

GAS CHROMATOGRAPHY–MASS SPECTROMETRY DETERMINATION OF THE MIGRATION OF PHTHALATE PLASTICISERS FROM POLYVINYL CHLORID IN FOOD ALIMENTS

M. O. BOUSSOUM¹, N. BELHANECHÉ-BEMSEMERA²

(1) Faculte des Sciences de la Nature et de la Vie, Université Ibn Khaldoun, Tiaret, Algeria.

Email : idir_boussoum@yahoo.fr;

(1, 2) Laboratoire des Sciences et Techniques de l'Environnement, Ecole Nationale Polytechnique, BP 182 El-Harrach, Alger, Algeria.

ABSTRACT

In this study, the specific migration of epoxidized sunflower oil (ESO) and di-octyl phthalate (DOP) was addressed by using gas chromatography coupled with mass spectrometry. The test conditions were 12 days. Twelve circular samples of plasticized PVC were immersed in 120 ml of olive oil. A circular sample and 10 ml of food stimulant were taken off every day to be analyzed. The rate of mass variation was followed.

We first searched for the optimum operating conditions for the analysis of additives in question (ESO and DOP) in based on the measurement of retention time to increase the sensitivity and specificity of the chromatographic system chosen.

Key Words: plasticized PVC, migration, DOP, ESO, CG/SM.

NOMENCLATURE

Subscripts :

ESO: Epoxidized sunflower oil ;

PVC : Polyvinyl chloride

DOP: Di-octyl phthalate;

GC / MS: Gas chromatography coupled with mass spectrometry

1. INTRODUCTION

Polyvinyl chloride (PVC) is one of the most widely used polymeric materials in medicine. Flexible PVC is used for the manufacture of blood and blood component storage bags, intravenous solution dispensing sets, blood tubing, and so on. As PVC per se is a rigid polymer, additives in the form of plasticizers are incorporated into it to increase its flexibility and low-temperature properties [1]. Phthalates are a well-known group of plasticizers required to make polyvinylchloride (PVC) plastic materials pliable. Most PVC products contain DOP plasticizers in the range from 30 to 80 wt %. Since DOPs are not chemically bound to the plastic, they raise serious environmental contamination issue by easily leaching to the surrounding medium or fluids [2]. Phthalate esters are widely used as industrial plasticizers. In particular, di-octyl phthalate (DOP) is used in the manufacture of polyvinyl chloride (PVC) products and other plastics to achieve the desired softness, flexibility and

stability for specific applications. PVC is employed in the production of floor tiles, food wrapping film, industrial tubing, and medical devices, and is the most widely used polymer because of its availability [3].

In this study, the specific migration of epoxidized sunflower oil (ESO) and di-octyl phthalate (DOP) was addressed by using gas chromatography coupled with mass spectrometry. We first searched for the optimum operating conditions for the analysis of additives in question (ESO and DOP) in based on the measurement of retention time to increase the sensitivity and specificity of the chromatographic system chosen.

The use of capillary columns results in certain system-level injection and detection. Indeed, the volume of samples should be low to avoid saturating the stationary phase. For this, a comparison between a Split injection (injector splitter) and a Splitless injection (injection without divider) was made. The techniques of external and internal standard were compared in the case of the analysis of the DOP. Finally, two extraction solvents of different polarities were used: hexane and chloroform to determine the best extraction solvent. Sunflower oil epoxidised (ESO) was obtained by epoxidation of commercial sunflower oil; this epoxidation reaction was developed as part of a research project as part of national research programs (NRP) [4]. Its main objective is to obtain an additive (thermal stabilizer) non-toxic, from a local raw material which is sunflower oil. This addendum is intended for the plastics industry in general and that of plastic packaging in particular those intended to come into contact with foodstuffs, pharmaceuticals, cosmetics, etc.

In addition, HTE meets the new guidelines in the production of additives where the current trend is to develop new products known as green, i.e. non-toxic and do not cause harm to the environment during the discharge of materials to use outside the state of waste. Thus, there is a tendency towards replacing based stabilizers of heavy metals such as lead or cadmium, widely used until now [5], but have the disadvantage of being toxic and ecopersistants.

Preliminary studies [6, 7] have allowed, firstly, highlighting the properties of ESO as thermal stabilizer of PVC. The study of its alimentarity was raised in the case of rigid PVC [8] and plasticized PVC [9, 10]. An acute toxicity study of ESO was made. It has helped to advance the non-toxicity of the substance in the short term [11]. In all these studies, the estimated global migration is below the regulatory limit of 10 mg/dm² surface.

2. EXPERIMENTAL METHOD

2.1. MATERIALS

The PVC resin of K-Wert value of 70 produced by CIRES (Portugal), dioctyl phthalate (DOP) produced by SGP (Tunisia), the complex of stearates Zn and Ca produced by Aldrich (France) and the stearine produced by SO.G.I.S.SPA (Italy) is commercial products used without preliminary purification. The sunflower oil epoxydized (ESO) was especially prepared as described previously [12]. The level of oxirane oxygen was 5.2%. Plates were carried out according to following proportions' (the contents are expressed in grams for 100 g of PVC): 2 % for the stearate complex of Zn and Ca, 1 % for stearine, 10 % of the ESO and 40 % for the DOP (formulation of PVC plasticized: F40). PVC and additives were mixed in a two-roll mill at 140 °C and melt compressed at 170 °C under a pressure of 300 kN/m². Then circular samples having a diameter of (2 ± 0.1) mm and a thickness of (22 ± 0.1) mm were cut.

2.2. METHODS

PVC discs cut out in a plate of the F40 formulation are pre-soaked in n- heptane. A of the intervals of times and temperature determined, a disc left solvent. It is weighed before and after pre-soaking then dried during a given time.

2.3. GAS CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY

This technique has been used to identify the nature of the substances present in the simulator and quantify additives in PVC samples. The analysis gas chromatography coupled with mass spectrometry (GC / MS) was used in the case of the following additives: DOP & ESO.

2.3.1. MATERIAL USED BRAND

- ♣ Chromatograph Perkin Elmer PE-5MS;
- ♣ Mass spectrometer brand Perkin Elmer;
- ♣ Capillary column of internal diameter of 0.25 mm, length 30 m and a film of 0.25 μm (polar phase: 5% diphenyl 95% dimethyl polysiloxane.);
- ♣ Automatic injector.

2.3.2. CONDITIONS FOR ANALYSIS BY GC / MS**2.3.2.1. PLASTICIZER DOP**

- ▶ Mode: electron impact;
- ▶ Pressure: 31 kPa;
- ▶ Ionization potential: 70 eV;
- ▶ Carrier gas: Helium;
- ▶ Scan interval: 50 - 450 uma;
- ▶ Injection volume: 1.0 μl (injection);
- ▶ Interface temperature: 280 °C;
- ▶ Temperature programming: In the beginning, 3 min at 90 °C, then rising by 6 °C to 250 °C and maintained at 250 °C for 13 min.
- ▶ Etalon interne: Dibutyl phthalate (DBP), density of 1.04 and molecular weight of 278.35 g / mol derived from ALDRICH.

2.3.2.2. THERMAL STABILIZER ESO

- ▶ Interface temperature: 300 °C;
- ▶ Temperature programming: At first, 1 min at 90 °C, then rising 10 °C to 300 °C and maintained at 300 °C for 20 min.
- ▶ Internal standard Methylnonadecanoate (C₂₀H₄₀O₂) (ALDRICH).

2.3.3. PROCEDURE FOR IDENTIFICATION AND QUANTIFICATION WITH GC / MS**2.3.3.1. PLASTICIZER DOP**

Sample preparation for analysis was conducted according to the protocol described by Wang and Strom [13]:

Take about 0.2 g of PVC pellet and put in a soxhlet apparatus for 8 hours using 3 / 4 volume soxhlet extraction solvent (hexane or chloroform), then transferring the extract into a vial measure, complete with solvent extraction and an aliquot taken for analysis.

2.3.3.2. SUNFLOWER OIL EPOXIDISED ESO

Sample preparation for analysis was conducted according to the protocol described by Wang and Strom [13] and Simoneau Fautoni and [14] which includes the following steps:

- ◆ Take about 0.2 g of PVC pellet and dissolve in 8 ml of THF;
- ◆ PVC precipitate by adding methanol (volume of THF / methanol of 1: 2.5 v / v);
- ◆ The filtrate is separated from the PVC and then dried at 80 °C for 30 min;
- ◆ Dissolve the residue in 1 ml of nitric acid supra pure.

3. RESULTS**3. ANALYSIS OF DOP****3.1. COMPARISON OF INJECTION METHODS**

Samples must have a sufficient concentration so that they can be analyzed with sufficient reproducibility. Two injection methods were compared:

- Injection split the sample is divided into two streams one of which enters only in the column and the other escapes through a leak.
- Injection splitless: the solution is injected vanished then dragged into the capillary column where it condenses.

By comparing the chromatograms of samples analyzed by both methods, we find that the splitless injection mode ($t_r = 40$ min) gave retention times shorter than those obtained by split injection ($t_r = 71$ min), which we can choose the operating conditions to apply.

3.2. CHOICE OF SOLVENT EXTRACTION

The choice of solvent meets two criteria: it must have a great ability to not only solvent to extract the substance almost completely, but also to make this transfer in a reduced volume to facilitate concentration. The second quality is the volatility of the solvent extraction is interesting that during the partial evaporation thereof.

The results obtained by GC / MS analysis of the internal standard of DOP is dibutyl phthalate (DBP), whose initial concentration is 2.4 ppm by the two solvents namely hexane and chloroform are given in Table 2.1.

	Temps de rétention (min)	Surface (μm^2)
Hexane	40,26	12219
Chloroforme	28,79	87193

Table 2.1: Choice of extraction solvent.

From this table, it appears that chloroform extract has a retention time of DBP less than that of hexane. In addition, the surface of the chloroform extract of the standard peak DBP is greater than that of the extract of the hexane, chloroform which can be considered as a solvent of choice for extraction of the additives in question. The differences obtained are due to the fact that he is unlike polar hexane.

3.3. COMPARISON OF METHODS OF INTERNAL AND EXTERNAL CALIBRATION

To assess the amount of plasticizer (DOP) in PVC cylinders witnesses and those who have suffered the migration test at 40 °C with and without pre-soaking in n-heptane, two techniques of internal and external calibration were compared. The technique of external calibration is based on the preparation of solutions of different concentrations of DOP alone, while the internal calibration technique is based on the initial introduction of a mixture of internal standard (DBP) and DOP with different concentrations. Figure 2.1 shows the chromatograms of different samples analyzed.

The method of internal calibration gave better results because it facilitates the positioning of the peak of the samples analyzed.

By comparing the results obtained, we find that areas of the peaks of standards assayed in DOP olive oil are larger than those in aqueous ethanol, which means that concentrations of the latter are more important in the case environment simulator bold. The determination of the DOP in both environments simulators is achieved by GC / MS by measuring each of the chromatograms obtained the area of peak of standard DOP. A calibration curve was established, on the Y axis of the peak areas of standard DOP ($m/z = 149$ and $r = 28.77$) and the X axis the different concentrations of DOP. The values of DOP concentrations are given in Table 2.2.

Milieux simulateurs		Ethanol aqueux		Huile d'olive brute			
		Extrait par le chloroforme		Extrait par le chloroforme		Extrait par l'hexane	
		ppm	%	ppm	%	ppm	%
Concentration [DOP]	0 jours	2,2300	34,1000	2,2300	34,1000	0,0160	0,2450
	11 jours sans prétrempage	1,2400	18,9602	0,8300	12,6900	0,0042	0,0660
	11 jours avec prétrempage	0,7200	11,0100	0,0300	0,4600	0,0027	0,0413

Table 2.2: Number of DOP migrated from the plastic formulation F40.

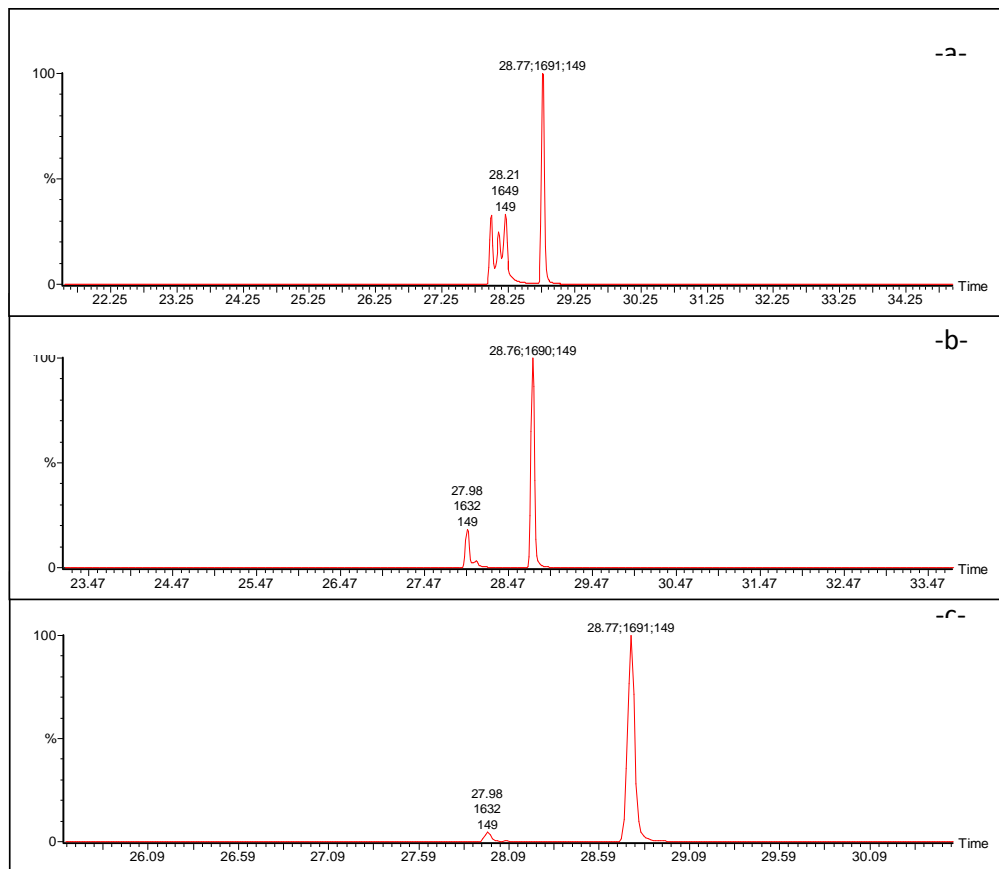


Figure 2.1: Chromatogram of the product by chloroform extraction of the specimen PVC F40:

- a- witness.
- b- in contact with ethanol for 11 days without pre-soaking.
- c- placed in contact with ethanol for 11 days with pre-soaking.

According to this table, it appears that:

- The best solvent is chloroform as hexane for extraction of additives considered.
- The amount of DOP migrated in the case of specimens tested with migration in olive oil is greater than that determined in aqueous ethanol, which means that the nature of the simulator environment plays a very important role in the transfer of DOP, since each simulator has a different behavior by its physicochemical properties (degree of affinity presented vis-à-vis the DOP).
- The pre-soaking decreased migration of DOP.

4. ANALYSIS OF THE ESO

Quantifying the ESO was performed by GC / MS (electron impact mode IE), using $m / z = 74$ which corresponds to the peak of the standard ESO [15, 16] and $m / z = 281$ which is characteristic peak of methyl esters of ESO C18: 2 [17]. The analysis was performed on samples of the three formulations studied and the samples tested migration. The ESO was found in the three formulations. Figure 3.1 shows the chromatograms of different samples analyzed.

For each chromatogram, determine the concentration of ESO by establishing a calibration curve (peak area according to the different concentrations).

The results are summarized in Table 3.1.

<i>Formulations</i>	<i>F</i>		<i>F0</i>		<i>F40</i>	
	ppm	%	ppm	%	ppm	%
<i>[HTE] migrée</i>						

0 jours	1,6238	99,2700	1,6025	97,7134	1,3030	96,4185
12 jours sans prétrempage	0,7125	43,4450	0,4800	29,2683	0,3550	21,6463
12 jours avec prétrempage	0,3138	19,1340	0,1575	9,6037	0,1500	9,1643

Table 3.1: Number of ESO migrated into olive oil (extracted by chloroform).

According to this table, it appears that:

- The quantity of migrated ESO in the case of the formulation F is greater than other formulations (F0 and F40) and this can be explained by the presence of other additives in PVC test formulations and F0, F40 slow the migration of the ESO.
- The pre-soaking decreased migration of ESO.

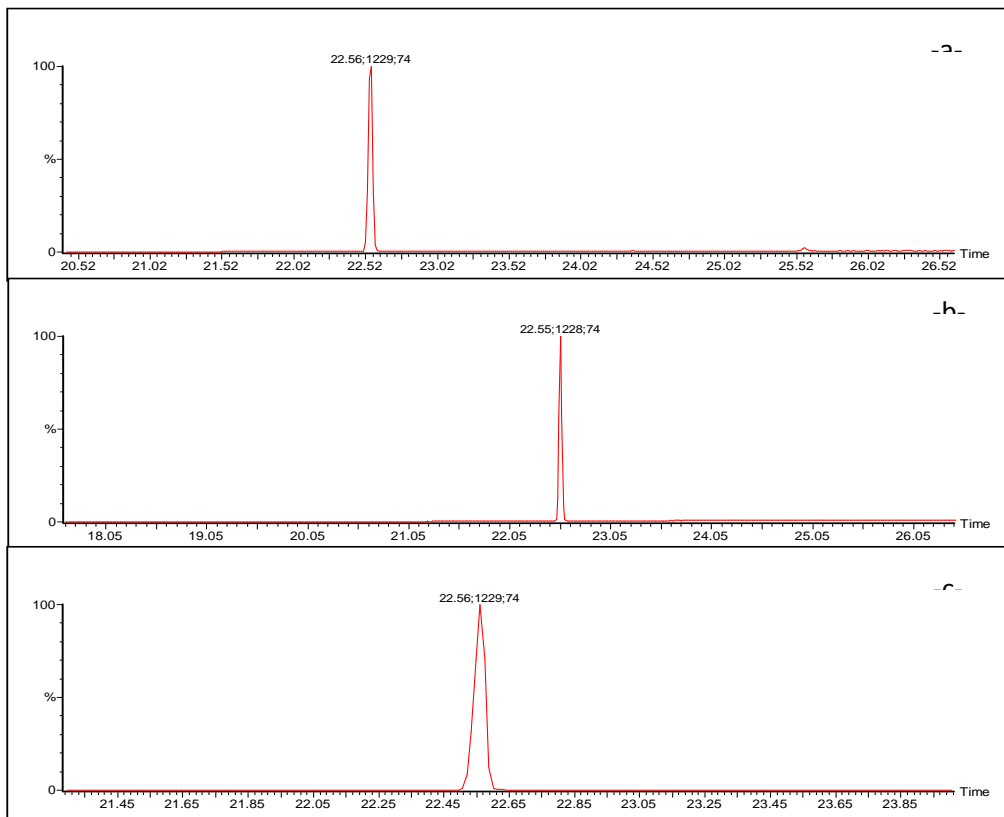


Figure 3.1: Chromatogram of the product by chloroform extraction of the specimen PVC F: - witness.
 - Without pre-soaking in contact with raw olive oil for 12 days.
 - With pre-soaking in contact with raw olive oil for 12 days.

5. CONCLUSION

The analysis by GC / MS, allowed:

- To select the operating conditions and injection mode (splitless injection) to be applied to the analysis of the DOP and the ESO.
- Obtain the chromatograms of the DOP, the ESO, witness and specimens that have undergone testing migration.

- Consider chloroform as the best solvent for the hexane extraction of additives in question and the method of internal calibration as the best method of analysis of methyl esters.
- The amount of DOP migrated in the case of test specimens (F40) who tested for migration into olive oil is greater than that determined in aqueous ethanol.
- The quantity of migrated HTE in the case of the formulation F is greater than other formulations (F0 and F40).

Overall, this study has confirmed that the migration took place and that the pre-soaking reduces the migration of additives in PVC samples.

REFERENCES

- [1]: I.Rie, N.Hiroyuki, "High-throughput determination of mono- and di(2- ethylhexyl)phthalate migration from PVC tubing to drugs using liquid chromatography–tandem mass spectrometry", *Journal of Pharmaceutical and Biomedical Analysis* 39 (2005) 1036–1041
- [2]: Y. C. Ling, C. Y. Chen, A.V. Ghule, "Rapid identification of phthalates in blood bags and food packaging using ToF-SIMS", *Applied Surface Science* 231–232 (2004) 447–451.
- [3]: W. Huber, B. Grasl-Kraupp, Hepatocarcinogenic potential of DEHP in rodents and its implications on human risk. *Crit. Rev. Toxicol.* 26, 365–481. (1996).
- [4] : Projet de recherche N° AE 197/05 intitulé «Epoxydation de l'huile de tournesol et applications», Premiers Programmes Nationaux de Recherche (PNR1), (1998-2001).
- [5] : Livre vert de la communauté européenne COM (2000) 469, 26/07/2000.
- [6] : M.T.Benaniba, «Epoxydation de l'huile de tournesol et application à la stabilisation thermique du polychlorure de vinyle », Thèse de doctorat d'état, Université de Sétif, (2003).
- [7]: M.T.Benaniba, N.Belhaneche-Bensemra, G.Gelbard, «Stabilizing effect of epoxydized sunflower oil on the thermal degradation of PVC », *Polym.Degr & Stab*, N° 74, PP 501-505 (2001).
- [8]: D.Atek, N.Belhaneche-Bensemra, « FTIR investigation of the specific migration of additives from rigid poly (vinyl chloride) », *Eur. Polym. J.* 41, PP 707-714, (2005).
- [9] : M.O.Boussoum, D.Atek, N.Belhanache-Bensemra, « Etude des interactions contenant -contenu dans le cas polychlorure de vinyle stabilisé à l'huile de tournesol époxydée », *Projet de Fin d'Etude*, Ecole Nationale Polytechnique, (2003).
- [10]: M.O.Boussoum, D.Atek, N.Belhanache-Bensemra, «Interactions between Poly (vinyl chloride) stabilised with expoxidized sunflower oil and food simulants », *J. Polym. Degrad. and Stab.*, N° 91, PP 579-584, (2006).
- [11]: D.Atek, « Etude de la migration spécifique et de la toxicité de l'huile de tournesol époxydée », *Mémoire de magister*, Ecole Nationale Polytechnique, (2002).
- [12]: D. MESSADI, N. FERTIKH and A. E. H. GHEID, "Study of exchanges between a non-solvent and plasticizer disperse in a plastic disc," *Eur. Polym. J.* Vol. 27, No. 11, PP. 1187-1193, (1991).
- [13]: Qian Wang, B.K.Storm, "Separation and analysis of low molecular weight plasticizers in poly (vinyl chloride) tubes", *Polymer Testing* N° 24, PP 290-300, (2005).
- [14]: L.Fantoni, C.Simoneau, "European survey of contamination of homogenized baby food by expoxidized soybean oil migration from plasticized PVC gaskets", *Food Additives & Contaminants*, Vol.20, N° 11, PP 1087-1096, (2003).
- [15]: M.V.Gonzalez-Rodriguez, « Determination of antioxidant migration levels from low-density polyethylene films into food simulants », *Journal of Chromatography A*, N° 1018, PP 53-62, (2003).
- [17]: G.CAMERON, "A new approach to the analysis of phtalate esters by GC/MS", *Agilent Technologies Inc.*, Palo Alto, Californie, État-Unis, (2001).
- [19] : Norme ENV 1186-4, «Détermination des esters méthyliques d'acides gras », (1994).