Study of the migration phenomena from milk polypropylene bottles

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The aim of this work is to study the interactions between polypropylene (PP) bottles and milk.. For that purpose, the migration tests were carried out for 10 days at two different temperatures (20 and 40°C), with and without agitation and by using two food simulants: n-octane and sunflower oil. The mass variation of PP samples with time was followed. The phenomena of migration were studied by using Fourier transform infrared spectroscopy in attenuated total reflexion mode (FTIR-ATR), atomic absorption spectrometry (AAS) and gas chromatography- mass spectrometry (GC-MS), .

The results showed the influence of contact time, temperature, storage conditions and simulant nature on migration phenomena from food package. .

Keywords: PP; migration; milk; liquid simulant; FTIR-ATR; AAS

1. Introduction

The presence, in the food or in the environment, low quantities of potentially toxic products is it dangerous to man? In the absence of scientific certainty, can we establish a legislation?

This is the reason for which the units of scientific research are focusing more on the safety and quality of food packaged to protect the health of the consumer. In effect, packaging play a revealing and indicator role of the life level of societies. By its technological and marketing functions, the packaging makes life less requiring it would be essential for the consumer. But, it can cause damaging nuisance that it must nearby look, even if we can't prove the existence of a cause-effect relationship between exposition to a substance and the appearance of a disease for the low doses.

It is in this context that the study of the content containing interactions has extended the field of food to the pharmaceutical, hereafter the scientific evidences made at the end of the 60 years involving the packaging as a source of foods contamination [1].

At front of the multiplicity of products, the constraints of conservation, the amenities of use and today the requirements related to the environment, there is a wide variety of materials and packaging systems forming part of our lives [2]. In effect, a direct contact of a plastic packaging with a food can be a source of reciprocal interactions between content and container causing quality defects; flavor or aroma of food is able to pass from the product to the outside (aromatic loss). In addition, additives contained initially in the polymer can also migrate to the food; then there is contamination of the product [3-7].

Our work is devoted precisely to highlight the context of the migration of additives contained initially in the bottles of milk, to study the factors favoring this process and finally to identify the migrating substances.

In this work, migration testing have been carried out in two food simulants, sunflower oil and n-Octane, with and without agitation a tow different temperature. The migration phenomenon has been firstly analyzed by a preliminary study based on the rate of mass variation of samples which were in contact with the two food simulants at 20 and 40°C and using three analytical techniques of analysis Fourier transform infrared (FTIR-ATR) atomic absorption spectrometry (AAS) and gas chromatography-mass spectrometry (CG-MS).

2. Materials and Methods

2.1 Migration testing

Samples having a diameter of 20 ± 0.1 mm and average mass (0, 1600±0.001) g were cut from the selected PP bottle into squares. Migration tests were carried out for 10 days at two different temperatures (20 and 40°C), with and without agitation and by using two food simulants: n-octane and sunflower oil (directive 82/711EEC). Ten samples of PP were immersed in 100 ml of food simulant. A squares sample and 10 ml of food simulant were taken off every day. The rate of mass variation was calculated according to the following equation:

$$\tau(\%) = [(m_t - m_0)/ m_0] * 100 \qquad (1)$$

Where:

m_0= initial mass before immersion

m_t = mass of the sample at the time t.

The weights were measured to an accuracy of 10^{-4}g.

2.2 FTIR-ATR spectroscopy analysis

This technique has been used for the purpose to confirm the nature of the polymer used in the manufacture of the selected bottles and to perform a semi-quantitative estimation of the migration phenomenon by identifying the migrant species. A polymeric film (PP) was recovered and analyzed directly with a Perkin–Elmer model *Spectrum One*. The resolution was 2 cm^{-1}.

2.3 AAS Atomic absorption spectrometry analysis

PP samples were first mineralized out as follows [8]:

- Weigh a 0.4 g sample in a porcelain crucible.
- Insert the crucible in a muffle furnace at 900 ° C for 2 hours until white ash is obtained.
- Leave the crucibles cool.
- Add 2 mL of supra pure nitric acid.
- Dissolve the residue with distilled water and complete with the same solvent up to 20 mL.

The concentrations of Zn, Pb, Cu, and Cd were determined using a Perkin–Elmer analyst spectrometer.

2.4 GC-MS analysis

GC-MS analysis was performed on a Perkin–Elmer GC connected with a MS detector. A 30 m capillary column PE-5MS (5% diphenyl, 95% dimethyl polysiloxane), i.d = 0.25 mm; df = 0.25 µm, Perkin–Elmer) was used. The analysis was carried out using electron impact mode and an ionization potential of 70 eV. The carrier gas was helium with a flow of 2 ml/min.

The separation of DOA from PP was done by Soxhlet extraction with chloroform according to the method developed by Wang and Storm [9]. The analysis was conducted under the following conditions: 90 °C held for 3min, heated up to 250 °C at a rate of 6 °C/min and held for 13min. Molecular mass in the range 50–450 amu was scanned. The identification of different peaks was deduced by searching in the MS library (NIST) and further confirmed by running the known chemical for DOA

Calibration curve for DOA was prepared in chloroform at concentrations that covered the concentration range found in the polymer extracts. The resulting line was linear with correlation coefficient of 0.9977. Three analytical replicates were analyzed for each concentration.

3. Results and discussion

3.1 Study of changes in the rate of mass change

The rate of mass variation as function of time gives information about the phenomenon which occurred between the samples and the food stimulants.

Figure 01show the evolution of the rate of mass variation with time of contact under the influence of agitation and a temperature in the case of the sun flower oil and n-octane. It can be noted that (τ) increase during the first 6 day of contact who indicate the penetration of the two liquid simulants in the free volume. Then after this duration the shape of all curves decreases, which confirm that migration of additives occurred in both food simulants. However, we note that the rate of mass variation is higher in the case of the sun flower oil. Due to the good solubility of the plasticizer in fatty stimulant, and also to its low solubility in aqueous stimulant [10, 11].

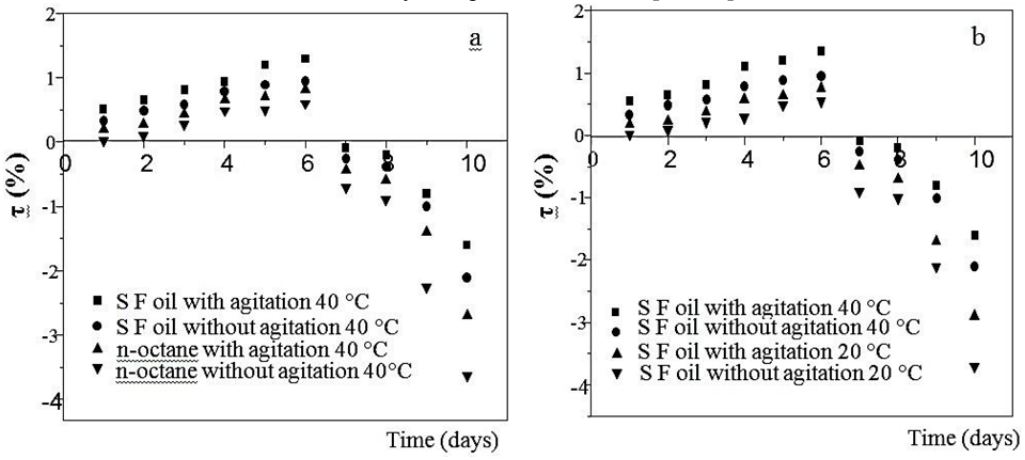

Fig. 1 Evolution of the rate of mass variation versus time of contact in the case of sunflower oil and n-octane with and without agitation at 20 and 40 °C. **a)** highlight the influence of the agitation and the nature of food simulant; **b)** highlight the influence of temperature

The study of the rate of mass variation allows us to deduce:

- The food stimulant has a real influence on the phenomenon of migration.
- The agitation affects the variation of mass in the tow food stimulant by the renewal of the contact surface of the plastic material.
- The temperature is an important factor favoring the phenomena of interaction between polypropylene (PP) bottles and milk.

3.1.1 Estimate of the overall migration

The table 1 shows the values of the overall migration in the sun flower oil and in the n-octane. All values of overall migration determined are lower than the maximum overall migration established by the EEC: 10 mg/dm^2, which means that the migration has not affected the quality of the food stimulant.

Table 1 Values of overall migration in mg/dm^2.

	Sunflower oil, 40°C		**n-octane, 40°C**		**Sunflower oil, 20°C**	
	With agitation	Without agitation	With agitation	Without agitation	With agitation	Without agitation
Overall migration (mg/dm^2)	-0.434	-2.745	-2.998	-2.810	-1.496	-3.894

In addition, the smaller values of overall migration are obtained in the case of samples having been in contact with the sunflower oil; this can be explained by the good solubility of plastizer in oil while its solubility in the n-octane is very low due to the low viscosity of the latter, which confirmed the influence of the nature of food stimulants in the migration phenomenon. Moreover, the most important rate of migration was observed at 40 °C under the influence of agitation and a temperature. After the results showed, we can conclude that all factors studied have a real influence on the phenomenon of migration.

3.2 Migration analysis by infrared spectroscopy

In order to follow the evolution of the characteristics bands of additives present in the formulation of the polymer constitutive of this bottle we have study the ATR spectra of samples of bottles were in contact with food simulants at 0 day (witness), 6th day and 10th day at two different temperatures 20 and 40°C with and without agitation.

A semi quantitative estimation of the migration of additives was done. For that purpose, the following absorbance's ratios were calculated: A 1166 /1372, A 1338/1372, A 1455/1372 and A 2853/1372

In our case, we considered the band at 1372 cm^{-1} corresponding to the vibration of the deformation of CH_3 of PP [12] as the more stable band which is taken as a reference band.

An initial increase is first observed in all absorbance ratios indicating the penetration of the food simulant in the PP samples, followed by a decrease of all absorbance ratios, their decrease in intensity corresponds to a migration of one or more components in the food simulants. The report calculated in the case of tests with agitation are lower than those measured for the tests without agitation. Most of the monomers and additives are lipophilic, and the migration is a function of the affinity between the migrant and the packaged product, migration is generally more important in a fat medium than in an aquous.

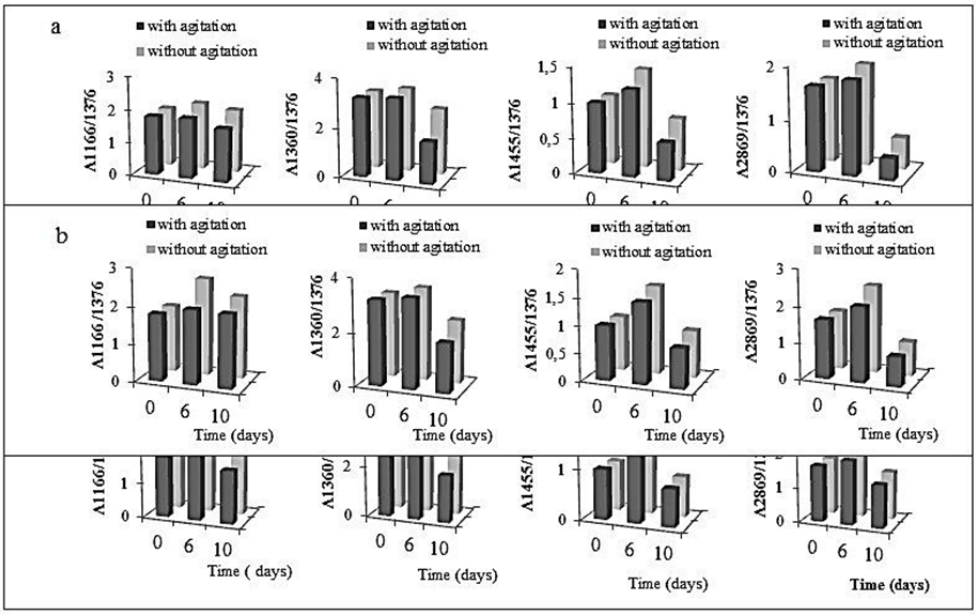

Fig. 2 Variation of absorbance's ratios as a function of time of contact with: a) Sunflower oil at 40°C; b) Sunflower oil at 20°C; c) n-octane at 40°C

3.3 Atomic absorption spectrometry analysis

The atomic absorption spectrometry was first used to determine the concentration of Zn, Pb, Cd and Cu in the PP samples. The results showed in Tables 2, 3, and 4 shows their presence. The presence of this element would be linked to the additives present in the formulation or to residues of the polymerization (catalysts). In addition, the presence of zinc is probably due to the fact that the heat stabilizer used during the manufacture of the bottle is zinc stearates; its characteristics bands have been also detected by infrared spectroscopy.

Table 2-4 Concentrations (µg /l) of metals present in the samples which were in contact with: Sunflower oil (40°C and 20°C) and n-octane at 40°C.

2	**Sunflower oil (40°C)**							
	With agitation				**Without agitation**			
Concentration (µg/L)	[Zn]	[Pb]	[Cu]	[Cd]	[Zn]	[Pb]	[Cu]	[Cd]
2 days	610	0,31	61,5	11,07	1465	1,32	132,7	11.61
4 days	550	0,21	55,5	6,69	1325	1,15	96,5	10.63
6 days	510	0,15	52,6	5,06	780	0,82	77,4	7.35
8 days	450	0,11	48	4,78	635	0,38	65,05	5.68
10 days	380	0,08	37,6	4,69	410	0,10	55,25	5.31

3	**Sunflower oil (20°C)**							
	With agitation				**Without agitation**			
Concentration (µg/L)	[Zn]	[Pb]	[Cu]	[Cd]	[Zn]	[Pb]	[Cu]	[Cd]
2 days	1290	1,91	183,4	10,70	1915	1,78	260,9	14,89
4 days	1110	1,75	122,05	8,35	1805	1,77	200,7	12,795
6 days	1270	1,685	56	6,635	1720	1,76	41,8	12,235
8 days	980	1,535	50,60	6,505	1575	1,74	40	9,515
10 days	685	1,185	45,39	6,455	1490	1,70	37,55	8,77

4	**n-octane (40°C)**							
	With agitation				**Without agitation**			
Concentration (µg/L)	[Zn]	[Pb]	[Cu]	[Cd]	[Zn]	[Pb]	[Cu]	[Cd]
2 days	1600	1.03	226.4	8.33	1975	3.08	448.4	17,17
4 days	1545	0.70	102.3	5.71	1720	1.23	334.4	12,58
6 days	1495	0.50	50.25	5.67	1680	0.65	151.1	12,23
8 days	1325	0.35	47.5	4.85	1405	0.60	141.1	8,50
10 days	1355	0.31	32.9	4.66	1255	0.55	103.5	8,16

According to the results shown by the Tables 2, 3 and 4 It can be noted that the residual concentrations in the PP samples decreased with time. By comparison between the values showed in case of samples which were in contact with sunflower oil and those found in the n-octane, we note that there is an effect of affinity which shows the influence of the food simulant on the migration phenomenon. In addition, the comparison of the results shown in tables 2 and 3 confirm the influence of the temperature and the agitation which increase the mobility of the molecules of the additives and promote their migration in the food simulants.

3.4 Application of the GC/MS to the study of the specific migration

In order to identify the various additives contents in the composition of the formulation of the milk bottles having been used for migration tests, we proceeded to the analysis of the pellet witness and those having undergone migration testing in the two environments simulators -sunflower oil and the n-octane with and without an continued agitation and at two different temperatures 20 and 40°C using the method of extraction by the chloroform. It should be noted that the technique of the internal standard has been used in this study. Figures 3 and 4 represent, respectively, the chromatograms obtained and their corresponding fragmentations.

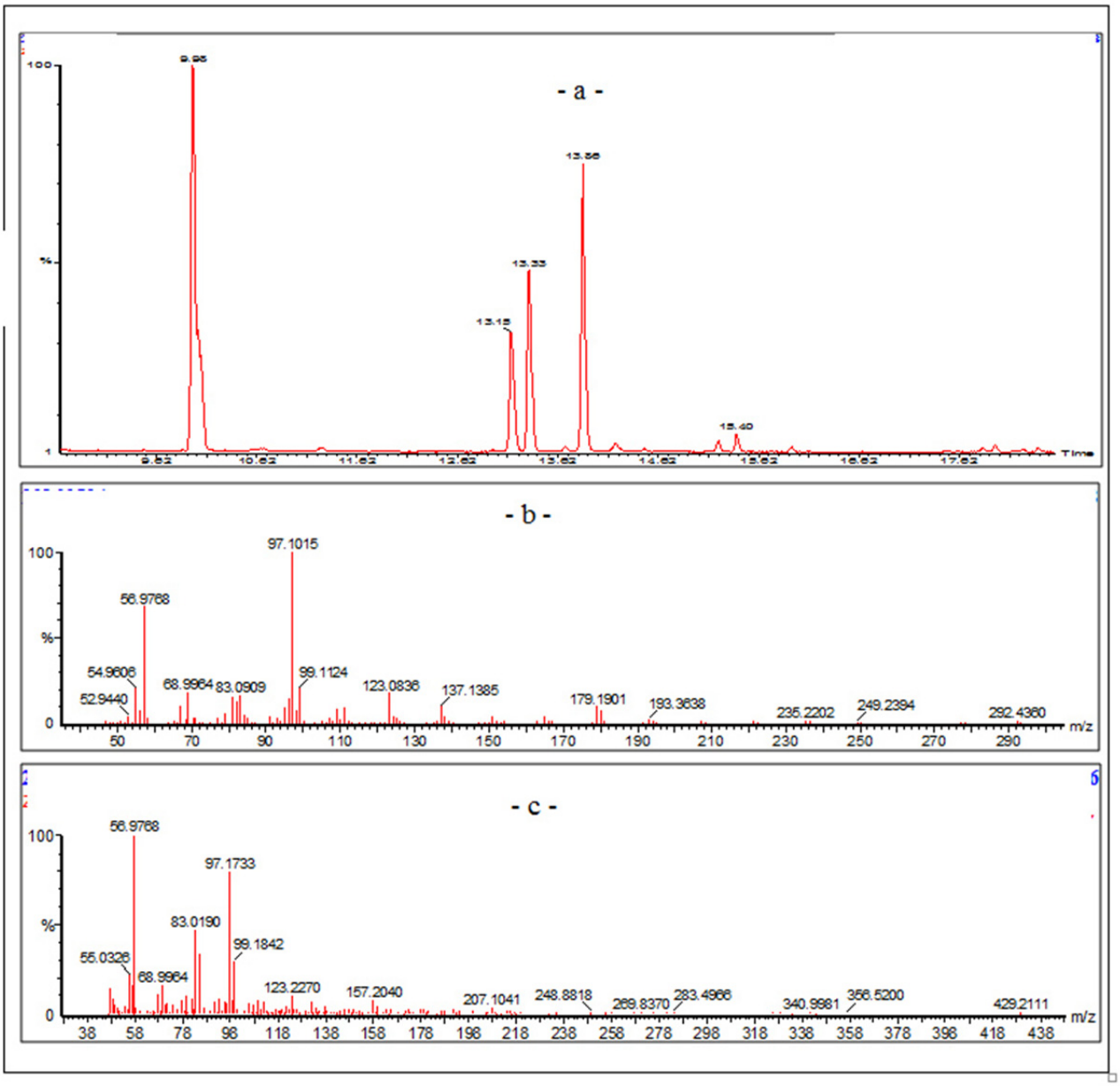

Fig. 3 **a)** Chromatogram of the sample in contact with the sunflower oil for 10 days without agitation at 20°C; **b)** Fragmentation of the peak retention time of 9.98min; **c)** Fragmentation of the peak retention time of 13.86min.

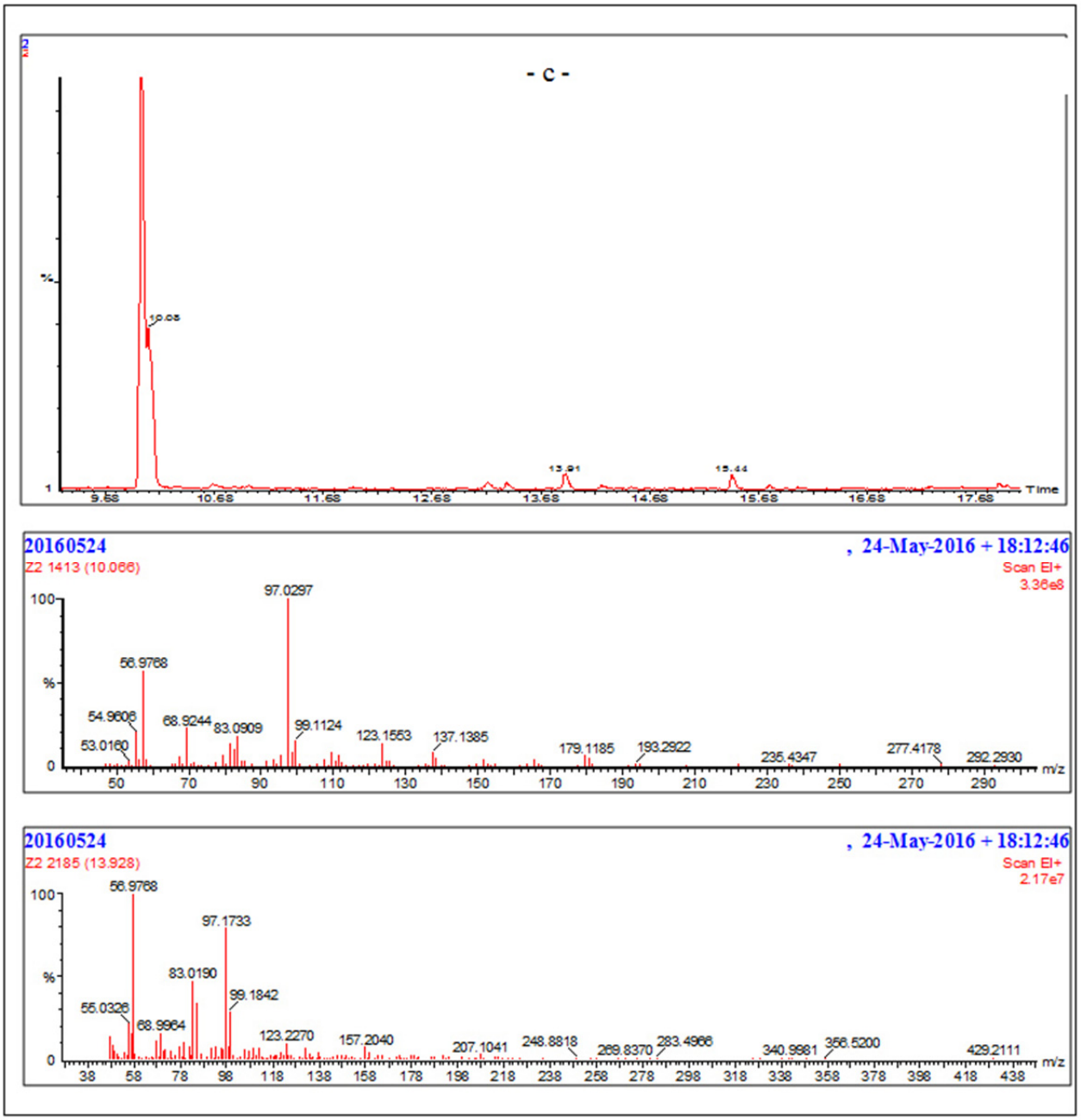

Fig. 4 **a)** Chromatogram of the sample in contact with the sunflower oil for 10 days without agitation at 40 °C; **b)** Fragmentation of the peak time retention of 10.01min; **c)** Fragmentation of the peak time retention of 13.91min.

We note the presence of two major peaks; the first has a retention time equal to 9.98 minutes with a report m/z equal to 97,10 and the second has a retention time equal to 13.86 minutes with a report m/z equal to 56.98 which correspond to the standard peak of bis 2-ethyl HexylAdipate.

From the chromatograms of the PP pellet extract and the mixed standard analyzed (Benzyl Butyl Phthalate, Bis (2-Ethyl Hexyl) Phthalate, Bis 2-Ethyl hexyl adipate, DN-Butyl Phthalate, Di-N- Octyl phthalate, diethyl phthalate, dimethyl phthalate) by GC / MS under the same operating conditions, it can be noted that the peak having the m / z ratio equal to 97 with tr = 9.98 min has substantially the same Retention of Di-Octyl Adipate (tr = 10 min). Through these spectra, it can be confirmed that the plasticizer used in the formulation of the PP pellets is Di-Octyl Adipate.

Table 5 illustrates the quantity migrated from Di-Octyle Adipat (DOA) in sunflower oil to two different temperatures, namely, 20 and 40°C.

Table 5 Migrated quantity of DOA.

Sunflower oil without agitation 20°C	Tr	9.98	13.86
	Surface	434426976	231373024
	Concentration (ppm)	$6.12*10^{-3}$	$4.23*10^{-3}$
Sunflower oil without agitation 40°C	Tr	10.01	13.91
	Surface	261922608	7731452
	Concentration (ppm)	$3.36*10^{-2}$	$2.17*10^{-1}$

From this table, we note that the areas of the peaks of samples measured in sunflower oil at 20°C are more important than those at 40°C, which means that the concentrations of DOA are more important at 20°C. In addition, the results of Table 6 highlight the influence of the temperature on the phenomenon of migration.

4. Conclusion

The monomers of the basic material or the additives incorporated in plastic can be transferred in the food, with consequences on the organoleptic plans or toxicological consequence. as the migration is a function of the affinity between the migrant and the packaged product, the phenomenon of migration depends on the composition of packaging (concentration of molecules, nature and volatility) but also that of the food.

Some of the constituents of the food are capable to get about into the packaging and change its structure; also they can activate the migration of plastic compounds. The packaging may be permeable to environmental contamination which can also alter the quality of food.

In this context, the present work had the following objectives:

- To study the interactions bottles of milk /food.
- Quantify the quantity of Di Octyl Adipate acid (DOA) migrated by the GC/MS.

In this study the phenomenon of migration to the Interfaces packaging of milk - food simulant has been studied. The migration tests have been carried out with and without agitation at 20 and 40°C in two food simulants: Sunflower oil and n-Octane.

This study has required the intervention of different techniques of analysis namely Fourier-transform infrared spectroscopy (FTIR-ATR), the atomic absorption spectrometry (AAS) and gas chromatography-mass spectrometry (GC/MS) as well an estimate of overall migration.

The applications of the FTIR spectroscopy-ATR which is a very simple technique to the analysis of samples which have undergone the tests of migration allow identifying the PP as the polymer constitutive of these bottles. The follow of the variation of the characteristics bands of this additive in function of the time of contact between the samples and food simulants has shown that a phenomenon of migration of this additives occurred.

The AAS allowed the determination of some elements attributed to the additives present in the formulation of this bottle which are: the Ca, Pb, Cd and Zn.in the samples having undergone the migration tests.

The follow of the variation of the residual of metals in the samples has highlighted the migration of additives throughout the duration of contact.

The analysis of the plastic of the selected bottle which has undergone the tests of migration by the GC/MS has confirmed what has been obtained in the study of the phenomenon of migration by the FTIR and by the AAS, because it has allowed:

- To identify the different additives contents in the formulation of the plastic used in the manufacture of these bottles which is the plasticizer (DOA)
- To clarify the migration of additives which is the DOA.
- To quantify the concentration of the DOA in the samples which have undergone the tests of migration.
- To highlight the influence of different parameters tested on the migration of additives from bottles which were in contact with the two food simulants.

Broadly, this study has therefore confirmed that the phenomenon of migration occurred to the interface bottles of milk - physiological fluid. In addition, it has shown the influence of certain parameters such as: temperature, nature of the food simulant and the agitation.

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