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Note

Determination of slip agents in polyolefins by non-vaporizing cold on-column injection and the use of an immobilized phase capillary column

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Slip agents are commonly used as additives in the production of polyolefin films to enhance surface migration and therefore to facilitate the release of two overlying layers during use[1]. Long-chain aliphatic amides, mostly oleamide and erucamide, are generally used[2].

Their concentration, however, needs to be carefully monitored in order to avoid problems during the production process or in application. The type of amide is also important because it determines the surface migration rate. The techniques used for quantitative analytical problems generally require extraction of the polyolefin (in some instances by re-precipitation and filtration[3]), followed by instrumental analysis of the extract.

These analyses are usually performed by infrared spectroscopy[3,4] or by gas chromatography (GC)[5–8]. Previous GC determinations, however, require the amides to be previously converted into more volatile derivatives as their direct injection does not give satisfactory results[9]. Conversions into nitriles[5] or methyl esters[10] are the most popular reactions used for this purpose.

None of the GC methods used previously matched our requirements as they involved tedious, time-consuming sample preparation and long analysis procedures, and gave unsatisfactory accuracy and precision.

Frisina *et al.*[11] reported a method for amide extraction and precipitation followed by GC determination with direct injection of the extract into a packed column. Their results showed good agreement with those obtained by infrared spectroscopy. The results are accurate and reliable, but the method is still too sophisticated and time consuming for our purposes.

The method proposed in this paper overcomes these disadvantages as the polyolefin is extracted directly and the extract is injected into a capillary column by the

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non-vaporizing cold on-column injection technique[12–14]. The method is simple, rapid, selective and precise.

EXPERIMENTAL

Chemicals

Acetone and chloroform (analytical-reagent grade, Carlo Erba, Milan, Italy), oleamide (technical grade, AKZO Chemie) and erucamide (technical grade, Croda) were used.

Apparatus

A Carlo Erba Model 2960 gas chromatograph, fitted with a non-vaporizing cold on-column injector and a flame-ionization detector (FID) was used. Identification and integration of peak areas were accomplished with a Varian CDS 401 data system.

A Pulverisette 14 (Fritsch) was used to powder the samples.

The column was a home made 15-m Duran glass capillary wall-coated open tubular column coated with PS 255 (methylsilicone + 1% vinyl silicone), film thickness 0.15 μm, immobilized according to the procedure described by Grob and coworkers[15–17]. The stationary phase was obtained from Petrark. The carrier gas was helium at an inlet pressure of 0.5 kg/cm^2. The injection temperature was 180°C, the column temperature was held for 5 min at 180°C then programmed at 5°C/min to 220°C, and the detector temperature was 250°C.

Method

The sample must be previously powdered to permit uniform extraction; films should be cut in small fragments. A 5-g amount of sample is placed in the extraction apparatus and refluxed with 200 ml of acetone; 2–3 h are generally sufficient for complete extraction of the additive, whereas about 12 h are required when diethyl ether is used.

The extract is transferred quantitatively into a 40-ml beaker and evaporated to dryness on a water-batch. The residue is dissolved quantitatively in chloroform and transferred into a 10-ml graduated flask; 0.001 g of internal standard is added and the solution is diluted to the mark with the solvent. A 1-μl volume of this solution is injected into the chromatograph.

RESULTS AND DISCUSSION

Fig. 1 shows a chromatogram obtained by injecting an extract containing the amides as such directly into a capillary column under the conditions mentioned in the Experimental section. Sample introduction was effected by means of a non-vaporizing cold on-column injector[12] incorporating a secondary cooling system[13,14] of the initial part of the column while the oven was kept at 180°C. In this way the sample was injected into the cooled initial part of the capillary and its components started to vaporize much more quickly than during the injection technique into a completely unheated column.

The advantages offered by the combined use of the non-vaporizing cold on-

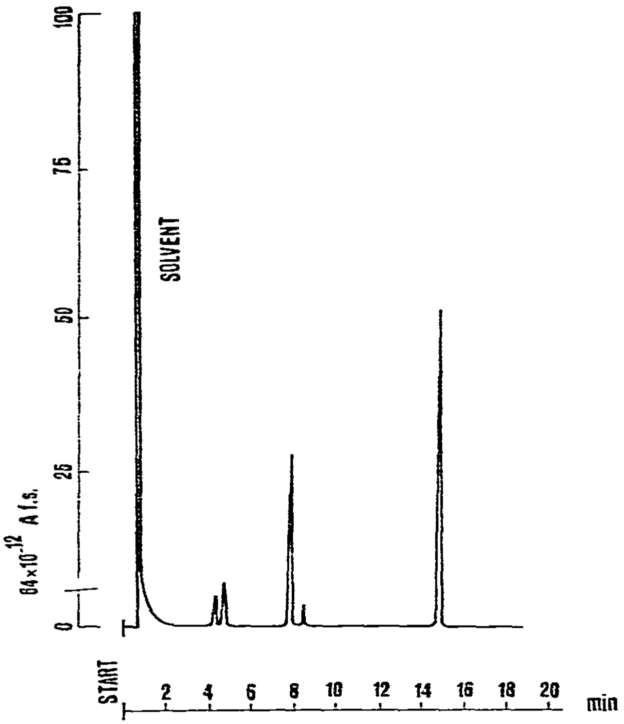

Fig. 1. Chromatogram obtained by injecting an extract containing oleamide (15 μg/ml) and erucamide (40 μg/ml) directly into a capillary column. For conditions, see Experimental.

column injector and capillary column over conventional packed columns are evident in terms of both sample preparation and analysis time (Table I).

To establish the accuracy of our method, the GC results for a sample of commercially available polyethylene grains were compared with those obtained by other techniques (see Table II). Slightly higher results were obtained by infrared (IR) analysis, probably owing to interfering components which affect the absorbance measurement.

TABLE I

ADVANTAGES OF THE PROPOSED METHOD OVER THE BEST GC METHOD DESCRIBED IN THE LITERATURE FOR THE DETERMINATION OF SLIP AGENTS IN POLYOLEFINS

Proposed method		*Literature method*[11]	
Step	*Time required*	*Step*	*Time required*
Powdering	15 min	Solubilization	48 h
Extraction	3 h	Precipitation	
Concentration	30 min	Filtration under vacuum	
Dilution	15 min	Rinsing	
GC analysis	15 min	Concentration	
		Dilution	
		GC analysis	120 min

TABLE II

COMPARISON OF RESULTS OBTAINED WITH DIFFERENT TECHNIQUES FOR A COMMERCIAL SAMPLE OF POLYETHYLENE

Technique	*Oleamide (ppm)*
High-resolution GC (on-column injection and capillary column)	416
IR (6.05-μm band)[3]	460
Potentiometric titration[18]	420
GC (analysed as methyl esters on a packed column)*	425

* 3-m × 2 mm I.D. column packed with 20% diethylene glycol succinate on Chromosorb P AW (80–100 mesh) at 200°C. Carrier gas: nitrogen (30 ml/min).

Compared with IR spectroscopy, the GC method eliminates the interferences caused by antistatic agents or polyethers, which are often present in the extract. It also permits the rapid qualitative and quantitative analysis of the various amides used as slip agents.

Despite the unconventional injection conditions (120°C above the boiling point of the solvent), used in order to shorten the analysis time, the use of the secondary cooling system permitted good quantitative results to be obtained. Repeated on-column injections of samples with an amide concentration in the range 200–1000 ppm resulted in a relative standard deviation of 3.6%. Calibration was carried out by the peak-area ratio method, using as the internal standard an amide not present in the sample.

An even better relative standard deviation (below 1%) can be obtained by injecting the sample at a temperature slightly higher than the boiling point of the solvent. As already mentioned, this will obviously result in a longer analysis time.

CONCLUSIONS

The proposed method can be easily used in industrial application laboratories for the routine quality control of slip agents in polyolefins. The non-vaporizing on-column injection with secondary cooling combined with the high resolution of capillary columns permit accurate quantitative analyses to be completed in a very short time. This time can be halved by using hydrogen as the carrier gas. In our work, however, helium is preferred for safety reasons.

The good separation shown in Fig. 1 is very convenient when analysing real samples that also contain antioxidants and UV stabilizers whose retention times are close to that of the amide.

A GC investigation of different additives contained in polyolefins is currently in progress.

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