

CHROM. 11,716

Note

Gas chromatographic analysis of fatty acid amides in polyolefins

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(Received November 20th, 1978)

Frequently a fast analysis of fatty acid amides (C_{14} – C_{22}), used as slip agents in polyolefins, is required in industrial analytical laboratories. Such analyses are usually performed, after extraction of the polymer with suitable solvents, by infrared¹ or ultraviolet² spectroscopy or, more frequently, by gas chromatography (GC). The GC determination of extracted amides has mostly been carried out by the "reaction GC" technique (reaction in the column to form the related nitriles^{3–5}), or after prior conversion of amides into suitable derivatives (*e.g.*, methyl esters or trifluoroacetyl derivatives⁶).

The direct analysis of long-chain fatty acid amides has been less investigated^{7–9} and separation between saturated and unsaturated amides with the same chain length has not always been possible.

A rapid method is described here that allows the analysis by direct injection into the column of the polymer extract and the separation, identification and determination of fatty acid amides, both saturated and unsaturated.

EXPERIMENTAL

Reagents

Carbon tetrachloride, chloroform, methanol and absolute ethanol were obtained from Carlo Erba (Milan, Italy), palmitamide and stearamide from Fluka (Buchs, Switzerland) and oleamide and erucylamide from ICN Pharmaceuticals (Cleveland, Ohio, U.S.A.). Methyl esters of palmitic, stearic, oleic and erucic acids were reference substances for GC from Merck (Darmstadt, G.F.R.).

Extraction procedure

A weighed sample (15–20 g), in pellet, film or powder form, is extracted with carbon tetrachloride (*ca.* 250 ml) under reflux and with magnetic stirring, the extraction time being chosen according to the type of polymer: low-density polyethylene is completely "dissolved" in about 30 min, whereas high-density polyethylene and polypropylene (pellets) may require 48 h; ethylene-propylene copolymers or powdered polymers require intermediate times.

After cooling, the sample suspension is vacuum filtered using a Gooch crucible (Permax 26 D-R3 type), thoroughly washed with chloroform-ethanol (1:1) (which allows the precipitation of low polymers), and the extract is concentrated, re-filtered

and diluted to exactly 10 ml with carbon tetrachloride. This extract is injected directly into the gas chromatograph.

Gas chromatographic analysis

A Carlo Erba Model GV gas chromatograph equipped with a flame-ionization detector and direct injection into the column was employed.

The column dimensions (glass tubes) were (A) 3 m \times 2 mm I.D. for oleamide, palmitamide and stearamide and (B) 1 m \times 2 mm I.D. for erucylamide. The stationary phase was 3% Dexil 300 GC (carborane-siloxane-type structure; Analabs, North Haven, Conn., U.S.A.) on Gas-Chrom Q (80-100 mesh). The column temperature was 190° and the injection block and detector temperature 300°. The carrier gas was helium (about 1.2 kg/cm² before the column).

RESULTS AND DISCUSSIONS

Under the above conditions, the elution order and retention times of the components were as shown in Figs. 1 and 2. Related peaks are symmetrical and reproducible. Amides with the most practical importance in the polymer field, *i.e.*, palmitamide, stearamide, oleamide and erucylamide were well separated, although a saturated and an unsaturated amide with the same number of carbon atoms were present (stearamide and oleamide).

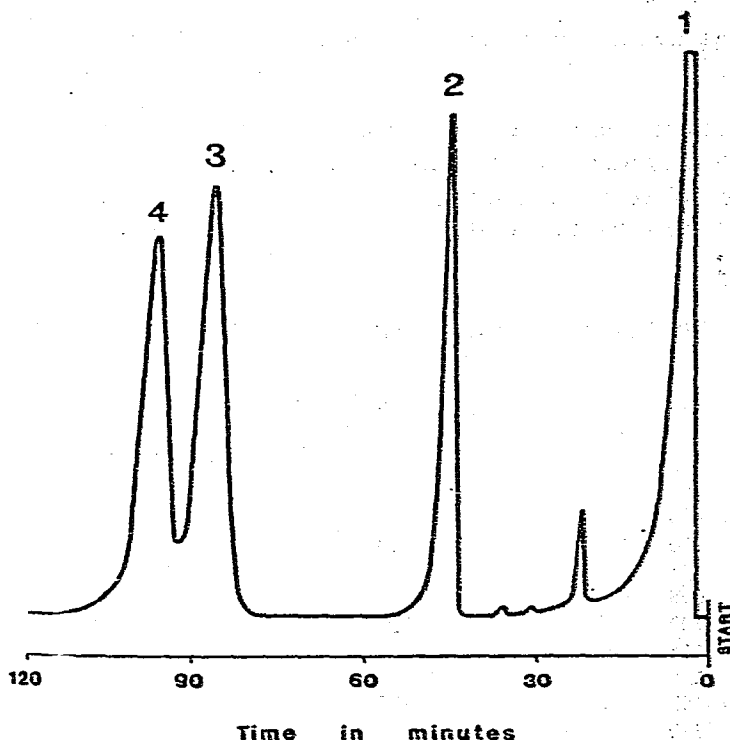


Fig. 1. Gas chromatogram of a mixture of amides in chloroform-ethanol obtained on column A. Peak: 1 = solvent; 2 = palmitamide; 3 = oleamide; 4 = stearamide.

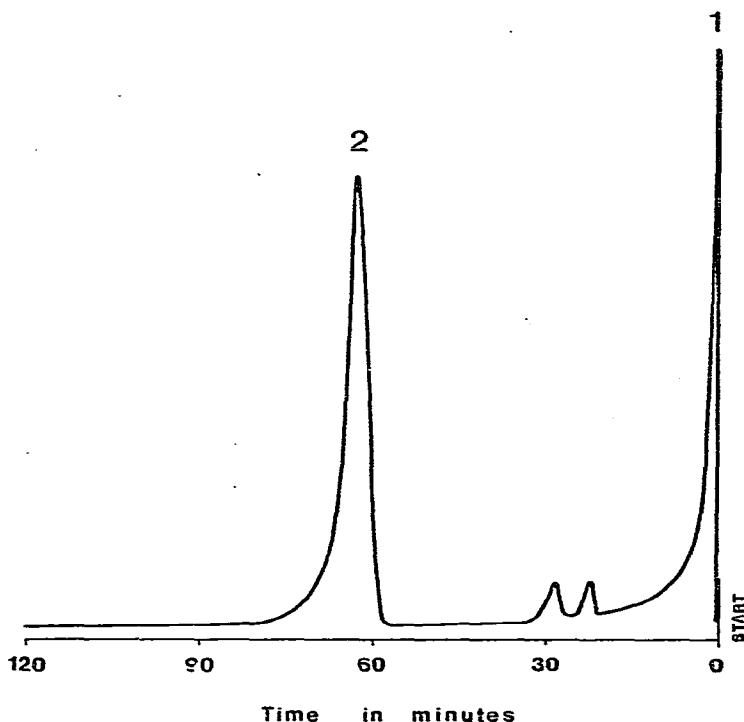


Fig. 2. Gas chromatogram of erucylamide in chloroform-ethanol obtained on column B. Peaks: 1 = solvent; 2 = erucylamide.

Quantitative determinations were made by the external standards method, *i.e.*, by comparison with known amides. As the titres of the long-chain fatty acid amides used as reagents were not reliable, it was necessary to determine their true titres by the following steps: (a) purification from free fatty acids; (b) quantita-

TABLE I

RECOVERY TESTS ON POLYMER SAMPLES AND COMPARISON OF INFRARED (IR) AND GC METHODS

Sample	Amide	Amide added (ppm)	Amide found (ppm)	
			IR method ¹	Proposed method
A	Palmitamide	50		45
	Oleamide	300		290
	Total	350	340	335
B	Palmitamide	95		115
	Oleamide	605		620
	Total	700	710	735
C	Palmitamide	115		115
	Stearamide	235		205
	Total	350	335	320
D	Palmitamide	230		210
	Stearamide	470		450
	Total	700	670	660

tive acidic hydrolysis; (c) conversion into methyl esters; (d) titre determination by direct comparison with commercially available related high-purity acid methyl esters. This calibration procedure could only be applied to saturated amides, because the unsaturated amides were not readily quantitatively hydrolysed in acidic medium; their methyl esters were obtained after alkaline saponification with methanolic hydroxide in Carius tubes at 130°.

The accuracy of the method and of the calibration procedure was found to be satisfactory through recovery tests, carried out on polymers (low-density polyethylene) with a known total amide content at two different concentration levels and analysed by infrared spectroscopy¹ and the proposed method. The results in Table I show that the agreement between the two methods and the recovery can be considered to be acceptable.

For the precision, we calculated, e.g., for oleamide, confidence limits (95% probability) of $\pm 5\%$ at a concentration of 500 ppm in the polymer.

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