lining (epoxy resins that leaches BPA) with adequate solution salinity. In this research, one of the aims was to investigate the concentrations of BPA in different Tomatoes brand without going further to reveal correlations between type and ingredients. These research does not focus on the quantity of tomatoes consumed on a daily basis, therefore, no knowledge is available about the true quantities consumed daily. The measured obtained maximum BPA Values using the developed method are higher than those values Reported in other countries like Canada [19], New Zealand [20], Belgium [21], Portugal [18], Turkey [22], US [23], UK [24], and France [25], and reported maximum BPA value in domestic canned food in japan [17]. Also, the obtained results are much above the specific migration limit of 0.05 mg of BPA per kg of food set by EU Commission (Commission Regulation EU 10/2011) [26]. The developed method showed excellent validation for selectivity where the internal standard (BPA-d) and target analyte (BPA) peaks were well resolved at retention times 5.77 ± 0.02 min and 5.707 ± 0.03 min, respectively, in calibration standards and canned food samples with no interfering peaks. The aforementioned compounds were also confirmed with their finger print mass fragments (224/242/284) and (213/228/312), respectively. Since varying trace or minor amounts of BPA were sometimes detected as expected in method blanks

since BPA is ubiquitous, one blank sample was carried out and analysed for a Batch of real samples, where minor amounts of BPA in method blank in the Batch were detected. The cause of migration of BPA to the food was not assessed in this research, the condition of storage of sample at the super market, which is unknown, might account for variation in the concentration results especially the temperature at which it is stored.

4. Conclusion

The results obtained in this work suggest that the identified phytochemical compounds are bioactive constituents therefore these plants are proving to be an increasingly valuable reservoir of bioactive compounds of substantial medicinal merit.

References

- [1] Selke, S.; Culter, J. and Hernandez, R. 2004. Plastic packaging: Properties, processing, applications, and regulations. *Hanser Pub.*, Munich, germany.
- [2] Ash, M., and Ash, I.: Handbook of Plastic and Rubber Additives. gower, Hampshire, UK, 1340 pp. 1995
- [3] Huang, Y.Q., Wong, C.K.C., Zheng, J.S., Bouwman, H., Barra, R., Wahlstrom, B., Neretin, L., and Wong, M.H.: Bisphenol A (BPA) in China: A review of sources, environmental levels, and potential human health impacts. *Environment International* 42:91-99, 2012.
- [4] Barnabe, S., Brar, S.K., Tyagi, R.D., Beauchesne, I., and Surampalli, R.Y.: Pre-treatment and bioconversion of wastewater sludge to value-added Products-Fate of endocrine disrupting compounds. *Science of The Total Environment* 407(5):1471-1488, 2009.
- [5] Crain D. A., Eriksen M., Iguchi T., Jobling S., Laufer H., LeBlanc g.A., and guillette Jr. L.J.: An ecological assessment of bisphenol-A: Evidence from comparative biology. *Reproductive Toxicology* 24(2):225-239, 2007.
- [6] Kumar, A., and Xagorarakis, I.: Pharmaceuticals, personal care products and endocrine- disrupting chemicals in U.S. surface and finished drinking waters: A proposed ranking system. *Science of the Total Environment* 408(23):5972-5989, 2010.
- [7] Hernandez, R.J. and Gavara, R. 1999. Plastic Packaging: Methods for Studying Mass Transfer

- Interactions. *Pira International, Leatherhead, UK*, pp 53.
- [8] Yoshida, T.; Horie, M.; Hoshino, Y. and Nakazawa, H. 2001. Determination of Bisphenol A in canned vegetables and fruit by high performance liquid chromatography. *Food Addi. and Cont.* 18: 69-75.
- [9] Paseiro-Losada, P.; Lopez-Cervantes, J.; Sanchez-Machado, D.I. and Simal-Lozano, J. 2003. Effects of compression, stacking, vacuum packing and temperature on the migration of Bisphenol A from polyvinyl chloride packaging sheeting into food simulants. *Chromatographia* 58: 327-330.
- [10] Szymanski, A.; Rykowska, I. and Wasiak, W. 2006. New ketoimine sorbents in solid phase extraction for HPLC analysis of Bisphenol A and other "endocrine disrupting" residues in drinking water. *Polish J. of Environ. Stud.* 15: 479-483.
- [11] Cao, X.L.; Dufresne, G.; Belisle, S.; Clement, G.; Falicki, M.; Beraldin, F. and Rulibikiye, A. 2008. Levels of Bisphenol A in canned liquid infant formula products in Canada and dietary intake estimates. *J. Agric. Food Chem.* 56: 7919-7924.
- [12] Maragou, N.C.; Makri, A.; Lampi, E.N.; Thomaidis, N.S. and Koupparis, M.A. 2008. Migration of Bisphenol A from polycarbonate baby bottles under real use conditions. *Food Addi. and Cont.* 25: 373-383.
- [13] Cao, X.L.; Corriveau, J.; Popovic, S.; Clement, G.; Beraldin, F. and Dufresne, G. 2009. Bisphenol A in baby food products in glass jars with metal lids from Canadian markets. *J. Agric. Food Chem.* 57: 5345-5351.
- [14] Krishnan, A.; Stathis, P.; Permuth, S.; Tokes, L. and Feldman, D. 1993. Bisphenol-A: An Estrogenic substance is released from polycarbonate flasks during autoclaving. *Endocrinology* 132: 2279-2286.
- [15] S. Arar, M. A. (2019). A New Solvent Extraction Method with Gas Chromatography Mass. *Acta Chromatographica*, 71-78. doi:DOI: 10.1556/1326.2017.00388