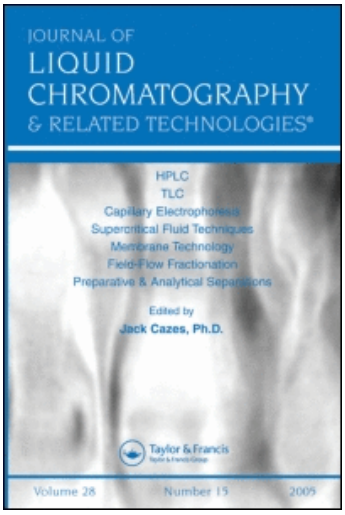


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# Determination of Polyolefin Additives by Normal-Phase High Performance Liquid Chromatography following Soxhlet Extraction

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# DETERMINATION OF POLYOLEFIN ADDITIVES BY NORMAL-PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY FOLLOWING SOXHLET EXTRACTION

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## ABSTRACT

Methods were developed for the determination of three classes of polyolefin additives. These classes are: mono and diglycerides, tertiary $C_{12}$-$C_{16}$ alkyldiethanolamines, and alkyldithiopropionates. Soxhlet extractions were performed on 50 g ground samples with chloroform for 2 hours. The extracts were concentrated and the additives were determined by high-performance liquid chromatography on a μ-Porasil stationary phase. The methods were studied with both polyethylene and polypropylene.

## INTRODUCTION

Recently a series of methods were published from this laboratory for the determination of additives in polypropylene and polyethylene by normal phase high performance liquid chromatography (HPLC) following hot decalin extraction (1-3). Decalin extraction can be performed in about an hour and can be used for many types of additives as long as the additives possess good chromophores (3). The present work describes methods based on Soxhlet extractions with chloroform which can be used for determining several additives which are not amenable to the decalin extraction/HPLC method.

## MATERIALS AND METHODS

Instrumentation The liquid chromatograph used in this study was a Waters Model 204 liquid chromatograph equipped with a model 6000A pump. The injectors were a Valco 6000 psi injector or a Micromeritics Model 725 Autoinjector, both equipped with 50µL sample loops. Elution was monitored with a Waters Model 450 variable wavelength ultraviolet absorption detector or a Waters Model 401 Differential Refractometer detector, and a 10 mV strip chart recorder. The column used was a 3.9 mm i.d. x 30 cm µ-Porasil column packed with 10 micron porous silica obtained from Waters Associates, Milford, Mass.

The grinder was a Wiley mill with 10 mesh screen, cooled with liquid nitrogen. The Soxhlet extractor used had a 500 mL capacity solvent flask. Ground sample was extracted from 45 mm x 123 mm cellulose thimbles obtained from Fisher Scientific.

Reagents Reagent grade chloroform, 1,2-dichloroethane, and absolute ethanol for use as HPLC solvents were filtered through Millipore type FH 0.5 micron filters prior to use. Ammonium hydroxide (27% aq) was obtained from Mallinkrodt and used as received. The extraction solvent was reagent grade chloroform and was used without pretreatment. Armostat 310 and Armostat 410 were obtained from Armak, Chicago, IL.; Atmul 84 was from ICI America, Inc., Wilmington, Del.; DLTDP and DSTDP were obtained from American Cyanamid Co., Bound Brook, N. J.

Procedure Portions of 50 g samples of polymer were weighed accurately after grinding to 10 mesh, and placed in Soxhlet thimbles. To prevent the samples from floating in the extraction solvent, the cutout tip of an extraction thimble and a 1 cm layer of 3 mm glass beads were placed above each sample. A 250 mL portion of extraction solvent was poured into each of the boiling flasks. After 2 hours extraction time, the extract solutions were transferred to 400 mL beakers and evaporated to about 10 mL on a steam bath. The solutions were transferred quantitatively to 25 mL volumetric flasks and diluted to volume with chloroform. The

TABLE I
Chromatographic Conditions Used for the Separation of Additives on μ-Porasil.

| ADDITIVE | MOBILE PHASE | RETENTION VOLUME, mL | DETECTOR |
|---|---|---|---|
| Armostat 310 | Chloroform:Ethanol: Ammonia (80:20:0.1) | 5.6 | Refractive Index |
| Armostat 410 | Chloroform:Ethanol: Ammonia (80:20:0.1) | 5.6 | Refractive Index |
| Atmul 84 | Chloroform:Ethanol: Ammonia (95:5:0.05) | 6.3 | Refractive Index |
| DLTDP | 1,2-Dichloroethane | 7.9 | UV, 230 nm |
| DSTDP | 1,2-Dichloroethane | 6.3 | UV, 230 nm |



solutions were allowed to sit for several minutes until any small polymer particles present floated to the top, leaving a clear solution near the bottom of the flask. Using a Pasteur pipet, 1-5 mL portions of the clear bottom solutions were transferred to 20 mL scintillation vials, from which the HPLC injections were made.

The HPLC conditions used for the determination of the additive are listed in Table I. Duplicate injections of each standard and sample solutions were made. Peak heights were measured to the nearest 0.5 mm, and in cases where the peak widths for sample extracts were not uniform, area measurements were made by measuring also the peak widths at half the peak heights to the nearest 0.1 mm using a peak magnifier. The amount of each additive was determined from each sample injection by comparing peak heights or areas for sample and standard.

## RESULTS AND DISCUSSION

A requirement for the determination of additives by the decalin extraction/HPLC method (1-3) is that the additives possess a strong chromophore above 230 nm, in the region where a mobile phase solvent such as dichloromethane does not absorb ultraviolet

radiation strongly. Typically levels of such additives in decalin following extraction range from about 0.02-0.2 mg/mL. This is about two orders of magnitude too dilute for HPLC determination following decalin extraction of the five common additives which are the subject of this work. These are Atmul 84 (mono-and diglycerides), DLTDP (dilaurylthiodipropionate), DSTDP (distearyl-thiodipropionate), Armostat 310 (ethoxylated tallow amine), and Armostat 410 (ethoxylated coconut oil amine). Concentrations of these additives should be 1-10 mg/mL or greater. To obtain extracts with these concentration levels, an extraction procedure with a volatile solvent is required. Several such procedures have been described (4-6). Reported extraction times were as long as 48 hours (4).



In the present work, to determine the minimum amount of time required to extract the additives of interest from ground polyolefin matrices, Soxhlet extractions were performed with chloroform for time intervals ranging from 1-8 hours. The levels of additives were determined by HPLC following a 1:10 concentration of the extract solution. The amounts of additives extracted are listed in Table II. It is apparent from Table II that the extractions are almost complete following 1 hour and no significant additional amount of additives are extracted after 2 hours extraction time. All subsequent analyses were performed using 2 hour extraction times.

Response Linearity of response with peak height was established for injected amounts for up to 465 µg Armostat 310, 510 µg Armostat 410, 500 µg Atmul 84, 241 µg DLTDP, and 465 µg DSTDP. Some nonlinear response with peak height and area was observed between 241 µg and 482 µg DLTDP injected. This serves to illustrate that the region of linear of response should be established for the particular liquid chromatograph and detector used for this type of analysis.

Accuracy To ensure that the additives were being extracted in a quantitative manner studies were performed with polymers prepared

TABLE II
Weight Percent Additives Determined in 50 g Polymer Samples at Various Extraction Times

| ADDITIVE | POLYMER | TIME OF EXTRACTION, HOURS | WT % |
|---|---|---|---|
| Armostat 310 | PE | 1 | 0.12 |
| | | 2 | 0.14 |
| | | 4 | 0.15 |
| | | 8 | 0.16 |
| Armostat 410 | PP | 1 | 0.19 |
| | | 2 | 0.18 |
| | | 4 | 0.19 |
| | | 8 | 0.18 |
| Atmul 84 | PP | 1 | 0.28 |
| | | 2 | 0.30 |
| | | 4 | 0.28 |
| | | 8 | 0.31 |
| DLTDP | PE | 1 | 0.025 |
| | | 2 | 0.029 |
| | | 4 | 0.020 |
| | | 8 | 0.030 |
| DSTDP | PP | 1 | 0.26 |
| | | 2 | 0.26 |
| | | 4 | 0.24 |
| | | 8 | 0.24 |



with known amounts of additives. The results of this study are listed in Table III. The data in Table III indicate good recoveries for the additives.

Precision The pooled standard deviations for the additive determination were calculated and are listed in Table IV. These data indicate good precision for the Soxhlet extraction/HPLC method.

Limits of Detection Limits of detection for the method as written were calculated assuming 2 mm peak heights for both the RI detector set at 16X sensitivity and the UV detector set at 0.2 Absorbance. This represents a S/N level of about two. The limits of detection, expressed as wt. % in original samples were 0.002% Armostat 310, 0.004% Armostat 410, 0.02% Atmul 84, 0.003% DLTDP, and 0.007% DSTDP.

TABLE III

Results of Studies on Polymer Samples with Known Amounts of Additives.

| SAMPLE | ADDITIVE | SPECIFIED WT. % | DETERMINED WT. % |
|---|---|---|---|
| PE | ARMOSTAT 310 | 0.10 | 0.068 |
| | | 0.10 | 0.072 |
| | | 0.20 | 0.14 |
| | | 0.20 | 0.15 |
| | | 0.40 | 0.31 |
| | | 0.40 | 0.32 |
| | | 0.60 | 0.48 |
| | | 0.60 | 0.47 |
| PP | ARMOSTAT 410 | 0.05 | 0.034 |
| | | 0.05 | 0.034 |
| | | 0.10 | 0.083 |
| | | 0.10 | 0.085 |
| | | 0.20 | 0.18 |
| | | 0.20 | 0.18 |
| | | 0.40 | 0.39 |
| | | 0.40 | 0.38 |
| PP | ATMUL 84 | 0.10 | 0.068 |
| | | 0.10 | 0.068 |
| | | 0.20 | 0.18 |
| | | 0.20 | 0.17 |
| | | 0.40 | 0.43 |
| | | 0.40 | 0.42 |
| | | 0.80 | 0.76 |
| | | 0.80 | 0.75 |
| PE | DLTDP | 0.01 | 0.018 |
| | | 0.01 | 0.014 |
| | | 0.03 | 0.029 |
| | | 0.03 | 0.026 |
| | | 0.10 | 0.052 |
| | | 0.10 | 0.046 |
| | | 0.20 | 0.12 |
| | | 0.20 | 0.11 |
| PP | DSTDP | 0.05 | 0.070 |
| | | 0.05 | 0.052 |
| | | 0.10 | 0.092 |
| | | 0.10 | 0.088 |
| | | 0.20 | 0.26 |
| | | 0.20 | 0.24 |
| | | 0.40 | 0.42 |
| | | 0.40 | 0.45 |

TABLE IV

Precision Data for the Additives

| ADDITIVE | POOLED STANDARD DEVIATION[a] | RANGE OF VALUES, WT. % |
|---|---|---|
| ARMOSTAT 310 | 0.0089 | 0.068-0.48 |
| ARMOSTAT 410 | 0.0050 | 0.034-0.39 |
| ATMUL 84 | 0.0055 | 0.068-0.76 |
| DLTDP | 0.0063 | 0.014-0.12 |
| DSTDP | 0.020 | 0.052-0.45 |

a. Calculated from the data in Table III.



Interferences Usually more than one additive is used in a polyolefin formulation. Thus, in determining an additive, it is important to check possible interferences with other additives which could be present in the polymer. Studies indicated that BHT and Irganox 1010 do not interfere with the determination of Armostats 310 and 410. However, a peak due to a minor component in the additive Weston 618 might be an interference if this additive is present. A small component in Weston 618 also might interfere in the determination of Atmul 84. However, the additives DSTDP, DLTDP, BHT, and Ethyl 330 do not interfere in the determination of Atmul 84. In the determination of DLTDP and DSTDP, some potential interference was encountered with Topanol CA and Irganox 1010, however, the interference from the latter additive was slight. The additives CGL-144, Kemamide E, Irganox 1076, TNPP, and BHT do not interfere with the determination of DLTDP or DSTDP. In general, interference studies should be done with any other known additives present.

## CONCLUSION

The procedure described in this work should be amenable to several types of additives which do not possess good chromophores for sensitive detection in dilute solution. The 2 hour Soxhlet

extraction conceivably could be coupled with other specifically designed normal-phase HPLC systems, or nonaqueous reversed-phase systems as well.

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## REFERENCES

1. Schabron, J. F.; Fenska, L. E. Anal. Chem. 1980 52, 1411.

2. Schabron, J. F.; Bradfield, D. Z. J. Appl. Polym. Sci. 1981 26, 2479.

3. "Determination of UV Absorbing Polyolefin Additives by Gradient and Isocratic Normal-Phase High Performance Liquid Chromatography," Schabron, J. F.; Smith, V. J., Ware, J. L., submitted for publication.

4. Haney, M. A.; Dark, W. A. J. Chromatogr. Sci. 1980 18, 655.

5. Lehotay, J.; Danecek, J.; Liska, O.; Lesko,J.; Brandsteterova, E. J. Appl. Polym. Sci. 1980 25, 1943.

6. Walter, R. B.; Johnson, J. F. J. Polymer Sci.: Macromolecular Reviews 1980 15, 29.