AMPA [*O,O*-dimethyl [(trifluoroacetyl)amino]-phosphonate] had an HPLC retention time of 25 min, eluting just after derivatized glyphosate. The AMPA HPLC fraction from control asparagus samples gave only very small GLC peaks at the GLC retention time of derivatized AMPA. From the interfering peak size in comparison with that of a standard of derivatized AMPA, it appeared that AMPA analysis could proceed successfully by this method at levels of ca. 0.10 ppm and above in asparagus. However, this potential was not verified by fortification experiments.

We found that the HPLC cleanup step was a relatively simple adjunct to the analytical procedure for the two crops examined, adding approximately 2 h to the analysis time for each sample once the HPLC system was set up. It is also quite reproducible; we analyzed approximately 40 field-treated kiwi fruit and asparagus samples, including numerous repeats, at the University of California laboratory using a single HPLC column with no noteworthy change in column retention or efficiency characteristics. The selectivity afforded by HPLC cleanup suggests potential utility for glyphosate analysis on other "problem" substrates. The HPLC cleanup is not, however, essential for all crops. Experience at the Michigan State University laboratory showed that some crops (strawberries, cantaloupe, cucumber, and acorn squash) could be analyzed successfully for parent glyphosate by the procedure described herein, or minor modifications of it (a column at 5% Thermon 3000 on AW-DMCS Chromosorb W, 80–100 mesh, supplied by Shimadzu was used for GLC), without the secondary HPLC cleanup. The need for HPLC cleanup of derivatized glyphosate should thus be evaluated on an individual crop basis.

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Registry No. Glyphosate, 1071-83-6.

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A Gas Chromatographic Method for Rapid Determination of Food Additives in Vegetable Oils

A rapid and simple method for the simultaneous determination of five kinds food additives [dehydroxyacetic acid (DHA), 3(2)-*tert*-butyl-4-hydroxyanisole (BHA), 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT), *tert*-butylhydroquinone (TBHQ), and 4-(hydroxymethyl)-2,6-di-*tert*-butylphenol (Ionox-100)] in commercial vegetable oils was studied by means of high-resolution gas chromatogrphy with a fused silica capillary column. By use of this method, the separation between food additives and fatty components, the reproducibility of food additives' retention time, and peak area were greatly improved. Some vegetable oils contained about 4–5 ppm of DHA and less than 0.5 ppm of BHA but did not contain BHT, TBHQ, and Ionox-100 in the range of our experiments.

The addition of food additives such as 3(2)-*tert*-butyl-4-hydroxyanisole (BHA), 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT), dehydroxyacetic acid (DHA), *tert*-butylhydroquinone (TBHQ), 4-(hydroxymethyl)-2,6-di-*tert*-butylphenol (Ionox-100), and so on is effective for the purpose of conservation of food quality. For the determination of food additives, gas chromatographic (GC) techniques have been used since the 1960s.

Vacuum sublimation as a pretreatment for GC reported by MaCaulley et al. (1967) is convenient for decreasing the interference peaks on the chromatogram, but the analysis takes a long time. Kline et al. (1978) developed the use of a precolumn in order to prevent the appearance of oil component peaks when the diluted sample with solvents was injected directly into GC, and they measured a few ppm level of antioxidants contained in oils. But these methods have the disadvantage of not being able to determine DHA, which has been widely used.

If a column having a high power for separation of the oil components such as a capillary column and splitless mode was adopted, we thought that the DHA could be measured and the lower detection limit would be improved. Thus, studies on a rapid method for the simultaneous determination of five kinds of food additives including DHA in vegetable oils by means of a high-resolution GC with a capillary column were carried out.

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Table I. Reproducibility of Retention Time for Food Additives

food additive	1	2	3	4	5	6	$\bar{x}$	s	% SD
DHA	11.99	11.99	11.99	12.00	11.99	11.99	11.99	0.00408	0.0340
BHA	13.06	13.05	13.06	13.07	13.06	13.06	13.06	0.00632	0.0484
BHT	13.37	13.37	13.37	13.39	13.37	13.37	13.37	0.00816	0.0610
TBHQ	13.63	13.63	13.63	13.65	13.64	13.64	13.64	0.00816	0.0598
Ionox-100	15.62	15.63	15.63	15.64	15.63	15.63	15.63	0.00632	0.0405

MATERIALS AND METHODS

Reagents and Sample. Food additives (BHA, BHT, TBHQ, Ionox-100, and DHA) were purchased from Tokyo Kasei Kogyo (Tokyo) and acetone (99.7%) for spectroscopy from E. Merck (Darmstadt). Fifteen kinds of commercial vegetable oils were on the market in Japan and The People's Republic of China.

Preparation of Standard and Stock Solutions. A stock solution (I) containing 1000 ppm each of five food additives was prepared by accurately weighing 100 mg of each food additives and transferred into a 100-mL volumetric flask partially filled with acetone and made up to exactly 100 mL with acetone. A stock solution (II) was prepared by accurately taking 10 mL of stock solution I into a 100-mL volumetric flask and diluting to 100 mL with acetone. This stock solution II contained 100 ppm of each food additive. A standard solution for food additives was prepared by transferring 5 mL of stock solution II into a 100-mL volumetric flask and diluting to 100 mL with acetone. This standard solution contained 5 ppm of each food additive.

Gas Chromatograph. The samples were analyzed directly by means of a Hewlett-Packard Model 5840A gas chromatograph equipped with a capillary injector system at 200 °C and a flame ionization detector (FID) at 250 °C. The fused silica capillary was coated with cross-linked 5% phenylmethyl silicone. The column film thickness was 0.52 μm, inner diameter 0.31 mm, and length 25 m. The average linear nitrogen gas velocity was set at 26 cm/s. The column oven was held at 50 °C for 2 min, temperature programmed at 15 °C/min to 280 °C, and then held at the temperature for 20 min. The data were processed by 5840 terminal. To avoid the appearance of interference peaks, the contaminated quartz wool and glass insert were replaced by new ones at the end of each daily analysis. The contaminated quartz wool was dumped, but the quartz glass insert could be reused by washing.

Analysis of Food Additives. To examine the reproducibilities of a retention time and a peak area on chromatograms of each of the food additives, 1 μL of the standard solution was injected into the GC. To assess whether reactions between food additives and components in vegetable oils occur or not, 5 mL of stock solution I was added to 100 mL of a sesame oil 3 containing no food additives. This solution was stirred in water bath controlled at 25 °C, and each content of the food additives within a certain period of time was analyzed by means of GC.

To determne the concentration of food additives in 15 commercial vegetable oils, 1 mL of each vegetable oil was transferred into a 10-mL volumetric flask and made up to volume. One microliter of each of these solutions was injected into GC. The qualitative and quantitative analyses of food additives in samples were carried out, comparing the chromatogram obtained from samples with that from the standard solution.

RESULTS AND DISCUSSION

Representative chromatograms of a standard solution containing 5 ppm of each of the five food additives, sesame oil 3 free from food additives are shown in Figure 1.

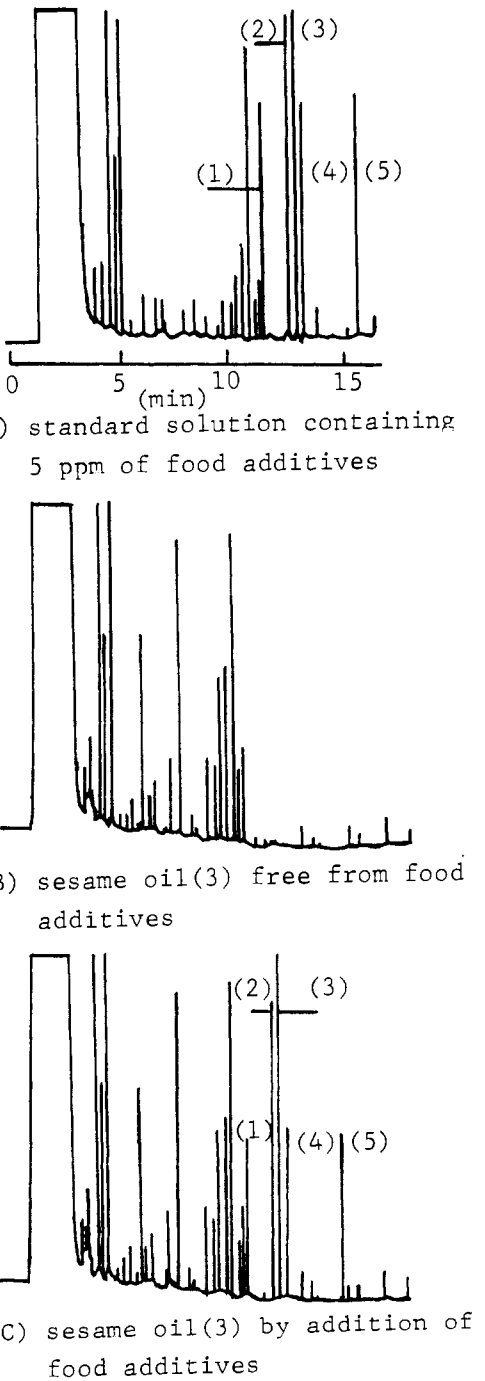

Figure 1. Capillary gas chromatogram obtained from the food additive standard, sesame oil 3, and sesame oil 3 with food additives. 1, DHA; 2, BHA; 3, BHT; 4, TBHQ; 5, Ionox-100.

Figure 1A shows each peak of DHA, BHA, BHT, TBHQ, and Ionox-100 well separated and each peak height is sufficient for easy detection. Figure 1B, which is an example of sesame oil 3 free from food additives, shows that many peaks due to some components contained in vegetable oils appeared within about 11 min. Similarly, many peaks that were shown in the chromatograms, obtained from other commercial vegetable oils, do not interfere with

Table II. Reproducibility of Absolute Peak Areas for Food Additives

food additive	1	2	3	4	5	6	$\bar{x}$	s	% SD
DHA	1329	1372	1132	1370	1434	1250	1314.3	108.0	8.22
BHA	3091	2685	2706	2755	2798	2507	2757.0	191.6	6.95
BHT	3589	2911	2960	2979	3078	2837	3059.0	271.5	8.88
TBHQ	1617	1617	1449	1435	1820	1506	1574.0	144.1	9.15
Ionox-100	2857	2656	2639	2799	2861	2661	2745.5	105.0	3.82

Table III. Change of Food Additive Concentration in Sesame Oil 3 through Various Reaction Times at 25 °C

time, min	DHA	BHA	BHT	TBHQ	Ionox-100
30	0.81	0.70	0.98	1.00	0.68
60	1.13	0.74	0.85	0.92	0.68
90	0.94	0.71	0.83	0.79	0.73
120	1.04	0.72	0.83	0.87	0.72
150	0.95	0.70	0.82	0.83	0.72
180	1.13	0.72	0.83	0.85	0.68

Table IV. Food Additives (ppm) Found in Commercial Vegetable Oils

vegetable oil	DHA	BHA
salad oil 1	ND[a]	ND
salad oil 2	ND	ND
salad oil 3	0.9	ND
salad oil 4	ND	ND
salad oil 5	ND	ND
corn salad oil	ND	ND
sesame oil 1	ND	ND
sesame oil 2	ND	ND
sesame oil 3	ND	ND
sesame oil 4	ND	ND
sesame oil 5	6.3	ND
spigadro oil 1	4.8	0.4
spigadro oil 2	4.5	0.4
olive oil	ND	ND
peanut oil	5.0	0.5

[a] ND = not detected.

the peaks of DHA, BHA, BHT, TBHQ, and Ionox-100. These results are also supported clearly by Figure 1C.

For a standard solution containing 5 ppm of each of the food additives in acetone, the results regarding to the reproducibilities of retention time and peak area in gas chromatograms are as shown in Table I; the standard deviation was very low, generally less than 0.06 %. As Table II shows, the absolute reproducibility in area counts for five food additives was just over 9% relative standard deviation, for six analyses. It might be said that the reproducibility of the absolute areas is also very good. This means that the external standard method can be used for these vegetable oils with confidence.

For five kinds of food additives, the relationship between reaction time and the percentage of residual food additive fraction against the amounts of added food additives to sesame oil 3 is as shown in Table III. It was found that the decrease of DHA concentration does not appear except at 30 min, but BHA, BHT, TBHQ, and Ionox-100 show a 70–80% concentration range, and these figures do not change throughout the reaction times. Therefore, BHA, BHT, TBHQ and Ionox-100 seemed to react with some components or denatured components in vegetable oils.

The concentration of DHA and BHA in 15 commercial vegetable oils is shown in Table IV. Some vegetable oils contained 4–5 ppm of DHA and less than 5 ppm of BHA. But, BHT, TBHQ, and Ionox-100 are not detected in all samples.

If the peak height, which is 3 times as high as the noise peak, is considered suitable for the quantitation, the lower limits of detection are estimated to be 0.5 ppm for DHA, TBHQ, and Ionox-100 and 0.3 ppm for BHA and BHT.

Registry No. DHA, 520-45-6; BHA, 25013-16-5; BHT, 128-37-0; TBHQ, 1948-33-0; Ionox-100, 88-26-6.

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Increased Specificity in Sorbic Acid Determination in Stored Dried Prunes

Two thermal degradation products produced from sugars in processed prunes during drying and protracted storage were isolated and identified by gas chromatography–mass spectroscopy (GC–MS). The compounds were 5-(hydroxymethyl)-2-furaldehyde and 2-furaldehyde. The gas chromatographic procedure was specific for sorbic acid and quantitation was not affected by these and other degradation compounds, but they appear to have affected to varying degrees the spectral methods used in this study.

Prior to 1950 dried prunes were stored and marketed at a water activity of about 0.65 (16–18% moisture), which obviated any need for preservatives. However, prunes are currently marketed at a water activity of 0.75 or greater (>28% moisture) to provide a product with a more tender texture. Food products stored at this water activity must be treated in some manner so that microbial proliferation will not occur. The main commercial procedure at present