Gas Chromatographic Determination of Acid-Catalyzed Transesterified Antioxidant Additive Irganox 1076® in Polypropylene

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Synopsis

The transesterification by means of methyl alcohol of a low vapor pressure antioxidant additive, *n*-octadecyl-β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, Irganox 1076® (produced by Ciba-Geigy) was studied. The classical method to prepare methyl esters from triglycerides in lipids was applied with use of sulfuric acid as a catalyst. The optimum reaction conditions were sulfuric acid concentration of 1 w/v% in methyl alcohol, temperature of 75°C, and time of 2 hours. The contents of the additive were determined by gas-liquid chromatography (GLC) of a portion of transesterificate using 10% SE-30 on Gaschrom Q (60–80 mesh) or 5% Silicone OV-17 on Shimalite W (80–100 mesh) as a packing reagent. Irganox 1076 in polypropylene was extracted with *n*-hexane. Many interfering substances in the GLC could be completely removed by the Florisil column treatment of *n*-hexane extract. The relative standard deviation was 2.7% for Irganox 1076 at levels corresponding to 0.0142 wt% in polypropylene. The limit of detection was 5 μg/g in polypropylene.

INTRODUCTION

n-Octadecyl-β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (Irganox 1076), a low vapor pressure white powder of molecular weight 530, has been generally used as an antioxidant for polyolefins.

Wims and Swarin[1] noted that the extract treated with tetrahydrofuran for 24 hours from 8 mesh polypropylene pellets could be separated by size exclusion chromatography (SEC) or normal-phase liquid chromatography. Schabron and Fenska[2] determined simultaneously the three kinds of antioxidant additives, BHT, Irganox 1076, and Irganox 1010 in polyethylene by high performance liquid chromatography (HPLC).

In the HPLC analysis, the column is considerably choked up in the developmental stage of the extract. Furthermore, the retention time is the only one method presently available for identification of components. Considering these two disadvantages, gas chromatographic analysis on a volatile derivative was considered to be effective. The paucity of reports on the gas-liquid chromatographic determination of Irganox 1076 promoted us to investigate it.

Many methods have been developed for the quantitative formation of methyl esters for the analysis of fatty acids in lipid mixtures. They are classified into two types. One type requires two steps, namely, the saponification of fatty acid esters such as glycerides, phosphatides, and sterol

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esters, followed by methylation by means of methyl alcohol in the presence of sulfuric acid,[3] hydrochloric acid,[4] *p*-toluene sulfonic acid,[5] or boron trifluoride[6] as catalysts, or methylation with diazomethane.[5]

This procedure has some disadvantages. The double bonds of the esters may change during saponification. In the reaction of fatty acids with diazomethane, the yield may be poor because of the formation of pyrazoline.[4]

The other method requires only one step; the formation of the methyl esters by the direct transesterification by means of methyl alcohol in the presence of sulfuric acid,[3] hydrochloric acid,[7] or boron trifluoride,[8] or by means of sodium methoxide[9] or potassium methoxide.[10]

The latter reagents proved to be easier to use and milder technically.

In the present work the specific determination method of an antioxidant additive Irganox 1076 commonly used in industry was developed. The method consists of a clean-up procedure by the Florisil column for *n*-hexane extract of polypropylene followed by the transesterification by methyl alcohol in the presence of sulfuric acid and the gas-liquid chromatographic analysis.

EXPERIMENTAL

Reagents

The antioxidants 2,6-di-*tert*-butyl-*p*-cresol (BHT), *tert*-butyl-4-hydroxy anisole (BHA), and stearyl alcohol were purchased from Tokyo Kasei Kogyo Co., Ltd. and *n*-octadecyl-β-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate (Irganox 1076) from Kasho Kogyo Co. Ltd (produced by Ciba Geigy). Ethyl ether, *n*-hexane, methyl alcohol, ethyl alcohol, and sodium sulfate for pesticide residue analysis were purchased from Wako Pure Chemical Industries Ltd. and Florisil of 60-100 mesh from Floridin Co. Ltd.

The antioxidant additives were used without further purification.

Other reagents were all analytical grade.

Apparatus

The gas chromatograph used in this study was a Shimadzu Model GC-4BM gas chromatograph equipped with a flame ionization detector. The GC-MS analyzer used was a Jeol Model JMA 200 Mass Data Analysis System. The fractionation with a Florisil column chromatography was done by a Toyo Kagaku Sangyo SF-160 Rectangular Balance-Operated Fraction Collector.

Materials

To satisfy the generality of our present work, the impure samples containing the more interfering substances were necessary. Therefore previously proven rather than newly produced materials were used. We collected some polypropylene lunch wares which had been employed in the field for one to ten years.

Solvent Extraction Procedure

For the extraction of additives from polypropylene, 5 cubes of 4 × 4 × 4 mm, were refluxed in a Kjeldahl-type flask with 100 mL of *n*-hexane for 8 hours at 80°C. The solution was then cooled to room temperature and was filtrated with a filter paper (Toyo Kagaku Sangyo, No. 5c) to remove the precipitate insoluble in *n*-hexane. The filtrate was evaporated under vacuum until just before the solvent completely disappeared and made up to 10 mL with *n*-hexane.

Florisil Column Chromatography

As a clean-up procedure, 5 g of Florisil was activated at 120°C for 20 hours and was prewet with about 30 mL of *n*-hexane. This Florisil was packed into a glass chromatographic column of 10 mm inner diameter (id) × 300 mm, and then was topped with about 10 mm anhydrous sodium sulfate. The column was eluted with a 50 mL portion of *n*-hexane at a flow rate of one drop per 2 seconds to remove the impure substances in Florisil and the extracted solution was entirely poured on the column. The excess amounts of solvent were allowed to flow out from the column. Irganox 1076 was eluted with 120 mL of 5% ethyl ether/*n*-hexane after eluting the column with 20 mL of *n*-hexane.

Derivative Formation

The eluate from the Florisil column was concentrated to below 5 mL by a rotary evaporator under vacuum, and the residue was transferred quantitatively into a 20 mL test tube and brought to the mark with *n*-hexane. A portion of this solution was put into a 17 mm (id) × 60 mm glass ampule reactor and the solvent was carefully distilled over a water bath at 40°C under a stream of nitrogen. Next, to an ampule reactor was added 10 mL of 1 w/v% sulfuric acid in methyl alcohol and sealed. This ampule was immersed into a 75±1°C water bath and shaken frequently for 2 hours, and then immediately cooled to below room temperature by a stream of water and opened carefully. The contents in the reactor were transferred into a 100 mL separatory funnel with 20 mL of chloroform without any loss of product and 60 mL of water was added. The separatory funnel was shaken vigorously for 10 minutes and an organic layer was separated.

This procedure was repeated two times to extract the aqueous layer with 15 mL of chloroform. The collected organic layers were washed by 20 mL of distilled water and dehydrated with about 10 of anhydrous sodium sulfate. After filtration, the solution was evaporated under vacuum until the solvent was completely removed, and then was made up to 5 mL with dichloromethane.

Gas-Liquid Chromatography

The two columns, 3 mm (id) × 2 mm, glass tubings packed with 10% SE-30 on Gaschrom Q (60–80 mesh), and 5% Silicone OV-17 on Shimalite W (80–100 mesh) were isothermally operated at 220°C.

The injector was maintained at 285°C. Nitrogen as a carrier gas was allowed to flow at the flow rate of 60 mL/min. The methyl derivative of Irganox 1076 showed a retention time of about 4 minutes in the former and of about 8 minutes in the latter.

GC-MS Analysis

The column, 2 × 2 mm (id), glass tubing packed with 10% SE-30 on Gaschrom Q (60–80 mesh) was isothermally operated at 274°C.

Helium as a carrier gas was allowed to flow at 1 kg/cm^2. The ionization voltage, current, and temperature of ion source were 70 eV, 300 μA, and 250°C.

The Calibration

The calibration curve obtained by the treatment procedure outlined above using a series of standard solution containing 0, 20, 40, 60, 80, and 100 μg of Irganox 1076 per 5 mL of chloroform.

RESULTS AND DISCUSSION

Florisil Column Chromatography

Irganox 1076 of 10.25 mg was eluted. Each fraction holding 10 mL eluent solvent was treated with the procedure mentioned above, and Irganox 1076 was converted to its methyl ester. The elution curve is shown in Figure 1. The eluted Irganox 1076 was present in the 4th to 12th fractions and the content in the 6th fraction was maximum. The curve (A) in Figure 2 shows the chromatogram of the first 20 mL fractions eluted by *n*-hexane from 5 g of polypropylene. This is the same chromatogram as the direct transesterificate of the extract which had many unknown components. In any following fraction, however, these complicated peaks were not present. Con-

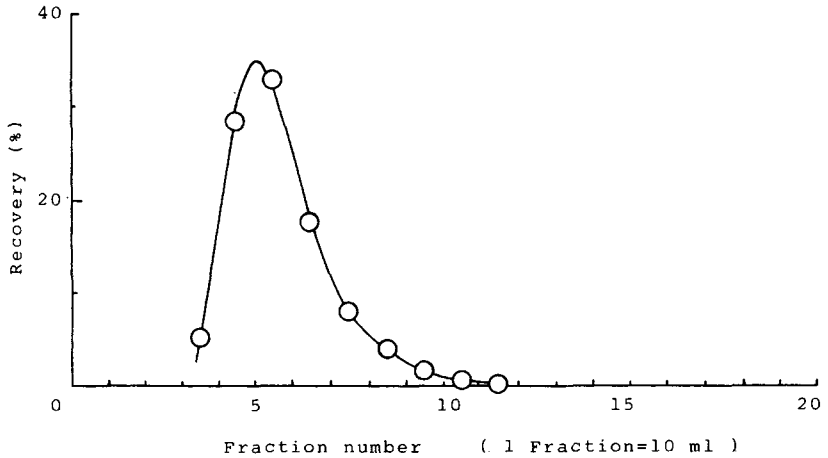

Fig. 1. Elution pattern of Irganox 1076 from activated Florisil column with 5% ethyl ether/*n*-hexane.

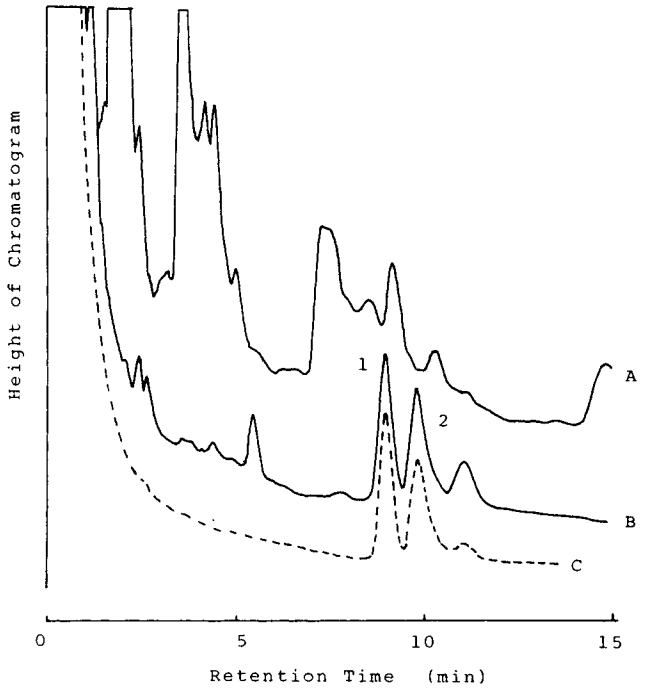

Fig. 2. Gas chromatogram of transesterificated products. A: Fraction 1 eluted with 20 mL of *n*-hexane from Florisil column. B: Fraction 2 eluted with 120 mL of 5% ethyl ether/*n*-hexane from Florisil column. C: 100 μg of Irganox 1076. GLC operating condition: column, 5% OV-17 on Shimalite W(80-100 mesh), 2 × 3 mm id, glass; temp, inj., 285°C; oven, 215°C; flow, N_2, 60 mL/min. Memo: peak 1 is methyl derivative from Irganox 1076. Peak 2 is stearyl alcohol.

sequently, 20 mL of *n*-hexane is quite satisfactory to remove the interfering materials. Further flow of 120 mL of 5% ethyl ether/*n*-hexane resulted in the complete elution of added Irganox 1076.

The recovery of Irganox 1076, BHA, and BHT from the mixture by controlled Florisil column treatment is shown in Table I. Both BHA and BHT in the eluate were at first determined by gas-liquid chromatography employing 10% SE-30 on Gaschrom Q (60–80 mesh) as a packing reagent. A part of the eluate was taken and Irganox 1076 was transesterified to its methyl ester. Although the mean value of recovery of Irganox 1076 detected

TABLE I
Recoveries of IRGANOX 1076, BHA, and BHT Eluted from Activated Florisil Column with 5% Ethyl Ether/η-Hexane

Compound	Amount added (μg/g)	Percent recovered (%)		
Irganox 1076	205	93.0	84.6	86.0
		101.7		
BHA	304	82.0	88.0	89.2
		91.1	86.0	
BHT	274	96.0	99.1	91.0
		101.3		

showed over 90%, the relative standard deviation was slightly higher than the other two additives. BHA and BHT showed good recoveries and lower deviation.

These results indicate that three additives can be eluted simultaneously from the controlled Florisil column.

The Optimum Conditions of Transesterification

Figure 3 shows the relationship between the reaction time and the yield of methylate. The first reaction was rapid as Jones and Lapworth[11] reported on the kinetics of the decomposition of acyl derivatives of phenol. At 5 w/v% H_2SO_4/MeOH, the yield of methyl ester decreased linearly after two hours and 1 w/v% H_2SO_4/MeOH, the rapid decrease was observed after 4 hours. At 0.1 w/v% H_2SO_4/MeOH, the yield was almost unchanged and higher than the others from 3 to 8 hours. The yield after 2 hours almost agreed with the others.

Figure 4 shows the relationship between the charged temperature and the yield under various acid concentrations. The ester formed by reaction with 0.1 w/v% H_2SO_4/MeOH increased linearly with increasing temperature. At both 1 w/v% and 5 w/v% H_2SO_4/MeOH solution, the yield–temperature relationships had shown a similar tendency with the maximum yield at 75°C in 1 w/v% H_2SO_4/MeOH solution. Heating at 90°C was too dangerous as the glass ampule was often explosive due to the low boiling point of methyl alcohol.

The optimum reaction time and temperature in 1 w/v% H_2SO_4/MeOH solution were 2 hours and 75°C. The higher and constant yield of methyl derivative was obtained and the added response relationship gave a straight line at a level of 20–200 μg of Irganox 1076.

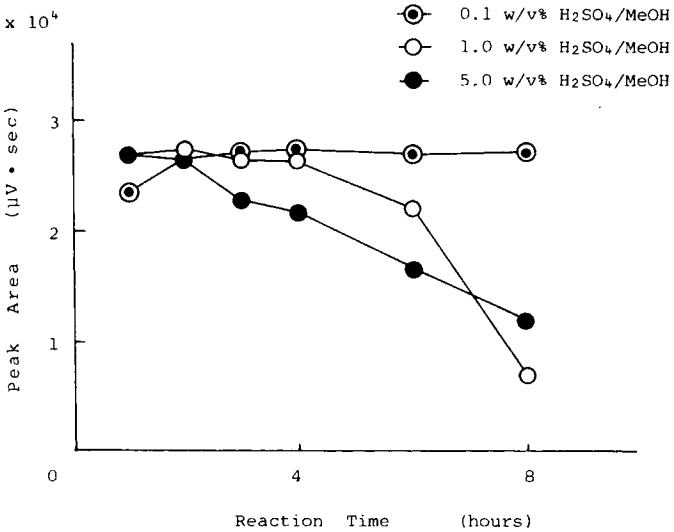

Fig. 3. Relationships between reaction time and yield of methylate derived from 610 μg of Irganox 1076 by acid-catalyzed transesterification at 90°C in the presence of three kinds of sulfuric acid concentrations.

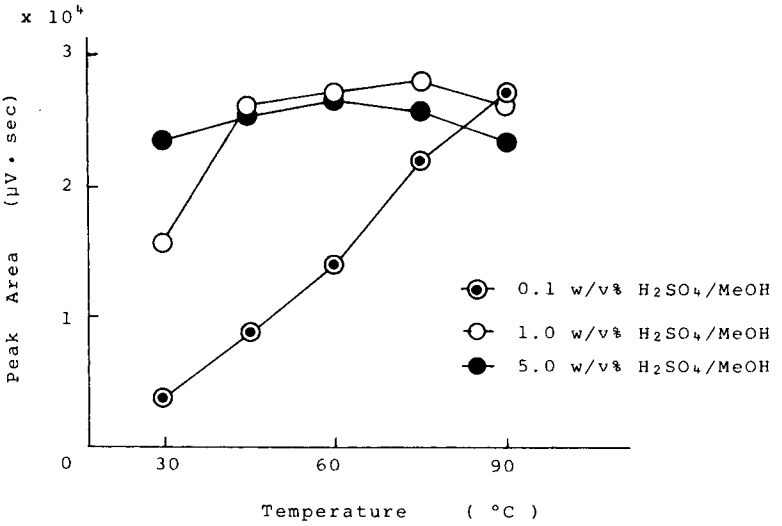

Fig. 4. Influence of reaction temperature on yield of methylate derived from 744 μg of Irganox 1076 by acid-catalyzed transesterification for 2 hours in the presence of three kinds of sulfuric acid concentrations.

From the above results the reaction was considered to proceed essentially with the same mechanism as the acid-catalyzed transesterification of lipid mixtures. However, the yield of ester decreased rapidly with time in 1 w/v% and 5 w/v% H_2SO_4/MeOH solution at 90°C (shown in Figure 3), although for stearyl alcohol the yield was constant with time as shown in Figure 5. This suggests the chemical transformation of the methyl ester of Irganox 1076 to another unknown compound with time at 90°C in higher sulfuric acid concentration.

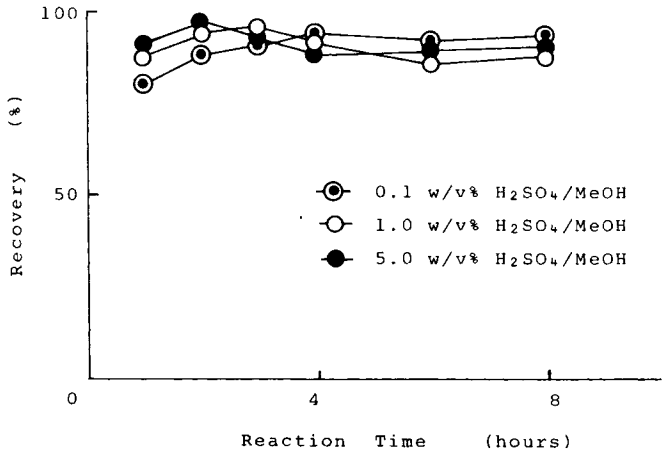

Fig. 5. Relationship between reaction time and recovery of stearyl alcohol obtained from 610 μg of Irganox 1076 by acid-catalyzed transesterification at 90°C in the presence of three kinds of sulfuric acid concentrations.

Gas-Liquid Chromatography

From preliminary experiments, the operation at relatively high temperature was necessaray to determine the methyl derivative of Irganox 1076 in the product. The influence of the polarity of the liquid phase on the shape of separation was studied. The gas-liquid chromatogram with 10% SE-30 on Gaschrom Q (60–80 mesh), 10% Silicone DC-200 on Gaschrom Q (80–100 mesh), and 5% Silicone OV-17 on Shimalite W (80–100 mesh) showed similar behavior and good separation, whereas 2% Silicone OV-17 on Gaschrom Q (60–80 mesh) packing reagent with low polarity was not suitable because of its tailing phenomenon.

Identification

Figure 6 shows the gas-liquid chromatographic separation of the transesterified product. Figure 7 shows the mass spectra of the peak component (A) of Figure 6. The considerable ion peaks were m/e = 292, 277, 219, 203, 189, 147, and 57, and the maximum in intensity was at m/e = 277. Figure 8 shows the spectra of Irganox 1076 which is extremely similar to the spectra shown in Figure 7 except for the upward ion peaks from m/e = 219, the parent ion peak at m/e = 530, and (M-15) fragment ion peak at m/e = 515.

The chemical structure of Irganox 1076 and the molecular weight of the methyl derivative of 292 were determined to identify the component (A) to be methyl-β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate.

On the other hand, the component (B) in Figure 6 perfectly agreed with the mass spectra of pure stearyl alcohol.

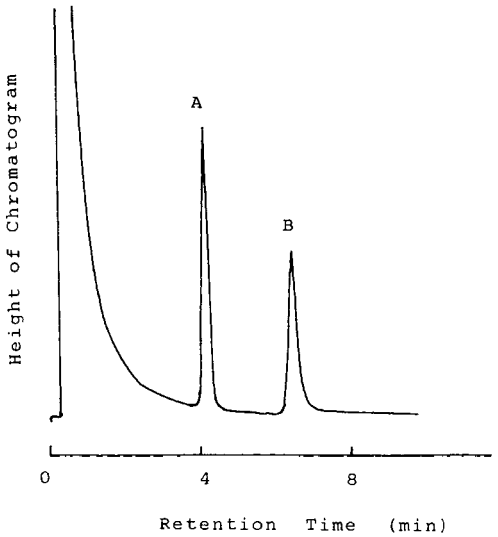

Fig. 6. Gas chromatogram of derivative from Irganox 1076. (A) Methyl-β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate. (B) Stearyl alcohol. GLC operating condition: column, 10% SE-30 on Gaschrom Q (60-80 mesh), 2 × 3 mm id, glass; temp, inj., 280°C; oven, 215°C; flow, N_2, 60 mL/min.

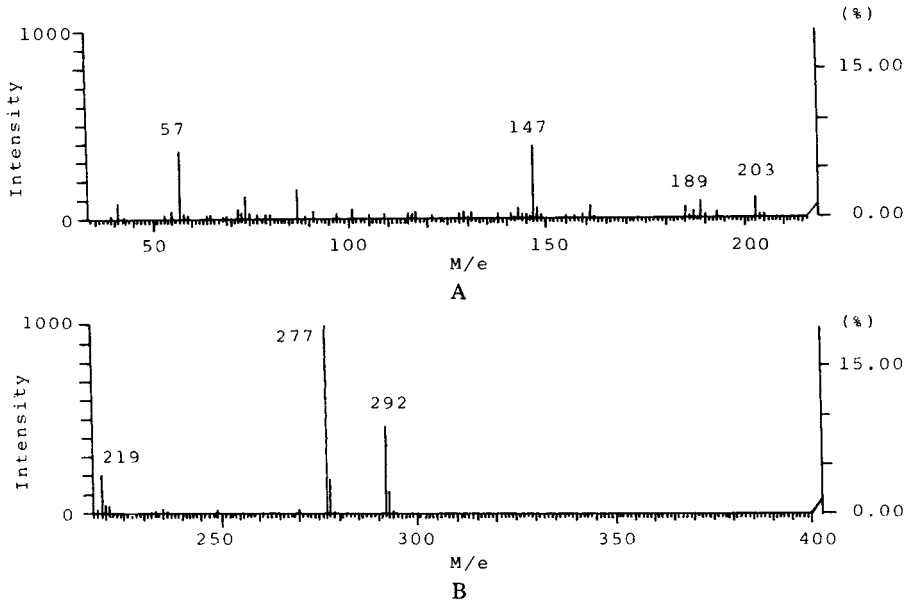

Fig. 7. Mass spectrum of derivative (A) from Irganox 1076. (A) Shown in Figure 6.

The Limit of Detection

The limit of detection of Irganox 1076 was about 5 μg/g in polypropylene. The limit is about 4 times lower than 0.002 wt% reported recently by Schabron and Fenska[2] with HPLC. The mass fragmentography in GC/MS, furthermore, might lead to the possibility for the trace amount analysis by using parent and fragment ions, although the limit of detection in a FID (flame ionization detector) is quite sufficient for the analysis at additive levels in polypropylene as mentioned in Ref. 2.

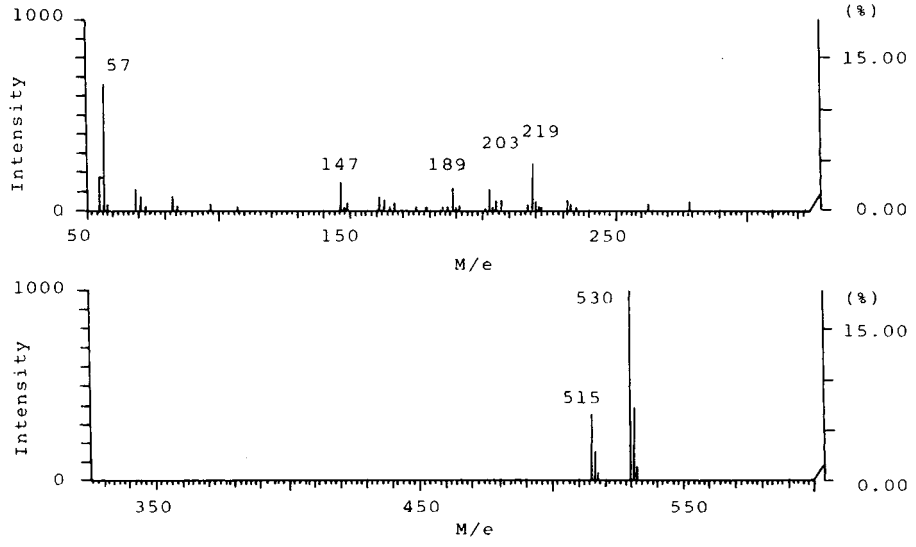

Fig. 8. Mass spectrum of Irganox 1076.

Application to Some Polypropylene Food Containers

As the elution from Florisil column gave good recoveries for the additive, we have analyzed those in the polypropylene food containers. That is, simultaneous determination of these three additives was performed mixing each 5 g of the four kinds of sample, followed by the solvent extraction with about 100 mL of *n*-hexane at 80°C. The extract was evaporated below 40°C under vacuum until just before the solvent completely disappeared and was made up to 50 mL with *n*-hexane.

Each 5 mL of solution was applied successively to the fractionation, transesterification, and gas-liquid chromatographic determination.

The results are shown in Table II. Good precision is seen for the method. The relative standard deviations were 2.7% for Irganox 1076 and 3.9% for BHT. The good reproducibility observed in applied studies indicates that our proposed analytical method is quite sufficient to determine the additive contents of most polypropylene samples with the exception of efficiency of solvent extraction.

Concerning the dependence of the efficiency on extraction conditions, the present paper could not describe this precisely. Spell and Eddy[12] have concluded that the extraction rate was a function of the particle size and the permeability of the solvent, which was shown to be inversely proportional to its polarity and the polymer density.

Furthermore, Wims and Swarin[1] found that 24 hours was sufficient to recover a number of antioxidants from polypropylene using a wrist action shake, and with the exception of a few studies, the methods involve the heating of polymer in the solvent to increase the efficiency of extraction.[13]

CONCLUSIONS

A method has been developed for the quantitative analysis of Irganox 1076, BHA, and BHT in polypropylene food containers.

The following conclusions are drawn from this study:

1. The formation of the methyl ester by means of acid-catalyzed transesterification is very good technique for the gas-liquid chromatographc determination of the low vapor pressure antioxidant additive Irganox 1076. The optimum reaction conditions to obtain the methyl ester in 1 w/v% H_2SO_4/MeOH solution are 75°C for 2 hours.

TABLE II
Results of Duplicate Analyses of Polypropylene Food Containers

	Amount found (μg/g)		
NO	IRGANOX 1076	BHA	BHT
1	138	ND[a]	106
2	142	ND	99.3
3	137	ND	96.3
4	145	ND	96.5
5	147	ND	98.0
Mean	142	ND	99.2
SD[b]	3.8	-	3.9

[a]ND= Not detected.
[b]SD= Standard deviation.

2. The gas-liquid chromatograms with 10% SE-30, 10% Silicone DC-200, and 5% Silicone OV-17 as packing reagents show similar patterns and good separations.

3. MS is especially useful for the identification of the additives in unknown polypropylene samples.

4. Florisil column chromatography showed the quantitative and simultaneous recoveries of Irganox 1076, BHA, and BHT, and also showed the considerable clean-up effect to remove the sample impurities.

5. The duplicate analyses in *n*-hexane extract of a sample mixture showed good precision. The relative standard deviations were 2.7% for Irganox 1076 at levels corresponding to 0.0142 wt% and 3.9% for BHT at levels corresponding to 0.0099 wt% in polypropylene.

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