# Adsorptive Capacity of Active Filter Aids for Used Cooking Oil

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**Many materials are purported to adsorb polar compounds that are the result of degradation of oils used for deep-fat frying. In the present study, the capacity of several of these adsorbents in terms of the amount of polar oil degradation compounds adsorbed by a given weight of material was determined. A significant difference in the adsorptive characteristics and capacity of the materials tested was demonstrated. Adsorptive capacity varied from 0 to over 150 mg of total polar compounds per gram of adsorbent. Some of the materials demonstrated selective adsorption characteristics. For these materials, only one class of polar compounds was adsorbed.**

KEY WORDS: Adsorbent, adsorptive capacity, filter aid, frying, oil degradation, saturation.

Deep-fat frying is a popular way to prepare a variety of foods. When food is fried in heated oil, many complex chemical reactions occur, and the oil begins to degrade (1). The triglyceride molecule breaks down into volatile and nonvolatile compounds, which are soluble in the oil. These components contribute to the flavor and odor (desirable and undesirable) of the food fried in the oil.

Whereas triglyceride oil is a nonpolar material, the products of oil degradation, as defined by International Union of Pure and Applied Chemistry (IUPAC) Method 2.507 (2), are polar materials. The polar fraction of a used oil is composed of free fatty acids, mono- and diglycerides, oxidized triglycerides, and oligomeric triglycerides (polymers).

Several European countries have placed legal limits on the amount of total polar material that may be present in an oil used for deep-fat frying (3). A definite relationship between the taste of food fried in oil and the concentration of total polar materials present has been presented (4).

As frying continues, the concentration of degradation products gradually increases until the oil is unfit for use. At the same time, the quality of food fried in the oil decreases until it is unacceptable for human consumption. It is common practice for restaurant owners to filter oil used for deep-fat frying to remove food debris, which may accelerate the decomposition of the oil. However, filtration alone does not remove oil-soluble degradation products. Simultaneous removal of particulates by filtration and soluble impurities by adsorption is desirable as it will extend the life of the oil and provide higher-quality fried foods.

Several materials have been purported to adsorb the polar degradation products of a heated oil. Among them are synthetic magnesium silicate (5), synthetic calcium silicate (6), aluminum oxide, diatomaceous earth, bleaching earth (7), activated carbon (8–11) and various forms of silica (11–15). The purpose of this study was to compare the adsorptive capacity of these materials for the polar compounds that result from degradation of a frying oil.

TABLE 1

**Adsorbents Selected for Evaluation**

| Material tested | Trace name and source |
|---|---|
| Activated carbon | Darco T-88, American Norit Co.<br>Jacksonville, FL |
| Activated alumina (basic pH) | LaRoche Chemicals,<br>Baton Rouge, LA |
| Activated alumina (neutral pH) | M. Woelm<br>Eschwege, Germany |
| Bleaching earth #1 | Filtrol 105, Harshaw-Filtrol<br>Cleveland, OH |
| Bleaching earth #2 | Tonsil Supreme, LA Saloman<br>Port Washington, NY |
| Calcium silicate | Silasorb, Manville Corp.<br>Denver, CO |
| Diatomaceous earth | FW-18, Eagle Picher<br>Reno, NV |
| Magnesium silicate | Magnesol XL, The Dallas Group<br>Liberty Corner, NJ |
| Silica #1 | Britesorb C200, PQ Corp.<br>Valley Forge, PA |
| Silica #2 | TriSyl, WR Grace & Co.<br>Baltimore, MD |
| Silica Gel[a] | Silica Gel 60<br>Baxter Scientific Products<br>Obetz, OH |

[a] Silica gel of type specified in IUPAC Method #2.507.

TABLE 2

**Common Physical and Chemical Properties of the Materials Tested**

| Material | pH | LOD (%) | LOI (%) | Surface area $m^2/g$ |
|---|---|---|---|---|
| Activated carbon | 8.00 | 4.8 | — | 824 |
| Basic alumina | 9.55 | 0.1 | 7.8 | 287 |
| Neutral alumina | 7.40 | 0 | 0 | 158 |
| Bleaching earth #1 | 3.80 | 15.2 | 3.2 | 311 |
| Bleaching earth #2 | 3.55 | 12.3 | 4.9 | 400 |
| Calcium silicate | 9.80 | 4.8 | 11.0 | 185 |
| Diatomaceous earth | 9.60 | 0.1 | 0.1 | <10 |
| Magnesium silicate | 8.50 | 10.8 | 9.9 | 619 |
| Silica #1 | 2.75 | 65.6 | 6.5 | 955 |
| Silica #2 | 7.80 | 59.2 | 3.1 | 499 |
| Silica Gel 60A | 6.50 | 7.0 | 2.8 | 430 |

## MATERIALS AND METHODS

Table 1 lists the specific products that were chosen to represent the materials listed above in this study. Table 2 lists the common physical and chemical properties of these materials: The pH is that of a 5% by weight suspension in deionized water. LOD is the percent weight loss on drying at 105°C for 2 h. LOI is the additional percent weight loss on ignition at 600°C for 1.5 h.

Surface area was determined by nitrogen adsorption (16) with a Model 2200 High Speed Surface Area Analyzer (Micromeritics Instrument Corp., Norcross, GA).

IUPAC Method 2.507 (2) is widely used for determination of the polar and nonpolar fractions of a used frying oil. However, Sebedio *et al.* (17) showed that adsorption in a Sep-Pak silica cartridge (Supelco, Bellefonte, PA)

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duplicates the IUPAC method, is more rapid, and utilizes less solvent.

Both White and Wang (18) and Perkins *et al.* (19) have shown that HPSEC (also known as high-performance gel permeation chromatography—HPGPC) is a facile method to separate and quantitate the high and low molecular weight components of a used frying oil.

The present study involved two modifications to these procedures: i) Each of the adsorbents to be evaluated was substituted for the silica gel in the solid-phase extraction tube (Supelco) and evaluated in triplicate. ii) The initial Stock Solution (see below) was passed through the solid-phase extraction tube until the adsorbent was saturated.

One gram of each adsorbent (as received from the vendor) evaluated was placed in a 6-mL solid-phase extraction tube, dried to a constant weight at 105°C (a dried sample is more representative of the material that would contact used frying oil because oil at frying temperature evaporates any volatiles present), lightly tapped (to settle the material and eliminate voids), and held in place with a filter pad.

A frying oil (partially hydrogenated soybean oil) which had been used to deep-fry breaded vegetables and cheese was obtained from a seafood restaurant. The oil had degraded to the restaurant's normal discard point. A stock solution of the oil was prepared at a concentration of 25 mg oil per mL of a nonpolar solvent consisting of petroleum ether/diethyl ether (87:13, vol/vol). This stock solution was passed through the adsorbent column in 10-mL portions. The total volume passed through the column was held constant at 150 mL for all materials.

Each 10-mL effluent fraction was collected separately in a tared vial and carefully evaporated to a constant weight to determine the weight of oil in the effluent. Each effluent oil residue was redissolved in tetrahydrofuran (THF) and analyzed by HPSEC (high-performance size exclusion chromatography) for quantitative determination of the components (see below).

After the 150 mL of stock solution had been passed through the adsorbent column, the column was rinsed with 20 mL of an 87:13 vol/vol solution of fresh petroleum ether/diethyl ether to remove all nonpolar triglycerides and any unadsorbed polar materials. This solvent solution is the nonpolar solvent system specified in IUPAC Method 2.507. This is the optimum solvent for removal of nonpolar triglycerides from adsorbent silica and is expected to give comparable results for other adsorbents.

The adsorbent column was then rinsed with polar solvents to remove any polar materials adsorbed. The polar wash consisted of 30 mL diethyl ether, followed by 25 mL of basic methanol (0.1N with sodium hydroxide). Each of these polar solvent washes was collected separately, carefully evaporated to a constant weight, dissolved in THF, and analyzed by HPSEC to determine the composition. The sodium hydroxide was extracted from the basic methanol eluate with water before solvent evaporation.

For both the effluent oil and the polar-solvent wash procedures, a 10-μL sample of the residue, dissolved in THF, was analyzed by HPSEC to determine the composition. The amount of THF used to dissolve the residues was adjusted to the weight so that 75 to 100 μg of residue was injected into the chromatographic system.

The HPSEC analysis system used in this study consisted of a Micromeritics Model 725 autosampler, a Varian model 5000 HPLC, a Varian RI-4 refractive index detector, and a Varian Model 4270 integrator (Varian Associates, Sugar Land, TX). THF with approximately 150 mg/L BHT added as a stabilizer was used for the mobile phase at a rate of 1.0 mL/min.

The column system consisted of 2 stainless steel columns (25 cm by 4.2 mm) packed with 5-μm diameter styrene-divinyl benzene polymer. The system was a Phenogel guard column (Phenomenex, Torrence, CA), followed by a G2500HXL column (500 Å) connected in series with a G2000HXL column (250 Å). Column temperatures were held at 30°C. Integration response factors were determined by analysis of a pure soybean oil (Wesson) and polymer and fatty acid standards obtained from Sigma Chemical Co. (St. Louis, MO).

## RESULTS AND DISCUSSION

HPSEC analysis of the initial oil (Fig. 1) indicates the presence of polar compounds (polymers, diglycerides and low molecular weight monoglycerides and free fatty acids) in the used oil.

Graphs of the composition of the effluent oil fractions (as determined by HPSEC) *vs.* the total eluant volume of stock solution passed through a column of diatomaceous earth are shown in Figure 2. All of the lines are parallel to the X-axis (the slope equals zero) indicating that no adsorption of any of the polar degradation products has occurred.

Graphs of the same information for the effluent from the columns of the active filter aids indicate adsorption has occurred because the first milliliters of effluent do not indicate the presence of polar materials. As the adsorptive sites are occupied, polar materials begin to appear in the effluent, and the concentrations increase until the lines become parallel to the X-axis, indicating that the adsorbent is saturated. Figure 3 shows such data for the synthetic magnesium silicate. This method was used to evaluate the effluent from all of the adsorbents to assure that the adsorptive sites were saturated.

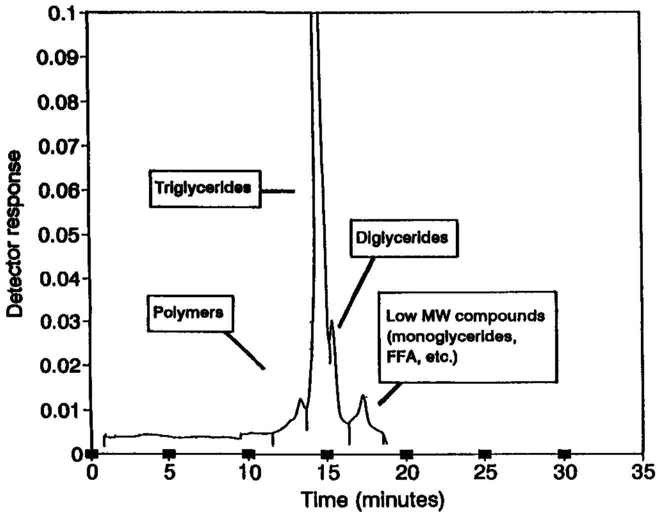

FIG. 1. HPSEC of the initial used frying oil. 25 cm SS columns; G2500HXL (500 angstrom) in series with G2000HXL (250 angstrom) 30°C; tetrahydrofuran at 1 mL/min; refractive index detection.

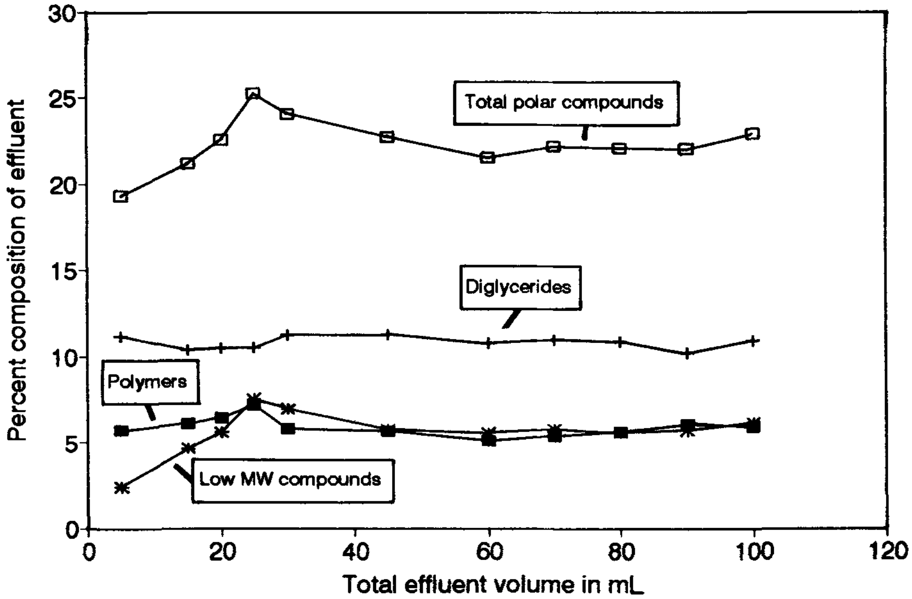

FIG. 2. Graph of the average percent composition of effluent fractions *vs.* total eluant volume for diatomaceous earth.

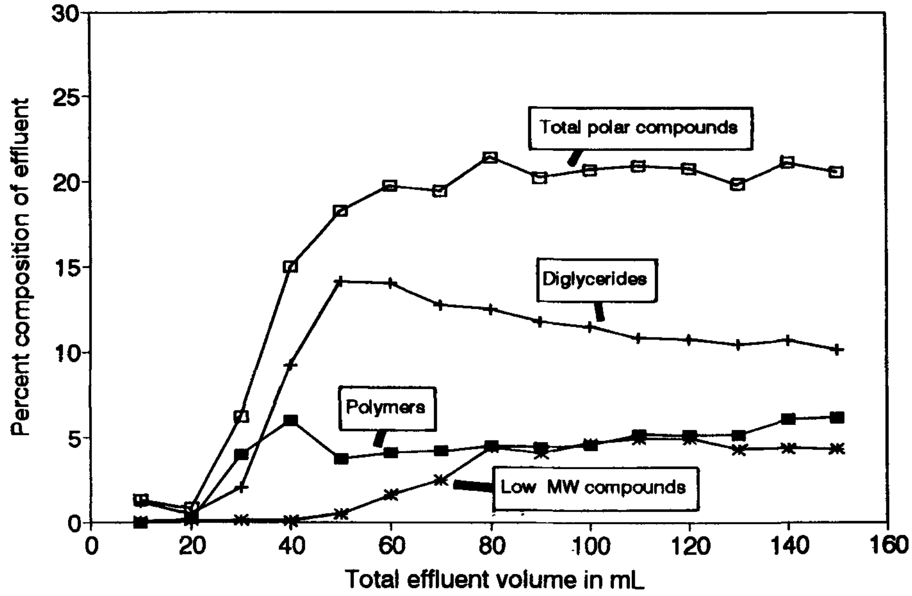

FIG. 3. Graph of the average percent composition of effluent fractions *vs.* total eluant volume for synthetic magnesium silicate.

HPSEC analysis shows that the residue removed from the adsorbents by the polar solvent elutions consisted almost entirely of polar oil degradation products. Figures 4 and 5 show HPSEC analysis of the polar elution residues for synthetic magnesium silicate. These polar elution residues were different in concentration and composition for each of the adsorbents tested.

Multiplying the percent composition of the residue from each polar elution by the total weight of residue gives the weight of each polar compound adsorbed. The combined weight of all of the polar components is the weight of total polar compounds adsorbed per gram of material. The average of the values for the three replicate analyses is presented in Table 3. As an error analysis, the procedure was performed on magnesium silicate (the material that adsorbed the highest amount of total polar material) five times. The standard deviations of the five analyses are included in Table 3.

The materials varied widely in adsorptive characteristics as indicated by the data shown in Table 3: i) The adsorptive capacity varied from no adsorption (diatomaceous earth) to adsorption of over 155 mg of total polar compounds per gram (synthetic magnesium silicate). ii) None of the materials tested had the highest adsorption capacity for all of the degradation products of a used frying oil. iii) Some of the adsorbents demonstrated

TABLE 3

**Milligrams of Polar Materials Removed from One Gram of Adsorbent by Polar Solvents**

| Adsorbent | Polymers | Diglycerides | Low MW[a] (Mg[b], FFA, etc.) | Total polars |
|---|---|---|---|---|
| Activated carbon | 1.5 | 17.4 | 19.6 | 38.5 |
| Basic alumina | 8.6 | 13.9 | 71.5 | 94.0 |
| Neutral alumina | 0.7 | 2.5 | 96.5 | 99.7 |
| Bleaching earth #1 | 41.0 | 10.5 | 36.9 | 88.4 |
| Bleaching earth #2 | 61.3 | 9.3 | 36.5 | 107.1 |
| Calcium silicate | 16.7 | 17.5 | 59.8 | 94.0 |
| Diatomaceous earth | 0.0 | 0.0 | 0.1 | 0.1 |
| Magnesium silicate | 59.7 ± 1.9 | 19.3 ± 1.6 | 77.6 ± 3.6 | 156.8 ± 3.0 |
| Silica #1 | 38.1 | 11.2 | 12.1 | 61.4 |
| Silica #2 | 49.5 | 12.8 | 21.5 | 83.8 |
| Silica Gel 60A | 64.0 | 54.3 | 21.3 | 139.6 |

[a] MW = molecular weight.
[b] Mg = monoglycerides, FFA, free fatty acids.

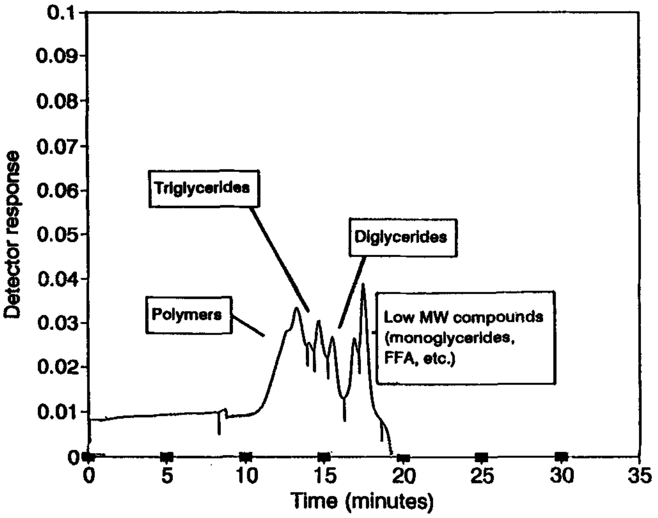

**FIG. 4. HPSEC of material from the first polar elution for magnesium silicate. 25 cm SS columns; G2500HXL (500 Å) in series with G2000HXL (250 Å) 30°C; tetrahydrofuran at 1 mL/min; refractive index detection.**

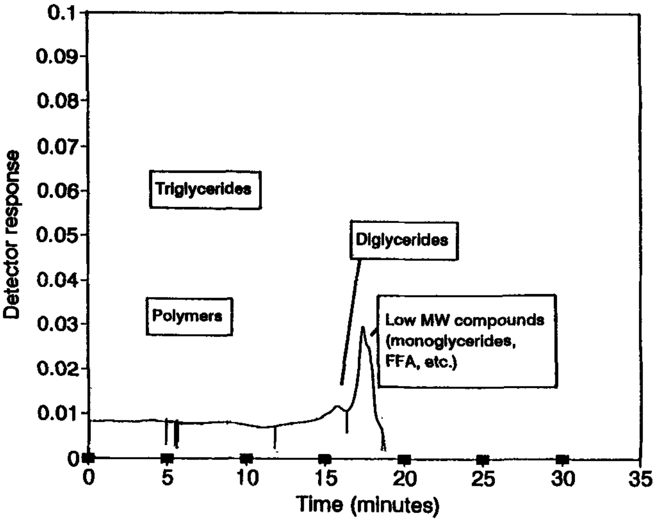

**FIG. 5. HPSEC of material from the second polar elution for magnesium silicate. 25 cm SS columns; G2500HXL (500 Å) in series with G2000HXL (250 Å) 30°C; tetrahydrofuran at 1 mL/min; refractive index detection.**

selective adsorptivity (*i.e.*, they primarily adsorbed only one class of polar compounds). The best example of this is neutral alumina, which primarily adsorbed free fatty acids.

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