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Extraction and Determination of Phthalates Content in Polyethylene Food Contact Materials on the Ghanaian Market

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Abstract
The use of polyethylene food packages in the food industry in Ghana as opposed to the traditional forms of packages is increasing with different designs and compositions. These materials contain compounds such as phthalates which have the tendency to leach into food during storage or processing. Phthalates are widely used in industry as plasticizers in everyday products like personal care products and food packages. These compounds, however, can be present in high concentrations in some materials. Thus, the determination of phthalates in polyethylene food contact materials was investigated using Gas Chromatography-Mass Spectrometry (GC-MS). Five different polyethylene food contact materials were purchased from markets within the Accra Metropolitan Assembly domain. These were soxhlet extracted and identified by a GC-MS instrument. Four phthalates at varying concentrations were detected in the five categories of the polyethylene food contact materials analysed. Benzyl Butyl phthalate (BBP) was detected in only one out of the 25 samples analysed with a concentration of 1.43mg/kg. Dibutyl phthalates (DBP) was detected in all samples analysed ranging from 3.59mg/kg to 15.45mg/kg. Diethyl phthalates (DEP) was detected in trace amounts ranging from not detected to 5.32mg/kg. Di 2-(Ethyl Hexyl) phthalates (DEHP) which is one of the common and most widely phthalates detected in food contact materials was detected in large amounts ranging from not detected to 14.30mg/kg. In conclusion, all the four phthalates under investigation were detected in the selected polyethylene food contact materials.
Keywords: Accra Metropolitan Assembly, Contact Materials, Gas Chromatography-Mass Spectrometry, Leaching, Soxhlet

1. Introduction

The use of packages to preserve or transport food is by no means a modern phenomenon. Broad plant leaves, animal skin, gourds and other forms of natural products were used as packaging materials by earliest civilization [1]. Although these forms of packaging are still employed in the food industry in Ghana, the practice has drastically reduced due to modern forms of packaging materials such as polyethylene. Different forms and designs of these modern materials are frequently used for packaging different everyday products compared with the traditional forms of packages. This is as a result of social and technological changes such as increased in the consumption of snacks, "takeaway foods" and convenience in eating [2]. Packaging materials protect food from biological and chemical changes, thus extending the shelf-life of the product. Packaging, therefore, has become an indispensable tool in the food industry [3].

The use of plastics in food handling and processing in the packaging industry has increased significantly since the introduction of plastics in the 1930s [4]. Polyethylene is the simplest and most widely used plastic packaging material [5] and it is used to wrap all kinds of raw and ready to eat foods in Ghana such as cooked rice and beans (waakye) and fried plantain and beans (red-red). These plastics may present a source of contamination through the leaching of toxic chemicals such as phthalates which can be deleterious to human health [4]. Furthermore, the migration of adventitious substances from food packaging materials into food has raised many concerns in both developed and developing countries. Technical reports by NTP (1980, 1982) in a toxicological study demonstrated the carcinogenic effect in rodents and potential estrogenic effect in humans from added plasticisers such as phthalates [3]. These Phthalates are easily leached and released from their products into the environment due to the weak bound to their incorporating substrate. Phthalates are man-made low molecular weight species added to plastic materials during processing to make them flexible. These phthalates have the tendency to leach into food from the food contact material during storage or heating [6]. There are evidence of adverse effects of these phthalates on the metabolism, neurological development, asthma and allergy in humans. [7].

Chemical contaminants that leach may affect the safety and quality of food depending on the nature of the food contact material [8]. Marsh and Bugusu (2007) further stated that the constant introduction of different packaging materials and designs with different compositions has, therefore, increased the hazards posed to humans due to the leaching of chemicals such as phthalates from the packaging material into food during processing or storage. The toxicity of these chemicals can be influenced by the mode of exposure such as ingestion, inhalation and absorption through the skin as well as intravenous administration [9]. These chemicals such as di-(2-ethyl hexyl) phthalates according to Bonini, Errani, Zerbinati, Ferri, and Girotti (2008) are toxic and can cause damage to reproduction and development, alter liver and kidney functions, damage the heart and lungs and also have an adverse effect on blood clotting.

A lot of countries especially from the European Union have established guidelines to help regulate and monitor the quantity of these phthalates added to food contact materials. In Ghana, however, these food contact materials are not only used to store food or transport food but foods such as kenkey and rice are sometimes cooked with these polyethylene food contact materials at very high temperatures. There is a paucity of data on phthalates in packaging materials in Ghana. Thus, the objective of this work is to determine four suspected phthalates namely; di-2 (ethyl hexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzylbutyl phthalate (BBP) and diethyl phthalate (DEP) in polyethylene food contact materials distributed on the Ghanaian markets.

2. Materials and Methods

2.1 Samples Collection and Preparation

Five different categories of polyethylene food contact materials specifically black polyethylene bags (BPB), plain polyethylene bags (TAB), thick plain polyethylene films/bags (TPB), polyethylene food containers (PFC) and polyethylene plastic bottles (PPB) were purchased from three different local markets: Madina, Makola and Kwame Nkrumah circle, all within the Accra Metropolitan Assembly. These food contact materials were each cut accurately into 3×3cm pieces and thoroughly mixed to give a representative sample.

2.2. Chemicals and Reagents

Ethyl acetate, acetone, acetonitrile and n-hexane, Di-(2-ethylhexyl) phthalate [99.8%], Benzyl butyl phthalate [99.7%], Diethyl phthalate [99.9%] and Dibutyl phthalate [99.8%] were procured from Paska Fine Chemical Industries (India), Riedel-de Haen (Germany), VWR, Prolab (France) and Wako Pure Chemical Industries Ltd (Japan). All glassware used were washed with detergent, rinsed thoroughly with distilled water and dried in an oven. The dried glassware were rinsed thoroughly with n-hexane and acetone before each use. All plastic laboratory materials were totally avoided to minimize contamination.

2.3 Phthalate extraction

2.0g each of the samples was accurately weighed into new extraction thimbles and extracted with 200ml ethyl acetate in a 500ml round bottom flask at the boiling point (77°C) of ethyl acetate for six hours thirty minutes (6hrs 30min) using the Gallen Kjeldahl apparatus. The samples were then allowed to attain room temperature and then concentrated to dryness using a rotary evaporator at a temperature of 40°C. The dried samples were reconstituted with 2ml ethyl acetate and picked into a GC vial after a minute of ultra-sonication. The samples were all analysed using a GC-MS equipped with an autosampler. Each batch of samples consisted of a sample blank and a spiked sample. The extraction process was repeated two more times for the same samples and analysed to check the effectiveness of the extraction process.

2.4 Phthalate Determination

The determination of phthalates in polyethylene food contact materials was conducted using a Varian CP 3800 Gas Chromatograph (GC) coupled to a Saturn 2200 mass spectrometer. The GC was fitted with a programmable splitless injector; the injector-port temperature was maintained at 280°C. The injector line was packed with glass wool to improve vaporization and also to provide a surface for the collection of any dissolved plastic. A varian HP-5 (30m × 0.25mm × 0.25µm) GC column temperature was programmed from 100°C to 260°C at 8°C/min, then to 300°C at 35°C/min and held for 8.86 minutes. The carrier gas, helium was set at a constant flow of 1mL/min. A volume of 2µL was injected at a normal speed with ethyl acetate as the rinsing solvent. A Saturn 2200 mass spectrometer equipped with a Varian CP8400 autosampler was operated in full scan mode for this analysis. The scanning parameters were across a range of m/z 45-300. The heated zones were set at 80°C for the manifold, 210°C for the ion trap and 260°C for the transfer line to prevent condensation of the analytes.

3. Results and Discussion

3.1 Quality Control Analysis

Each batch of samples was analysed with a sample blank and a spiked sample. The recovery rate of the method was evaluated by spiking some of the extracted samples with 1.0mg/L of a phthalate standard solution. The mean percentage recoveries of the spiked samples are shown in Table 1 with a recovery range from 67.10% to 125.20%. All compounds were satisfactorily recovered as shown below.

The effectiveness of the extraction process was determined by repeating the extraction of the same sample two more times and analysing it. The results indicated that the extraction was complete after the first extraction since phthalates were not detected in the subsequent extractions.

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Table 1: Analytical recoveries % of spiked samples at 1ppm

MATRIX	1ppm spiked	% recovery
Di-2-(Ethyl Hexyl) Phthalate (DEHP)	0.888	88.80
Di Ethyl Phthalate (DEP)	0.671	67.10
Benzyl Butyl Phthalate (BBP)	1.252	125.20
Di Butyl Phthalate (DBP)	1.170	117.00

3.2 Identification of DEHP, DEP, BBP and DBP in polyethylene packages

To identify the presence of the four phthalates: 2-di- (ethyl hexyl) phthalate (DEHP), di ethyl phthalate (DEP), Benzyl butyl phthalate (BBP) and Di-butyl phthalate (DBP), the stock standards were prepared and then analysed with a GC-MS to confirm their identities. The retention times of the various phthalates were also determined and use to identify the compounds. The polyethylene samples of the five different categories were extracted and analysed with the GC-MS using the same method settings used to analyse the standards as described above in the analytical test method. The fragmentation patterns of the various samples being analysed were compared with those of the phthalate standards. All the four phthalates under investigation were detected and identified with the help of the major fragmentation ions that corresponded with that of the Gas Chromatograms of the standards from the GC-MS and the identities of the phthalates confirmed using the GC-MS library database. The major fragmentation ion detected in all the phthalates was represented by a m/e ratio of 149. This was found to be the protonated phthalic acid anhydride ion. Other additional ions such as 177.0 and 176.0 for DEP, 205.0 for DBP, 91.0 and 206.0 for BBP and 167.0 for DEHP were all identified, and hence, were significant in the phthalates identification. The chromatograms of a mixed standard, a sample blank and a sample are shown below

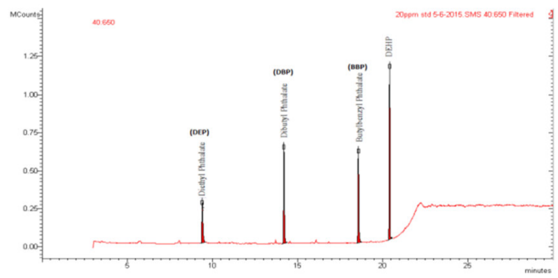


Fig. a. Chromatogram of a standard

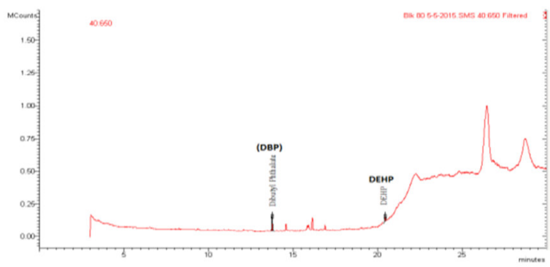


Fig. b. Chromatogram of a blank sample

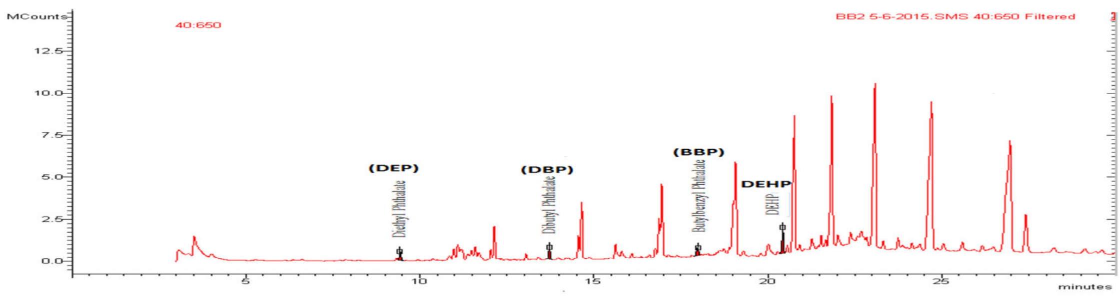


Fig. c. Chromatogram of a sample

3.3 Quantification of DEHP, DEP, BBP and DBP in polyethylene packages

All phthalates under investigation were detected in all the categories of polyethylene food contact materials with the exception of Benzyl Butyl Phthalate (BBP), which was detected in only one of the Black Polyethylene Bags (BPB) as shown in Table 2 and in Figures 1-5. Both di 2-(Ethylhexyl) Phthalate (DEHP) and dibutyl phthalate (DBP) were detected in significant quantities ranging from not detected to 14.30mg/kg and 3.59 to 15.45mg/kg respectively. DEHP and DBP are the common and most widely detected phthalates in food contact materials according to Wenzl (2009). A study on the migration of phthalates in printed polyethylene confectionery packages by Balfas, Shaw and Whitfield (1999) also reported DEHP and DBP as the predominant phthalates detected in all samples.

BBP was detected in only one out of the 25 food contact materials analysed with a concentration of 1.43mg/kg. The monoester metabolite of BBP is responsible for the reproduction and development effects of phthalates such as reduced sperm production in infants [9]. A study on the migration of phthalates into food simulants from plastic containers during microwave heating by Roders, Rudel, Just and Snedeker (2014) reported similar results where BBP was not detected in any sample. The short chain phthalates such as BBP are used in applications such as personal care, paints, adhesives and enteric-coated tablets [13].

Though di-ethyl Phthalate (DEP) was detected in all categories of the polyethylene food contact materials, it was detected in trace amounts compared to DBP and DEHP ranging from not detected to 5.32mg/kg as shown in table 2 and fig 1-5.

Di–2-(ethyl hexyl) phthalate (DEHP), which has the effect of altered zinc concentration and infertility in male infants [11] had the highest average concentration of 12.03mg/kg detected ranging from 9.89mg/kg to 14.30mg/kg.

Table 2. Phthalates concentration in polyethylene packaging materials

Polyethylene food contact materials	DEHP (mg/kg)	DEP (mg/kg)	BBP (mg/kg)	DBP (mg/kg)
BPB	9.89 -14.30	0.75 – 4.97	ND – 1.43	3.59 – 12.35
	*12.03	*2.19	*0.29	*8.03
TAB	ND – 7.99	ND – 5.32	ND	8.87 – 15.45
	*3.08	*2.47		*11.35
TPB	ND – 10.73	ND – 4.10	ND	5.71 – 13.86
	*5.84	*1.68		*9.94
PPB	ND – 10.60	0.37- 1.31	ND	5.11 – 9.66
	*4.94	*0.84		*7.43
PFC	ND – 12.08	1.05 – 1.73	ND	4.92 – 11.78
	*7.35	*1.26		*7.95

*mean concentrations ND- Not detected

From table 2 and fig 1-5, all the phthalates under investigation were detected in all the different categories of food contact materials. The predominant phthalates, DEHP and DBP were detected in significant concentrations ranging from 9.89mg/kg to 14.30mg/kg and 8.87mg/kg to 15.45mg/kg respectively. These concentrations were detected in the Black Polyethylene Bags (BPB) and the polyethylene bags/films popularly called 'take away bags' (TAB) for the DEHP and DBP respectively. A research report by Heise and Litz (2004) stated that out of the common phthalates, only two are regularly found in environmental samples. That is primary DEHP and to a lesser degree DBP. This research, however, detected higher concentrations for both DEHP and DBP.

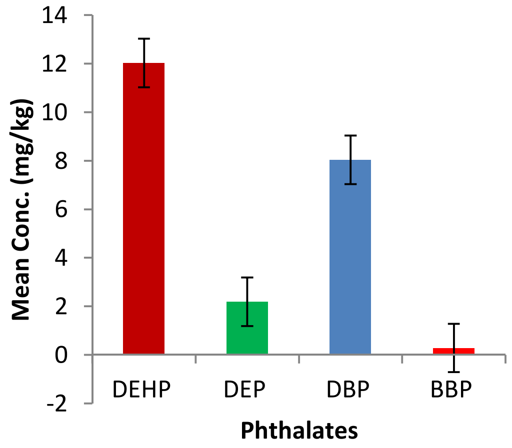


Fig 1 Phthalate concentrations found in BPB

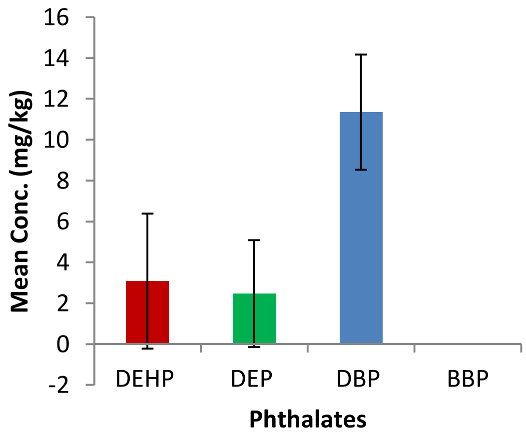
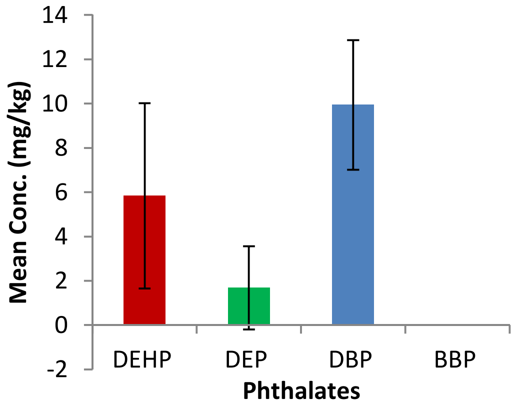


Fig 2 Phthalate concentrations found in TAB



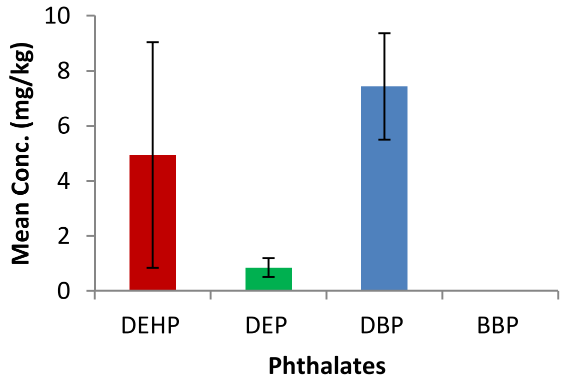


Fig 3 Phthalates concentration found in TPB

Fig 4 Phthalates concentrations found in PPB

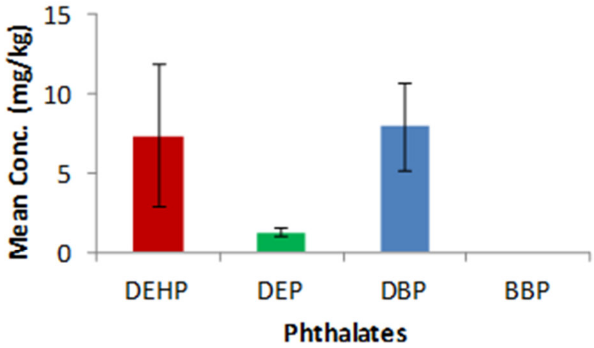


Fig 5 Phthalates concentration found in PFC

4. Conclusion

The study showed that the four phthalates; DEHP, DEP, BBP and DBP under investigations were all detected in the polyethylene food contact materials with DEHP and DBP showing very significant concentrations. DEP was detected in trace amounts compared to DEHP and DBP. BBP was the only phthalates detected in only one out of the 25 samples analysed. The average concentrations of the phthalates detected in the polyethylene food contact materials were 6.65mg/kg, 8.94mg/kg, 1.69mg/kg and 0.06mg/kg for DEHP, DBP, DEP and BBP respectively

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