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Characterization of polymer additives by supercritical fluid chromatography and by liquid chromatography

T. GREIBROKK*, B. E. BERG, S. HOFFMANN, H. R. NORLI and Q. YING
Department of Chemistry, University of Oslo, P.O.B. 1033, Blindern, 0315 Oslo 3 (Norway)

SUMMARY

Various polymer additives were characterized by chromatographic methods. As many of the additives lack chromophores for UV absorption, the detection has to be based mainly on refraction or light scattering in liquid chromatography (LC) and on flame ionization or light scattering in supercritical fluid chromatography (SFC). More than fifteen additives were analysed essentially by the same SFC method, except with varying density gradients, whereas two different columns and several different eluents were required in LC. This illustrates that SFC has an obvious advantage over LC for the characterization of this large group of lipophilic compounds.

INTRODUCTION

In order to improve the physical properties of synthetic polymers, most polymeric materials contain antioxidants, UV stabilizers, metal deactivators, slip agents, antiblock agents and antistatic agents. The need for such additives in polyolefins has been well studied[1]. Even if many additives have multiple functions, the number of additives routinely used in the manufacture of polyolefins exceeds 20, although not all added together, as some additives are better suited than others for a particular product or purpose. As the purity and amount of additive affect the properties of the polymer, there is a need for analytical methods to characterize the additive and also to determine the amount present. Further, many commercial additives are not single components, but may contain homologues or byproducts in significant amounts. For products used in food processing and packaging there is also a need to determine the amount of additives released to the foodstuff.

Owing to the relatively high molecular weights involved, liquid chromatography has been the most commonly used chromatographic technique for additives. Unfortunately, many additives show little UV absorption. Previously this led to the use of refractive index (RI) detectors, without gradient capability and with low sensitivity. Supercritical fluid chromatography (SFC) has recently been demonstrated to be valuable for this type of compound[2–5], particularly owing to the ability to use the mass-sensitive flame ionization detector.

In an industrial production control laboratory, there is always a need for several

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analytical techniques operating simultaneously, as many operators may use the systems around the clock. Thus, if one chromatographic system could be used for most of the additives, this would represent a major advantage over a system with dedicated instruments and methods for each additive. Based on earlier experience in SFC with some additives[2,5], the main purpose of this study was to examine if essentially one technique could be utilized for the purity control of most of the additives used in the manufacture of polyolefins. After having developed liquid chromatographic (LC) and SFC methods for most of the additives, the results for each additive were also compared to check whether one method had clear advantages for a particular additive.

The LC methods mainly involved the use of light-scattering detection (LSD) for compounds without strong chromophores, permitting the use of gradient elution where that was required. The combination of SFC and LSD, first reported by Carraud *et al.*[6], was included on some occasions in order to compare the results on open capillaries with packed columns or because other methods did not give a satisfactory result.

EXPERIMENTAL

SFC–FID

The instruments were either a Model 3000 supercritical fluid chromatograph (Carlo Erba, Milan, Italy) or a laboratory-built system based on a Model μLC-500 pump (ISCO, Lincoln, NE, U.S.A.)[7–9]. The latter was equipped with solvent venting injection[7–9], whereby 0.5-μl volumes were injected with venting times of approximately 20 s. The columns were 10 m × 50 μm I.D. SB-Phenyl-5 or SB-Biphenyl-30 with 0.5- and 0.25-μm films (Lee Scientific, Salt Lake City, UT, U.S.A.). The restrictors were ceramic frit restrictors from Lee Scientific or laboratory-made integral restrictors. The linear flow-rate in the columns was 2–4 cm/s and that in the precolumn (2 m × 50 μm I.D. coated with a 0.2-μm film of DB-1) was 15–20 cm/s. Carbon dioxide, grade 4.8, was obtained from AGA Norgas (Oslo, Norway).

SFC–LSD

The instrument consisted of a Carlo Erba Phoenix 20 syringe pump connected to packed fused-silica columns and a modified Varex VLSD-101 laser light-scattering detector. The modification, which has been published[5], consisted mainly in removal of the ordinary nebulizer and use of the drift tube as a column oven. The restrictor, which could be heated, functioned as the nebulizer. The detector time constant was set at 0.2 s. The injector could be heated by a jacket and a cartridge heater[5]. The laboratory-made integral restrictors had a thin (1 mm) ceramic frit at the inlet to prevent plugging by foreign particles[5]. *n*-Propanol was added to the carbon dioxide as a modifier, with another pump[5]. The fused-silica columns were packed[10] with different reversed-phase materials.

LC–LSD

The LC results were partly obtained on 4.6 mm I.D. columns connected to the unmodified Varex detector, and partly on packed 0.32-mm fused-silica columns connected to the detector which was equipped with a modified nebulizer to accommodate the low LC flow-rates. The modifications have been published[10]. The

LC pumps were Waters Assoc. Model 6000 A (Millipore–Waters, Milford, MA, U.S.A.). For the packed capillaries the pump was equipped with an open split to maintain a constant flow at the low flow-rates[10].

LC–UV detection

For the few UV-absorbing additives, the samples were injected on a packed fused-silica column which was connected to an SPD-2AM variable-wavelength absorbance detector (Shimadzu, Kyoto, Japan). The detector was modified for packed capillaries with a fused-silica capillary flow cell. The time constant was set at 0.2 s. The mobile phase was delivered by a Waters Assoc. Model 590 pump in the constant pressure mode, with an open split.

RESULTS AND DISCUSSION

Owing to their low solubility in aqueous solutions, very few of the additives can be chromatographed by ordinary reversed-phase methods in LC. In order to be able to run gradients, where this might be needed, non-aqueous reversed-phase and normal-phase elution on amino-modified silica was chosen for the LC experiments.

Irgafos P-EPQ (MW 979) is an organic phosphonite with aromatic substituents, allowing the use of UV detection. With non-aqueous reversed-phase chromatography, the choice of the C_{18} material had a considerable effect on the peak profiles (Fig. 1). With a packing material containing a relatively high density of residual silanol groups, most of the sample was adsorbed on the column (Fig. 1A). With more deactivated packing materials, the chromatograms mainly contained three peaks, in approximately the same ratio based on UV and LSD (Fig. 1B and C). Detection at 220 nm was chosen to reduce the influence of variations in molar absorptivities. With capillary SFC the resolution was improved, resulting in four major peaks and several minor peaks (Fig. 1D). One impurity is tris(2′,4′-di-*tert.*-butylphenyl) phosphite, another additive.

Irganox PS 802 (MW 683) is the distearyl ester of thiodipropionic acid, which has little UV absorbance. The purity tests showed that LC with LSD and SFC with flame ionization detection (FID) gave approximately the same results (Fig. 2).

Armostat 400, N,N′-bis(2-hydroxyethyl)-C_{12}–C_{16}-diamine, also lacks strong chromophores. Owing to the basic functions the mixture was best separated on the amino column in LC. The resolution was slightly better in LC than in SFC (Fig. 3). The retention on the Biphenyl-30 column was higher than that on the Phenyl-5 column, but the resolution of the mixture was not actually improved. Whether the secondary amino groups reacted with carbon dioxide, is not known, but so far there is nothing to indicate that this had happened.

Hostanox SE 10, dioctadecyl disulphide (MW 571), is a non-polar additive with few apparent impurities in LC. According to the chromatogram obtained by LSD, the purity was better than 90%. Better resolution was obtained with SFC, however, showing an actual purity of only 70% by using FID (Fig. 4).

In a routine industrial purity test with reversed-phase LC and RI detection, the three additives oleamide, stearamide and erucamide appeared to be essentially pure, with one peak each (Fig. 5A). This is the only example within the compounds tested where a small amount of water improved the peak shape in a reversed-phase system.

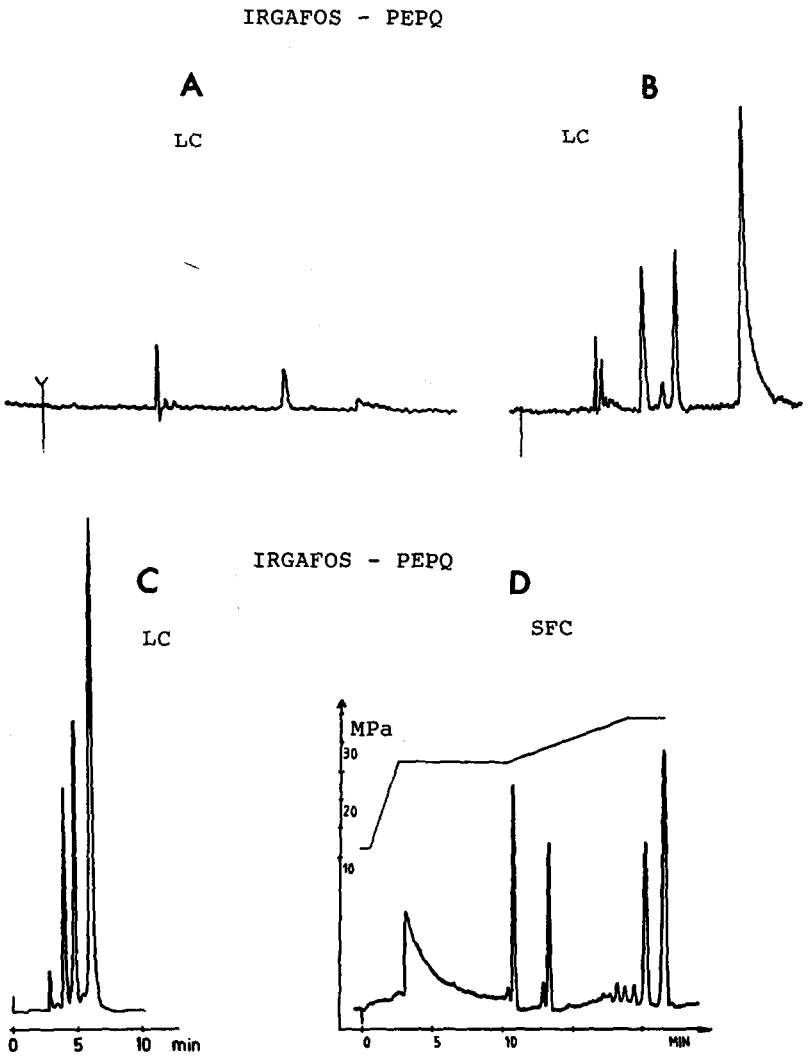

Fig. 1. Separation of Irgafos P-EPQ (0.1 μg) by LC on (A) 3-μm Spherisorb ODS, (B) 4-μm Novapak C_{18} in 20 cm × 0.32 mm I.D. packed fused-silica columns and (C) 5-μm Supelco LC-18-DB (25 cm × 4.6 mm I.D.) with acetonitrile–chloroform (65:35), with (A and B) UV detection (220 nm) and (C) LSD. Chromatogram D shows the SFC separation with carbon dioxide on the 50-μm Phenyl-5 column with FID.

The amino column could not be used owing to the strong retention of byproducts with acidic functions. With a standard SFC method the purities of the three fatty amides were determined to 90, 60 and 90%, respectively (Fig. 5B–D). The main impurity in stearamide was stearic acid.

Glyceryl monostearate is another additive without strong chromophores, making UV detection difficult. In LC with LSD the best resolution was obtained on an amino column with a small amount of methanol in dichloromethane. A gradient was required to elute the components in a reasonable time (Fig. 6A). The shortest elution

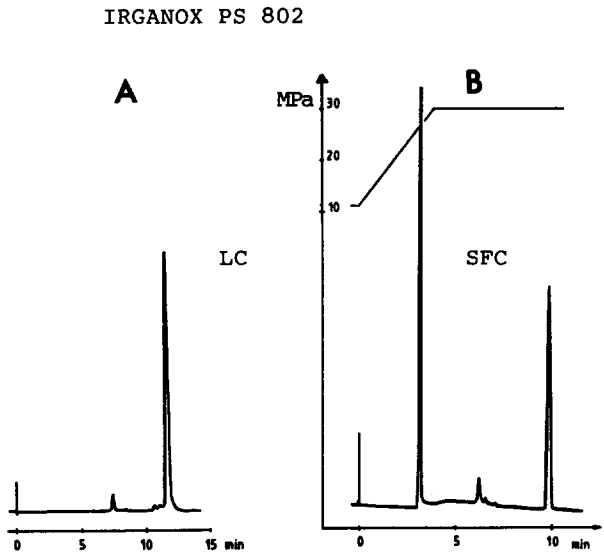

Fig. 2. Separation of Irganox PS 802 by (A) LC on a Supelco LC-18-DB column (25 cm × 4.6 mm I.D.) with acetone and LSD and (B) SFC with carbon dioxide on the Phenyl-5 column with FID. The first peak in B is a solvent peak.

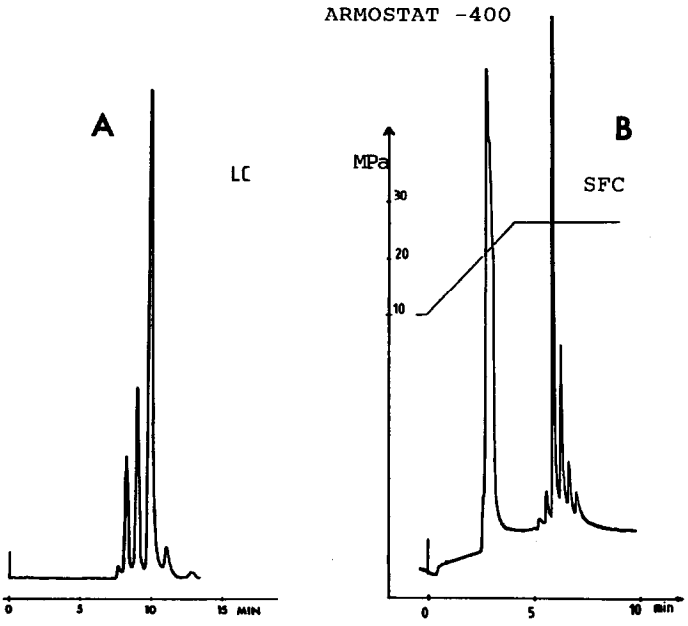

Fig. 3. Separation of Armostat-400 by (A) LC on a 5-μm Supelcosil LC-NH_2 column (25 cm × 4.6 mm I.D.) with hexane–methanol (95:5) and LSD and (B) SFC with carbon dioxide on the Biphenyl-30 column with FID.

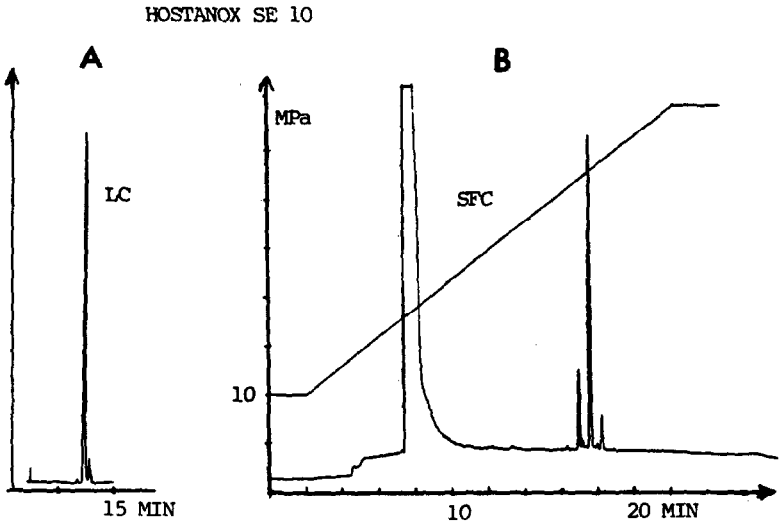

Fig. 4. Separation of Hostanox SE-10 by (A) LC on a Supelco LC-18-DB column (25 cm × 4.6 mm I.D.) with acetone and LSD and (B) SFC with carbon dioxide on the Phenyl-5 column with FID.

time was obtained on a packed column in SFC, with *n*-propanol-modified carbon dioxide and LSD (Fig. 6B). The best quantitative analysis, however, was achieved by SFC on an open-tubular column with FID (Fig. 6C). Owing to the non-linearity of the light-scattering detector, the amounts of triglycerides and other small peaks are misrepresented compared with the FID trace. The actual content of glyceryl monostearate in this technical-grade product was determined by FID to be only 30%. In SFC the elution pattern was similar on the packed and on the open-tubular column, according to the molecular weight, in contrast to the LC normal-phase pattern where the triglyceride peak eluted first.

N,N′-Ethylenebisstearamide is a fatty amide for which we could find no satisfactory LC separation method. The solubility in pure carbon dioxide was low, but the addition of *n*-propanol to the carbon dioxide, heated injection and LSD finally led to the separation of three components by SFC[5].

The following commercial additives were purity tested by SFC with pure carbon dioxide on a Biphenyl-30 or a Phenyl-5 column, with variations in the density gradient: Irgafos P-EPQ, Irgafos 168, Atmer 129, Hostanox SE-10, Sumilizer BHT, Armostat 400, Irganox 1010, Irganox 1076, Irganox MD 1024, Tinuvin 120, Tinuvin 327, Tinuvin 770, Irganox PS 802, Radiamuls 142, Crodamide OR, Crodamide ER and Crodamide SR. The Phenyl-5 column could be used for all the additives. The Biphenyl-30 column was tried only where stronger interactions with the stationary phase was expected to improve the resolution. Chromatograms with essentially one peak in both LC and SFC and some of the previously published SFC separations have not been included in this paper.

In order to test the purity of all the additives properly by LC, several different systems were needed (Table I), requiring much more instrumentation in product control compared with SFC. This illustrates that SFC had a definite advantage over LC for this group of lipophilic compounds.

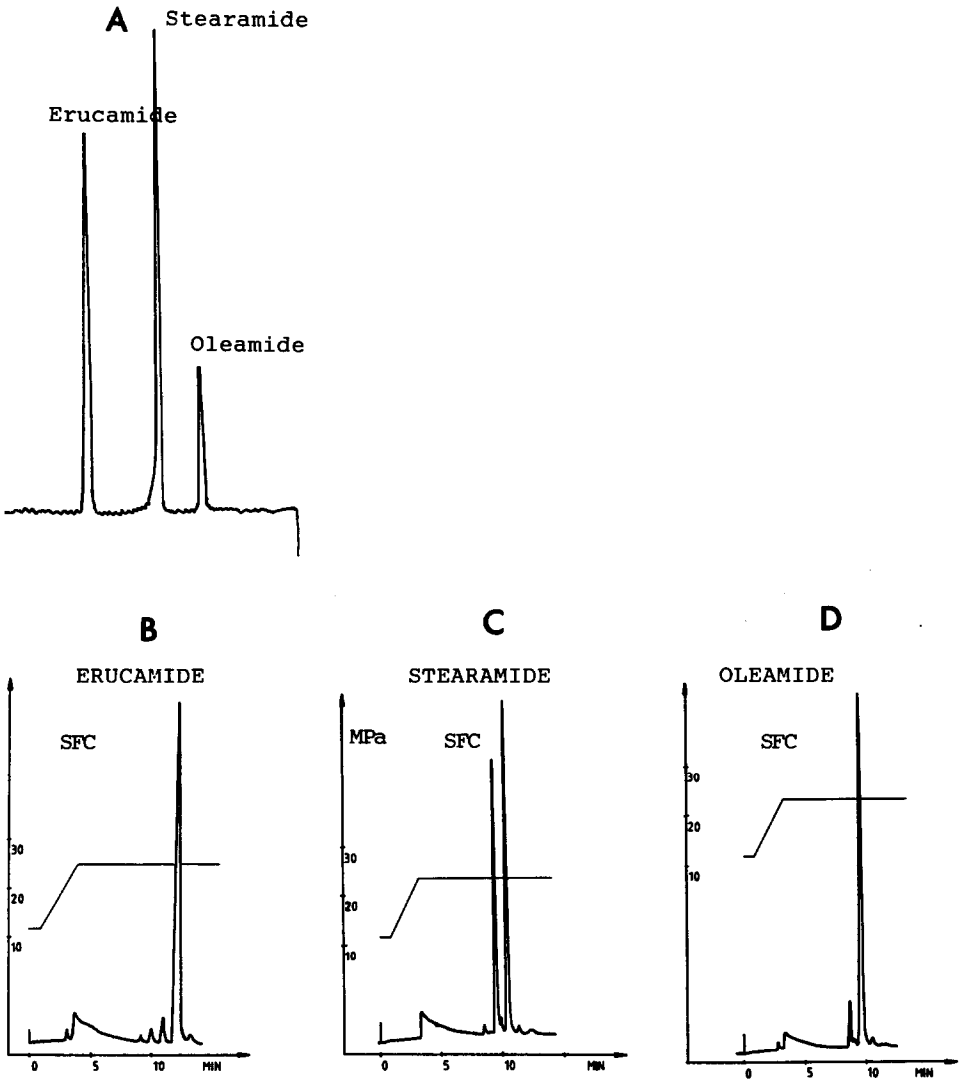

Fig. 5. Purity tests of erucamide, stearamide and oleamide by (A) LC on a 5-μm Spherisorb ODS column with water–methanol (4:95) and RI and (B, C, D) SFC with carbon dioxide on the Phenyl-5 column with FID.

Polyolefin pellets or films are routinely analysed for their additives content, often after Soxhlet extraction of the product. Examples of SFC analyses of the extracts of two different polyolefin products are shown in Fig. 7. By use of the solvent venting injection technique[7–9], volumes of up to 1 μl could be injected.

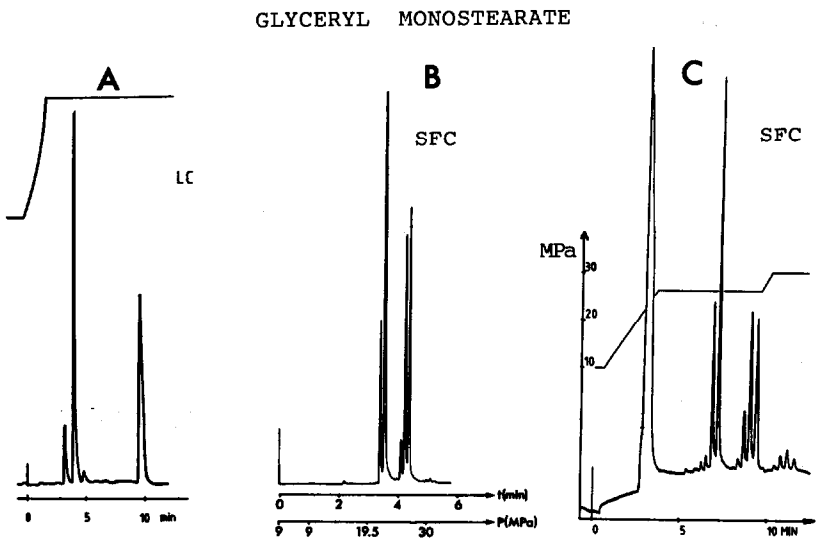

Fig. 6. Separation of technical-grade glyceryl monostearate by (A) LC on a Supelcosil-LC-NH_2 column (25 cm × 4.6 mm I.D.) with 0.6–3% methanol in dichloromethane and LSD, (B) SFC on a 4-μm Novapak-C_{18} column (10 cm × 0.32 mm I.D.) with 2.9 mol-% *n*-propanol in carbon dioxide and LSD and (C) SFC on the Biphenyl-30 column with carbon dioxide and FID.

TABLE I

LC CONDITIONS FOR CHARACTERIZATION OF ADDITIVES

Additive	*Column*	*Mobile phase*
Irgafos P-EPQ	C_{18}	Acetonitrile–chloroform (65:35)
Irgafos 168	C_{18}	Acetonitrile–chloroform (65:35)
Atmer 129	Amino	0.6–3% methanol in chloroform
Radiamuls 142	Amino	0.6–3% methanol in chloroform
Hostanox SE-10	C_{18}	Acetone
DSTDP	C_{18}	Acetone
Armostat 400	Amino	Methanol–hexane (5:95)
Sumilizer BHT	C_{18}	Acetonitrile–acetone (65:35)
Irganox 1010	C_{18}	Acetonitrile–acetone (65:35)
Irganox 1076	C_{18}	Acetonitrile–acetone (65:35)
Irganox MD 1024	C_{18}	Methanol–water (75:25)
Tinuvin 327	Amino	Methanol–dichloromethane (10:90)
Tinuvin 770	Amino	Methanol–dichloromethane (10:90)
Crodamide OR, ER, CR	C_{18}	Methanol–water (96:4)

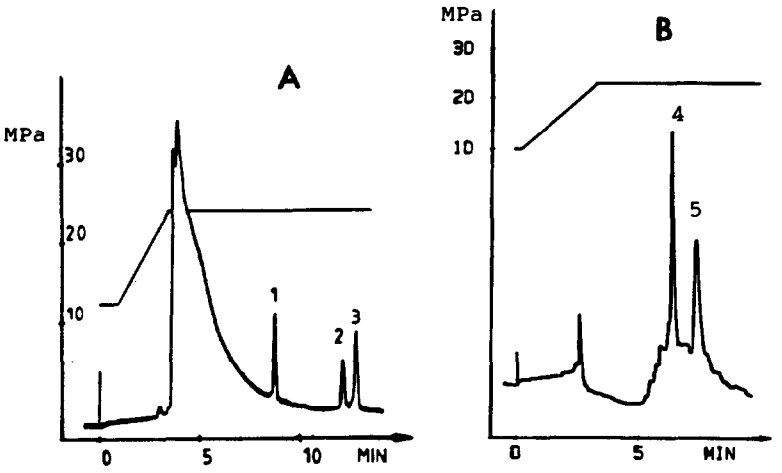

Fig. 7. Determination of the additives (1) Tinuvin 120, (2) Tinuvin 770, (3) Tinuvin 327, (4) stearamide and (5) erucamide in two extracts (A, B) from polyolefin pellets by SFC with carbon dioxide on the Phenyl-5 column with FID.

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