replaced by water on the mineral surface and consequently no bands indicating adsorbed glyphosate were found in the IR spectra of these minerals.

Registry No. Glyphosate, 1071-83-6; montmorillonite, 1318-93-0; nontronite, 12174-06-0.

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Determination of Fumigants and Related Chemicals in Fatty and Nonfatty Foods

James L. Daft

Mean recoveries for 22 fumigants and related industrial chemicals were determined from various fatty and nonfatty foods by liquid extraction and gas chromatography. Results were sorted according to sample type, e.g., fat or nonfat, and the extraction or cleanup techniques used. The overall mean recovery was 73% from fatty foods and 78% from nonfatty foods; the recovery from both sample types after further cleanup by Florisil chromatography was 55%. Actual fumigant residues were also determined in 549 samples examined; 849 residues were found in 372 samples; no residues were found in 177 samples. Findings were sorted and cross-referenced by sample type, i.e., fat, nonfat, grain-based, and nongrain-based. Findings included 10 different residues: carbon disulfide, carbon tetrachloride, chloroform, chloropicrin, ethylene dibromide, ethylene dichloride, methylene chloride, methylchloroform, tetrachloroethylene, and trichloroethylene. Mean finding amounts ranged from 7 to 799 ng/g. The average number of findings per fat and nonfat sample was 2.31 and 0.72 and per grain-based and nongrain-based sample was 2.22 and 1.04, respectively.

Traces of toxic fumigant residues are being found in several food products, e.g., spices (Stijve et al., 1976; Reeves et al., 1985), citrus fruit (Iwata et al., 1983; Tonogia et al., 1986) drinking and process water (Kroneld, 1986; Uhler and Diachenko, 1987), and dairy and grain-based products (Rains and Holder, 1981; Entz and Hollingfield, 1982; Heikes, 1987). Most residues are found in products containing 0–10% fat because existing methods work best on nonfat or low-fat foods and generally do not work well on high-fat types. For example, the acetone-soaking or back-extracting methods used for analyzing whole grain, milled products, and low-fat foods (Berck, 1974; Newsome and Panopio, 1977; AOAC, 1980; Clower, 1980; Daft, 1987) do not efficiently partition fumigants from samples containing more than 10% fat, e.g., corn chips, which contain 28% fat. Extractions from these high-fat-containing foods either contain too much fat or the excess fat is not completely soluble in the extracting solutions, resulting in lost determinations or low fumigant recoveries through poor, fat-distorted gas chromatography (GC).

Since the compounds used as fumigants are quite fat soluble, fat-containing foods that have been exposed to them would be expected to contain these kind of residues. Therefore, fumigant methods should be capable of analyzing all foods, including high-fat types.

In this study, the method used, a rapid aqueous–nonaqueous coextraction of sample with acetone and isooctane (Daft, 1988b), satisfactorily partitions halogenated fumigants and related chemicals from a wide variety of food types. The gas chromatograms from samples containing as much as 20% fat generally are free of fat effects such as band broadening and delayed retention times; further cleanup is not necessary.

Experimentally, however, several of these 20% or less fat extracts were taken through a Florisil cleanup step to determine whether the gas chromatography was improved or analyte recovery changed. An improvement seen was the removal of endogenous background peaks from gas chromatograms. An impairment seen was the lowering of

Department of Health and Human Services, Food and Drug Administration, 1009 Cherry Street, Kansas City, Missouri 64106.

recoveries to about 50% for several analytes.

Although further cleanup is not needed for the above samples, it is needed for samples containing higher amounts of fat (e.g., 21–70%). For these samples, the Florisil cleanup step is used routinely. It removes about half of the fat extracted from samples and permits suitable, semiquantitative determinations by GC.

Incurred residues were also determined from a variety of fatty and nonfatty foods during this study. Residues were found in 68% of the samples examined, ranging in amounts from 1 to 4400 ng/g. Most findings were in foods containing 1% or more fat. Apparently, fumigant residues exist in the majority of fatty and grain-based food types such as meats, dairy products, and baked goods. A few residues appear to exist in nonfatty types such as fruits and vegetables.

Further research is needed to develop methods that can sufficiently quantitate all residues from all high-fat foods. The rapid semiquantitative techniques used in this study suitably screen such samples for fumigants and related chemical contaminants. In this report, the mean recoveries and coefficients of variation for 22 analytes are listed relative to sample type, extraction, and cleanup. The mean amounts of the residues actually found in the foods examined are listed also.

MATERIALS AND METHODS

Sampling and Preparation. The foods selected for this research were obtained from the Food and Drug Administration's "market basket" collections (Gartrell et al., 1986; Reed et al., 1987; Pennington and Gunderson, 1987). Collections of 234 food items are made table ready by peeling, cooking, etc. Items are then composited by grinding, mixing, or blending and stored at approximately −4 °C until analysis.

Sample Fortification. Fortification of samples with the 22 analytes tested was done at two concentration levels, one for each detector used in making the determinations (see Table I). The detectors used were electron capture (ECD) and Hall electroconductivity (HECD). The analytes were added to all sample types, but not to each sample in replicate.

Method of Analysis. Slightly different techniques were used to extract samples based on sample consistency and fat content (Daft, 1988b). Clear beverages were extracted directly with purified isooctane. Food samples containing more than 70% fat or oil were diluted directly, or melted, and then diluted in isooctane. Most samples had a solid or pulpy consistency; these samples were coextracted with purified 20% acetone–5% NaCl in 25% phosphoric acid and isooctane. Most of the final extracts and dilutions (isooctanes) were analyzed directly by GC. The extracts from samples containing 21–70% fat were passed through micro-Florisil columns (0.3 g of Florisil gravity-packed in disposable pipets) to remove excess fat. (In this study, several nonfat and low-fat samples were also taken through the cleanup step. Samples were not analyzed in replicate.)

Nineteen analytes were determined on 3.6 m × 4 mm (i.d.) columns of 20% OV-101 and 7.5-m 10% SP-1000 with ECD and HECD detectors. The other three (1,2-dibromo-3-chloropropane, *o*-dichlorobenzene, *p*-dichlorobenzene) were determined on 1.8 m × 4 mm (i.d.) columns of 5% OV-101 with the same detectors. Identity confirmations were made on alternate (mixed-bed) columns with the same detectors. Multicomponent reference solutions were used throughout the study (Daft, 1985, 1987, 1988b). These solutions were made in an isolated hood following strict safety precautions (*Fed. Reg.*, 1979).

Quality Control. All reagents were purified to reduce GC background interferences or impurities. Also, samples were weighed-out in a contaminant-free hood; fortification of samples was done in the same hood. Reagent blanks were run with each set of samples analyzed. In addition, the laboratory environment was analyzed for potential contamination; the room air, product wrappings (Daft, 1987), and the processes for preparing samples (Daft, 1988a) were carefully monitored.

RESULTS AND DISCUSSION

Strict safety precautions and quality control were exercised during the study. The analyst wore safety gear approved by the U.S. National Institute of Occupational Safety and Health (NIOSH) and the U.S. Mine Health Safety Administration (MHSA) when working with hazardous, toxic fumigant compounds. During the study, the monitoring of our laboratory environment for potential contamination showed that essentially none existed. However, some reagents gave GC background response. During analysis, any apparent response that also appeared in the reagent blank was not determined.

Several trends could be seen in the 1151 recovery determinations made in the study, many related to sample type and method technique. For example, the direct extraction of clear beverages gave the best overall mean recovery, 82%. The aqueous–nonaqueous extractions of fatty and nonfatty foods gave the next best recoveries, 73% and 78%, respectively (see Table I). Use of the micro-Florisil cleanup step lowered the latter two to 55%.

Each analyte was also recovered somewhat uniquely. For example, when no Florisil cleanup was used, the recoveries for the following three analytes were still relatively poor from both sample types, respectively (see Table I): methyl bromide, 18 and 22%; methylene bromide, 59 and 59%; methylene chloride, 41 and 45%. When the cleanup step was used, the recoveries for chloroform and methylchloroform were approximately 23% better from nonfat than from fat samples. Conversely, the recoveries for 1,2-dibromo-3-chloropropane, *o*-dichlorobenzene, and *p*-dichlorobenzene were approximately 24% better from fat than from nonfat samples. Also, the recoveries for brominated compounds were comparatively lower after the cleanup step than for most chlorinated compounds. The brominated compounds may have eluted from the columns slower than the chlorinated compounds, thus, more incompletely. Of the 22 compounds tested, methyl bromide consistently gave the poorest mean recoveries from all the foods tested: ranging from 9 to 22% for both sample types. The methyl bromide recovery was often near zero from fatty foods. Tetrachloroethylene consistently gave the best recoveries throughout the study: ranging from 8 to 102% for both sample types.

The coefficient of variation (CV) varied widely for methyl bromide. Recovery of this compound appeared to be extremely matrix dependent. Recoveries of other compounds appeared to be matrix dependent to a lesser degree but was evident in most of the study because individual replicates were not done on samples. Limited analysis time was a factor here. The analysis of the 549 samples for incurred residues was done within a relatively short period of time. Although as many as three similar samples from different market baskets were examined at one time or another during the study, the fortifications were generally made on samples once. Thus, recovery determinations tended to vary for all the analytes simply because the sample matrices varied significantly. In some instances, variation appeared high because limited determinations were made on the analytes in question, e.g., only four determinations each for 1,2-dibromo-3-chloro-

Table I. Mean Recoveries (%) and Coefficients of Variation (CV, %) from Fatty and Nonfatty Food Types, Electron-Capture and Hall Electrolytic Detectors Combined

compound	fortificn level, ng/g		key: high–low, *mean* (CV), no. determinations					
			fatty		nonfatty		both	
	ECD	HECD	extracted	cleaned up[a]	extracted[b]	cleaned up	extracted	cleaned up
carbon disulfide	316		93–35, *66* (34), 5	63–30, *48* (27), 5	111–37, *72* (29), 20	87–30, *59* (32), 9	111–35, *71* (29), 25	87–30, *55* (31), 14
carbon tetrachloride	3.2	19.1	130–38, *82* (29), 15	99–44, *73* (23), 14	129–38, *88* (22), 27	110–46, *79* (25), 9	130–38, *86* (24), 42	110–44, *75* (23), 23
chloroform	14.8	11.9	136–34, *71* (41), 9	81–13, *45* (59), 6	161–178 *75* (37), 32	117–37, *70* (40), 13	161–17, *74* (38), 41	117–13, *62* (47), 19
chloropicrin	8.3	39.7	137–50, *78* (27), 17	95–24, *60* (38), 13	118–41, *87* (21), 37	180–0, *58* (69), 17	137–41, *84* (23), 54	181–0, *59* (57), 30
1,2-dibromo-3-chloropropane	12.6	251	93–66, *81* (12), 5	66–40, *56* (20), 5	102–58, *85* (21), 5	64–5, *36* (78), 4	102–58, *83* (17), 10	66–5, *47* (46), 9
o-dichlorobenzene	101	74.4	114–70, *93* (22), 4	113–49, *75* (39), 4	105–70, *95* (15), 5	78–11, *46* (63), 4	114–70, *94* (17), 9	113–11, *60* (51), 8
p-dichlorobenzene	125	75	116–81, *97* (15), 4	113–44, *72* (42), 4	108–91, *100* (6), 5	91–19, *51* (62), 4	116–81, *99* (10), 9	113–19, *62* (50), 8
1,1-dichloroethane	2350	17.6	71–40, *55* (23), 5	67–35, *46* (32), 4	93–55, *73* (20), 8	56–38, *44* (18), 4	93–40, *66* (24), 13	67–35, *45* (24), 8
2,3-dichloropropene	145	48.4	117–37, *74* (35), 6	68–40, *54* (22), 4	98–66, *79* (14), 7	74–29, *52* (37), 4	117–37, *77* (24), 13	74–29, *53* (28), 8
1,3-dichloropropene	85.2	42.6	69–45, *58* (18), 5	58–17, *43* (44), 4	112–53, *78* (26), 8	61–0, *35* (85), 4	112–45, *70* (28), 13	61–0, *39* (60), 8
ethylene dibromide	30.5	87.2	113–50, *72* (24), 17	90–14, *52* (44), 13	102–31, *78* (19), 37	82–0, *37* (81), 16	113–31, *76* (20), 54	90–0, *44* (63), 29
ethylene dichloride	1260	18.9	103–34, *68* (33), 22	70–29, *45* (29), 14	87–43, *62* (21), 26	58–4, *30* (71), 9	103–34, *65* (28), 48	70–4, *39* (46), 23
methyl bromide	115	46.1	67–0, *18* (114), 18	43–0, *11* (132), 13	71–0, *22* (99), 31	31–0, *9* (141), 11	71–0, *20* (103), 49	43–0, *10* (134), 24
methylchloroform	8	17.4	98–53, *76* (18), 13	78–30, *60* (24), 9	150–51, *89* (23), 30	130–47, *81* (30), 16	150–51, *85* (23), 43	130–30, *74* (32), 25
methylene bromide	4	44.7	91–40, *59* (31), 11	63–26, *47* (29), 9	98–31, *59* (28), 18	49–0, *37* (46), 8	98–31, *59* (28), 29	63–0, *42* (37), 17
methylene chloride	398	9.3	85–26, *41* (54), 6	73–17, *39* (65), 4	48–40, *45* (8), 5	32–8, *20* (85), 2	85–26, *43* (37), 11	73–8, *33* (71), 6
propylene dibromide	38.7	105	134–63, *86* (21), 14	82–25, *62* (32), 10	129–53, *91* (16), 29	107–0, *57* (61), 16	134–53, *90* (18), 43	107–0, *59* (50), 26
propylene dichloride	896	34.7	196–40, *79* (47), 14	90–32, *57* (30), 10	191–58, *86* (28), 28	128–0, *48* (68), 16	196–40, *83* (35), 42	128–0, *51* (54), 26
1,1,2,2-tetrachloroethane	49.4	49.4	118–50, *70* (23), 14	85–24, *58* (33), 10	122–49, *84* (20), 29	89–8, *57* (42), 16	122–38, *80* (23), 43	89–8, *57* (38), 26
tetrachloroethylene	8.1	24.3	166–57, *99* (20), 23	123–31, *88* (29), 13	138–68, *102* (12), 36	115–64, *94* (15), 17	166–57, *101* (15), 59	123–31, *91* (22), 30
1,1,2-trichloroethane	79.3	17.3	108–38, *74* (28), 14	66–25, *50* (29), 10	104–43, *76* (17), 29	75–0, *42* (64), 16	118–43, *74* (19), 43	75–0, *45* (51), 26
trichloroethylene	16.1	26.4	105–57, *89* (13), 21	91–29, *69* (25), 12	113–31, *82* (24), 23	81–40, *69* (20), 9	113–31, *85* (20), 44	91–29, *21* (23), 21
overall			196–0, *73*[c] (38),[c] 262	123–0, *55* (45), 190	191–0, *78* (33), 475	181–0, *55* (59), 224	196–0, *76* (35), 737	181–0, *55* (53), 414

[a] Extract cleaned up further with Florisil chromatography. [b] Beverages included. [c] Mean/262 determinations.

Table II. Frequency and Mean Amount of Residues Found in 549 Samples by Fat Content and Sample Type

food type	no. samples examined	no. having residues	no. residues determined	no. per samples	amount found, ng/g		
					high	low	mean[a]
fatty (all)	285	256 (90%)	659	2.31	1040	1	48/46
fatty (grain-based)	158	150 (95%)	418	2.65	1040	1	46/45
fatty (nongrain-based)	127	106 (83%)	241	1.90	760	1	52/48
nonfatty (all, including beverages)	264	116 (44%)	190	0.72	4400	1	111/61
nonfatty (grain-based)	78	51 (65%)	106	1.36	4400	1	115/90
nonfatty (nongrain-based)	186	65 (35%)	84	0.46	3000	1	105/43
grain-based (all)	236	201 (85%)	524	2.22	4400	1	60/56
nongrain-based (all)	313	171 (55%)	325	1.04	3000	1	66/46
overall	549	372 (68%)	849	1.55	4400	1	62/51

[a] 372/549 samples.

Table III. Frequency and Mean Amount of Ten Fumigants and Industrial Chemicals Found in 372 of 549 Samples Examined

compd	no. of determ	amount, ng/g high	low	mean
chloroform	302	830	2	71
tetrachloroethylene	265	230	1	12
methylchloroform	200	570	1	22
carbon tetrachloride	44	210	2	31
methylene chloride	21	4400	72	799
carbon disulfide	7	3000	100	738
trichloroethylene	5	94	2	49
chloropicrin	2	22	12	17
ethylene dibromide	2	11	2	7
ethylene dichloride	1	30	30	30

propane and *o*- and *p*-dichlorobenzenes through nonfatty cleanup (see Table I). In addition, the Florisil cleanup step caused the overall mean CV to increase from 35 to 53%. Evidently, this step yields cleaner sample extracts and gas chromatograms that are freer of background effects, but, at the same time, it adversely affects the accuracy and precision of determinations. Therefore, the identities of residues following the cleanup step are much more likely to be valid, but the amounts determined are lower than what is actually incurred.

Of the 549 food samples examined for actually incurred residues, 285 were fat and 264 nonfat types; 236 were grain-based and 313 nongrain-based types (see Table II).

Fatty foods contained 659 incurred residues; nonfatty contained 190 (see Table II). Fatty (grain-based) foods contained 418 residues; nonfatty (nongrain-based) contained 84. Mean amounts for each of 10 different residues found are shown in Table III. Ethylene dibromide (EDB) was detected twice, once each in peanut butter and whiskey, at very low levels. Chloropicrin, which gives erratic recoveries from most methods, was detected twice, once each in corn chips and flour tortillas. Methyl bromide, a highly volatile fumigant that gave relatively poor recoveries during this study, was not detected in any of the samples. Figure 1 shows typical residue determinations from a meat sample.

In fumigant analysis, the inability to reconcentrate samples by evaporation or to clean them up by chromatographic techniques without losing analytes makes the purge and trap (Heikes and Hopper, 1986) and headspace methods (Entz and Hollingfield, 1982; DeVries et al., 1985; McNally and Grob, 1985) desirable for this determination, even though special equipment is required. Residues are cleanly separated from the sample matrices by these methods. Yet, methods of liquid–liquid or solid–liquid extraction, which might yield more matrix and background effects, fit the existing equipment in most analytical laboratories. Methods of liquid extraction also permit relatively easy maintenance of quality control, e.g., prevention of potential background contaminations and interferences. In addition, these methods can be applied to a broad range of samples and analytes. Furthermore, they are fast. Most determinations are made immediately following the initial extraction of samples. In any case, 80–100% recovery of all analytes from all food types is difficult, if not impossible, with present methods.

In conclusion, the extraction techniques described in this report gave an overall mean recovery of 76% from assorted fatty and nonfatty foods for the 22 analytes tested. A Florisil cleanup of these extracts lowered this recovery to 55% for both food types. Yet, the cleaner sample extracts resulting from this step helped verify the 849 actual fumigant and industrial chemical residues found in the 549 food items examined. Of these findings 78% was from food containing 1% or more fat (e.g., meats, dairy products, and baked goods); the mean level was 51 ng/g. Nonfatty foods (e.g., fruits, vegetables, and beverages) were relatively free of residues.

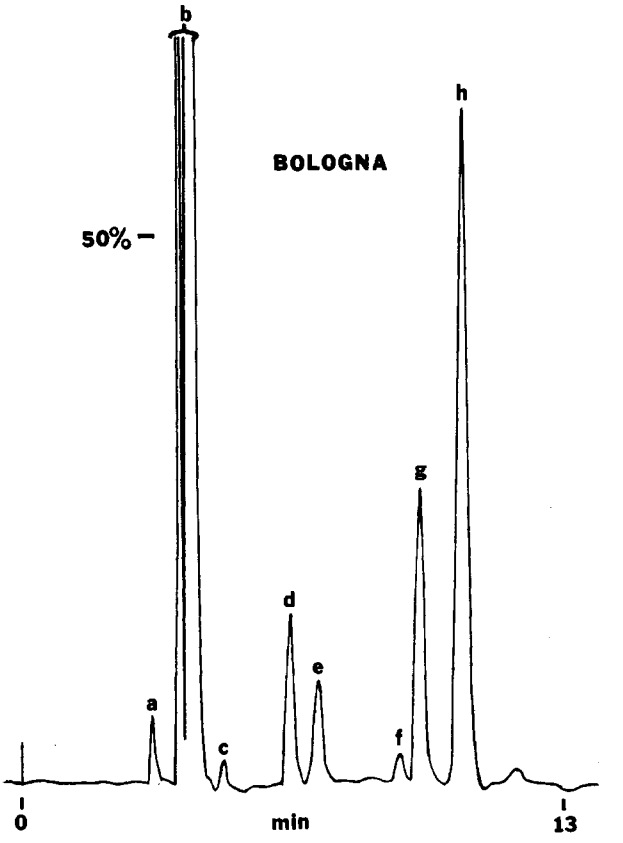

Figure 1. Chromatogram of meat sample containing 26% fat (8 mg sample equiv following Florisil cleanup of extract): (a) air; (b) acetone–isooctane solvent; (c) 100 ppb carbon disulfide; (d) 3 ppb methylchloroform; (e) 240 ppb methylene chloride background response; (f) 2 ppb trichloroethylene; (g) 8 ppb chloroform plus 10 ppb background response; (h) 12 ppb tetrachloroethylene. Conditions: 10% SP-1000 column, 120 °C, electron-capture detection.

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Registry No. Carbon disulfide, 75-15-0; carbon tetrachloride, 56-23-5; chloroform, 67-66-3; chloropicrin, 76-06-2; 1,2-dibromo-3-chloropropane, 96-12-8; *o*-dichlorobenzene, 95-50-1; *p*-dichlorobenzene, 106-46-7; 1,1-dichloroethane, 75-34-3; 2,3-dichloropropene, 78-88-6; 1,3-dichloropropene, 542-75-6; ethylene dibromide, 106-93-4; ethylene dichloride, 107-06-2; methyl bromide, 74-83-9; methylchloroform, 71-55-6; methylene bromide, 74-95-3; methylene chloride, 75-09-2; propylene dibromide, 78-75-1; propylene dichloride, 78-87-5; 1,1,2,2-tetrachloroethane, 79-34-5; tetrachloroethylene, 127-18-4; 1,1,2-trichloroethane, 79-00-5; trichloroethylene, 79-01-6.

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Some Problems with 1,2-Dibromoethane Residue Analysis

Takashi Suzuki,* Takashi Ishizaka, Kumiko Sasaki, and Yukio Saito

Imported fruits were assayed for EDB residues. The relative standard deviations among nine individuals in each lot were 100 (max) and 41% (min) in mango and were 90 (max) and 27% (min) in papaya, respectively. Blending of the sample for 30 s for homogeneity caused about 11-15% of decreased EDB residue levels. The analytical results for grapefruit after separation into pulp, seed, and peel showed that EDB residue levels are very high in seed (2550 μg/kg (max) of sample), low in peel (3.97 μg/kg (max) of sample), and negligible in pulp (0.51 μg/kg (max) of sample).

Since the introduction of the Mediterranean fruit fly [Diptera, Tephritidae, *Ceratitis capitata* (Wiedemann)] into California in 1980, the quarantine treatment by 1,2-dibromoethane [commonly referred to as ethylene dibromide (EDB)] to citrus fruits, papaya, and mango, which are produced in the Trypetidae-occuring area, has been needed prior to its acceptance to Japan. However, EDB residues in those agricultural products had to meet strict legal tolerance requirement by the Ministry of Health and Welfare in Japan, depending on the recommendation of the FAO/WHO Joint Meeting (FAO/WHO, 1967) that no residue of EDB treatment be allowed to reach the consumer because of its carcinogenicity.

There are many reports on determination of EDB, and they have been summarized by Newsome and Papino (1977), King et al. (1980), and Rains and Holder (1981).

National Institue of Hygienic Sciences, 18-1, Kamiyoga, 1-Chome, Setagaya-ku, Tokyo 158, Japan.

In Japan a method using the combination of a distillation apparatus, which had been devised by Bielorai and Alumot (1966), and steam distillation with *n*-hexane has been used as a Japanese official method since 1981 (Sekita et al., 1983).

This paper deals with some problems on EDB analysis depending on the results obtained by applying this method to fruits.

EXPERIMENTAL SECTION

Reagents. EDB was a product of Tokyo Chemical Industry Co. Ltd. Pesticide-grade hexane was purchased from Wako Pure Chemicals Industry Co. and showed several peaks on the gas chromatogram after exposure to air or keeping EDB standard solutions in refrigerator but did not interfere with the analysis of EDB. Florisil PR was a product of Floridin Co. and was used after overnight activation at 130 °C. Silicone oil was a product of Shinetsu Chemical Co. Purified water was obtained by a double distillation, using all-glass apparatus, of tap water passed

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