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Effect Of The Microwave Heating On The Stability Of Phthalate Plasticizers, Which Are Used In Plastic Packing Industry, In Aqueous Food Simulants.

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Abstract: Stability of di (ethyl hexyl) phthalate, di-n-octyl phthalate, diisobutyl phthalate and Dibutyl phthalate in the three aqueous food simulants: distilled water, 3%w/v acetic acid and 10%v/v ethanol., during microwave heating has been studied. the percent of recovery of each plasticizers was determined using direct HPLC method. Stability was dependent on heating (exposuring) time, microwave power setting, and the nature of the food simulant. In general, studied plasticizers appeared to be more stable in 10%v/v ethanol, then in distilled water., The 3%w/v acetic acid allowed good stability for the lower molecular weight compounds even at full power, but the higher molecular weight compounds decomposed very fast.
Key words: phthalate plasticizers, microwave, stability, migration, food simulant, HPLC.

1- Introduction:

Microwaving is becoming an increasingly used process for the heating of foodstuffs in both the industrial and home sectors. The microwave oven is used for a variety of purposes such as cooking, backing, frying, defrosting, reheating, pasteurization, sterilization..etc [1]. Microwave processing offers several advantages over conventional heating methods. These advantages include speed of operation, energy savings and precise process control [2, 3]. A variety of foods have been developed and modified over the past few years for the microwave market. Numerous of these food products are cooked along with the packaging material (container, wrapping film) in the microwave oven [4,5]. Such microwavable packaging material include plastics, paperboard and composites. However, during microwave cooking, the constituents of numerous of the above-mentioned packaging materials, i.e. plasticizers, antioxidants, stabilizers, monomers.. etc., may result in the deterioration of food quality and even promote toxicity [6]. Microwave migration studies represent a unique challenge because of their shorter cooking times, and microwave distributions can influence cooking times. Quite high package temperatures may be achieved when the package absorbs microwave energy and converts it to heat. Microwave cooking not only produces temperature increases in packaging and food, but there is also a microwave effect which could increase the magnitude of the migration process [7].

Four types of food simulants are stabilized to perform the migration test by Directives [8-11], three of them are aqueous simulants., A (distilled water), B (3% w/v acetic acid), and C (10%v/v

ethanol)., and the other is a fatty food simulant., simulant D (rectified olive oil., that could be replaced by sunflower oil or corn oil). An incomplete list of additives., that can be used in the manufacture of plastic materials and articles that are intended to come into contact with foodstuffs., is established by Directives [12, 13], which also lays out specific migration levels (SML) according to their individual toxicity that must not be exceeded in the migration tests.

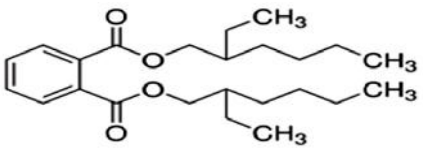
To carry out the specific migration test, plastic material is put in contact with food simulant, under determined temperature and time conditions. However, it must be considered that this value will not be representative of the real migration level from the packaging if the analyte is not stable during the test. While considerable researches have been focused on the stability of plastic additives during processing, there is a lack of studies on the stability of additives in food simulants [14-20]., therefore, the stability study in food simulants is necessary to know the types of additive that may undergo degradation in food simulants and their degradation products, as well as on the type of media or heat exposure to which they are more sensitive.

In the present work the stability of four plasticizers (di-n octyl phthalate (DnOP), di (ethylhexel) phthalate (DEHP), di butyl phthalate (DBP) and diisobutyl phthalate (DIBP) has been studied in the four food simulants after they have been exposed to microwave at full power (≈ 1450 w) and medium power (≈ 725 w)., because the phthalates plasticizers are the most common additives used in the polymers processing and applications [21, 22]. The chemical structures of these phthalates are shown in figure 1.

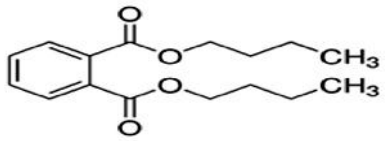
2-Experimental procedure:

2.1-Materials: Di-n octyl phthalate (DnOP), di (ethylhexel) phthalate (DEHP), dibutyl phthalate (DBP) and diisobutyl phthalate (DIBP) (99%) were obtained from Sigma-Aldrich (Aldrich, Milan ,Italy), methanol (HPLC- gradient grade) was supplied by (Panreac -EU), acetonitrile and ethanol (HPLC-gradient grade) were obtained from Sigma-Aldrich (Germany), 2-propanol (HPLC-gradient grade) was supplied by shamlab (Syria), acetic acid (HPLC-gradient grade) was supplied by Scharlaus ChemiesA (Barcelona, Spain). Distilled water (water was purified in our lab, Damascus university).

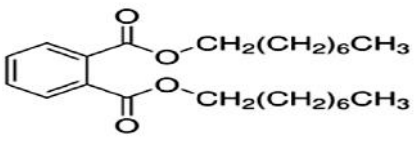
Figure 1: The chemical structure of the studied phthalates.



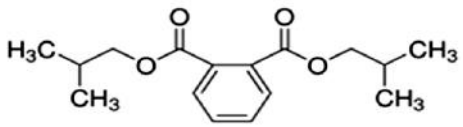
Di (ethylhexel) phthalate (DEHP)
Mw= 390.56 g/mol



Dibutyl phthalate (DBP)
Mw= 278.35g/mol



Di-n octyl phthalate (DnOP)
Mw= 390.56 g/mol



Diisobutyl phthalate (DIBP)
Mw= 278.35g/mol

2.2-Apparatus: 2.2.1-The Microwave Oven: Watter (WST-61) domestic microwave oven (Watter microwave has been opend from its top and then acondensing apparatus has fixed on it.)

2.2.2-Micro lab ultrapure water system: Hamilton Laboratory Glass, LTD.

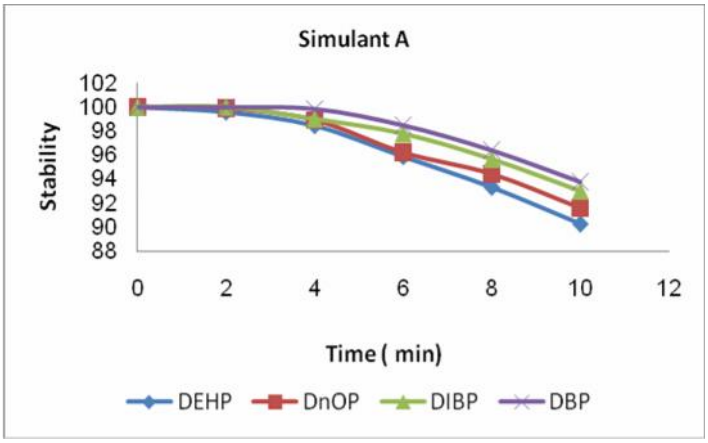
2.2.3-The High Performance Liquid Chromato graphic (Shimadzu, Japan, Kyoto). The device was supplied with; pump was model(LC-20AT), the oven was model (CTO- 20A); DEHP, DnOP, DBP, and DIBP were completely separated using a stainless steel column of dimension (4.6 × 250 mm^2) packed with symmetry C_{18} and 4 µm particle size (Merck , Germany). The detection system was model (SPD - M20A, UV-PDA), the signal acquired from detector was recorded by a personal computer to operated by using LC solution program. Micro liter syringe for HPLC (Hamilton- Bonduz, Schweiz, Switzerland, 100µl).

2.3-Chromatographic Experiments: The chromatographic experiments for analysis of the aqueous simulant samples were carried out as the described below method:

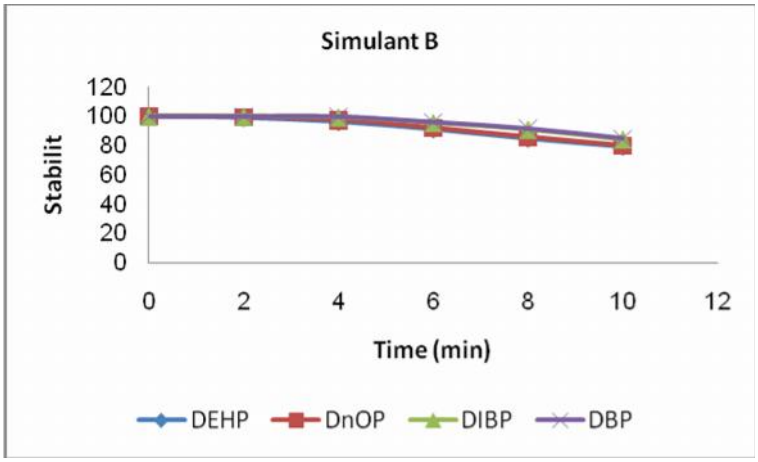
***Mobile phase:** Acetonitrile and methanol (90 : 10)., *column oven temperature: 30°C., *injection volume: 20 µl., *flow rate: 1ml/min for(DEHP, DnOP) and 0.8ml/min for (DBP, DIBP)., *wave length: 273nm.,. The aqueous simulants and 95% Ethanol were analyzed directly. DEHP, DnOP, DBP, and DIBP were identified by comparison of theirs retention time with corresponding peak in the stander solution and its UV spectrum. Quantification was carried out using a calibration plot of external standard.

2.4- Stability test procedure and preparation of samples: for stability test., individual stock standard solution of each plasticizer (1000mg/L) was prepared in 2-propanol, then, this stock solution was diluted with 2-propanol to obtain individual working solution(100mg/l)., this working solution was used to spike individual samples solutions around specific migration limit for each plasticizers (3ppm) in simulant A, simulant B, simulant C [12]. The samples solutions of the aqueous simulants were kept in glass ware and exposed to a microwave oven at full power (≈1450 w) and medium power (≈725 w).

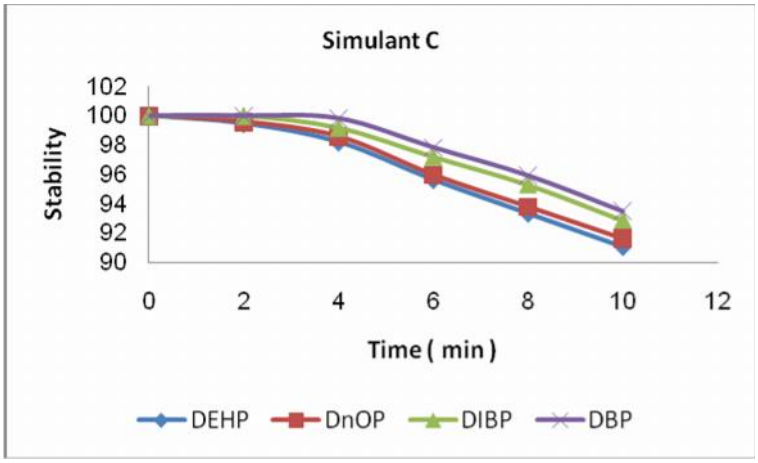
Figure 2: Stability of phthalate plasticizers in aqueous food simulants at medium power level of microwave oven.



Stability of phthalate plasticizers in simulant A at medium power level of microwave oven.



Stability of phthalate plasticizers in simulant B at medium power level of microwave oven.



Stability of phthalate plasticizers in simulant C at medium power level of microwave oven.

3- Results and Discussion:

The analysis of additives from food contact materials is commonly performed by gas chromatography (GC) [23-25] or high performance liquid chromatography (HPLC) [26-27]. In this study, a rapid screening method to test the stability of food contact materials was achieved using HPLC.

The present work has been interested to study the stability of the four plasticizers in aqueous food simulants by exposing to a microwave oven irradiation at full power (≈1450 w) and medium power (≈725 w) for 2, 4, 6, 8, 10 min.

Figures 2-3 show the results obtained in the stability test of each plasticizer in simulants A, B, and C, in a time interval 2, 4, 6, 8, 10 min, after they have been exposed to microwave irradiation at full power (≈1450 w) and medium power (≈725 w). The percent of recovery of each plasticizers has been calculated as the ratio between concentration of each plasticizers in simulant at affixed time and the concentration of them at the end of test. It was considered that, a recovery < 50% of the initially added amount of substance in simulant shows that the substance is not stable in that simulant at specified test conditions [14].

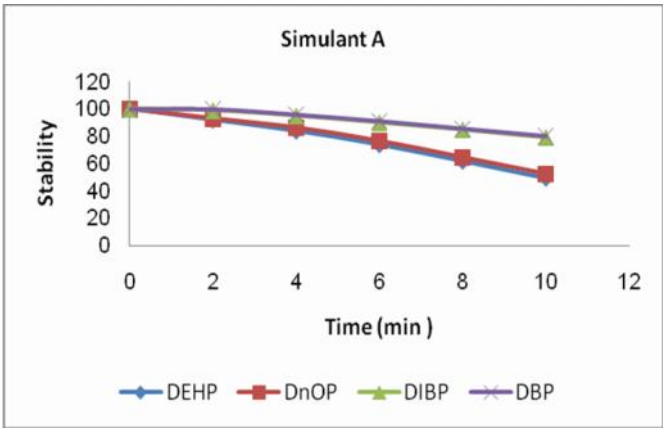
Figure 2 shows the results obtained at medium power (725w)., in simulants A and C, all studied plasticizers DEHP, DnOP, DIBP and DBP were stable and the percent of the stability when they were heated by exposing to a microwave irradiation at medium power for 10 min as follows: In simulant A; 93.5067% for DBP, 92.8800% for DIBP, 91.5922% for DnOP and 90.2489% for DEHP., In simulant C; 93.7233% for DBP, 93.0257% for DIBP, 91.6156% for DnOP and 91.0600% for DEHP. In simulant B., the most stable plasticizers were the compounds of the lower molecular weight (84.1867% for DBP and 84.6400% for DIBP., at medium power for 10 min.)., on the other hand, the compounds of the higher molecular weight DnOP and

DEHP showed a recovery around 80.0711% and 78.9956% consequently).

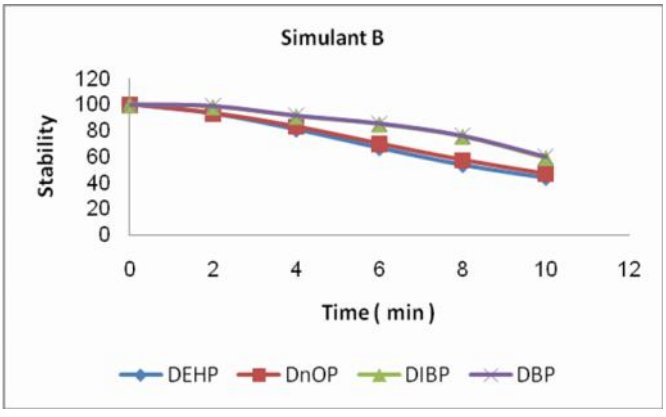
At high power (1450 w)., Figure 3., DBP and DIBP (phthalate compounds of the lower molecular weight) appeared to be stable during the entire assay, in simulant A., similar to the way they showed in simulant C, "the stability in the end of the test was: In simulant A; 80.1533% for DBP and 79.5233% for DIBP". In simulant B., the stability was decreasing in the first minutes of assay until 60.1433% for DBP and 59.1933% for DIBP that kept constant until the end of the test. DnOP and DEHP " phthalate compounds for higher molecular weight" appeared to be stable during the entire experiment in simulant C (63.0522% for DnOP and 60.3856% for DEHP., at 10 min). In simulant A., DnOP was stable during all the entire experiment (its stability in the end of the test was 52.3633%)., while DEHP appeared to be stable., but suffered a fast decomposition by increasing exposure time to 10 min (the stability was: 49.7867%). In simulant B; DnOP and DEHP were stable, but at the end of the test the stability of the compounds decreased making them unstable (46.9078% for DnOP and 43.5744% for DEHP., at 10 min).

Observing the power level of the microwave oven irradiation effects on the stability of phthalate plasticizers, it can be seen., in general, that the rise in power level causes an increase of degradation, although there are difference between simulants. So, degradation increases substantially with the power level of the microwave oven in simulants B and A, whereas, phthalate plasticizers are hardly affected in simulant C. The stability of low size phthalate plasticizers DBP and DIBP is quiet good even at high power level, and the stability decreases up to 50%. The high molecular weight plasticizers DnOP and DEHP are the most degradated compounds at high power level.

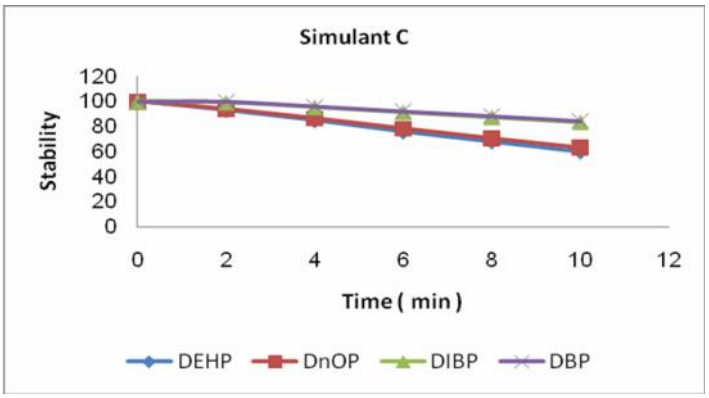
Figure 3: Stability of phthalate plasticizers in aqueous food simulants at full power level of microwave oven.



Stability of phthalate plasticizers in simulant A at full power level of microwave oven.



Stability of phthalate plasticizers in simulant B at full power level of microwave oven.



Stability of phthalate plasticizers in simulant C at full power level of microwave oven.

The results which has obtained show that the stability of the studied plasticizers does not related to the test conditions and their molecular weight only., but also related to construction of the alcohol series. The straight long series alcohol (DnOP., DBP) are more stable than the branched series alcohol compounds (DEHP., DIBP).

Comparing the obtained results with other published works, it has been seen that consulted references do not show many data about stability of the plasticizers that have been studied in this work (using microwave oven), only one study about DEHP and DBP but with using conventional heating has been found [28].

4- Conclusions:

- Comparing the results for each simulant when the power level of the microwave oven is increased, it can be seen that, in general, plasticizers are less stable at high power. In simulants B and A, this power level effect is higher than that in simulant C.
- Comparing the effect of each simulant on plasticizers stability at a fixed power level, it is noted that simulant C is the simulant that allows the highest stability of the studied compounds. All considered plasticizers are stable in simulant C during 10 min at medium and high power of the microwave oven.
- The straight lined phthalate plasticizers are more stable than their branched isomers.

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References

1- Giese. J., (1992)., Advances in microwave food processing., Food Technol., 46 (9): 118-123.

2- Knutson. K. M., Marth. E. H., Wagner. M. K., (1987)., Microwave Heating of Food., Lebensm Wiss Technol. 20:101-110.

3- Potter. N. N., (1986)., Food Scieence., 3rd edn. A V I publishing, west port, conn, 320-326.

4- Freedman. G., (1990)., Prcceedings of the Microwave packaging symposium, 23- 24 April., Philadelphia, Pa, USA.

5- Harisson. P., (1989)., The role of packaging in achieving microwave browning and crisping., Packag Technol Science., 2: 5-10.

6- Anastasia. B. Badeka., Michael. G. Kontominas., (1996)., Effect of microwave heating on the migration of dioctyladipate and acetyltributylcitrate plasticizers from food-grade PVC and PVDC/PVC film into olive oil and water.

7- Galotto. M. J. and Guarda A., (1999)., Comparison between thermal and microwave treatment on the overall migration of plastic materials indended to be in contact with foods., packaging technology and science., 12: 277- 281.

8- OJEC (Official Journal of European Communities)., Council Directive on the approximation of the Laws of the Member States relating to materials and articles intended to come into contact with foodstuffs (89/109/EEC)., 1989., L40. 38.

9- OJEC (Official Journal of the European Communities)., Commission Directive relating to plastic materials and articles

intended to come into contact with foodstuffs (90/128/EEC)., 1990., NO.L75. 19.

10- OJEC (Official Journal of the European Communities)., Commission Directive modifying 90/128/EEC, 92/39/EEC, and 93/9/EEC., (95/3/EC)., 1995., NO. L41.44.

11- OJEC (Official Journal of European Communities)., Commission Directive relating to materials and articles intended to come into contact with foodstuffs (82/711/EEC)., 1982., L279.26.

12- OJEC (Official Journal of European Communities)., Commission Directive relating to materials and articles intended to come into contact with foodstuffs (2002/72/EEC)., 2002., L220. 18.

13- Regulation (EC) the European Parliament and of the Council on materials and articles intended to come into contact with food., and repealing Directives 80/590/EEC and 89/109/EEC Official Journal of the European Union., 1935/ 2004., L 338.4.

14- Pérez – Lameal. C., Rijk.R., and simal – Gàndara. J. J., (1998). Stability of the secondary antioxidant bis (2,4 –di – tert – butyl phenyl) pentaerythritol diphosphile in food simulants., J. Agric food chem., 46., 687.

15- Demertzis. P.G., Franz. R., (1998). Development of an HPLC method for measurements of the stability of Irganox type polymer antioxidants in fatty food simulants., food addit contam., 15., 93.

16- Quinto-Fernández. E. J., Pérez-Lanela. C., Simal-Gándara. J.,(2003). Analytical methods for food-contact materials additives in olive oil simulant at sub-mg/kg level., Food Additives and Contaminants., 20., 678-683(6).

17- Spyropoulos. D. v., (1998). Stability testing of the plastics additives 2,4-dihydroxy-benzophenone, 2,2'- dihydroxy-4- methoxy benzophenone, 2-hydroxy-4-n-octyloxy benzophenone, 2-etoxy-2-ethyl oxanilide (tinuvin 312) and 2,2'- mehylenebis (4-methyl-tert-butyl phenol) in aqueous and fatty simulants ., Journal of Food Additives and Contaminants., 15., 362-369(3).

18- Zhi-Wei. W., Xiu-ling.H., and Chang-ying. H., (2009). A systematic study on the stability of UV ink photo initiators in food simulants using GC., Journal of Packing Technology and Science., 22; (3)., 151-159.

19- Poustková. I., DobiáŠ. J., Steiner. I., Poustka. J., and Voldrich. M., (2001). Stability of Bishenol A diglycidyl ether and Bisphenol F diglycidyl ether in Water-based food simulants., European Food Research and Technology., 219; (5)., 534-539.

20- Philo. M., Jickells. S., Damant. A., and Castle. L., (1994). Stability of Plastics monomers in food-simulating liquids under European Union Migration test conditions., J. Agric food chem., 42; (7)., 1497-1501.

21- Wypych. G., Handbook of plasticzers., Chem. Tec publishing., Toronto. Newyork., 2004.

22- D'Mello.J.P.F., Food Safety, Contaminants and Toxins., CABI Publishing., (2003)., 282-283.

23- Perlstein. P., Orme. P., (1985)., Determination of polymeric hindered – amine light stabilizers in plastics by pyrolysis–gas chromatography. Journal of chromatography., 325., 87 – 93.

24- Dilettato., D., Arpino. P.J., Nguyen. K., and Bruchet. A., (1991)., Investigation of low molecular mass oligomers and polymer additives from plastics., part II: Application to polyolefin soxhlet extracts., Journal of high Resolution Chromatography., 14.,335 – 342.

25- Demertzis. P. G., Simal – Gndara. J., and Franz. R., (1995)., A Convenient group method for the gas chromatographic determination of aliphatic diamines in the four official EC Food simulants., Deutsche lebensmittel– Rundschau., 91., 35 – 38.

26- Giust. J. A., Seipelt.T., Anderson. B. K., Deis. D. A., and Hinders. J. O.,., (1990)., Determination of bis(2-ethylhexyl) phthalate (DEHP) in cow's milk and infant formula by high performance liquid. Chromatography., Journal of Agricultural and food chemistry., 38., (2)415 – 418.

27- Aignasse. M. F., Prognon. P., Stachowicz. M., Gheyouche. R., and Pradeau. D.,(1995)., Anew simple and rapid HPLC method for dotermination of DEHP in PVC packaging and releasing studies., International Journal of pharmaceutics., 113., 241 – 246.

28- Alkadi. H., Chehadeh. A., Hamo. S., (2012). Effect of temperature and exposure time on the stability of Plasticizers, which are used in plastic Packing Industry, in food stimulants, Part (I)-Stability of Diethylhexyl phthalate (DEHP) and Dibutyl phthalate (DBP)., Damascus University Journal for the Basic Science., (1).

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