Determination of Dimethylpolysiloxanes in Fats and Oils[1]

W.G. DOEDEN, E.M. KUSHIBAB[2] and **A.C. INGALA**, Swift and Company, Research and Development Center, 1919 Swift Drive, Oak Brook, Illinois 60521

ABSTRACT

A direct aspiration, flame atomic absorption method has been developed for the determination of dimethylpolysiloxanes (DMPS) in fats and oils. The detection limit of the method is approximately 1 ppm with a standard deviation for samples containing 1-10 ppm DMPS of 0.3. The technique is reasonably rapid, requires a minimum of sample preparation, and is applicable to the analysis of both hydrogenated and nonhydrogenated products.

INTRODUCTION

Dimethylpolysiloxanes (DMPS) or methyl silicones are commonly added to fats and oils to prevent oxidative foaming in products used in frying applications. In spite of their widespread use, methodology for their determination in hydrogenated products remains relatively limited.

In general, the methods employed for their determination in fats and oils require an isolation of the DMPS from the fat followed by an atomic absorption (AA) determination of silicon in the isolates. One of the more frequently applied techniques was developed by Neal and coworkers (1) who reported on the low temperature extraction of DMPS from fats and oils with petroleum ether followed by AA analysis of the extract. This technique, while successfully applied in some laboratories, is a reasonably tedious and technique-dependent method for the determination of DMPS.

More recently Kundu (2) reported on a method employing flameless AA. In this work, the fat is converted to a soap, the siloxanes extracted into an organic solvent and the extract analyzed for silicon. This technique is also relatively time consuming and technique-dependent. Freeman (3) eliminated the need for an isolation step by employing a direct aspiration flame AA technique for estimating the DMPS content of sunflower seed oil. While applicable to the analysis of lightly hydrogenated oils, this method is not directly applicable to the analysis of more heavily hydrogenated products.

In contrast, the procedure detailed below is relatively rapid and is applicable to the analysis of both hydrogenated and nonhydrogenated fats and oils. The detection limit is ca. 1 ppm with a standard deviation of 0.3 for samples containing 1-10 ppm DMPS.

EXPERIMENTAL PROCEDURES

Apparatus

A Perkin-Elmer model 403 atomic absorption spectrophotometer was used in conjunction with a silicon hollow cathode lamp. Instrumental parameters were: wavelength 251.6 nm, recorder response 3, slit 4 (0.7 nm). The instrument was used in the concentration mode at an expansion setting of 900 (ca. 0.01 absorbance units full scale). A nitrous oxide-acetylene flame was used with flow rates of 13 liters/minute for nitrous oxide and 7 liters/ minute for acetylene. Data were collected on a 10 MV recorder. A 70 C water bath was used to heat sample and standard solutions prior to analysis.

The selection of a wider slit setting than that recommended by the manufacturer, combined with proper alignment of the cork gasket in the nebulizer head so that it did not even partially block the gas inlets, enabled us to obtain a reasonably stable baseline at a sensitivity of 0.01 absorbance units full scale.

Heating both sample and standard solutions to 70 C prior to analysis reduced solution viscosity, increased the aspiration rate and consequently improved the sensitivity of the method.

Materials

Dow Corning 200 was used as the dimethylpolysiloxane standard, and a DMPS-free hydrogenated soybean oil was used to match the viscosities of the standards to those of the samples.

Industrial grade mineral spirits with a boiling range of 157-197 C as supplied by Central Solvents and Chemical Co., Chicago, Illinois, was used as a solvent for both standards and samples.

Standards

Working standards were prepared by pipetting 10, 8, 6, 4 and 2 ml of a 20 μg/ml Dow Corning 200 in mineral spirits solution into separate 50 ml volumetric flasks each containing 20 g of DMPS-free fat and diluting to volume with mineral spirits. These solutions contained 10, 8, 6, 4 and 2 μg DMPS per gram of fat, respectively. A solution containing 40% fat and 30 μg DMPS per gram of fat was also prepared for use in the optimization of the instrument.

Procedure

Sample solutions were prepared by dissolving 20 g of melted fat in mineral spirits and diluting to 50 ml. Both standard and sample solutions were then placed in a water bath at 70 C and allowed to equilibrate for ca. 1 hr.

Aspiration rate, flame conditions and burner position were optimized while aspirating the unheated 20 μg/ml DMPS stock solution. An absorbance of ca. 0.04 was generally considered desirable. The heated 30 μg DMPS per g of fat solution was then aspirated and the nebulizer adjusted to yield the maximum response.

The standard and sample solutions were then alternately removed from the 70 C bath and immediately aspirated into the flame. Mineral spirits at ambient temperature was continually aspirated between sample and standard solutions.

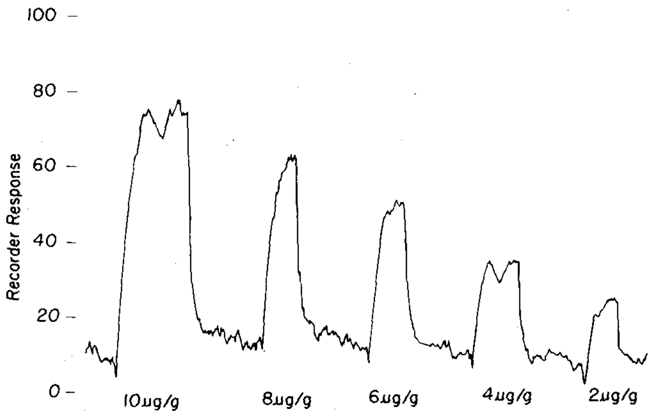

FIG. 1. Recorder response obtained for DMPS working standards. Concentrations are in μg DMPS/g of fat.

---

[1] Presented at a symposium of the North Central Section, March 28, 1979.

[2] Present address: Evans Food Products Co., Chicago, Illinois.

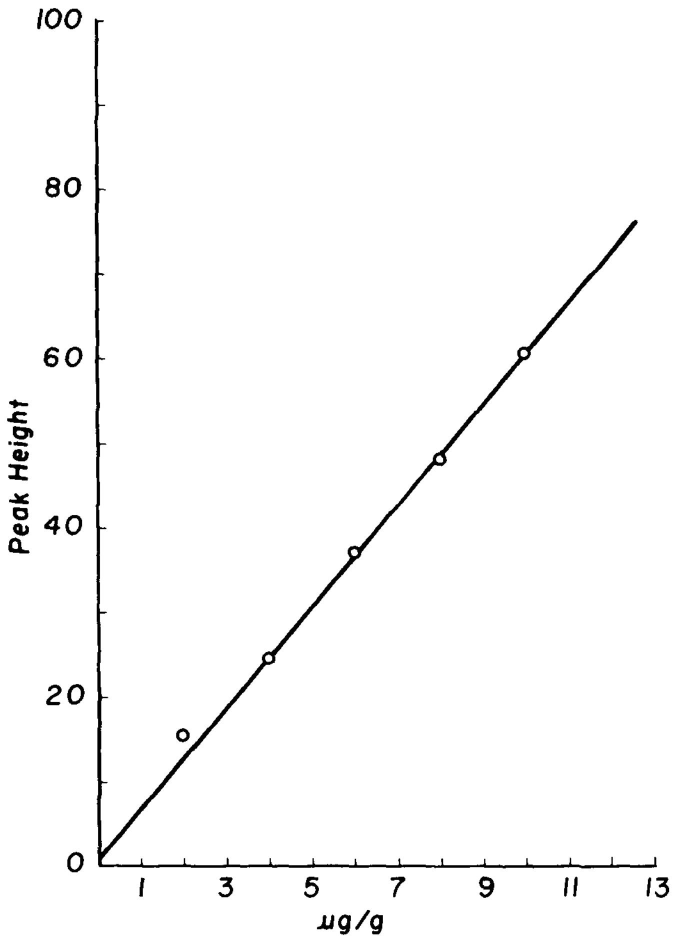

FIG. 2. Calibration curve obtained from DMPS working standards. Concentrations are in µg DMPS/g of fat.

RESULTS AND DISCUSSION

Instrument Calibration

The recorder tracings obtained for standards containing 2, 4, 6, 8 and 10 µg DMPS per gram of fat are presented in Figure 1. A calibration curve was prepared by plotting average peak height vs. concentration in µg DMPS per g of fat for these standards. The curve is presented in Figure 2. The DMPS content of the fat or oil is read directly from the calibration curve.

Recovery Studies and Sample Analyses

A sample of DMPS-free, hydrogenated fat was fortified with known levels of Dow Corning 200 and analyzed in triplicate. The results obtained are presented in Table I. Single determinations were also made on a second set of samples containing known amounts of DMPS. The results are presented in Table II. In both instances the precision and recovery data are satisfactory. Three frying fats of unknown DMPS concentration were also analyzed in duplicate on two different days. These results are presented in Table III.

Based on the data obtained in these and other studies, the standard deviation of the method was found to be ca. 0.3 over the range of 1-10 ppm DMPS or ±0.6 ppm at 95% confidence. The detection limit of the method, defined as a response equal to twice noise, was found to be below 1 µg DMPS per gram of fat. In those instances when optimum instrument performance was obtained, it was possible to achieve a detection limit as low at 0.5 ppm DMPS.

TABLE I

Replicate Determinations of Dimethylpolysiloxane in Hydrogenated Vegetable Oil[a]

Dimethylpolysiloxane (ppm)			
	Found		
Added	1	2	3
—	ND[b]	ND	ND
2.0	1.9	2.0	2.1
4.0	3.8	4.0	3.9
7.0	6.7	6.7	7.0
10.0	9.0	9.6	9.6

[a] IV-65.

[b] ND = None Detected.

TABLE II

Recovery of Dimethylpolysiloxane from Hydrogenated Vegetable Oil[a]

Dimethylpolysiloxane (ppm)			
Added	Found	Added	Found
0.5	0.8	7.0	6.7
1.0	1.1	7.0	6.6
3.0	3.0	9.0	8.7
5.0	4.6	11.0	10.4
5.0	5.1	13.0	12.6
5.5	5.4		

[a] IV-65.

TABLE III

Dimethylpolysiloxane in Commercial Frying Fats

	Dimethylpolysiloxane (ppm)			
	Day I		Day II	
Sample	I	II	I	II
1	5.3	5.1	5.0	5.1
2	3.9	3.8	3.4	3.6
3	2.5	2.4	2.2	2.1

This method is relatively rapid and has been used successfully in our laboratory to monitor the uniformity of DMPS distribution in a product, to determine its fate in frying studies and to detect cross contamination of product streams.

REFERENCES

1. Neal, P., A.D. Campbell, and D. Firestone, JAOCS 46:561 (1969).
2. Kundu, M.K., Fette, Seifen, Anstrichm. 79:170 (1977).
3. Freeman, I.P., F.B. Padley, and W.L. Sheppard, JAOCS 50:101 (1973).

[Received September 7, 1979]