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Identification of Organic Migrants from Some Plastic Food Packaging used in Saudi Arabia using Water as Food Simulant

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In this study, the authors are interested in organic migrants originating from plastic food-packages used widely in the Saudi market. Instead of using the food itself to conduct experiments food simulant is used, this is to avoid any spectral interferences. Deionized water was used as food simulant which is made to come into contact with the polymer material under desired conditions. GC-MS analysis was used to identify migrants. Many alkyl phthalates and hydrocarbons were found to have been migrated into the food simulant.

Key Words: Polymer food packaging, Food stimulant, Organic migrants, GC-MS analysis, Alkyl phthalates.

INTRODUCTION

Wide varieties of materials are being used for food packaging. Examples are metal, polymer and paper-based packages. Polymer based packages has grown in popularity and are used all over the world for various applications. Recently, numerous studies showed that packaging might pose a problem through migration of contaminants from the packaging material into food. Two major categories of migrants can be identified, organic and inorganic species. Migration of elements from polymer packaging into food has been studied by many researchers and is still an active area of research[1-3]. Migration of organic matter is also an active area of research due to wide variety of organic species that could migrate from the packaging material into food.

Modelling studies try to simulate and predict the nature of the migration process. In these studies, the packaging material is subjected to extreme conditions and possible contamination has been studied[4]. Other studies concentrate on qualitative and quantitative aspects of the migrants[5,6]. Extracting the possible migrants from packaging material is another way to study food contamination[7-9]. In their study Castle *et al.*[8,9] extracted certain migrants from paperboard packaging material. In a study by Begley *et al.*[10], nylon packaging material was dissolved in organic solvents and possible migrants were studied.

Contaminants can originate from the main packaging material itself (the polymer) as monomer, dimers, trimers etc. or from additives used to improve the quality of the package. Both types of migrants were studied by some authors, for example, styrene dimer and trimers migrated from disposable lunch boxes were quantitatively determined by Sakamoto *et al.*[5]. Contaminants from additives such as plasticizers and thermal stabilizers were studied by many investigators and many migrants were identified[11-14]. Migration of antioxidant additives from polymer packages into organic food simulants was studied under different temperatures. Migration was shown to increase at higher temperatures[15]. A study of migration from recycled paper packaging materials was conducted at 70 and 100°C at various time intervals[16]. Along with the actual determination and identification of organic migrants, methods for rapid testing, determinations and identification are reported[16,17].

EXPERIMENTAL

GC/MS spectra were taken on QP-7000 Shimadzu, with a fused silica capillary column (30 m × 0.25 mm ID), film (5% phenyl, 95% methylsilicon) thickness 0.25 µ and the output is an IBM computer with software class 5000 and GC-MS library for comparison.

Five samples of plastic packaging of different origins were collected from the local market. Samples were cut into 3 × 3 cm pieces; a total of 5 pieces were used in every experiment bringing the total area to 45 cm^2. Samples were immersed in 100 mL deionized water as food stimulant in Pyrex glass cups for 4 h. Experiments were conducted at 0, 20, 40, 60 and 80ºC using a water bath to control the temperature. After 4 h, the plastic sample was removed and then the aqueous solution for every experiment was extracted into diethyl ether (3 × 50 mL), dried over magnesium sulfate, filtered and evaporated *in vacuo*. The residue was dissolved in 1 mL of pure diethyl ether and subjected to GC-MS analysis to identify organic compounds.

For each experiment a reagent blank was prepared. The reagent blank contains deionized water only without any plastic packaging material. The reagent blank was run parallel to the actual samples into GC-MS to secure that the measured organic compounds are transferred only from packaging material, not from other sources.

RESULTS AND DISCUSSION

The purpose of this investigation is to identify the range of migration of some organic compounds from plastic packaging material which are used to save and transfer food. To perform experiments, water was used instead of actual food as a medium to measure contamination caused by

the transfer of matter from the packages into food. Because food contains so many compounds, spectral interferences are unavoidable. To get around this problem often a food simulant of some kind is used. Various food simulants have been used for specific applications *e.g.*, organic solvents, olive oil, cooking oil and acetic acid.

A survey for types of plastic packaging used to save and transfer food in Saudi Arabia was performed. Five samples were chosen from common plastic packaging types and used for the purpose of this investigation. Samples representative of various applications were selected. Sample type, origin, application and basic polymer material are shown in Table-1.

TABLE-1
PACKAGING SAMPLE INFORMATION

Sample	Origin	Application	Type	Polymer material
1	Jeddah, Saudi Arabia	Hot-cold drink	Small cup	Polystyrene
2	Thailand	Hot food	Plastic bag	Polyethylene
3	Jeddah, Saudi Arabia	Water	Water gallon	High density polyethylene
4	Jeddah, Saudi Arabia	Hot food	Plastic box	Polyethylene
5	Jeddah, Saudi Arabia	Hot-cold drink	Large cup	Polystyrene

GC-MS was used to investigate migration. Each GC-MS run results in a GC-MS chromatogram which is analyzed utilizing a built-in database. By examining the resulting chromatograms and data from GC-MS analysis, one can draw conclusions about migration under different conditions. Fig. 1 shows a typical GC-MS chromatogram and mass spectrum. Possible compounds present are identified by comparison between the GC-MS library and the actual spectrum of each component.

Analysis of data obtained for samples 1-5 at different temperatures show different peaks related mainly to various alkyl phthalate derivatives in different ratios (amounts) depending on the derivative. In addition to alkyl phthalate derivatives some long chain hydrocarbons appear to be present in the solutions.

Tables 2-6 show name, molecular weight, formula and retention time (Rt) of compounds believed to have been migrated into water from different packaging samples under investigation. One can notice the minute differences in the retention times of the same compound investigated under various temperatures.

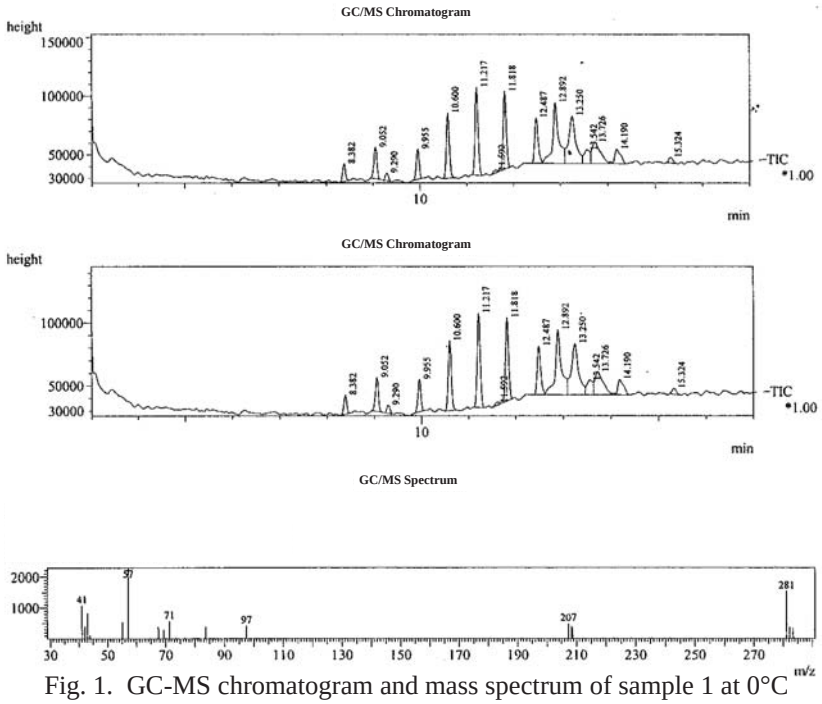

Fig. 1. GC-MS chromatogram and mass spectrum of sample 1 at 0°C

TABLE-2
MOLECULAR WEIGHT, FORMULA AND RETENTION TIMES OF MIGRANT COMPOUNDS AT VARIOUS TEMPERATURES FOR SAMPLE 1

Compound	m.w.	m.f.	0ºC	20ºC	40ºC	60ºC	80ºC
Dibutyl phthalate	278	$C_{16}H_{22}O_4$	8.38	8.53	-	10.11	10.12
Di*iso*butyl phthalate	278	$C_{16}H_{22}O_4$	9.04	9.23	-	10.80	10.79
2,6,10,14-Tetramethyl heptadecane	296	$C_{21}H_{44}$	9.95	10.18	-	-	-
Tridecyliodide	310	$C_{13}H_{27}I$	10.59	-	-	-	-
7-*n*-Hexyl eicosane	366	$C_{26}H_{54}$	11.20	-	-	-	-
Octadecane	254	$C_{18}H_{38}$	11.81	-	-	-	-
1,1,1-Triphenyl-2-decanol	386	$C_{28}H_{34}O$	-	-	-	12.36	12.37
Eicosane	282	$C_{20}H_{42}$	12.48	-	-	12.98	12.98
Di-*n*-octyl phthalate	390	$C_{24}H_{38}O_4$	12.89	-	-	-	-
Di*iso*octyl phthalate	390	$C_{24}H_{38}O_4$	13.70	13.33	-	14.55	14.55

TABLE-3
MOLECULAR WEIGHT, FORMULA AND RETENTION TIMES
OF MIGRANT COMPOUNDS AT VARIOUS TEMPERATURES
FOR SAMPLE 2

Compound	m.w.	m.f.	0ºC	20ºC	40ºC	60ºC	80ºC
Dibutyl phthalate	278	$C_{16}H_{22}O_4$	-	8.54	8.37	8.37	8.37
Di*iso*butyl phthalate	278	$C_{16}H_{22}O_4$	9.04	9.23	9.04	9.04	9.03
Heptadecane	240	$C_{17}H_{36}$	9.94	-	10.59	9.95	10.58
Eicosane	282	$C_{20}H_{42}$	11.20	10.85	12.46	10.59	11.20
7-*n*-Hexyl eicosane	366	$C_{26}H_{54}$	12.47	-	11.20	12.47	-
1,1,1-Triphenyl-2-decanol	386	$C_{28}H_{34}O$	-	-	11.70	-	-
Di-*n*-octyl phthalate	390	$C_{24}H_{38}O_4$	12.65	-	12.86	12.75	12.87
Di*iso*octyl phthalate	390	$C_{24}H_{38}O_4$	12.87	13.33	13.70	13.55	-
Tetradecamethyl hexasiloxane	458	$C_{14}H_{42}O_5Si_6$	-	-	-	14.27	-

TABLE-4
MOLECULAR WEIGHT, FORMULA AND RETENTION TIMES
OF MIGRANT COMPOUNDS AT VARIOUS TEMPERATURES
FOR SAMPLE 3

Compound	m.w.	m.f.	0ºC	20ºC	40ºC	60ºC	80ºC
Dibutyl phthalate	278	$C_{16}H_{22}O_4$	-	8.57	8.39	8.36	8.38
Di*iso*butyl phthalate	278	$C_{16}H_{22}O_4$	9.05	9.25	9.05	9.03	9.05
Heptadecane	240	$C_{17}H_{36}$	9.95	11.50	-	9.94	9.95
Eicosane	282	$C_{20}H_{42}$	10.60	12.90	-	11.20	10.59
8-Heptyl-pentadecane	310	$C_{22}H_{46}$	11.22	-	-	-	-
Tetracosane	338	$C_{24}H_{50}$	11.82	-	-	-	-
Di-*n*-octyl phthalate	390	$C_{24}H_{38}O_4$	12.90	13.12	12.90	12.74	12.87
Di*iso*octyl phthalate	390	$C_{24}H_{38}O_4$	-	13.60	13.23	13.20	-
9-*n*-Octyl-eicosane	394	$C_{28}H_{58}$	-	14.12	-	-	-

TABLE-5
MOLECULAR WEIGHT, FORMULA AND RETENTION TIMES
OF MIGRANT COMPOUNDS AT VARIOUS TEMPERATURES
FOR SAMPLE 4

Compound	m.w.	m.f.	0ºC	20ºC	40ºC	60ºC	80ºC
Di*iso*butyl phthalate	278	$C_{16}H_{22}O_4$	-	10.10	8.36	-	-
Dibutyl phthalate	278	$C_{16}H_{22}O_4$	9.04	10.77	9.02	9.04	9.05
Heptadecane	240	$C_{17}H_{36}$	9.95	-	-	10.58	9.95
Eicosane	282	$C_{20}H_{42}$	11.20	12.34	11.80	11.20	11.81
2,6,11-Trimethyl-dodocane	212	$C_{15}H_{32}$	12.48	-	12.46	12.47	-
Tetracosane	338	$C_{24}H_{50}$	-	-	-	-	-
Di-*iso*octyl Phthalate	390	$C_{24}H_{38}O_4$	12.88	14.40	12.73	12.73	12.89
Di-*n*-octyl phthalate	390	$C_{24}H_{38}O_4$	-	14.53	12.86	12.85	13.22

TABLE-6
MOLECULAR WEIGHT, FORMULA AND RETENTION TIMES
OF MIGRANT COMPOUNDS AT VARIOUS TEMPERATURES
FOR SAMPLE 5

Compound	m.w.	m.f.	0ºC	20ºC	40ºC	60ºC	80ºC
Di*iso*butyl phthalate	278	$C_{16}H_{22}O_4$	-	8.55	8.38	8.36	8.35
Dibutyl phthalate	278	$C_{16}H_{22}O_4$	9.04	9.25	9.04	9.04	9.04
Heptadecane	240	$C_{17}H_{36}$	10.59	-	11.80	9.95	9.95
Eicosane	282	$C_{20}H_{42}$	11.20	-	12.47	10.59	10.59
2,6,10,15-Tetramethyl-heptadcane	296	$C_{21}H_{44}$	-	12.15	-	-	-
7-*n*-Hexyl eicosane	366	$C_{26}H_{54}$	11.80	13.76	-	-	11.80
Di*iso*octyl phthalate	390	$C_{24}H_{38}O_4$	-	-	12.74	12.87	12.88
Di-*n*-octyl phthalate	390	$C_{24}H_{38}O_4$	-	13.35	12.88	13.21	13.20

As for the effect of temperature on migration it appears that temperature has little effect on quantities of migrants. This may be due to the random mobility change of the polymeric chains with temperature. At higher temperatures, coiling and some entanglements may be occurring and this may result in hindering the release of additives.

Conclusion

GC-MS was used to study migration of organic compound from polymer packaging material into food. It appears that additives mainly migrate into the food simulant. Effect of temperature seems to be minimal. Extensive studies are still needed to absolutely identify compounds using standards and nuclear magnetic resonance technique. Quantitative determination of migrants can also be a field of study. Health effects of theses migrants are another area of concern.

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