Animal Health Research Journal Vol. 6, No. 1, March 2018 pp. 116-128

ISSN: 2356-7767

Effect of milk and dairy products preservation In plastic packages

Arwa, H.M. Nassar* and Azza, A. Hassan**

Food Hygiene Dept.* Biochemistry and Nutritional Deficiency Dept.**Animal Health Research Institute- Mansoura Lab.

Received in 10/1/2018
Accepted in 13/2/2018

Abstract

Dairy products including milk, Rayeb, cheese and cream are consumed widely , people are concerned about their safety However some contaminants in the packaging materials might migrate to the food. Phthalates have been used in most of plastic covering containers. It is not strongly bound in these products and can therefore leach out and combined with fatty foods, because its solubility in fat.A total of thirty two samples were analyzed for contamination by using Gas chromatography to detect the presence of phthalate. Di ethyl hexyl phthalate (DEHP) is considered a carcinogen and human exposure to it should be avoided. DEHP contaminate all examined samples by concentration of 0.733 ± 0.036, 0.679 ±0.013, 61.22± 0.54 and 10.83 ±0.24 µg/L for plastic packaged milk, Rayeb, cheese and cream after one month from production date respectively, while after two months from production the concentration were 0.79 ± 0.036, 0.8± 0.047, 65.86± 0.94 and 11.68±0.19 µg/L respectively. The critical toxic effects of DEHP that appear at the lowest exposure level relate to reproduction. Also (di-methyl phthalate DMP – di- ethyl phthalate DEP –Di- butyl phthalate DBP, di -n –octylphthalate DOP and Benzyl butyl-phthalate BBP) were measured in milk, cheese, Rayeb and cream and calculate TDI comparing it with international standard. The results obtained were discussed in the light of toxicological problems connected with plasticizers.

Key words: *milk, cheese, cream, phthalates, Gas chromatography.*

Introduction

Milk and dairy products contain many nutrients and provide a quick and easy way of supplying a relatively few calories, Chemical contaminants in milk comprise chemical hazards that may introduce during milk production, dairy processing or packaging (**Khaniki, 2007).**

Phthalate are chemical which is difficult to avoid because they are often not labeled and also unregulated and considered of high hazardous level.

Phthalate is a group of the most famous plasticizers and according to International Union of Pure and Applied Chemistry (IUPAC), a plasticizer is a substance or material incorporated in with anther (plastic, for instance) to increase its flexibility, work ability or stretch ability (**Huang *et al.,* 2008).**

Phthalates are used in many industrial and consumer products to make plastics more flexible and soft, it account more than 90% of the worldwide plasticizers consumption (**Daniels *et al*., 2005 and Murphy, 2001)** and its content can be up to 50 % by product weight **(Earls *et al*., 2003).**

The study tested the migration of phthalates from plastic packages to its contents of milk and dairy products as it is the most dangerous by-product.

(Wendi *et al*., 2009) reported that on processing, the DEHP Di (2-ethylhexyl) phthalate contaminated – milk and dairy products lead to

high concentrations of DEHP in the yielded cream, whereas low fat milk contained the less concentrations of phthalate plasticizers. Also, **(Yong *et al.* 2005)** exhibited that the detection limit for the phthalate DEHP was from 0.31 to 3.3 ng/g for samples contained up to 10.8% fat. Phthalates can be measured by HPLC or GC-MS.

The HPLC-MS method is used less often than GC-MS, possibly because it uses more potential contamination sources such as plastic filters, tubing, and solvents for the mobile phase (**Khedr, 2013)**. Although these methods have been successfully applied for the analysis of phthalates in whole milk and derivative products, most studies determined only free phthalates that occurred in solution of milk samples. Some phthalates have been found at higher levels in fatty foods such as dairy product, oils, fish and sea foods stored in plastic package due to non-covalent bound between phthalates and their parent materials which lead to bioaccumulation and release of phthalates esters into the packaged consumed food (**Koch *et al.*, 2003 and Wittassek *et al*., 2011).**

Phthalates in milking mother can reach her breast milk, through blood circulation as well as infant formula containing phthalates may also contribute to infant phthalate hazard **(Mortensen *et al.*, 2005*)*** Children whose mothers had the highest levels of phthalate had IQs (intelligent question) on average seven points below those whose mothers.

The toxicity of phthalate has been the subject of keen interest in recent decades. DEHP (diethylhexyl phthalate) is without doubt the best known plasticizer from the toxicological point of view. Its acute toxicity is quite low and it was considered for a long time to be quite safe as it was discovered in the 1980s, the National Toxicological program in the USA stated that oral administration of DEHP may cause liver tumors in rats and mice ***(*Kluwe *et al.*, 1982).**

New light has been shed on the DEHP action mechanism: its primary metabolic by-product known as, mono (2ethylhexyl) phthalate (MEHP), showed good affinity to retinoic acid receptors in several human tissues ***(*Russo *et al.*, 2015**) and retinoids are well known teratogenic agents. Since no affinity to retinoic acid receptors has been observed for DEHP, detailed description of the kinetics of metabolic conversion of DEHP to MEHP is essential.
This study aimed to search for the most popular phthalate (di-methyl phthalate DMP – diethyl phthalate DEP –Di- butyl phthalate (DBP) Benzyl butyl-phthalate (BBP)– diethylhexyl phthalate DEHP and di- n – octylphthalate DOP) contaminating plastic packaged pasteurized milk and the dairy products of fermented milk (Rayeb), Domiate cheese and cream sold in local markets .

Materials and Methods

Chemicals and materials:

The glass wares were used in this work to prevent blank problems from plastic wares **(Anja and Koni, 2007)** the glass wares were washed by ultrapure water and dried, then steeped by acetone for one hour, and dried by 200C° for two hour. Acetic acid, ethyl acetate, and methanol were (lab scan) grade. Phthalates standards (DMP, DEP, DBP, BBP, DOP, and DEHP); purchased form Sigma Aldrich with assay (>98 %).

Sample preparation:

Thirty two samples, each of milk ,fermented milk (Rayed), cheese and cream packaged in plastic bottles were purchased from local supermarket at Mansouracity, El Dakhlia Governorate, Egypt and stored at 4°C until used in this study .Before extraction of free phthalates, the proteins and lipids in milk samples removed because those components could affect extraction efficiency and interfere with the instrumental analysis.

Total phthalates extraction (Wang and Zuo, 2011).

In this study, a milk sample (5.0 mL) was pipetted into a 10-mL glass centrifuge tube; then, 1.0 mL of 10% (vol/vol) acetic acid was added,

mixed well, and heated in a sand bath at 70°C for 10min. The mixture was then cooled to room temperature and centrifuged for 10 min at 1,500× g. An aliquot of the supernatant was decanted out and filtered through a 0.45-µm nylon filter membrane. Then, 5 mL of filtrate was pipetted into a 10-mL glass vial and extracted with 1.0 mL of ethyl acetate3 times. The ethyl acetate extracts were combined, passed through anhydrous MgSO4packed in a Pasteurpipet to remove the residual water, and collected into a 5-mL glass vial. The extracts were then completely dried under a stream of nitrogen gas. Finally, 0.5 mL of methanol was added and vortexes for 1.0 min and the solution was transferred into a clean 2-mL minivial for instrumental analysis.

To analyze the total phthalates in milk samples, the bound phthalates adsorbed on the proteins and other solid components must be desorbed before pretreatment to remove general protein and lipids. Previously, ultrasonic radiation, a type of low frequency energy was extensively studied for improving almost all sample preparation and pretreatment processes, including cleaning, degassing, digestion, leaching, crystalliza-tion, precipitation, and extraction **.**

Gas chromatographic analysis:(EPA, 1984)
Phthalates identified individually by comparison of the retention times and target ions of the respective peaks in the sample chromatogram With the substance peaks of a reference solution measured under the same conditions. The phthalates fraction was injected into a gas liquid chromatography in (chemistry administration) Varian model CP – 3800- mass detector Varianmodel 320-MS, column (30m – 0.25mm) internal diameter 0.25 um.

GC operating conditions were as follows:Injector temperature were 275 ° C, initial oven temperature 40°C hold for 3.5 minutes raised at 5°C / min and then held at 250°C for 10min . Raised again at 2°C /min and held at 280°C for 5 min. The carrier gas was helium at flow rate 1ml/min.

Statistical Analysis : Statistical Analysis Were performed using SPSS Statistical program according to ***(*Petrie and Watson, 2013*)***

Results and Discussion

Table (1). Concentrations (µg/L) of different phthalate residues detected in milk stored for one month and two month from the production date [N=8 (4of each)]

Phthalate type	Phthalate concentration		Phthalate concentration	
	Milk after one month (µg/L)	±SEM	Milk after two month (µg/L)	±SEM
Di-methyl phthalate (DMP)	ND	0.00	ND	0.00
Di- ethyl phthalate (DEP)	0.394	0.028	0.513*	0.034
Di- butyl phthalate (DBP)	0.366	0.0345	0.365	0.035
Benzyl butyl-phthalate (BBP)	ND	0.00	ND	0.00
Di-ethyl hexyL phthalate (DEHP)	0.733	0.0368	0.79	0.036
Di- n Octyl phthalate (DOP)	ND	0.00	ND	0.00

ND: non detectable -SEM: standard Error of Mean P*<0.05 by using t-test.

Table (2). Concentrations (µg/L) of different phthalate residues detected in Rayeb milk stored for one month and two month from the production date [N=8 (4of each)]

Phthalate type	Phthalate concentration		Phthalate concentration	
	Rayeb after one month	±SEM	Rayeb after two month	±SEM
Di-methyl phthalate DMP))	ND	0.00	ND	0.00
Di- ethyl phthalate DEP))	0.280	0.015	0.407*	0.039
Di- butyl phthalate(DBP)	ND	0.00	ND	0.00
Benzyl butyl-phthalate(BBP)	ND	0.00	ND	0.00
Di-ethylhexyL phthalateDEHP)	0.679	0.013	0.800*	0.047
Di- n Octylphthalate DOP	ND	0.00	ND	0.00

ND: non detectable -SEM: standard Error of Mean P*<0.05 by using t-test.

Table (3). Concentrations (µg/kg) of different phthalate residues detected in cheese stored for one month and two month from the production date [N=8 (4of each)]

Phthalate type	Phthalate concentration		Phthalate concentration	
	Cheese after one month	±SEM	Cheese after two month	±SEM
Di-methyl phthalate (DMP)	ND	0.00	ND	0.00
Di- ethyl phthalate (DEP)	6.04	0.5	6.5	0.4
Di- butyl phthalate (DBP)	14.24	0.063	15	0.23
Benzyl butyl-phthalate (BBP)	3.37	0.085	3.6	0.19
Di-ethyl hexyL phthalate (DEHP)	61.22	0.54	65.86*	0.94
Di-n Octyl phthalate (DOP)	6.9	0.3	6.68	0.2

non detectable -SEM: standard Error of Mean P*<0.05 by using t-test.

Table (4). Concentrations (µg/kg) of different phthalate residues detected in Cream stored for one month and two month from the production date [N=8 (4of each)]

Phthalate type	Phthalate concentration		Phthalate concentration	
	Cream after one month	±SEM	Cream after two month	±SEM
Di-methyl phthalate (DMP)	ND	0.00	ND	0.00
Di- ethyl phthalate (DEP)	1.71	0.006	1.68	0.046
Di- butyl phthalate (DBP)	ND	0.00	ND	0.00
Benzyl butyl-phthalate (BBP)	3.055	0.067	3.23	0.014
Di-ethyl hexyL phthalate(DEHP)	10.83	0.24	11.68*	0.19
Di- n Octyl phthalate (DOP)	ND	0.00	ND	0.00

ND: non detectable -SEM: standard Error of Mean P*<0.05 by using t-test.

Table (5). Previously established Tolerable Daily intake levels for phthalates.

Phthalate	Current TDI, EFSA 2005 mg/kg bw/day	Current TDI, SCHR ,2008 mg/kg bw/day
DBP	0.01	0.01
DEHP	0.05	0.05
BBP	0.50	0.5
DEP	ND	ND

ND: non detectable
TDI : Total daily intake
EFSA: European Food Safety Authority
SCHR: Scientific committee on health and environmental risk.

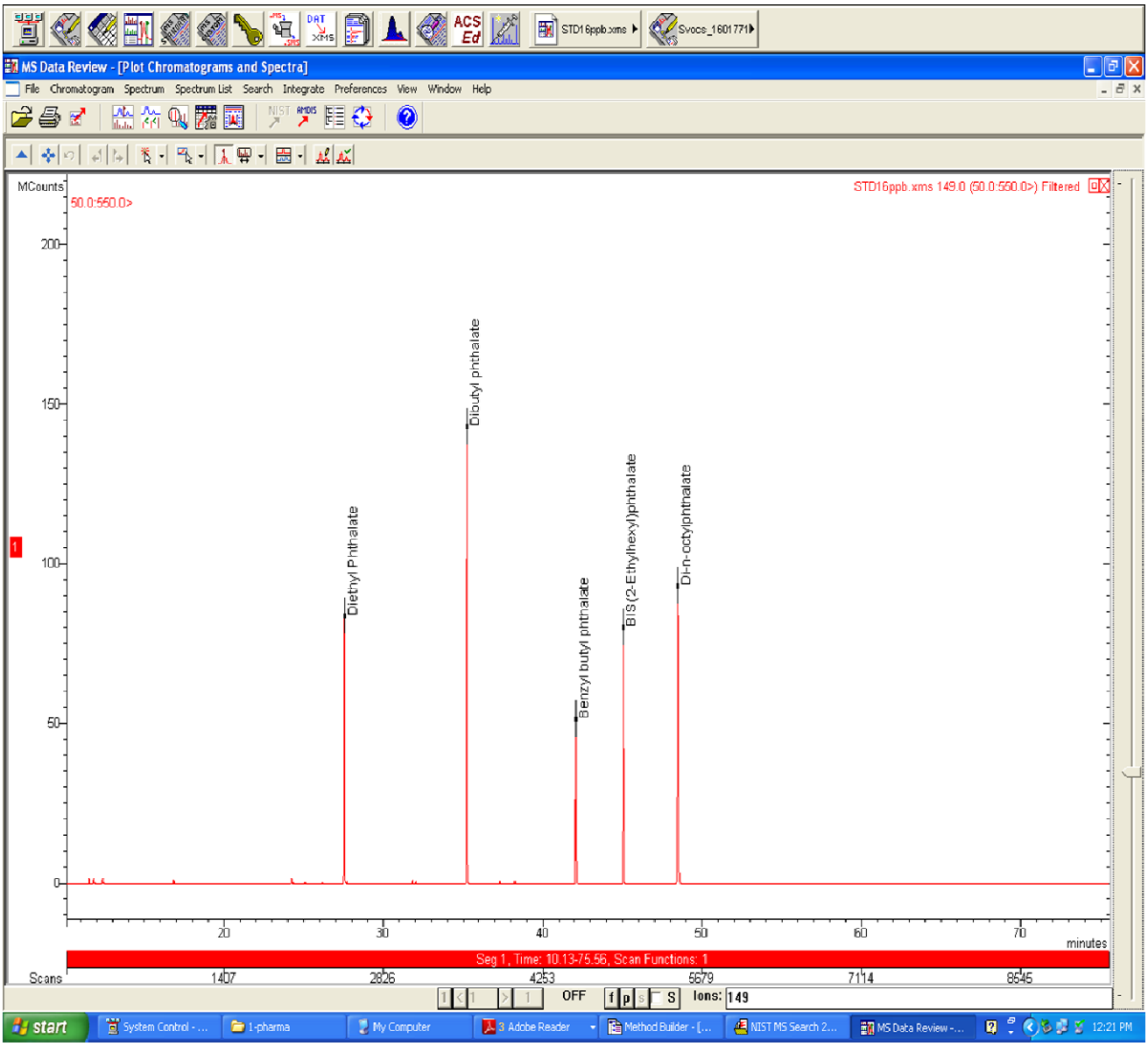
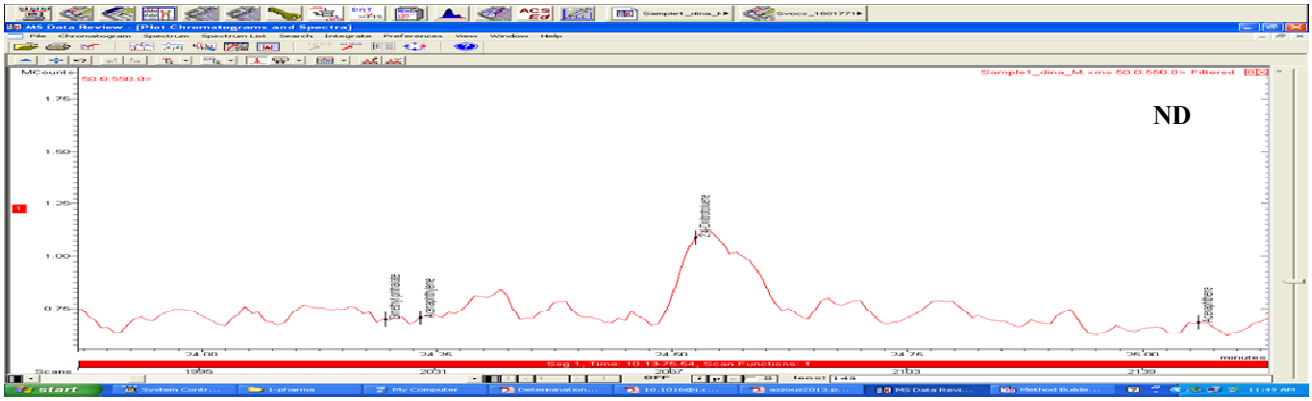
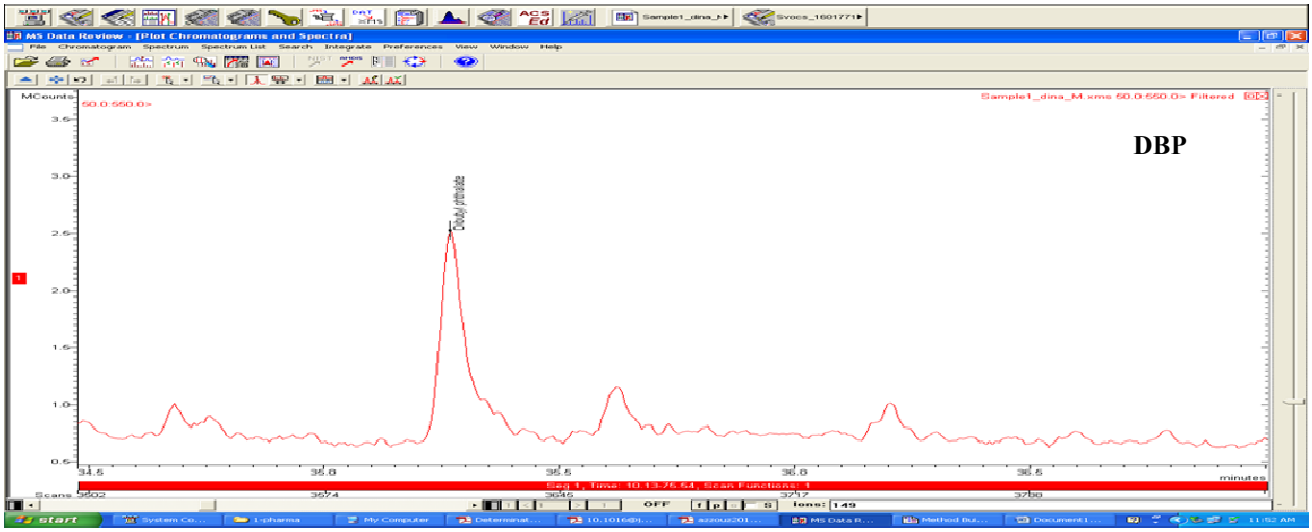
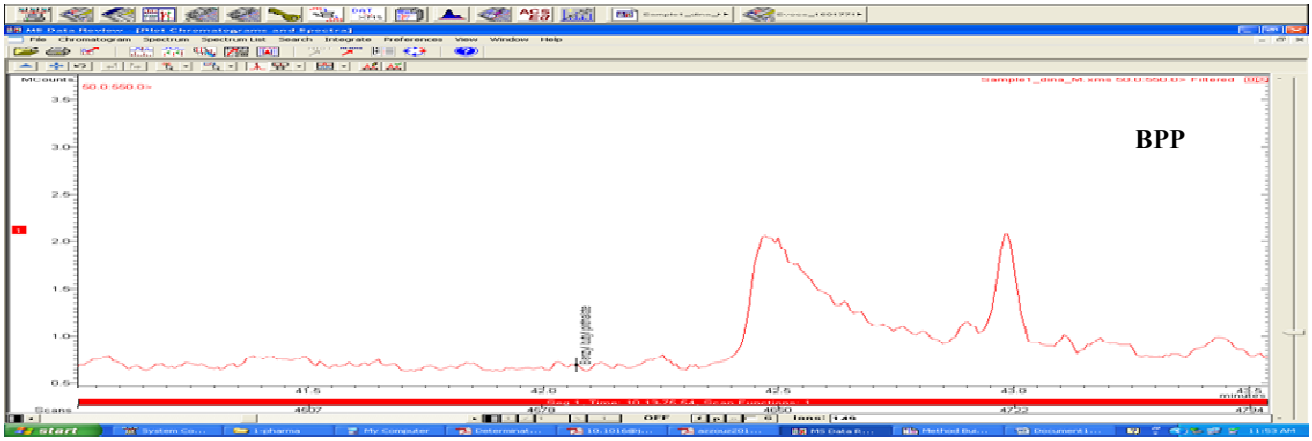


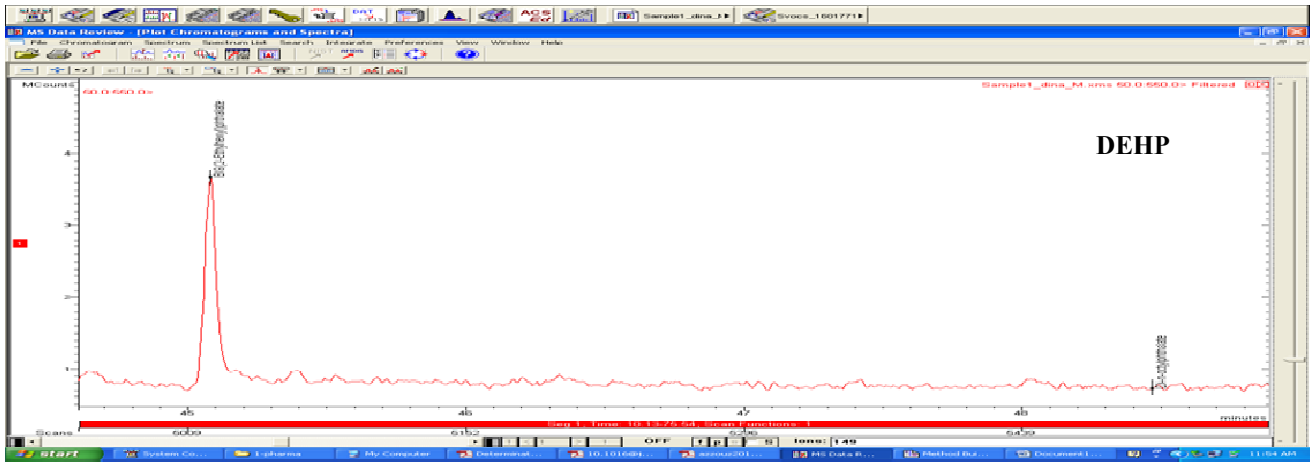
Figure (1). Gas chromatogram of calibration curve for mix of phthalate standard

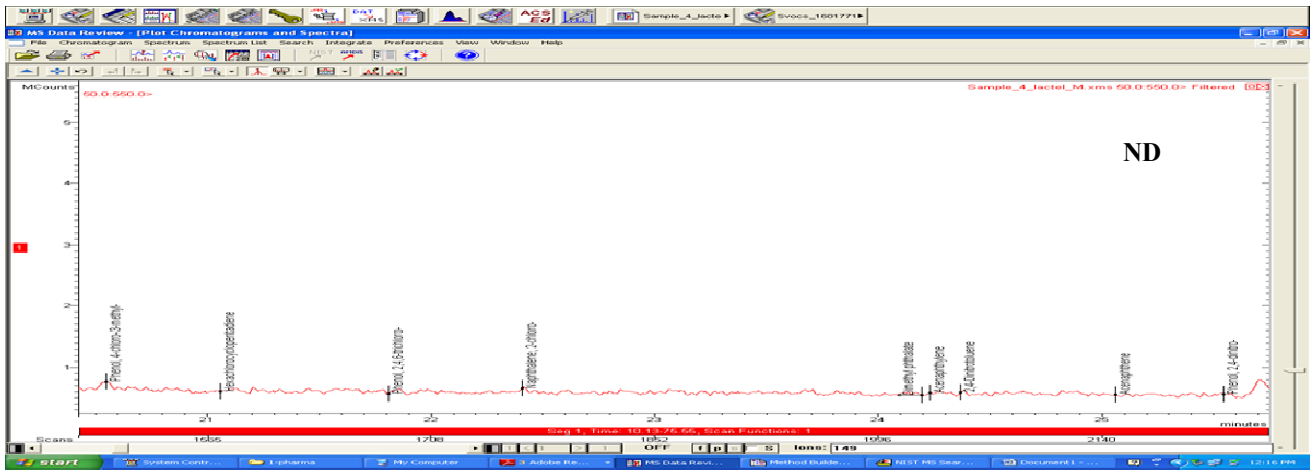

ND

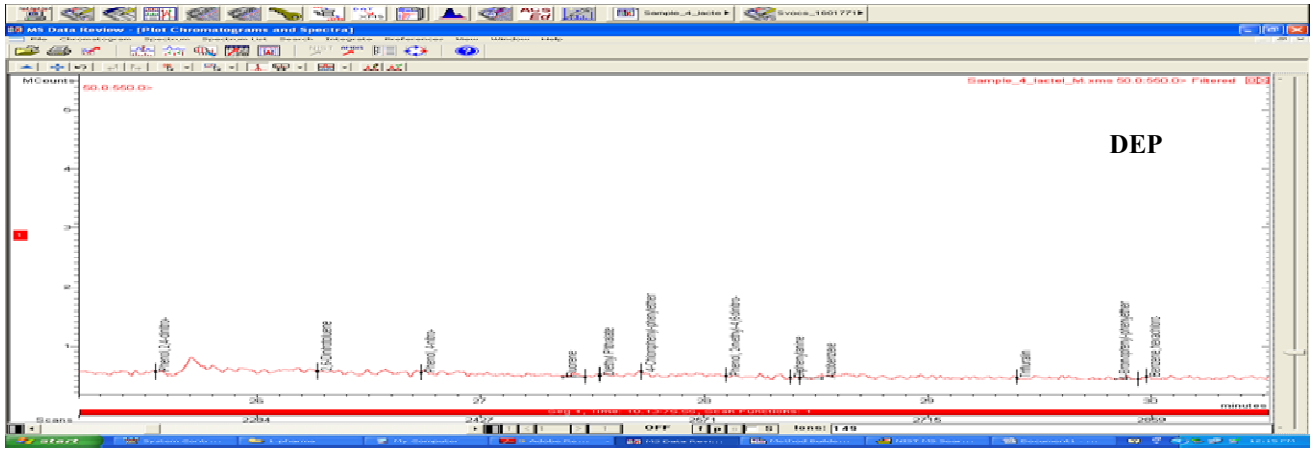

DEP

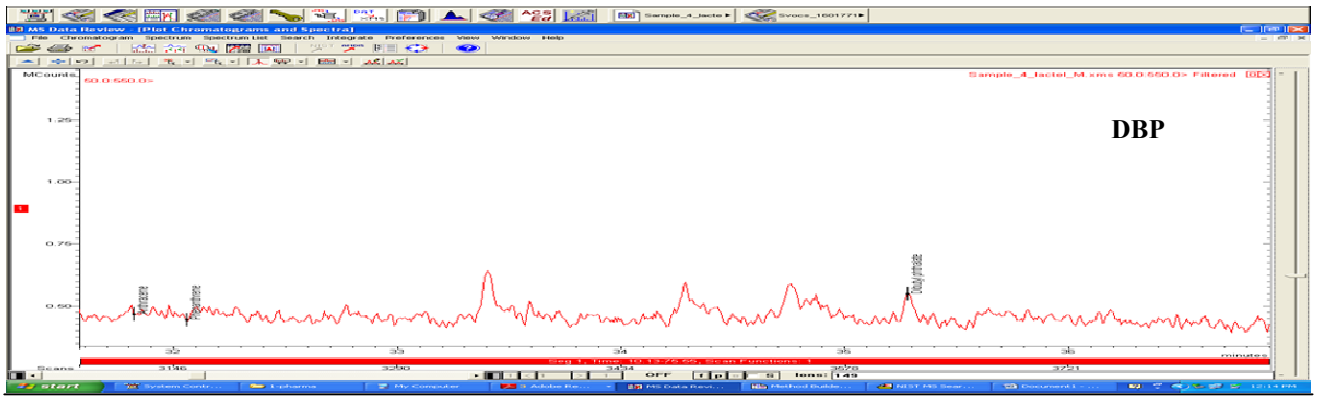

DBP


BPP


DEHP


ND


DEP


DBP

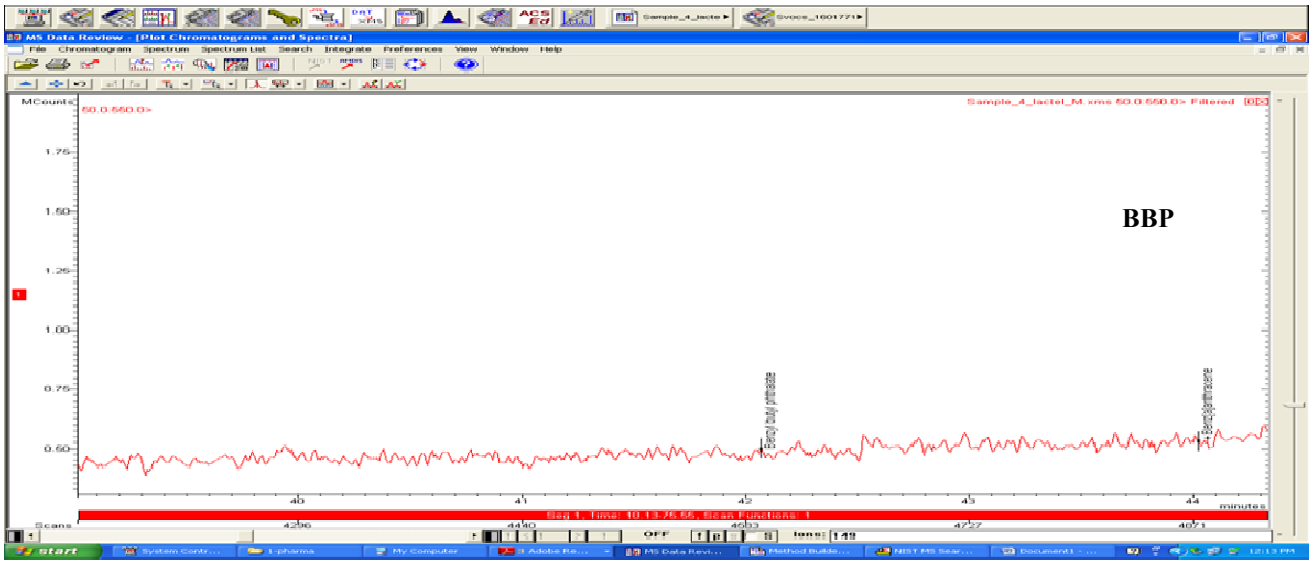
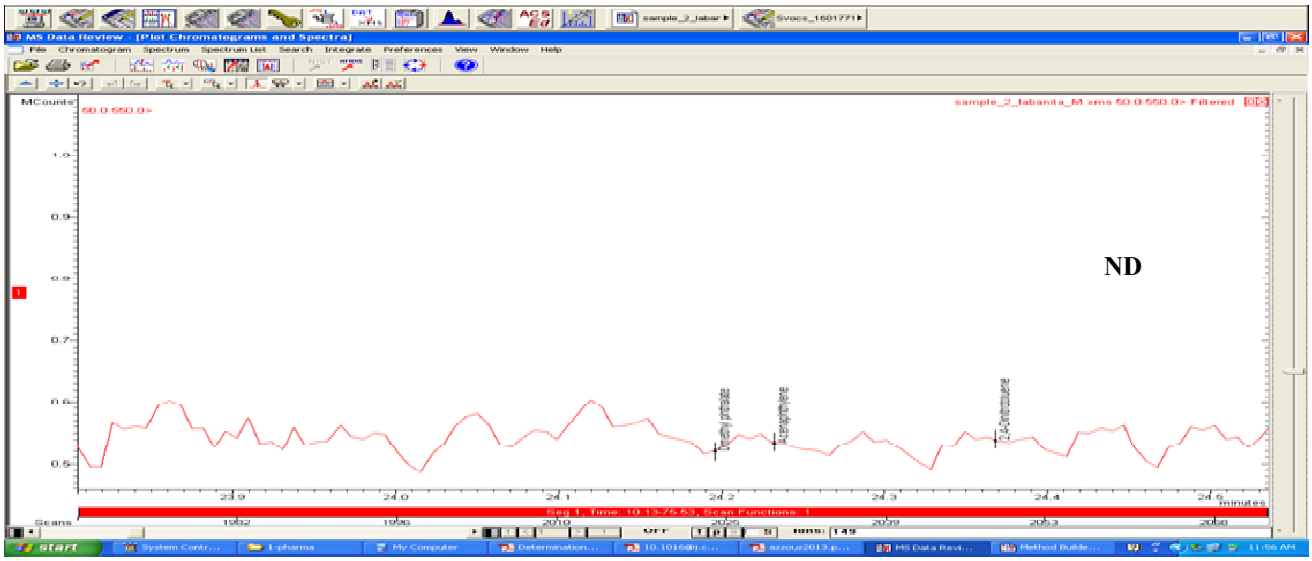
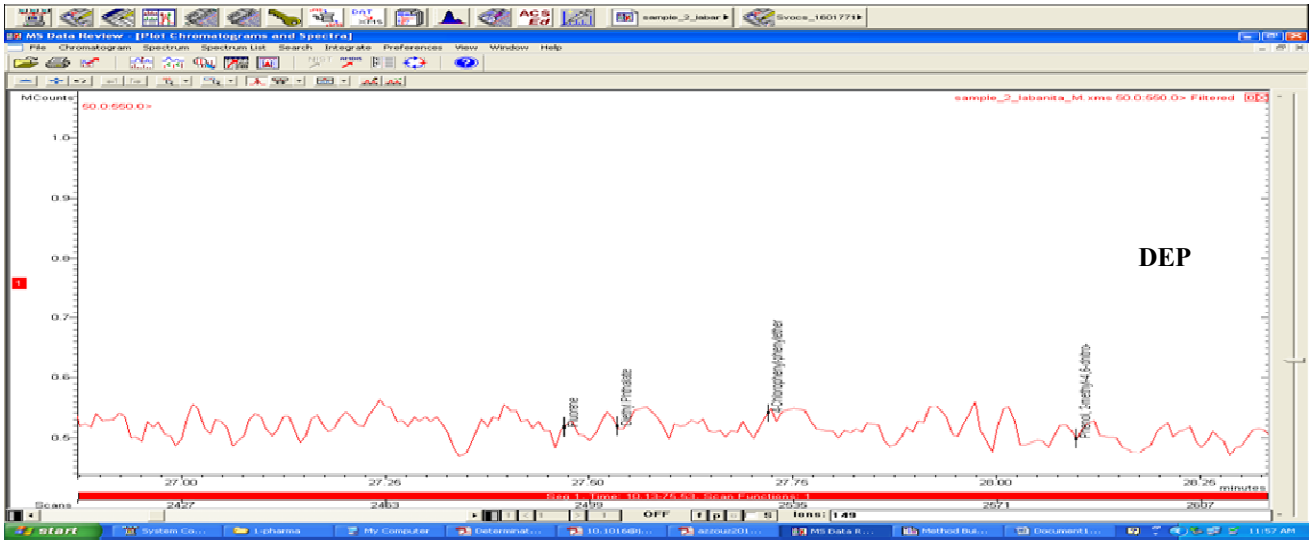


Figure (2). Gas chromatogram curves for phthalate of examined milk samples containing different residue of phthalate





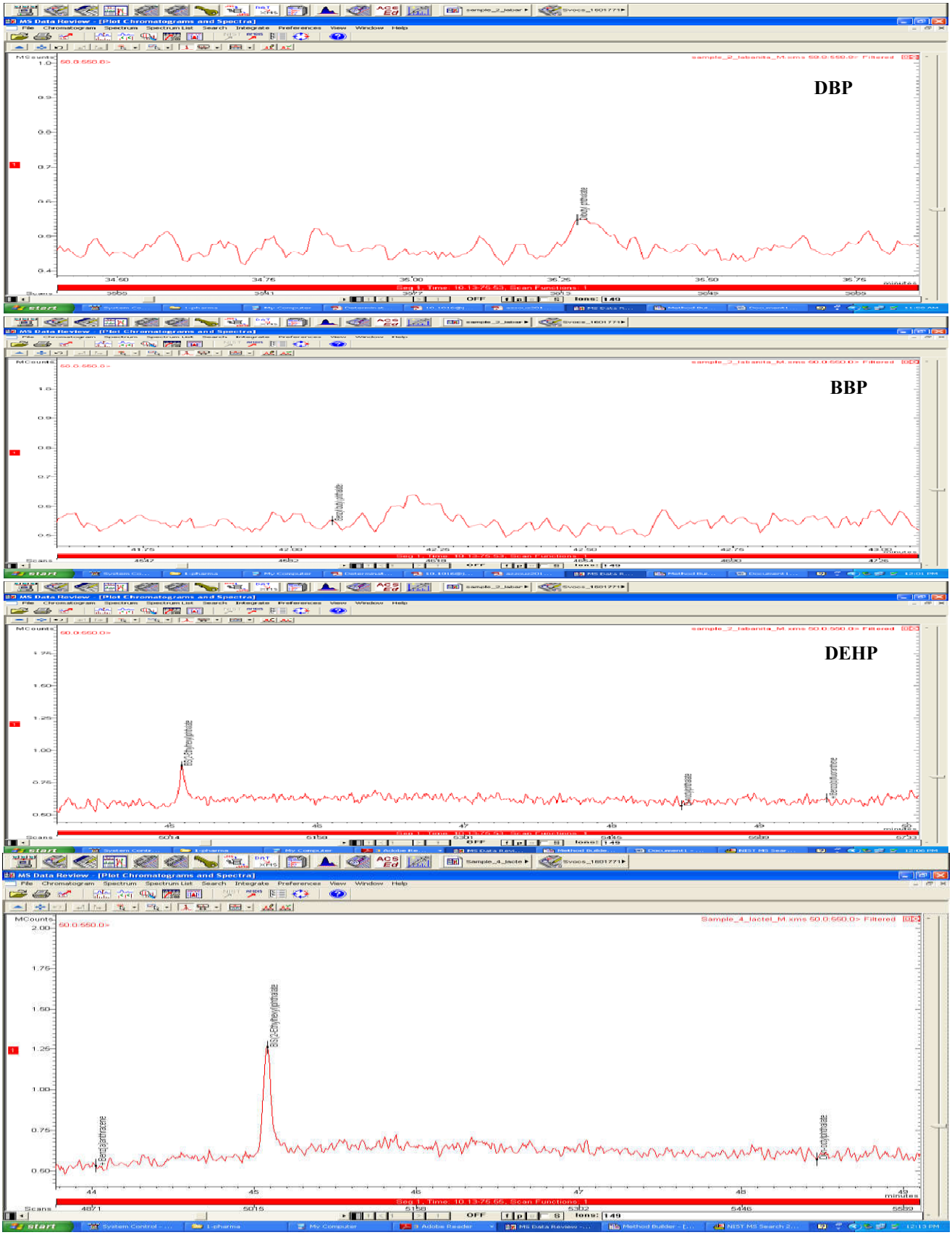


Figure (3). Gas chromatogram curve for phthalate of examined milk containing Di – Ethyl hexyl phthalate and Din-Octyl phthalate.

Phthalates ester is the most abundant man made chemical pollutants in the environment. It is commonly used to increase the flexibility of plastics in a wide array of consumer products. More than 470 million pounds of phthalates are produced or imported in the United States each year.

Detection of six phthalates esters namely DMP, DEP, DBP, BBP, DEHP and DOP in plastic packaged milk after one month and two month from the production date by Gas chromatography, it is clear from table(1)DMP , BBP and DOP not detected in all examined milk samples by using GC-Mass detection while DEP, DBP and DEHP were detected at concentration of 0.39± 0.028 , 0.36±0.034 and 0.73± 0.036 µg/L respectively after one month while after two month the concentration were 0.513±0.034, 0.365±0.035 and 0.79±0.036 µg/L respectively .Similar results were obtained by Food Standards Agency **(FSA, 2012)** survey as they examined 20 food groups including milk and dairy products and failed to detect DMP in any food groups. The obtained results were higher than **(Saad *et al., 2015*)** and **(Lin *et al.,* 2015**) higher results were reported by (**Wendi *et al.,* 2009**), **(Farajzadeh *et al.,* 2012)** detected DEHP in the range of 187-201ng/ml.

Page and Lacroix (1995) detected DEHP, DBP, BBP by concentration of 830, 0.00, 260ng/g.

Results given in table (2) revealed that the concentration of phthalate in examined plastic packaged Rayeb milk samples after one month were 0.28 ± 0.01 and 0.679 ± 0.013µg/L for DEP and DEHP respectively .But the concentration increased after two month from the production date to be 0.4 ± 0.039 and 0.800 ± 0.047 µg/L respectively. Significant increase in DEP after two month than month, on the other aspect DMP , BBP and BBP were not detected (fig.2) after one and two month in the examined Rayeb milk samples . lower results recorded by **(Saad *et al.,* 2015**)

The data presented in table (3) showed that five of the examined six phthalate were detected in examined Domiate cheese samples in concentration of 61.22±0.54, 14.24±0.063, 3.37±0.085, 6.04±0.5 and 6.9±0.3 for DEHP, DBP, BBP, DEP and DOP after one month respectively, while after two month the concentration were 65.86±0.94, 15±0.23, 3.6±0.19, 6.5±0.4 and 6.68±0.2 respectively. But DMP was not detected in all examined Domiate cheese samples table (3). Lower results were recorded by **(Saad *et al.,* 2015**) DEHP in cheese significant increase after two month than one month.

Obtained results in table (4) showed the concentration for phthalate group in examined cream samples were 10.83±0.24, 3.055±0.067, 1.71±0.006 µg/L for DEHP, BBP, DEP respectively after one month from the production date, while after two month, the results were 11.68±0.19, 3.23± 0.014 and 1.68±0.046. DEHP show significant increase in cream.

As demonstrated in table (4) we find that DMP, DBP and DOP were not detected after one and two month from production date in all examined cream samples. Higher results were recorded by **(Wendi *et al.,* 2009)**, they reported that on processing, the DEHP contaminated milk and dairy products lead to high concentrations of DEHP in the yielded cream, whereas low fat milk contained the less concentrations of phthalate plasticizers**.**

EFSA (2005) Considered a total daily intake of 0.05 mg/kg body weight per day table (5), resulted in a high Level of toxic phthalate in selected foods and represented high risk, as compared with acceptable daily intake (ADI).

The most dangerous compound of phthalate group is DEHP (Fig. 3) as it affect fertility and induces severe testicular effects including testicular atrophy **(Committee on Toxicity (COT, 2014)** which constituted the largest concentration in all examined samples. Similar results were recorded by (**Wormuth *et al.,***

2006 and Fierens *et al.*, 2012).
By observing the existed results we find that phthalates are increase by increasing storage period due to long time of contact between milk or dairy product and the inner wall of plastic packaged. Similar results were recorded by **(Saad *et al.*, 2015).**

The highest concentration of phthalates occur in Domiate cheese, which contain the highest amount of salt (Nacl) in the examined dairy products this is probably because of many reasons. Firstly the adsorption strength of phthalate is much greater than that of chloride, weakly adsorbing ions will be more sensitive to very small changes in the surface purity and surface reactivity. Secondly retention strength of weakly held chloride ions increase in the presence of phthalate anions .thirdly ion – exchange model introduced here for phthalate plus various competing ions is not definitive. **(Schulthess and Ndu, 2017**) finally the chloride ions and phthalate anions were found to exhibit a competitive reaction with the surface. (**Ndu and Schulthess, 2014) *in*** addition **(Russo *et al.*, 2015)** stated that Nacl increasing phthalate adsorption.

Food might be contaminated with phthalates through the migration from packaging materials via different commodities where fatty and oily foods are more susceptible to contamination due to their accumulative lipophilic character. Phthalates are also widely spread in milk, meat and other foods **(European Commission, 2010)**. It is likely that quantitative phthalate profile was different in milk, Rayeb, cheese and cream that may be attributed to different fat percent in each product.

There might be four reasons that most of phthalate were not found in similar percent in milk and dairy product . firstly some phthalate such as DEHP used in food packaging materials are now forbidden in some countries as China. secondly, it is not all phthalate were added in food packing materials only a few kind of phthalate would be added as the plasticizers. Thirdly, the other kinds of plasticizers, instead of phthalate, might be used in plastic products, finally different fat percent in examined dairy products.

Phthalate regulation
The European union regulates all food contact materials, as their constituents may not contaminate food and endanger consumer health. In contrast to plastics which are regulated by positive lists of authorized ingredients **(Stormer and Franz, 2009).** The **(European commission, 2010)** classified substances according to maximum residue limits (MRL) in food stuffs of animal origin, explained that DEP and DMP have no MRL because these substances when found at any limit constitute a hazard to human health. ***EU 10/2011*** explain that total specific migration limit shall not exceeding 60milligrams per Kg of food stimulant which is the permitted sum of particular substances enter in food, as regards food contact materials there was a general agreement regarding the need for EU level guideline to support the risk assessment, enforcement and compliance of such materials.

Conclusion and Recommendations
The migration of phthalates from packaging material to dairy products was discussed since examined product contain high amount of fat enable phthalates to migrate easily. In order to avoid this contamination, it should be store milk and dairy products in glass containers rather than plastic ones or use a new plastic material, like edible films. Science edible films have a lot of advantages like pollution free, flavor retaining, gas barrier, edible and biodegradable, they were used to package cheese for instance **(Pintado *et al.*, 2010).** However, due to their immature manufacturing process and high cost, their application to package dairy product is quite limited. Strict periodical monitoring of phthalate content in milk and dairy product should be applied. Good manufacturing practices and minimize using of phthalate must be implemented to save guard consumers.

Reference

Anja, F. and Koni, G. (2007). Blank problems in trace of diethylhexyl and dibutyl phthalate . Reviews in Environmental Contamination and Toxicology .175, 1-46.

COT (Committee on Toxicity) of chemicals in foods consumer products and the environment (2014). Cot statement on dietary exposure to phthalates - date from the total diet study (TDS) http://www.food.gov.uk/science/surveillance/

Daniels, C.A.; Summers, J.W.; Berard, M.T. and Wilkes, C.E. (2005). "PVC Handbook", Carl Hanser Verlag, Munich Cincinnati second edition.

Earls, AO.; Axford, I.P. and Braybrook, J.H. (2003). Gas chromatography–mass spectrometry determination of the migration of phthalate plasticisers from polyvinyl chloride toys and child care articles. J. Chromatogr. A, 983: 237-246.

European Commission, (2009). Methods for the determination of phthalates in food. Outcome of a survey conducted among European food control laboratories- Institute for Reference Materials and Measurements, EUR 23682 EN, Geel, Belgium

EU NO 10/2011 Commission Regulation (2011). Plastic materials and articles intended to come into contact with food OJ L 12, 15.1, p.1.

EFSA (European Food Safety Authority) (2005). Opinion of the Scientific Panel on Food Additives, Flavorings, Processing Aids and Materials in Contact with Food (AFC) on a request from the Commission related to butyl benzyl phthalate (BBP) for use in food contact materials. The EFSA Journal 241, 1-14 Available at: http://www.efsa.europa.eu/en/scdocs/scdoc/241.htm

EPA (U.S. Environmental Protection Agency) A (2012). Phthalates Action Plan. Washington, DC: U.S. EPA. http://www. epa.gov/oppt/existingchemicals/pubs/actionplans/phth alates_actionplan_revised_2012-03-14.pdf.

EPA (U.S. Environmental Protection Agency) (1984). Method 625: Base/Neutrals and Acids. http://www.epa.gov

Fierens, T.; Servaes, K.; Van Holderbeke, M.; Geerts, L.; De Henauw, S. and Sioen, I. (2012). Phthalates in food—Part 1: Analysis in food products and packaging materials sold on the Belgian market. Food Chem. Toxicol 50(7): 2575–258

Farajzadeh, M.A.; Djavanshir Djozan Mohammad Reza Afshar, Mogaddam and Jamal Norouzi (2012). Determination of phthalate esters in cow milk samples using dispersive liquid–liquid micro extraction coupled with gas chromatography followed by flame ionization and mass spectrometric detection . Journal Sep. Sci., 35, 742-749.

FSA, 2012 (Food Standards Agency). Determination of phthalates in foods and establishing methodology to distinguish their source. Available :http://www.food. gov. uk/science/science/research /contaminants research/envcont/organic-co

Huang, Po-Chin, Chien-Jung Tien, Yih-Min Sun, Cha-Yi Hsieh, Ching-Chang Lee, (2008). Occurrence of phthalates in sediment and biota: Relationship to aquatic factors and the biota-sediment accumulation factor. Chemosphere, 73(4): 539-544

Lin, J.; Chen, W.; Zhu, H. and Wang, C. (2015). Determination of free and total phthalates in commercial whole milk products in different packaging materials by gas chromatography-mass spectrometry Journal Dairy Sci. 98: 1–7

Khedr, A. (2013). Optimized extraction method for LC-MS determination of bisphenol A, melamine and di(2-ethylhexyl) phthalate in selected soft drinks, syringes, and milk powder. J. Chromatogr. BAnalyt. Technol. Biomed. Life Sci. 930: 98–103

Khaniki, J.R. (2007). Chemical Contaminants in Milk and Public Health Concerns: A Review. International Journal of Dairy Science, 2: 104-115.

Kluwe, W.M.; Haseman, J.K.; Douglas, J.F. and Huff, J.E. (1982). The carcinogenicity of dietary di (2-ethylhexyl) phthalate

(DEHP) in Fissher 344 rats and B6C3F1 mice. J. Toxicol. Environ. Health 10: 797 - 815.

Koch, H.; Drexler, H. and Angerer, J. (2003). An estimation of the daily intake of di (2-ethylhexyl phthalate) (DEHP) and other phthalates in the general population. Int. J. Hyg. Environ. Health, 206: 77-83.

Mortensen, G.K.; Main, K.M.; Andersson, A.M.; Leffers, H. and Skakkebaek N.E. (2005). Determination of phthalate monoesters in human milk , consumer milk , and infant formula by tandem mass spectrometry (LC-MS-MS) .Anal Bioanal Chem., 382(4) : 1084-92.

Murphy, J. (2001). "Additives for plastics handbook", 2nd ed., Elsevier, New York

Ndu, U. and Schulthess, C.P. (2014). The stoichiometry of proton, chloride and phthalate adsorption on goethite. Soil sci. Am. J.; 78: 465-472.

Page, B.D. and Lacroix, GM. (1995). The occurrence of phthalate ester and di-2-ethylhexyl adipate plasticizers in Canadian packaging and food sampled in 1985–1989: a survey. Food Addit Contam 12: 129–151.

Petrie, A. and Waston, P. (2013). Stastics for veterinary and animal science, 3 rd. edition Wiley –Blackwell .

Pintado, C.M.; Ferreria, M.A. and Sousa, I. (2010). Control of pathogenic and spoilage microorganisms from cheese surface by whey protein films containing malic acid, nisin and natamycin. Food Control, vol. 21, pp. 240-246, March.

Russo, M.V.; Avino, P.; Perugini, L. and Notardonato, I. (2015). Extraction and GC-MS Analysis of Phthalate Esters in Food Matrices: a Review RSC Advances published in 31 march pp. 1-38

Saad, M.M.; Ahmed, M.B. and Sultan, Y.Y. (2015). Phthalate residues in plastic packaged milk and dairy products. World Journal of Pharmaceutical Research. 4:1799-1807.

Scientific committee on health and environmental risk, (**SCHR) (2008)**. Phthalates in school supplies copy right©, DG Health and consumers of the European commission. http: //www.greenfacts.org/

Schulthess, C.P. and Ndu, U. (2017). Modeling the adsorption of hydrogen, sodium chloride and phthalate on goethite using a strict charge –neutral ion – exchange theory May 2 Journals. PLOS.org tenth anniversary.

Stormer, A. and Franz, R (2009). Migresives : a research project on migration adhesives in food packaging materials in support of European legislation and standardization . Food Additives and Contaminants, vol. 26, NO. 1581-1591.

Wang, C. and Y. Zuo (2011). Ultrasound-assisted hydrolysis and gas chromatography-mass spectrometric determination of phenolic Compounds in cranberry products. Food Chem. 128:562–568.

Wendi, A.; Reed, L. and John, G. (2009). Levels of DEHP and total Phthalate esters in milk, cream, butter and cheese. J. Food Additives. & Contaminants, 111(3): 375-385.

Wittassek, M.; Koch, H.; Angerer, G. and Brüning, T. (2011). Assessing exposure to phthalates – The human biomonitoring approach. J. Mol. Nutr. Food Res., 55: 7–31.

CICAD (Concise International Chemical Assessment) Document 52. **(2003).** World Health Organisation Diethyl Phthalate. Available at: http://www.who.int/ipcs/publications/cicad/en/cicad52.pdf

Wormuth, M.; Scheringer, M.; Vollenweider, M. and Hungerbühler, K. (2006). What are the sources of exposure to eight frequently used phthalic acid esters in Europeans? Risk Anal 26(3): 803–824.

Yong, L.; Jiping, Z. and Robert, S. (2005). Development of headspace of SPME method combined with GC-MS for the determination of phthalate esters in cow milk. J. Anal. Chem. Acta,; 538: 41-48.