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Time-dependent Migration of Elements from Plastic-packaging Material into Food

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Packaging is important for the food industry. Migration of elements from packaging material into food has attracted interest because of possible contamination of the food. In this paper behavior of migration with time was studied. Ca, Mg, Zn and K were used as examples for migration into food simulant. The study shows that polymer material, time of contact and type of migrating element affect the migration process.

Key Words: Packaging, Migration, Food.

INTRODUCTION

Polymer based packages have grown in popularity and are used all over the world for various applications. Packaging is essential to the food industry. It is used in a variety of applications, from simple containment of food to designed packages to prolong the shelf-life of the product. Along with the main polymer material, additives are often used to improve the performance of the package and to make it useful for specific applications. Examples of additives are coloring agents, plasticizers, stabilizers, anti-static agents, lubricants and antioxidants.

When the package comes into contact with food, two-way mass transfer takes place. Mass is transferred from the polymer into food; on the other hand mass is transferred from food into the polymer. These two processes are related and could be affected by many physical and chemical factors.

Recently, numerous studies showed that packaging might pose a problem, through migration of contaminants from the packaging material into food. Modeling studies try to simulate and predict the nature of the migration process. In these studies packaging material is subjected to extreme conditions and possible contamination is studied[1]. Other studies concentrate on qualitative and quantitative aspects of the migrants[2, 3]. Extracting possible migrants from packaging material is another way to study food contamination[4–6]. In their study Castle *et al.*[4, 5] extracted certain migrants from paperboard packaging material. In a study by Begley *et al.*[6], nylon packaging material was dissolved in organic solvents and possible migrants were studied.

Along with the main packaging material itself (the polymer), additives to the polymer used to improve the quality of the package can be a source of

contamination. Contaminants from additives such as plasticizers and thermal stabilizers were studied by many investigators and many migrants were evaluated[7, 8]. Contaminants studied in these studies are of organic nature.

Migration of elements from food packages into food was considered by some authors; Wang *et al.*[9] studied the determination of antimony in the resin and products of polyethylene terphthalate. Thompson *et al.*[10, 11] suggested neutron activation analysis to investigate the migration of trace elements from packaging material into food. In their study of food contamination, Castle *et al.*[4, 5] screened trace element contaminants using ICP-mass spectrometry. Knezevic[12] studied metal traces in paper products intended for packaging using atomic absorption spectrometry.

The study of potential contaminants is very important for contamination evaluation; however, food packaging practices may play an important role in the degree of the transfer of the contaminants from the package to the food. Among other factors, time of contact, temperature and type of food could affect the migration process.

Food packaging practices vary from country to country. In Saudi Arabia plastic and paper packaging is widely used in food industry. Wide range of plastic bags are used by restaurants for take-away food along with the usual paper and aluminium packaging as many people prefer to take away food instead of dining at restaurants. Food packages are being used to hold and transfer all types of food under different conditions. In this study the polymer material is made to come into contact with deionized water as food simulant to allow migration, after the contact, concentrations of migrant elements are followed using either ICP-atomic emission (ICP-AES) or flame atomic absorption (FAA).

EXPERIMENTAL

Samples of different origins were collected from the local market. 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 food	Plastic bag	Polyethylene
2	Riyadh, Saudi Arabia	Hot food	Plastic bag	Polyethylene
3	Jeddah, Saudi Arabia	Hot-cold drinks	Small coloured cup	Polyethylene
4	Jeddah, Saudi Arabia	Hot-cold drinks	Large cup	Polyethylene
5	Thailand	Hot food	Plastic bag	Polyethylene
6	Jeddah, Saudi Arabia	Water	Water gallon	H.D. polyethylene

ICP-atomic emission spectrometer of the type Optima 4100 and atomic absorption spectrometer of the type Analyst 800 both manufactured by Perkin, Elmer were used to follow the extent of migration of elements from packaging

material into food. Potassium was determined by atomic absorption while Ca, Mg and Zn were determined by ICP-AES. Samples intended for food contact were cut into 3 × 3 cm pieces; a total of 6 pieces were used in every experiment providing an area of approximately 54 cm^2. Samples were immersed in the food simulant for 1, 2, 3 and 4 h at room temperature. At the end of each period about 5 mL of the aqueous solution were transferred to a glass container and trace elements were determined by the appropriate method of analysis. All containers used are made of Pyrex glass.

A blank was run parallel to the actual samples; in the blank the deionized water comes into contact with the container with no polymer present. Readings from the blank were subtracted from concentrations obtained for the samples. This procedure will correct for any migration originating from sources other than the polymer. Multi-element standards provided by Perkin-Elmer were used to test the reliability of the analysis procedure.

Food simulants

Spectral interferences often do not allow the use of actual food in the experiments to test migration, although in some instances these interferences could be avoided, the use of neutron activation analysis to follow elemental migration from polymer packaging into food is noted as an example of such situation[10, 11]. To avoid spectral interferences, food simulants are used. Variety of food simulants have been used for contamination studies; examples are water, olive oil, acetic acid, ethanol, organic compounds. Mixtures of compounds can also be used. Water is best suited for use as food simulant in this study as spectral interferences during the determination of elements by ICP-AES or FAA can be serious if olive oil or other organics are used. In this study double-distilled deionized water was used as food simulant.

RESULTS AND DISCUSSION

Polymer digestion by burning at *ca.* 700°C and dissolving using 5% HNO_3 suggest that the elements Ca, Zn, Mg and K can be followed as migrants into the food simulant. It should be pointed out that recovery of elements using this digestion method is not complete; the results are used only as an indication for the elements that could be followed as migrants and not to determine the actual concentration of trace elements in the fibre material of the package.

In order to study migration of elements present in quantities below the detection limits of ICP-AES and FAA one has to resort to ICP-mass spectrometry (ICP-MS), or for some elements graphite furnace atomic absorption would be a suitable choice. In general ICP-MS has a much lower detection limit than ICP-AES or FAA. The detection limits for Ca, Mg, Zn and K are 0.08, 0.08, 1 and 2 μg/L respectively using ICP-AES or FAA.

Table-2 shows migration trends with the increase of contact time between the polymer material and the food simulant. Concentration values of zero indicate little or no migration as the detection limits are approached. One clear conclusion from the table is that there is no steady increase in migration with time of contact.

For example, a steady increase in migration of calcium in samples 4 and 5. On the other hand, potassium migration decreases with time in sample 1.

TABLE-2
TIME DEPENDENT MIGRATION RESULTS*

	Contact time (hours)	Ca (μg/L)	Mg (μg/L)	Zn (μg/L)	K (μg/L)
Sample 1	1	101	6	13	188
	2	96	7	0	168
	3	97	7	16	73
	4	123	10	18	153
Sample 2	1	86	8	26	241
	2	50	3	0	338
	3	59	4	10	250
	4	66	4	15	973
Sample 3	1	272	10	21	296
	2	292	10	0	89
	3	297	10	18	3
	4	91	6	13	405
Sample 4	1	49	0	5	72
	2	60	2	0	160
	3	67	2	6	392
	4	96	4	7	117
Sample 5	1	29	3	2	132
	2	57	4	0	468
	3	63	4	7	321
	4	69	5	6	521
Sample 6	1	214	10	14	224
	2	124	10	0	278
	3	116	10	17	208
	4	148	12	21	210

*All concentrations have a relative standard deviation (% RSD) of < 10

Some samples show a stable rate of migration within the time frame of the experiment, for example, magnesium migration is almost constant in samples 3, 5 and 6. Although the digestion study indicates similar concentrations of Ca and Zn in sample 2, calcium migrates in quantities larger than zinc. This might be because of the differences in sizes of the two elements, as it is known that diffusion of the migrants through the polymer lattice is among the factors that affect migration[13]. One should point out though that a tested digestion method is required to asses the exact amounts of elements present in the polymer lattice for the comparison to be more accurate.

From migration results in Table-2 it is also obvious that at some point of time the reverse migration prevails after which migration comes back to its original value or even increases, this behaviour is clear in zinc migration in all samples and potassium migration in sample 3.

Conclusion

Migration of Ca, Mg, Zn and K into deionized water was followed using ICP-AES and FAA. Results suggest that migrations do not follow a general trend; instead it depends on the type of the polymer material, migrating species, and time of contact. Calcium and potassium migrate in larger quantities than Zn and Mg. In many instances Zn and Mg concentrations are close to the detection limits of the instrument used, which indicate little or no migration.

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