Low Temperature Separation of Trace Amounts of Dimethylpolysiloxanes From Food

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Abstract

Dimethylpolysiloxanes, which are difficult to determine in fatty foods, can be separated at low temperatures by special freeze-out apparatus. Final determination is made by atomic absorption, visible or ultraviolet spectrometry. Recoveries from cottonseed oil and cake mix ranged from 95% to 110%.

Introduction

Dimethylpolysiloxanes (DMPS), common antifoaming agents added to foods and feeds, have been determined by various techniques, including application of baseline technique to the gem-dimethyl silicon peak in the infrared, wet ashing, atomic absorption spectroscopy and conventional column techniques. All these methods have disadvantages. An examination of the melting points of pure DMPS (<-65 C) revealed that they were even substantially lower than the freezing points of common food fats and oils in petroleum ether. On this basis it seemed feasible to separate DMPS from fats by a low temperature technique using petroleum ether and dry ice. This general procedure has been used by McCully and McKinley (1) to precipitate fats from acetone at low temperatures in a clean-up procedure for the determination of chlorinated pesticide residues.

The purpose of this communication is to describe a device used in the low temperature separation of DMPS from foods and its application to the separation of DMPS from fats and oils, as well as a cake mix. Dimethylpolysiloxane (DMPS, TGA standard) is obtained from the Toilet Goods Association, Washington, D.C.

The complete extraction assembly is shown in Figure 1. The freeze-out column was designed and constructed from a glass column with a coarse glass frit in the authors' laboratories, and it can now be obtained from Kontes Glass Company. The column was designed to contain 10 g of oil, cake mix, etc., distributed on 20 g of powdered cellulose. The dimensions given in Figure 1 are general; however, larger columns may require a longer freeze-out period.

Experimental Procedures

Four grams of dry cellulose powder (Whatman column Chromedia cellulose powder, CF-1) are placed in the column (see Fig. 1); 30 ml of petroleum ether (bp 30–60 C) are added and the cellulose is tamped into a pad. The material to be extracted is mixed with enough cellulose powder to form a friable mixture (usually 2 g/g of lipid) and transferred to the column (during mixing, oils may be distributed over the surface of the cellulose powder more completely by addition of a little petroleum ether). The column is placed in a Dewar flask containing a dry ice-heptane mixture (about -70 C) and frozen (about 30 min). Enough petroleum ether is added to cover the cellulose powder and successive portions (total of 400 ml) of cold (-70 C) petroleum ether are passed through the column by suction into a Kuderna-Danish concentrator (Kontes Glass Co.). The extract is concentrated to dryness, dissolved in methyl isobutyl ketone, and diluted to 10 ml. The DMPS is analyzed directly by atomic absorption spectrophotometry (2,3) using a Perkin-Elmer 303 atomic absorption spectrometer with Intensitron cathode, Si lamp, nitrous oxide burner and digital readout. Alternatively, the extract, after concentration and wet digestion with fuming sulfuric and nitric acids, may be analyzed by visible or ultraviolet (4) spectrophotometry, using a Beckman DU-2.

Separation of DMPS From Fats and Oils

A solution containing 1 μg of DMPS per milliliter of hexane was prepared from the TGA calibration standard. Two 10 g portions of cottonseed oil, combined with 20 and 40 μg of DMPS, respectively, were mixed with cellulose powder, transferred to the low temperature column, and extracted as described above. The extracts were concentrated and analyzed for silicon either by atomic absorption (2,3) or by ultraviolet spectrophotometry (4) after wet ashing (Table I). Usually no more than 0.2–0.3 g of soluble residue remained in the cleaned up extract from 10 g of cottonseed oil.

Separation of DMPS From Cake Mixes

To ensure the absence of DMPS, an experimental cake mix was made up using carefully prepared laboratory ingredients, taking precautions to eliminate any possible contaminations with DMPS. The composition of this cake mix was as follows: 12 g of flour, 2 g of dried egg, 2 g of dried milk, 2 g of crude peanut oil and 2 g of sugar. Experimental samples were prepared by adding 20, 40 and 100 mg of SiO_2 (1 μ average diameter, W. R. Grace Davison Chemical Co.) directly to the mix, and DMPS at 20 or 50 μg levels were added by dissolving them in peanut oil before adding to the mix. The prepared samples were mixed with 6 g of cellulose, added to

TABLE I

Analysis of DMPS in Fortified Samples

Samples and weight used	DMPS added, μg	DMPS observed		Determination Method
		μg	%	
Cottonseed oil, 10 g	0	0	....	Atomic absorption
Cottonseed oil, 10 g	20	19	95	Atomic absorption
Cottonseed oil, 10 g	40	40	100	Atomic absorption
Cake mix, 20 g	20	18	90	UV
Cake mix, 20 g	50	50	100	Atomic absorption
Cake mix, 20 g + 40 mg SiO_2	0	2.5	.....	UV
Cake mix,[a] 18 g + 40 mg SiO_2	0	0	.....	Atomic absorption
Cake mix, 20 g + 20 mg SiO_2	20	22	110	UV
Cake mix, 20 g + 100 mg SiO_2	50	52	104	Atomic absorption

[a] This cake mix did not contain any added fat.

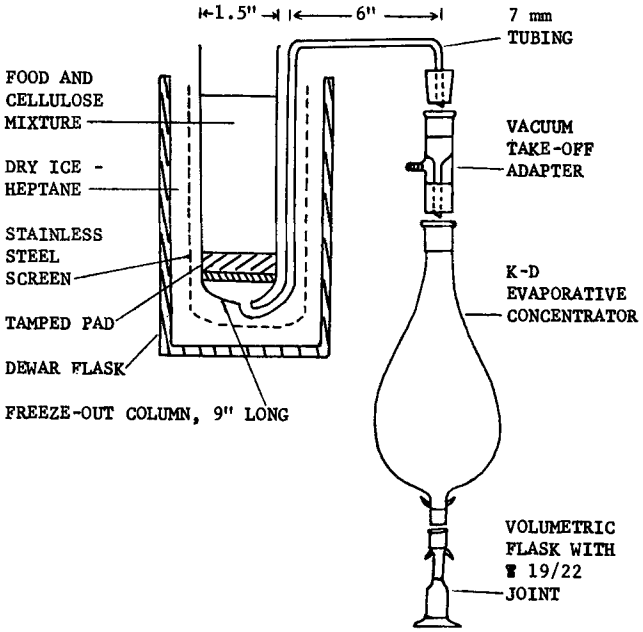

FIG. 1. Freeze-out column extraction assembly.

the column, extracted as described in the general procedure, and analyzed for silicon by ultraviolet or atomic absorption spectrophotometry (Table I).

The results in Table I indicate that DMPS can be quantitatively extracted from oils and cake mixes by the low temperature separation procedure described here. The silicates and 97–99% of the oils present in foods were retained on the cold column. An experiment was conducted to show that even finely divided silicon dioxide (1 μ average diameter) was retained on the cold column by irradiating SiO_2 for 30 min at a thermal neutron flux of 10^{13}n/cm^2 sec; 0.1 g of the neutron-activated SiO_2 dispersed in 15 g of cellulose powder was added to the low temperature column and eluted in the usual manner. No silicon was detected when the eluate was analyzed for total silicon by gamma ray spectroscopy. Thus the separation and determination of DMPS in the presence of high levels of silicates is feasible. The analytical time required for separation of one sample is about 1.5 hr; however, four to six separations can be performed simultaneously. It is anticipated that this technique can also be applied to the separation of pesticides and polynuclear hydrocarbons from fatty foods.

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