Microwave-assisted extraction by fast sample preparation for the systematic analysis of additives in polyolefins by high-performance liquid chromatography

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Abstract

This paper presents a new approach for complete and systematic analysis of organic additives in polyolefins. The proposed procedure is a convenient combination of sample preparation, performed by microwave-assisted extraction (MAE), and direct chromatographic evaluation of extract by high-performance liquid chromatography coupled with ultraviolet and evaporative light scattering detection. In particular two microwave-assisted processes are reported and discussed: the one-step MAE, useful for additives with low–medium dipolarity (like stabilizers, flame retardant, antistatics, slip and processing agents), and the two-step MAE, useful for additives with either high dipolarity (like organic salts, antigasfading, antiacid, nucleating agent) or high molecular mass (like polymeric hindered amine light stabilizers). Both the proposed processes have been tested on representative additives in five commercially common polymeric matrices, demonstrating their satisfactory analytical results, in terms of repeatability and percentage recoveries, and their good performances, in terms of safety and time/solvent consumption, in comparison with those of traditional extraction methods. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyolefins are the most widely used thermoplastic polymers and are employed in an extremely wide range of applications. Commercial polyolefins need the addition of suitable amounts of additives to prevent their degradation both during processing and their lifetime and to get best performances in their specific end-use applications. Commonly used additives are organic and inorganic products belonging to different chemical classes that can be grouped in the following main families: primary and secondary stabilizers, antiacids, UV stabilizers, antistatics, an-

tigasfadings, nucleating agents, slip agents, flame retardants, surfactants, mineral fillers and pigments.

Evolution of additive packages, and progressive use in food/medical packaging, leads to improved end-use performance but requires the resolution of analytical problems in terms of swiftness of response, more accurate quantification and more understanding of degradation and/or interaction between additives present in the same polymeric matrix.

The analytical evaluation of the additives can be performed with different techniques, mainly

1. Spectrophotometry (ultraviolet, infrared) [1], that has to be directly applied to the polymer. This technique is not applicable to matrices containing fillers or strongly pigments. Moreover, when

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many additives are present in the same sample, it is often unable to give reliable quantification, and it is not specific enough to distinguish between degraded and undegraded compounds present contemporarily in the same polymer.

2. Atomic absorption [2], X-rays fluorescence [3], Kjeldahl digestion used for the determination of elementary components characterising the additive. These techniques are highly sensitive but not specific, and only useful for a few additives.

3. Chromatographic techniques: gas chromatography (GC) [4–7] and, mainly, high-performance liquid chromatography (HPLC) coupled with ultraviolet (UV) [8–14] or evaporative light scattering detection (ELSD) [15,16] or mass spectrometric (MS) detection [17,18], in recent years, have begun to be the most common way to determine additives in polyolefins. The techniques, although only applicable to organic compounds, give high sensitivity and specificity on qualitative and quantitative evaluation of complex additive mixtures, but need laborious sample preparation involving long and difficult solvent extractions of the relevant compound from polymeric matrices [19,20].

In fact, extraction of additives is traditionally performed in the following ways:

1. Three 6-h refluxing of chlorinated solvents, under magnetic stirring.

2. Twelve 16-h boiling with chlorinated solvents in a Soxhlet apparatus [21].

3. Dissolution of polymer with either substituted aromatic or hydrogenated naphthalene solvents followed by coagulation with alcohol [22].

4. Extraction in aliphatic solvents using ultrasonic apparatus [23].

Extraction of additives, before the chromatographic analysis, often needs a complicated second step involving reprecipitation of the polymeric fraction.

The introduction in recent years of either supercritical fluid extraction (SFE) [24] or pressurised liquid extraction (PLE; Dionex trade name accelerated solvent extraction) [25–27] techniques has given, in comparison with traditional procedures, enormous reductions in solvent volume and sample treatment time. Nevertheless, they require grinding of polymeric matrix; moreover, in many cases, they do not have simplified procedures to eliminate soluble oligomeric fractions of polyolefinic matrix solubilized in extraction liquids and, besides, they do not give complete recovery of organic additives with high polarity e.g. organic salts.

Therefore, the demand to have a rapid, efficient and cheap method capable of making a complete extraction of all organic additives from different kinds of polyolefins prompted us to investigate the promising performances of the microwave-assisted extraction (MAE) technique. In fact, the aim of this study was to develop the existing MAE methods [28,29] and set microwave-assisted processes (MAP) from different kinds of unground polyolefinic matrices by using solvent mixtures with the lowest toxicity, heated through microwave energy.

A crucial aspect of the setting up of MAPs was to obtain additive extraction with minimal solubilization of the oligomeric fraction, giving extracts ready for direct HPLC injection.

Most types of commercial polyolefins e.g. polypropylene (homo) (PP), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), ethylene–propylene copolymer (EP) either crystalline or with a high level of amorphous fraction and poly-1-butene (PB) have been tested.

For each type of polymer, two MAPs, named, respectively one-step microwave-assisted extraction (OSM) and two-step microwave-assisted-solvent extraction (TSM) were set up. OSM procedures are useful for low–medium polarity additives and TSM for medium–high polarity additives.

The validity of both OSM and TSM procedures was verified on five representative additives for polyolefins and the effectiveness was tested with the most common additives belonging to different chemical classes. All the OSM and TSM extraction solutions were monitored by reversed-phase liquid chromatography (RPLC) with either UV or ELSD.

The extraction and sample preparation times, relative volumes of solvent consumption, safety aspects and additive recoveries of proposed MAPs were compared with the traditional extraction methods.

2. Experimental

2.1. Chemicals

All the extraction solvents: acetone, *n*-hexane *n*-heptane, methanol, isopropanol and ethyl acetate

were of analytical quality and were obtained from Carlo Erba (Milan, Italy). Acetonitrile, water, iso-propanol, methanol and trifluoroacetic acid reagent, used for the HPLC analysis were all of LC grade and were obtained from Merck (Darmstadt, Germany).

The additives: Irganox PS802 (thiodipropionic acid, dioctadecyl ester), Irgafos 168 [tris(2,4-di-*tert.*-butylphenyl)phosphite], Irganox 1010 (pentaerythritol tetrakis [3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propionate], sodium benzoate and Irganox 1425 (3,5-di-*tert.*-butyl-4-hydroxybenzyl phosphonic acid, monoethyl ester, calcium salt), were bought from Ciba (Basle, Switzerland).

2.2. Equipment

MAEs were performed using a MES-1000, 950-W, laboratory microwave extraction system (CEM, Mathews, NC, USA) equipped with 12-vessel position carousel: the instrument controls either pressure (P) or temperature (T), depending on which parameter reached its control set point first. The tested polymers, after addition of the relevant additives, were dry-mixed in a laboratory mechanical mixer and pelletized at 230–360°C by a TR30 single screw Bandera extruder (Milan, Italy).

The porosity and superficial areas of TSM extracted polymers were performed with a Sorptomatic 1900, Carlo Erba nitrogen porosimeter.

The X-ray crystallinity of TSM extracted polymers were taken by a PW 1710, Philips (Eindhoven, The Netherlands) X-ray reflection powder diffractometer. The photos of micronized polymers were taken by a SEM 515, Philips scanning electron microscope (SEM).

HPLC analysis of MAP extracts were done by a model 9012 Varian (Palo Alto, CA, USA) ternary gradient liquid chromatograph equipped with a Rheodyne model 7125 (Cotati, USA) manual injection valve and a Polychrome 9065 (Varian), UV diode array plus a Sedex 45 S.E.D.E.R.E. (Alforville, France) evaporative light scattering detectors connected in series.

A LiChroCart RP18 code 15539, 250×4 mm I.D. column prepacked with 5.0 μm C_{18} microspher (Merck) were used for the HPLC analysis of Irgafos 168, Irganox PS802 and Irganox 1010. A LiChroCart RP8 code 16052, 125×4 mm I.D. column prepacked with 4.0 μm C_8 superspher endcapped (Merck) was

used for the HPLC analysis of sodium benzoate; a LiChroCart RP-8 code 50332, 250×4 mm I.D. column prepacked with 5.0 μm C_8 microspher (Merck) was used for the HPLC analysis of Irganox 1425.

HPLC quantitative measurements were given by a Star, Varian, workstation and were performed in external standard mode, by comparing appropriate additive standard solutions.

2.3. Polymer samples

MAPs were performed on different kinds of either granular or Spheripol form polymers, all produced by Montell Polyolefins. A 3-kg amount of each testing polymer was dry-mixed for 5 min with the additive package of interest and pelletized at 230–260°C.

In particular the OSM extraction tests were performed on matrices with the following composition
1. Isotactic PP containing about 5% (w/w) of 25°C xylene soluble fraction
2. HDPE containing 1.3% of methyl groups per 100 carbon atoms.
3. LLDPE containing 14.0 and 8.0% (w/w) propylene and 1-butene, respectively.
4. Ethylene–propylene heterophasic copolymer (HECO) containing 10.2% (w/w) ethylene.
5. Ethylene–propylene heterophasic copolymer and ethylene–propylene amorphous copolymer blend (Supersoft) containing 23.8% (w/w) ethylene and 67.0% (w/w) of a fraction soluble in xylene at 25°C.
6. PB.

The PP, HDPE, LLDPE, HECO and Supersoft polymers were stabilized with Irganox 1010, Irganox PS802, Irgafos 168 plus G.M.S. 40 (dispersing agent) and calcium stearate (antiacid agent) mixture; while PB was mixed with Irganox 1010 and Irgafos 168 only.

The TSM extraction tests were performed on PP matrices containing Irganox 1010, Irgafos 168, sodium benzoate (1000 ppm) and Irganox 1425 (1000 ppm) and pelletized under the same conditions as the OSM samples.

All the OSM and TSM polymers contained a small amount (100–200 ppm) of processing stabilizer Irganox 1076 (octadecyl 3-(3,5-di-*tert.*-butyl-4-hydroxy phenyl) propionate).

2.4. MAP description

2.4.1. OSM conditions

Duplicate samples of 2.5 g of polymer were put into the microwave extraction vessel, mixed with 25 ml of ethyl acetate–*n*-hexane (75:25, v/v) and finally, heated for 15 min in a microwave oven with 1000 W microwave power supplied.

The extraction temperatures were: 125°C for PP, HDPE and HECO; 100°C for LLDPE and Supersoft; 80°C for PB.

The time required for reaching the set temperature depends on the number and type of samples put in the carousel contemporarily and is not included in the extraction time reported below. After the extraction, the vessels were allowed to cool to ambient temperature before opening.

Before injection on the HPLC each extract was filtered using a 0.45-μm porosity PTFE membrane syringe filter.

2.4.2. TSM conditions

The extraction of both organic salts sodium benzoate and Irganox 1425 from PP samples was performed by setting up own TSM. The first step (micronizing) gave the solution and then the recrystallization of the polymer as very small particles with dimensions of 1 μm or less. The second step (leaching) dissolved the additive via the addition of a suitable amount of an organic polar solvent in the same extraction vessel.

2.4.2.1. First step (micronizing)

In Table 1 the microwave oven heating conditions, the volume and kind of micronizing solvent mixtures useful for different polymeric matrices are shown.

2.4.2.2. Second step (leaching)

After the micronizing treatment, the vessels were allowed to cool to about ambient temperature, then opened, mixed with 25 ml of methanol, reclosed and, finally, shaken by hand for 15–20 s. In this way in both cases sodium benzoate and Irganox 1425 were completely solubilized.

Similarly to the OSM, a suitable amount of extraction solution was filtered by a 0.45-μm porosity PTFE membrane syringe filter before being injected in a HPLC system for analysis of extracted additives. The heating time necessary to obtain the polymer micronization depends on the number of samples in the microwave oven carousel heated contemporarily. The heating times, reported in Table 1, refer to two samples treated contemporarily.

2.5. HPLC–UV/ELSD analysis

2.5.1. Analytical conditions for OSM extracts

The standard and the sample solutions were injected into the chromatograph by means of a 10-μl sample loop. The chromatographic conditions were as follows: flow-rate, 2.0 ml/min; column temperature, 50°C; eluents of the mobile phase, water, acetonitrile, isopropanol; the eluent gradient is reported in Table 2. UV detector: wavelength, 273 nm; ELSD: temperature 40°C, gain 6, pressure of nebulizing gas 2.5 bar.

The identification of each compound present in the sample solution was made by comparing its retention time with that of the corresponding peak in the standard solution. Quantification of the UV absorbent additives Irganox 1010 and Irgafos 168 was carried out by comparison with an external standard solution of the pure additives. Quantification of Irganox

Table 1

Micronizing step conditions of the TSM procedures used for different kinds of polymeric matrices: polymer sample amount: 2.0 g; microwave power: 1000 W; solvent mixture volume: 25 ml

Polymer	Solvent mixture		Temperature (°C)	Heating time (min)
	Constituents	(v/v)		
PP	Acetone–*n*-hexane	25:75	130	30
HDPE	Acetone–*n*-heptane	20:80	135	40
LLDPE	Isopropanol–*n*-heptane	25:75	125	30
HECO	Acetone–*n*-hexane	25:75	125	30
Supersoft	Acetone–*n*-hexane	50:50	125	30
PB	Ethyl acetate–*n*-hexane	75:25	140	30

Table 2
Ternary gradient elution program for HPLC analysis of organic additives extracted from polymers by OSM procedure

Time (min)	Water (%)	Acetonitrile (%)	Isopropanol (%)
0	12	88	0
0.1	5	65	30
10	0	65	35
18	0	65	35

PS802 (non-UV absorbent) was carried out using a suitable calibration curve obtained by analysis of at least five solutions with different concentrations of pure additive.

2.5.2. Analytical conditions for TSM extracts

The standard and the sample solutions with sodium benzoate were injected into the chromatograph by means a 10-µl sample loop. The chromatographic conditions were as follows: flow-rate, 1.0 ml/min; column temperature, 50°C; isocratic elution with water containing 0.05% (v/v) of trifluoroacetic acid–acetonitrile–methanol (60:20:20, v/v); UV detector wavelength, 230 nm.

To maintain the original performances of stationary phase over time, it is important to wash the column for at least 2 h with isocratic elution with acetonitrile–isopropanol (65:35, v/v) at a flow-rate of 1 ml/min after about 5–6 analysis runs. In fact this washing step causes the elution of the other organic additives (e.g. stabilizer, slip and antistatic agents) and their degradation products not eluted during the elution run of sodium benzoate.

The standard and the sample solutions containing Irganox 1425 were injected into the HPLC chromatograph by means of a 500-µl sample loop and eluted using the on column sample enrichment (OCSE)

method. The chromatographic conditions were as follows: flow-rate, 1.0 ml/min; column temperature, 50°C; the eluents of the mobile phase were water, acetonitrile and methanol. The eluent gradient was performed in three steps as listed in Table 3. The UV wavelength of the detector was 282 nm. Identification and quantification of Irganox 1425 was carried out by comparing in external standard mode with a suitable methanolic calibration solution of pure additive.

3. Results and discussion

3.1. OSM extract analysis

Fig. 1 shows two HPLC chromatograms, respectively obtained by UV and ELS detectors, relative to a quantitative analysis of additives extracted by OSM from a PP pelletized sample.

Table 4 reports the concentrations of additives, present in OSM extracts obtained from the six polymeric matrices tested. The data demonstrate the efficiency of all OSM extractions and the low concentration of polymeric fraction solubilized in the same extraction liquids.

The repeatability of the HPLC–UV quantitative evaluation of Irganox 1010 and Irgafos 168, respectively, evaluated on the basis of six independent OSM extractions from the same PP sample, gave the following results: average value (ppm, w/w): $x=$ 490, relative standard deviation (RSD)=9.8%, confidence limits (95% probability) for a single analysis (ppm, w/w): ±19.6 ($\pm4.0\%$); average value (ppm, w/w): $x=1010$, RSD=20.2%, confidence limits (95% probability) for a single analysis (ppm, w/w): ±40.4 ($\pm4.0\%$).

Table 3
Ternary gradient elution program for HPLC analysis of Irganox 1425

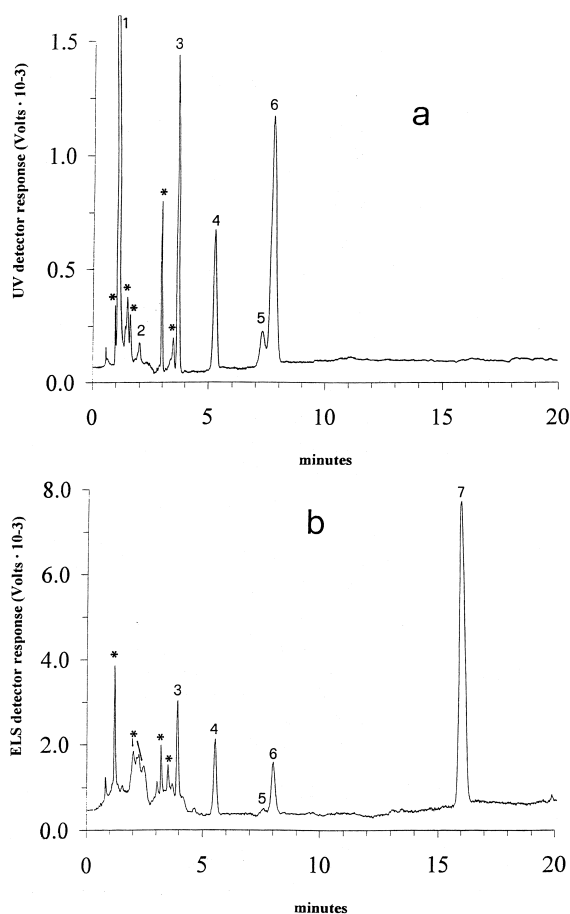| Elution step	Time (min)	Water (%)	Acetonitrile (%)	Isopropanol (%)
On column sample enrichment	0	0	80	20
of Irganox 1425	2	0	80	20
Elution of Irganox 1425	4	30	0	70
	9	30	0	70
Column reconditioning	9.1	0	80	20
	16	0	80	20

Fig. 1. HPLC chromatograms of OSM extraction solutions from polypropylene sample; (a) trace of the UV detection response, (b) trace of the ELSD response; peaks: 1=OSM solvent, 2=2,4 di-*tert*.-butylphenol (hydrolysis product of Irgafos 168), 3= Irganox 1010, 4=Irgafos 168 phosphate (oxidizing product of Irgafos 168), 5=Irganox 1076, 6=Irgafos 168, 7=Irganox PS802, *=unidentified degradation products of Irganox 1010; see text for HPLC–UV/ELSD conditions and additive concentrations.

The repeatability of the HPLC–ELSD quantitative evaluations of Irganox PS802 evaluated in the same PP sample gave the following values: average value (ppm, w/w): $x=3060$, RSD=153%, confidence limits (95% probability) for a single analysis (ppm, w/w): ±306 (± 10.0%).

3.2. Criteria to set up the OSM conditions

During the setting up of the OSM, the following parameters were optimized

- ratio between polymer amount and solvent mixture volume
- extraction temperature
- heating time in order to obtain a procedure as similar as possible for all tested polymeric matrices, but allowing both a high additive recovery and giving minimum solubilization of the oligomers extracted from polymeric matrix.

3.2.1. Ratio between sample weight/solvent mixture volume

It was noted that 2.5 g of polymer and 25 ml of solvent extraction mixture are optimum amounts to obtain efficient extractions for each kind of polymer. In fact these quantities allow, on one hand, a highly representative sampling of the polymer and, on the other hand, they do not produce an excessive dilution of the extracted additives for the HPLC sensitivity limits. Moreover they allow the direct HPLC injection of the extraction liquids without further concentration.

It has been demonstrated that with a polymer amount >2.5 g, for the same volume of extraction solvent (25 ml), effective and complete extractions may not be obtained, especially from polymeric matrices with high content of amorphous fraction (e.g. LLDPE, Supersoft). In fact this kind of matrix, because of a partial fusion effect suffered by heating treatment impedes a complete transfer of some additives from polymer to extraction liquid.

3.2.2. Extraction temperature

It is known that the temperature is an important parameter in all liquid–solid extraction processes. Because of heating, the polymer, suspended in OSM liquid, undergoes a 'swelling' effect that, making it more permeable to the solvents, helps with the extraction of additives. In the extraction of a polymer based on pelletized PP by the traditional refluxing procedure (69°C) under magnetic stirring with the same solvent mixture used for OSM, an acceptable recovery of Irgafos 168 (>95%) was observed only after 6 h of heating and insufficient recovery (90– 93%) of Irganox PS802 and Irganox 1010 was obtained even after 12 h of extraction.

It has been demonstrated that a temperature of 125°C is optimum for a good extraction of additives from highly crystalline matrices like PP and HECO.

Table 4
Additive concentrations and related recoveries (%) given by duplicate HPLC analysis of the OSM extract liquid from six tested polymers

Polymer	Irganox 1010			Irgafos 168			Irganox PS802			Polymeric fraction soluble (gr.%)[b]
	Expected (ppm)	Found (ppm)	Recovery (%)	Expected (ppm)	Found[a] (ppm)	Recovery (%)	Expected (ppm)	Found (ppm)	Recovery (%)	
PP	500	480	>95	1000	1040	>95	3000	3100	>95	0.8
HDPE	300	310	>95	800	820	>95	1000	1050	>95	0.2
LLDPE	400	410	>95	1000	1020	>95	2000	1850	93	0.5
HECO	500	530	>95	1000	1040	>95	3000	2900	>95	0.6
Supersoft	500	500	>95	1000	1100	>95	3000	3300	>95	0.7
PB	600	540	>95	2000	2020	>95	–	–	–	1.0

[a] Concentration given by the sum of Irgafos 168 and Irgafos 168 phosphate (its oxidative degradation product).
[b] W/w with respect to polymer put in extraction.

Temperatures >125°C, even if the extraction time becomes shorter, could cause polymer collapse or fusion, which could obstruct the extraction efficiency. On the other hand, temperatures <125°C can give an insufficient swelling effect on these matrices, consequently with an incomplete recovery of additives with medium–high polarity like Irganox 1010 in the short times foreseeable for OSM. Instead, matrices with high content of amorphous fractions (e.g. LLDPE, Supersoft) must be extracted at a temperature <125°C, because at this temperature they collapse or show phenomena of seeming fusion or they become excessively soluble in the OSM liquids, thus causing a loss of additives via encapsulation in the polymer when it coagulates at room temperature.

3.2.3. Heating time

The extraction time of the additives in OSM depends both on the kind of treated polymeric matrix and on the chemical nature of the extracting compound. In particular, the matrices with crystalline structure (e.g. PP or HDPE) are extracted with the most difficulty and that the compounds with high polarity (e.g. Irganox 1010) show the slowest extraction rates. In contrast, extraction from matrices with low crystal structure (e.g. LLDPE) or with high content of amorphous fractions (e.g. Supersoft) requires, for each kind of additive, very short extraction times: from 2 to 5 min. The need to make the OSM conditions uniform for all kinds of polymeric matrices suggested a time of 15 min as suitable.

Figs. 2 and 3, respectively show the percentage recoveries of the OSM extraction times, related to the three tested additives extracted from PP and HDPE pelletized samples. Irgafos 168 is rapidly extracted from both polymers (in about 2 min), Irganox PS802 shows an acceptable recovery after 10 min and a satisfactory recovery of Irganox 1010 after only 15 min.

3.3. TSM extract analysis

3.3.1. Sodium benzoate and Irganox 1425

Comparing the results of HPLC analysis (see representative chromatograms in Figs. 4 and 5) with those calculated by X-ray fluorescenc determination of sodium or calcium, respectively, on PP original sample, the accuracy of the analytical quantification of both additives, sodium benzoate and Irganox 1425 extracted by TSM, appears satisfactory, giving in any case recovery levels better than 95%.

In particular, the repeatability of HPLC analysis of sodium benzoate, evaluated on the basis of six independent TSM extractions from the same PP sample containing theoretically 1100 ppm of additive, gave the following results: average value (ppm, w/w): $x=1085$, RSD=32.1%, confidence limits (95% probability) for a single analysis (ppm, w/w): ±64 (±5.9%)

The HPLC repeatability of Irganox 1425, also evaluated on the basis of six independent TSM extractions from the same PP sample containing theoretically 1100 ppm of additive, gave the following results: average value (ppm, w/w): $x=1048$, RSD=17.7%, confidence limits (95% probability) for a single analysis (ppm, w/w): ±35 (±3.4%).
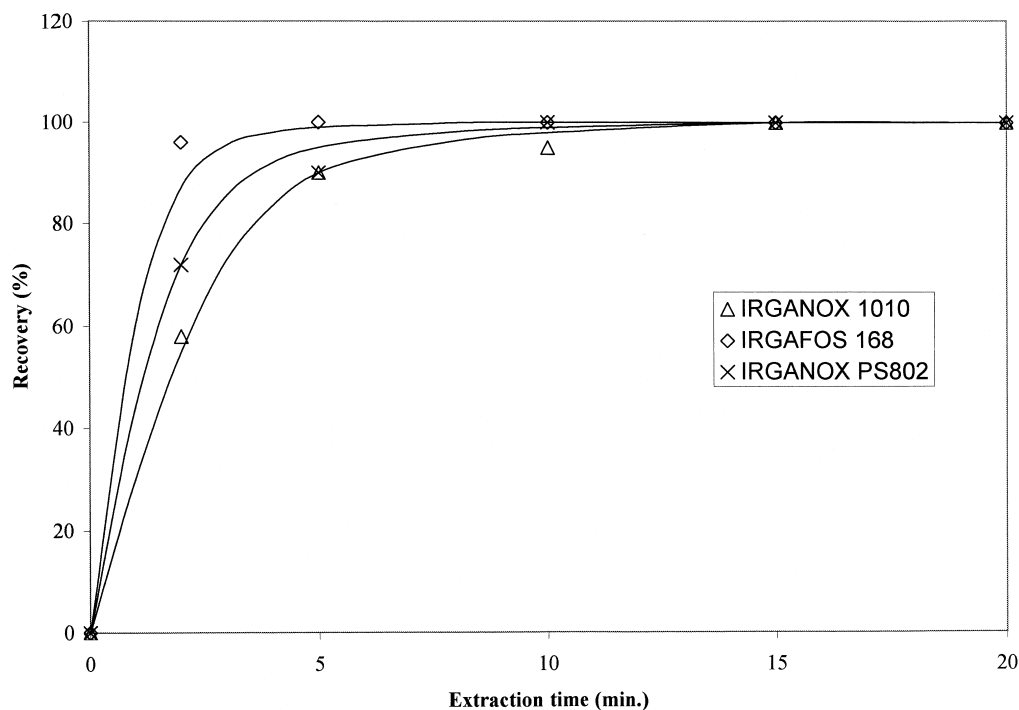
Fig. 2. Recoveries of additives extracted from pelletized PP sample; data from HPLC analysis of the OSM extracts after different heating times.

3.4. Set-up of TSM conditions

3.4.1. First step

The organic polar compounds, e.g. sodium benzoate or Irganox 1425, are very difficult to extract quantitatively from polyolefinic matrices, because of the reduced 'swelling' and the consequent poor diffusion effects of the solvents in which they are soluble. To solve this problem a polymer sample is prepared with a very high specific superficial area so as to increase the diffusion of polar solvents into the polymeric macrostructure.

This aim, in an analytical laboratory, can be achieved via three main procedures of polymer sample preparation: cryogenic grinding, solubilizing and coagulating, microwave dissolution at high temperature in closed vessel and recrystallization.

This work has demonstrated that the latter procedure gave the best results in terms of polymer surface area produced, recovery of additives, time and volume of solvent consumed. Using this pro-

cedure, the polymer in the suitable solvent mixture is at first completely solubilized by microwave heating and then, during cooling, recrystallized into very small particles or lamellar stacks. This particular crystallization procedure has been called 'micronizing'. With this new morphology, the polymer releases polar additives into the solvent mixture which although insoluble, are outside of macromolecular structures.

The micronizing morphologies are different among the polymers. As the SEM picture Fig. 6a shows, PP gives pseudo rhombic particles (quadrites) well known in the literature [30] with dimensions smaller than 1 μm, high X-ray crystallinity (more than 70%), high porosity (0.893 ml/g) and high superficial area (207.3 m^2/g). The polyethylene based micronized polymer instead shows 'lamellar stacks', also known as 'axialites' which have been well studied and characterised [31,32]. The ethylene and polypropylene based copolymers show micronized foams with both quadrites and axialites mor-
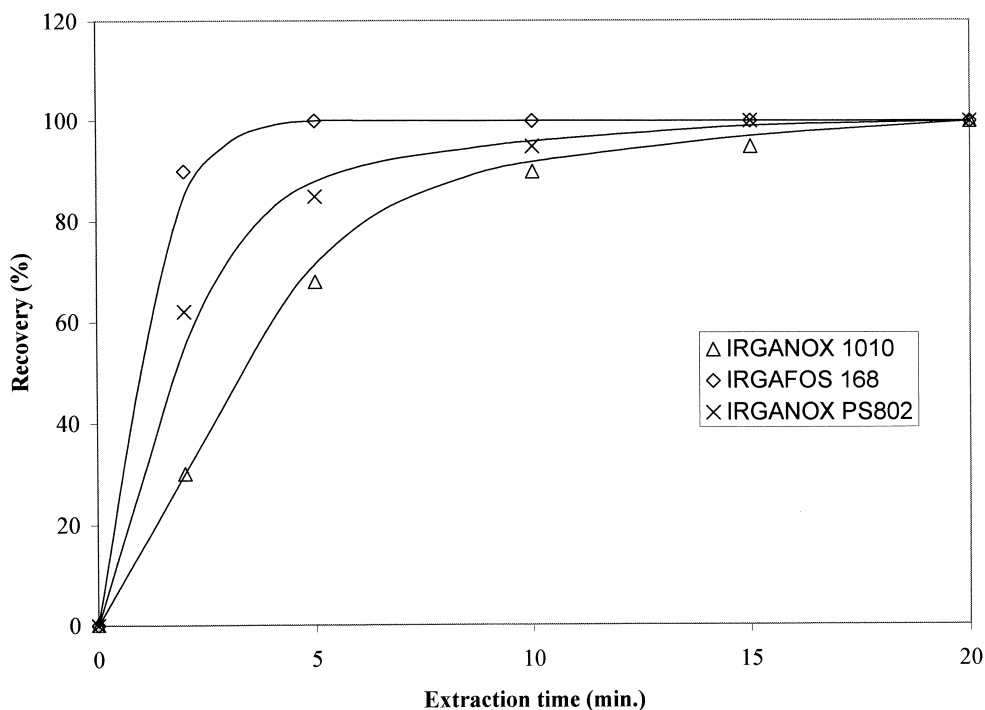
Fig. 3. Recoveries of additives extracted from pelletized HDPE sample; data from HPLC analysis of the OSM extracts after different heating times.

phologies. Finally the PB matrices show microalveolates foams with thick polymeric particles of 1–4 μm and 65% X-ray crystallinity.

The solubilization time needed by the polymer during the micronizing step depends on the number of the samples put in the carousel oven and heated in the same micronization run.

The heating times of the TSM seen in Table 1 are needed to micronize two polymer samples contemporarily. To micronize more than two samples, a longer heating time is required. The type of solvent and the ratio were chosen to obtain a homogeneous micronized bulk in any case, avoiding clots or compact fractions of fused polymer.

3.4.2. Second step

The polar solvent, added to the vessel containing the micronizing mixture, easily solubilizes the polar organic additive that is suspended in the previous solvent mixture. Thus a good recovery can easily be obtained by a short manual shaking (leaching action)

to get the final additive solution homogeneous. Therefore in this case, the second step can be called 'leaching step'.

The solubilization or the recovery of organic polar additives obtained by the second step of TSM can be reached not only by a leaching action, but also after a chemical reaction. In fact, it is possible that the good extraction of some difficult organic additives needs the addition to the second step solvent of oxidation (e.g. 2,6 di-*tert.*-butylhydroperoxide), saponification (e.g. tetrabutylammoniumhydroxide), hydrolyzation (e.g. phosphoric acid) or derivatization (e.g. 1,4-dibromoacetophenone) reagents [33]. In those cases the second step can be called an oxidation, saponification, hydrolyzation or derivatization step.

A good example of analysis by TSM extraction, coupled with chemical reaction, is given by the analysis of fatty acid salts (e.g. calcium stearate).

It has been verified that, if 25 ml of ethyl acetate and 25 ml of 2% (w/v) aqueous solution of ortho-
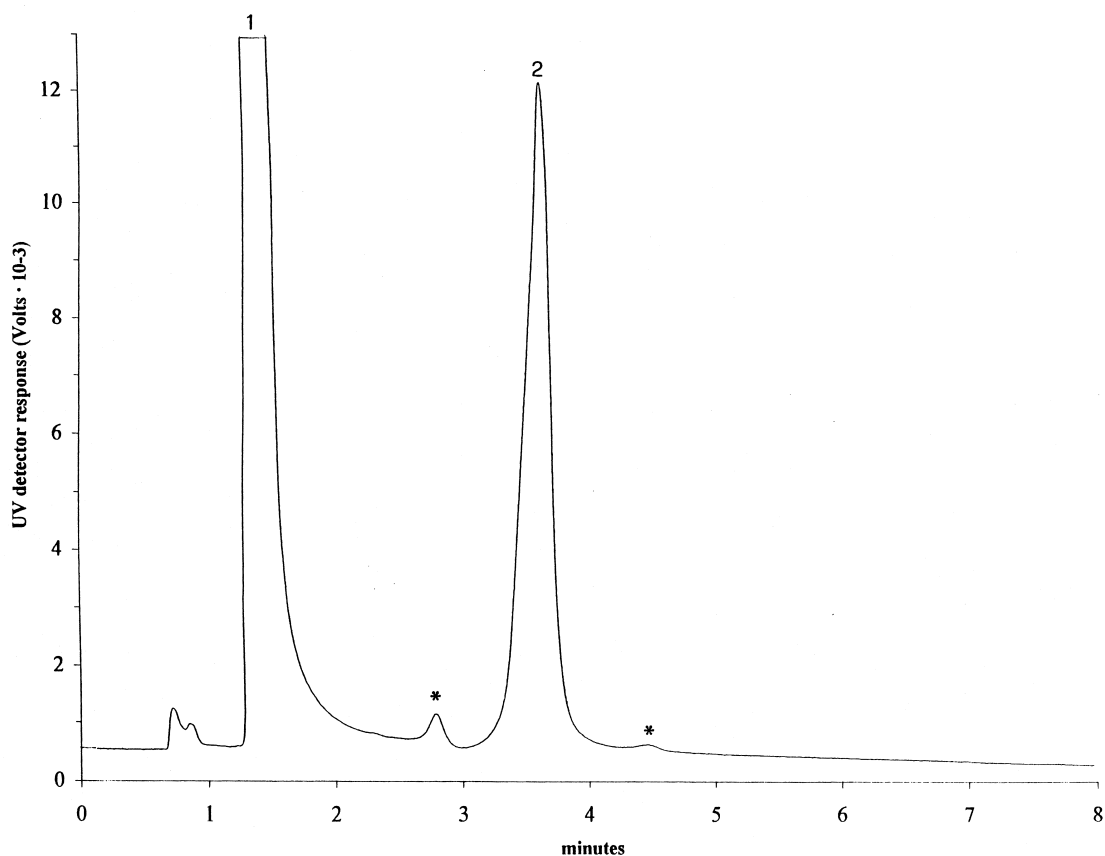
Fig. 4. HPLC chromatograms of TSM extraction solutions from polypropylene sample containing 1000 ppm of sodium benzoate (nucleating agent); peaks: 1=TSM solvent, 2=sodium benzoate, *=unidentified degradation products of Irganox 1010; see text for HPLC–UV/ELSD conditions and additive concentrations.

phosphoric acid are added to the micronizing mixture, after about 5 min of manual shaking of the reaction vessel, there is a complete transformation of fatty acid salts into the corresponding acids. The free fatty acids (mainly stearic, palmitic and myristic) are completely solubilized in the top layer of the organic solvent mixture inside the microwave vessel and determined quantitatively by HPLC–ELSD [34].

The amount of salt originally added to the polymer, can be checked by stoichiometric calculation according to relative cation determination.

3.5. Selection of the polymers

The MAPs set up in this work were carried out on samples with a structure and a composition repre-sentative of the most common commercial PP, PE and PB based polymers. In fact, the MAE conditions can be applied, without any variation, to either polypropylenic resin with different molecular mass distribution, grade and content of atactic fraction or copolymers with compositions different from those of respected tested samples. Furthermore it has been confirmed that the same MAE conditions can be applied, with equally good results, to similar poly-olefinic matrices containing high levels of fillers or strongly pigmented.

The inspection of the morphology of the OSM extracted polymers is the valid gauge to check if the conditions of extraction used give a complete recovery of additives. In practice optimal extractions have been confirmed when swollen polymer particles
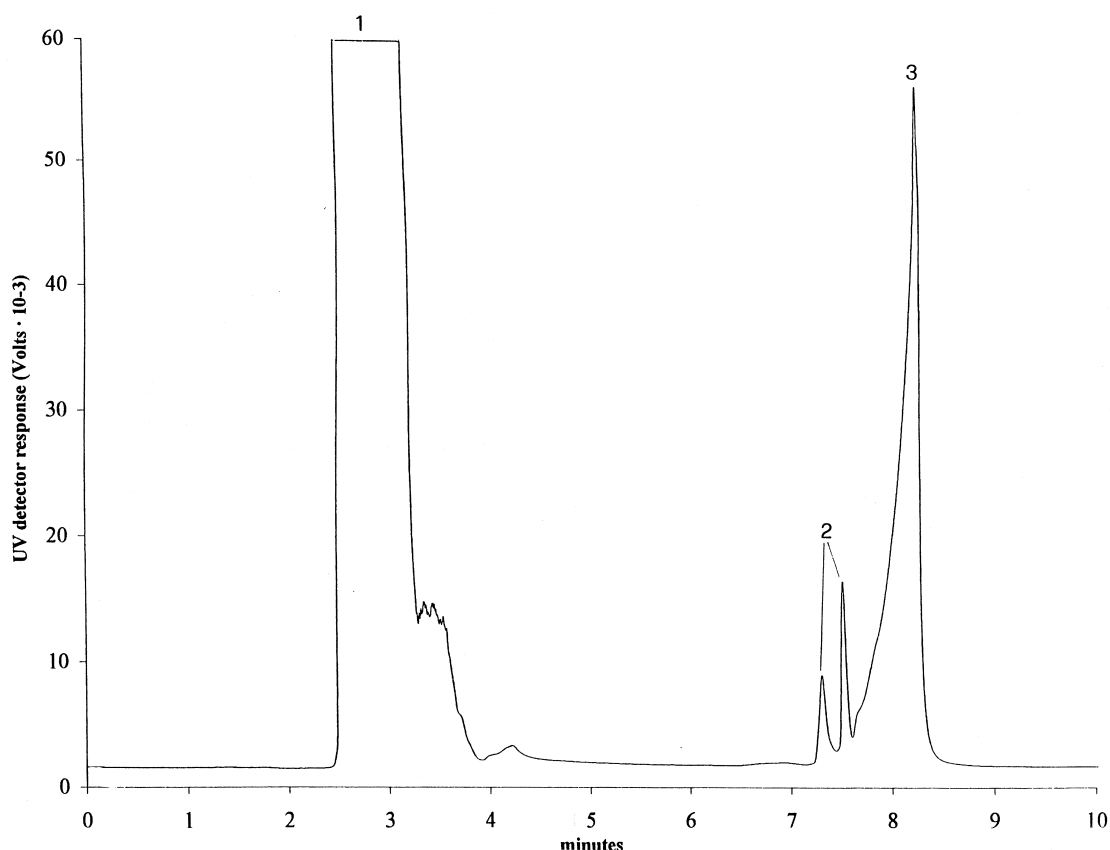
Fig. 5. HPLC chromatograms of TSM extraction solutions from polypropylene sample containing 1000 ppm of Irganox 1425 (antigasfading agent); peaks: 1=cumulative peak of TSM solvents, Irganox 1010 and Irgafos 168, 2=peaks present in the elution gradient, 3=Irganox 1425.

with few clots can be seen. A lack of swelling or the presence of compact fused polymer indicates a bad recovery, an account of incomplete extraction or encapsulation of additives. In most cases, adjustment of the extraction temperature, e.g. 110 rather 100 or 125°C, is sufficient to give good results. About TSM procedures, the right micronizing effect is obtained when, in the microwave vessel, polymer as homogeneous foam, without clots or fused fractions can be seen.

3.6. Selection of the solvents

A proper selection of the organic solvents is the most important key to successful extraction of additive from polymeric matrices.

Solvent choice was detected taking into account, on one hand the following solvent properties
1. the solubilization capacity for compounds (additives) of interest
2. the microwave absorption (the ability to convert electromagnetic energy to thermal energy) and, on the other hand, the following objectives
3. the lowest toxicity
4. to cause the right degree of polymer swelling at high temperature
5. to dissolve the smallest quantity of polymer at room temperature.

It is known [35] that the magnitude of the solvent dipole moment is the main factor that correlates with the microwave heating characteristics of the organic solvent. It is also known [36] that the heating pattern
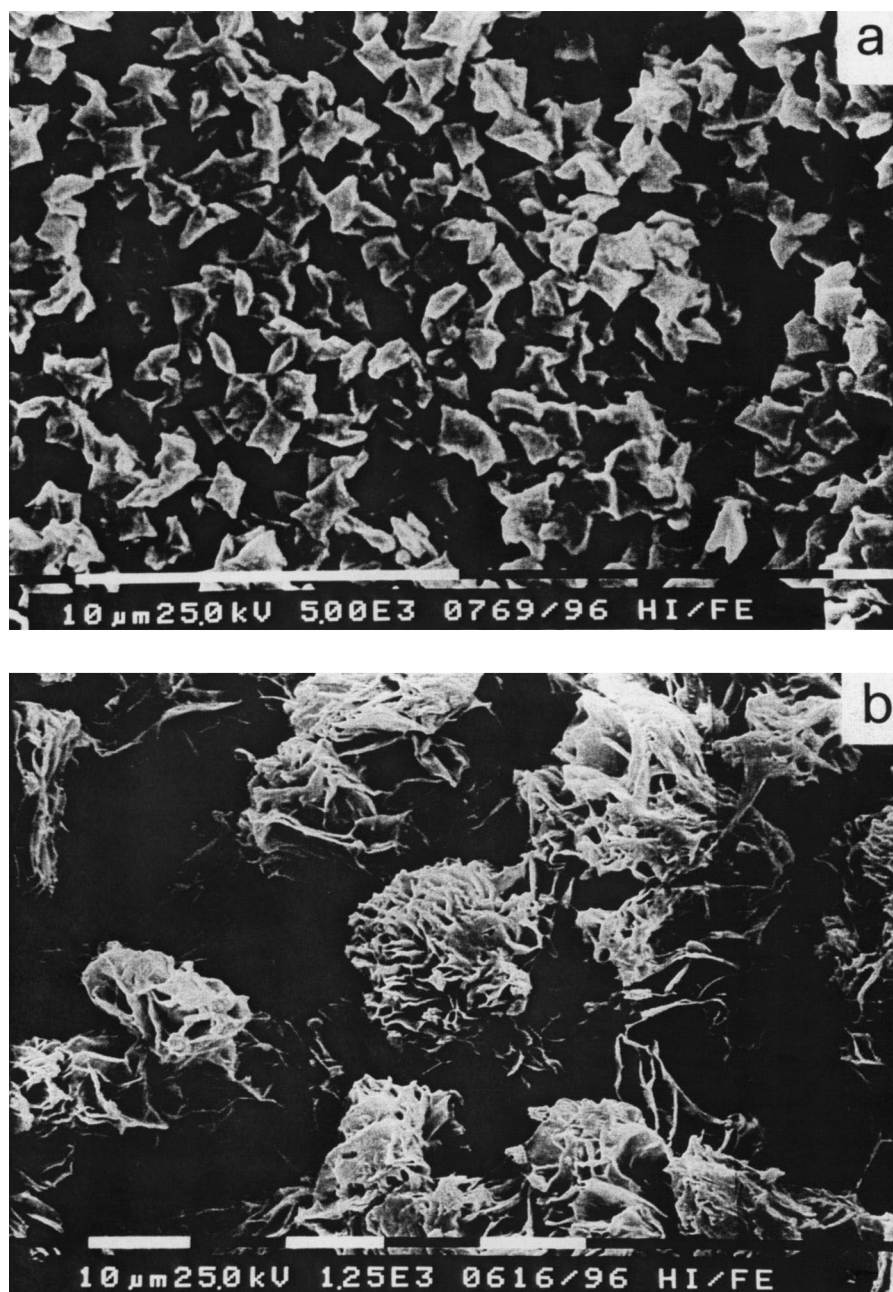
Fig. 6. Scanning electron microscope (SEM) pictures of micronized polymers obtained by the TSM procedure. (a) PP, magnification 5250×; (b) HDPE, magnification 1330×.

of a solvent that is heated with microwave energy will depend, in part, upon the dissipation factor of the same solvent.

The dissipation factor or loss tangent (tangent δ) is given by the following equation:

$$\tan \delta = \frac{\epsilon''}{\epsilon'}$$

where ϵ' = dielectric loss coefficient (the measure of ability of the sample material to convert electromagnetic to thermal energy), ϵ'' = dielectric constant (the ability of sample material to absorb the microwave energy).

Therefore in the binary solvent mixtures of either OSM or TSM micronizing step procedures, one apolar component (n-hexane or n-heptane), gives high swelling-melting power to polymer but does not heat under microwave irradiation. The second polar component (ethyl acetate, acetone, and isopropyl alcohol) has a sufficient dipole moment to facilitate heating under the microwave field and produces a shrinkage effect on the polymer macrostructure, preventing its solvatation.

The right ratio of the two solvents and the useful time and temperature set-up procedures give optimal swelling — good extraction in the case of OSM and optimal solubilization — good micronizing effect in the case of TSM. In the setting up of the MAP, solvents having high toxicity, e.g. chlorinated or aromatic compounds, were excluded.

3.7. Selection of additives

The choice of the useful compounds to verify the effectiveness of MAP has been guided by many years of experience using traditional extraction methods, in the field of additive analysis in polyolefins in the analytical department of Montell G.Natta Research Centre.

First of all attention has been focused on very common polyolefins additives; in particular, to test OSM, selecting the following:

1. The tetraphenolic primary stabilizer Irganox 1010, because it is the most commercially common antioxidant for polyolefins and, since it has accentuated dipolarity, shows poor solubility in hydrocarbon solvent. It therefore needs a high swelling grade of polymeric matrix to be completely extracted.

2. The phosphite aromatic secondary stabilizer IRGAFOS 168 is not difficult to extract but has a high level of antioxidant activity as hydroperoxides decompositor and suffers a fast degradation at temperatures >140°C. It decays via oxidation to give the phosphonate by-product and, less frequently, via hydrolysis to give 2,4-di-*tert.*-butylphenol (2,4-DTBP) [37,38].

3. The thioester aliphatic secondary stabilizer Irganox PS802, because it shows poor solubility in the OSM solvent mixture and, since it has a chemical structure particularly similar to polyolefinic matrices, shows a difficult recovery from either amorphous polymeric structures or from oligomeric fractions coagulated in the extraction vessel after OSM treatment.

To test TSM procedures, we have selected, as a representative of very organic polar additives, the nucleating agent sodium benzoate and the antigasfading agent Irganox 1425. Both compounds are easily leached with methanol and they require HPLC analysis by direct injections of extraction solutions via two different elution ways: isocratic elution in the case of sodium benzoate and OCSE plus ternary gradient elution in the case of Irganox 1425.

Extraction tests on PP matrix have demonstrated negligible additive degradation during OSM extraction. In fact, as can be deduced from HPLC analytical results, reported in Table 5, with Irgafos 168 stabilizer, in comparison with conventional ways, the OSM extraction gives the best recovery. It shows degradation effects as low as those of ultrasonication extraction procedure, the measured additive decay being essentially due to its antioxidant activity during the processing (extrusion) step of the polymer and not to microwave heating treatment.

In comparison with traditional ways, the TSM also gives the highest recovery and has the lowest time/solvent consumption.

With regard to Irganox 1425 analysis, Table 6 shows that recoveries as high as those of TSM extractions can be obtained only after polymer dissolution with xylene, its coagulation with methanol, an intermediate washing with acetone (solvent with intermediate dipolarity between xylene and methanol) and multi-washings with methanol of the coagulated polymer.

Therefore the MAP can be effectively applied to most of the organic additives for polyolefins and

Table 5
HPLC duplicate analysis results of Irgafos 168 and its by-products extracted from PP by different procedures (concentration of stabilizer added to original polymer: 1000 ppm; amount of each sample treated: 2.5 g)

Extraction procedure	HPLC analysis results		
	Irgafos 168 (undecayed additive) (ppm)	Irgafos 168 phosphate (oxidizing product) (ppm)	2,4-DTBP (hydrolyzing product) (ppm)
(1) OSM	810±20	195±4	5
(2) Ultrasonication for 1 h with 50 ml of anhydrous *n*-hexane at room temperature plus coagulation with anhydrous acetone, from=1 mm ground polymer	800±20	190±4	6
(3) 6-h refluxing under stirring with 40 ml of chloroform plus oligomer coagulation with 60 ml of acetone	780±19	210±4	25
(4) 80 ml of xylene dissolution plus 120 ml of methanol coagulation, distillation to dryness and redissolution with acetone	720±18	280±6	32

conveniently adopted for systematic analysis of organic additives in polyolefins. Its validity has been tested by comparing the OSM with a traditional extraction procedure (by 6-h refluxing chloroform) for the following additives:

1. Phenols: BHT, BHA, Cyanox 1790, Irganox

Table 6
Comparison of time/solvent consumption and percentage recoveries between conventional and TSM extraction procedures; HPLC duplicate analysis of Irganox 1425 performed in 2.0 g of PP sample

Extraction procedure	Time (h)	Solvent		Irganox 1425 recovery range (%)
		Kind	Volume (ml)	
(1) TSM	1.5–2	Acetone *n*-Hexane Methanol	6.25 18.75 25.00	99–103
(2) Cryogenic grinding of polymer <1.0 mm 6 h extraction by refluxing under magnetic stirring, concentration of extract	7–8	Methanol	80–100	60–65
(3) Xylene dissolution and crystallisation Multistep methanol washings, filtering and concentration of extract	4–5	Xylene Methanol	80 160	75–86
(4) Xylene dissolution and coagulation with methanol Acetone washings Multistep methanol washings, filtering and concentration of extract	5–6	Xylene Acetone Methanol	80 80 160	95–102

3114, Irganox 1330, Irganox 1076, Irganox MD 1024, Santonox, Topanol CA, Santowhite powder, Sanduvor EPU (primary antioxidants).
2. Aliphatic and aromatic phosphites: Ultranox 399, Ultranox 618 (secondary antioxidants).
3. Aliphatic tyoesters: Irganox PS800, Tyox (secondary antioxidants).
4. Benzotriazoles and benzophenones: Cyasorb UV 531, Tinuvin 120, Tinuvin P, Tinuvin 328, Tinuvin 327, Tinuvin 326 (UV stabilizers).
5. Monomeric hindered amine: Tinuvin 770, Tinuvin 144, Hostanox TMN 20 (light stabilizers).
6. Glycerol monoacyl esters: GMS 40, ATMER 129, Witconol MST (antistatic agents).
7. N,N′-Diethanol aliphatic amines: Atmer 163, Armostat 400 (antistatic agents).
8. Fatty amides: Crodamide ER, Unislip 1759, Unislip 1753 [39] (slip agents).
9. Halogen derivatives: Dechlorane plus-515, Saytex 102, Saytex 120, Saytex 111 (flame retardants).

Besides sodium benzoate and Irganox 1425, TSM procedures gave excellent recovery results for the following additives, extracted using the leaching mode:
1. ADK-STAB/Na-11, Mark M-10: aromatic phosphonate salts (nucleant agents).
2. Millad 3905, Millad 3940, Millad 3988: sorbitol derivatives (nucleant agents).
3. Chimassorb 944, Cyasorb UV 3346: polymeric hindered amines (light stabilizers),
   for the following additives, on extracted via hydrolytic mode:
1. Fatty acid salts (antiacid agents)
2. Adipic acid (nucleant agent adipic acid/zeolites based) for Tinuvin 622 (polymeric hindered amine light stabilizer) via saponifying mode [40], and for Ultranox 626 and Sandostab P-EPQ (aromatic phosphite and phosphite–phosphonite mixture stabilizers, respectively) via oxidizing mode.

The last two additives are highly effective for hydroperoxide decomposition and also decay at temperatures lower than 60–70°C. Therefore they are present partially oxidized in polymer matrices.

Thus, notwithstanding their high solubility on unpolar organic solvents, they cannot be correctly extracted by heating extraction procedures, OSM included, because they do not give the actual unde-

cayed additive present in the polymer. Therefore, the extraction method for these additives remains ultrasonication at room temperature, with anhydrous *n*-hexane or acetone from 1 mm cryogenically ground polymer particles. TSM extraction, on oxidizing mode, becomes an easy way for quantification of additive originally added to polymer.

During the present study, it was observed that the OSM and TSM also show, in comparison with traditional methodologies, a very high efficiency for degradation products of additives. This offers HPLC–MS equipped with modern interfaces, as a concrete contribution to the broadening of knowledge about the activity mechanisms of stabilizers and about side products resulting from degradation and/or interaction of additives [41–48].

4. Conclusions

The study demonstrated that the combination of MAE and HPLC–UV/ELS is a convenient way for systematic, complete and accurate analysis of organic additives in polyolefins. In particular the proposed MAPs, in comparison with traditional extraction methodologies, allow the following advantages
1. use of solvents with lower toxicity and environmental adverse effects (avoiding chlorinated or aromatic solvents)
2. hugely reduced solvent volume and time of sample treatment
3. direct extraction from pelletized matrices (no grinding)
4. fast and total recovery of either 'difficult' or high polar compounds
5. direct HPLC injection of extraction solutions (no coagulation, washing, concentrating)
6. appreciable accuracy improvement of analytical evaluations
7. negligible decomposition of stabilizers (with rare exceptions)
8. extraction of a very wide dipolarity range of organic compounds
9. increased knowledge about chemical mechanisms of action, degradation and interaction of additives during processing and end-use of polymers.

Acknowledgements

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