Adsorbent Treatment of Frying Oil and the Impact on Health and Nutrition

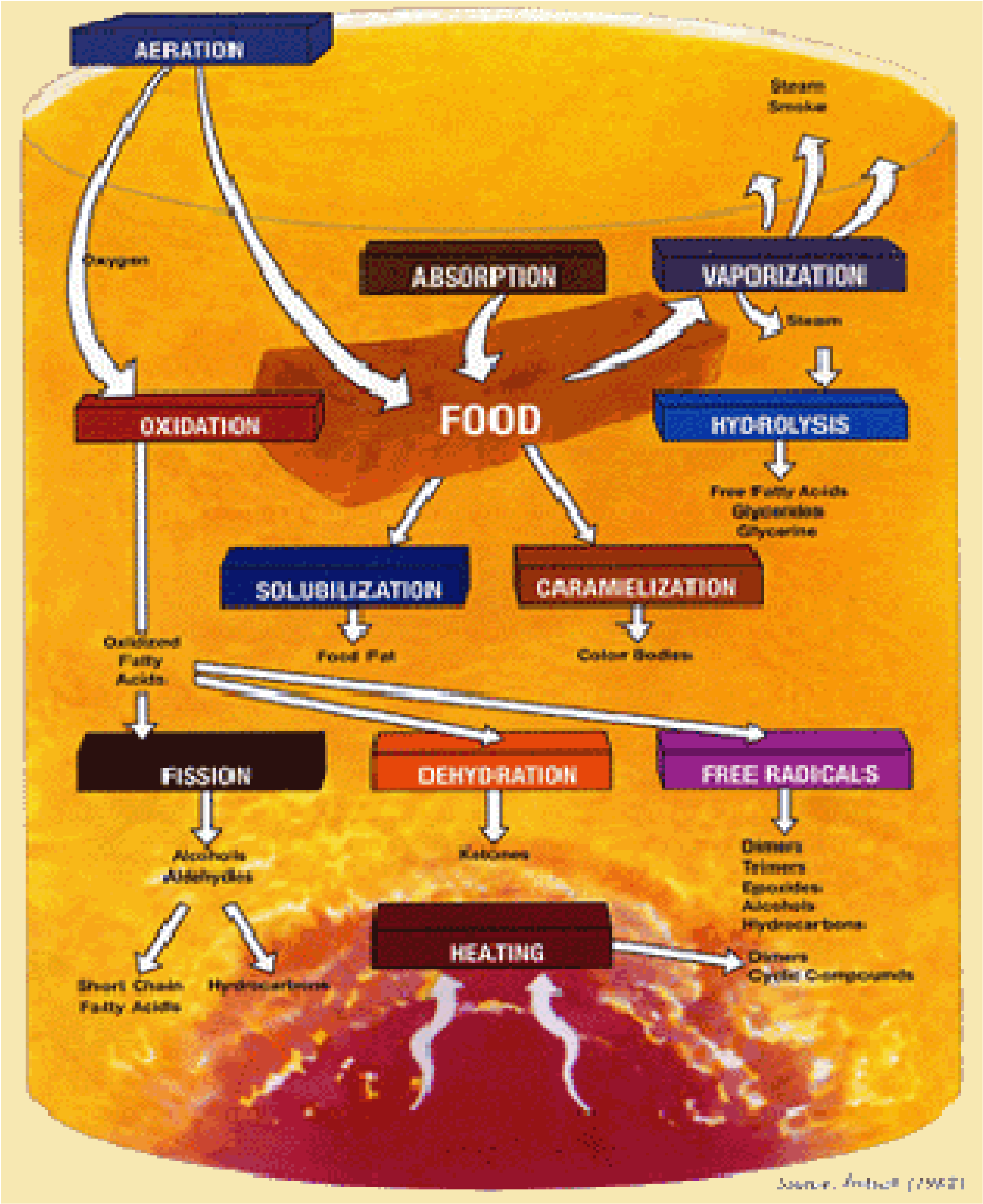
Brian S. Cooke
The Dallas Group America, Inc.

Outline

- Frying Oil Degradation
- Filtration of Frying Oils
  - Active versus Passive
- Adsorption of Polar Compounds
  - Packed Column
  - Batch Treatment
  - Temperature-Programmed Desorption (TPD)
- Controlled Frying Studies
  - French Fries
  - Chicken
- Field Results
  - Restaurant
  - Commercial
- Health and Nutrition
  - Treatment of Dietary Heated Fats

Frying Oil Degradation

- Deep-fat frying is very popular because it yields foods with good taste and is readily available.
- During Frying, Triglyceride molecules break down to form polar compounds.
  - Contribute to the flavor, odor and quality of the oil and the food being fried.



AERATION
Steam
Smoke
Oxygen
ABSORPTION
VAPORIZATION
Steam
FOOD
OXIDATION
HYDROLYSIS
Free Fatty Acids
Glycerides
Glycerine
SOLUBILIZATION
CARAMELIZATION
Food Fat
Color Bodies
Oxidized
Fatty
Acids
FISSION
DEHYDRATION
FREE RADICALS
Alcohols
Aldehydes
Ketones
Dimers
Trimers
Epoxides
Alcohols
Hydrocarbons
HEATING
Dimers
Cyclic Compounds
Short Chain
Fatty Acids
Hydrocarbons

Frying Oil Degradation

- Triglyceride molecules are non-polar.
- Products of oil degradation are polar.
  - Free fatty acids, mono- and di-glycerides, oxidized triglycerides, polymers, aldehydes, ketones, etc.

Frying Oil Degradation

- Free Fatty Acids
  - Decrease smoke point of frying oil
  - Further catalyze oil degradation
  - Decrease shelf stability of finished product
- Polymers
  - Increase potential for oil foaming
  - “Polymer buildup” effects heat exchange
  - Increase oil absorption

Frying Oil Degradation

- Color Bodies
  - Darkening of finished product
- Flavors
  - Scorched flavor due to inadequate filtration
  - Scorched flavor due to high temperature
  - Carryover of flavors

Frying Oil Degradation

- Concentration of polar materials increase until the oil becomes unfit for use
  - Relationship between the taste and quality of fried foods and the concentration of polar materials has been established
  - Legal limits on the amount of polar materials that may be present in oil used for deep-fat frying

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Filtration of Frying Oils

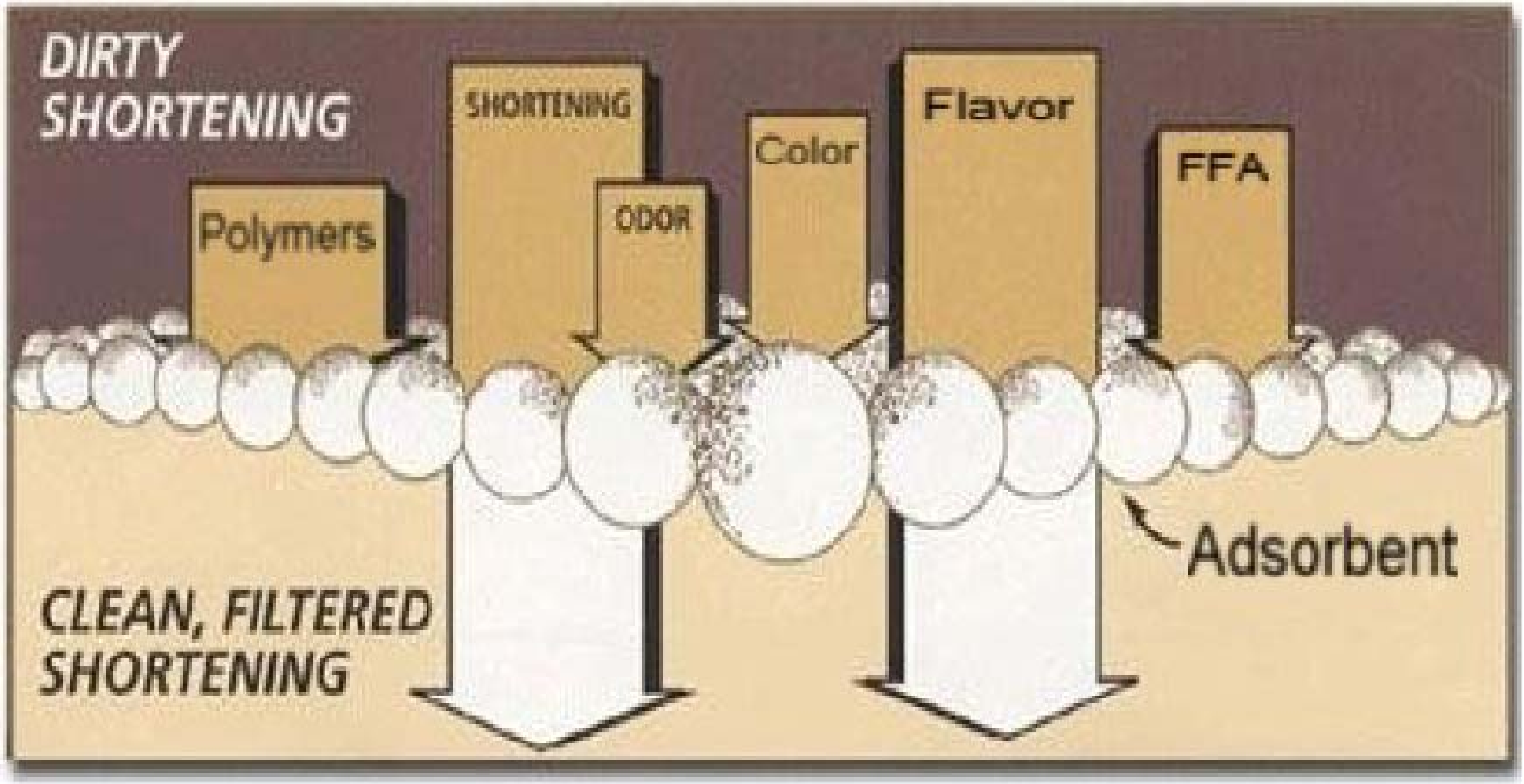
- Passive Filtration has long been used in the frying industry for removal of particulates from used oils
- Active Filtration is more desirable, as it removes both particulate and soluble impurities

Filtration of Frying Oils

- Passive Filtration
  - Removal of particulate from oil with a steel screen, cartridge or filter paper
    - 5 micron particles
  - Depth - removal of particulate with a porous pad or a "cake" of filter-aid-type materials (diatomaceous earth, perlite)
    - 1 micron particles

Filtration of Frying Oils

- Active Filtration by Adsorbent
  - Removes soluble degradation products by attracting polar products and holds them for removal in filter
  - Slows oil degradation
  - Acts as depth filter
  - Higher quality fried foods
  - Extend life of frying oil


DIRTY SHORTENING
SHORTENING
Polymers
ODOR
Color
Flavor
FFA
Adsorbent
CLEAN, FILTERED SHORTENING

Filtration of Frying Oils

- Benefits from Adsorbent Treatment
  - Reduction in oil use, potential elimination of oil discard
  - Reduces downtime
  - Reduces energy usage
  - Reduces cleanup costs
  - Improves finished product quality and shelf stability

Filtration of Frying Oils

- Adsorbents
  - Activated Alumina
  - Activated Carbon
  - Bleaching Clays
  - Calcium Silicate
  - Magnesium Silicate
  - Silica

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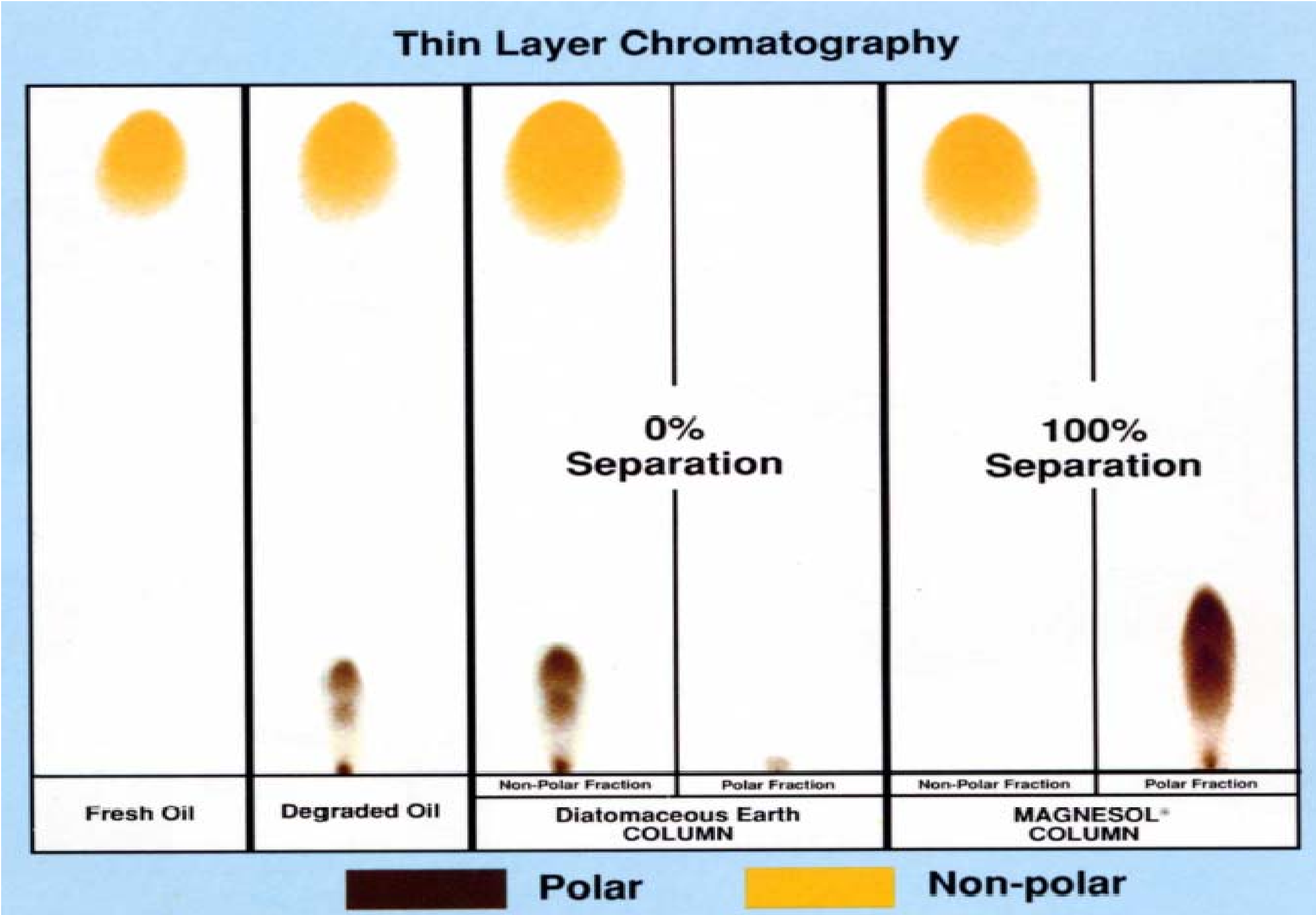
Adsorption of Polar Compounds in Frying Oil using a Packed Column

- International Union of Pure and Applied Chemistry (IUPAC) Method 2.507: Determination of Polar Compounds in frying fats
  - Packed column with adsorbent to be tested
  - Degraded frying oil passed through the column
  - The efficiency of the fractionation was assessed by the use of thin-layer chromatography (TLC).
  - The results were quantified using High Performance Size Exclusion Chromatography (HPSEC).

Adsorbents Tested

Material	Trade Name	Manufacturer
Activated Carbon	Darco T-88	American Norit Co., Jacksonville, FL
Basic pH Alumina	A-2	LaRoche Chemicals, Baton Rouge, LA
Neutral pH Alumina		M. Woelm Eschwege, Germany
Bleaching Earth #1	Filtrol 105	Harshow Filtrol, Cleveland, OH
Bleaching Earth #2	Tonsil Supreme	LA Saloman, Port Washington, NY
Calcium Silicate	Silasorb	Manville Corp., Denver, CO
Diatomaceous Earth	FW-18	Eagle Picher, Reno, NV
Magnesium Silicate	MAGNESOL XL	The Dallas Group, Whitehouse, NJ
Silica #1	Britesorb C200	PQ Corp., Valley Forge, PA
Silica #2	Trisyl	Grace & Co., Baltimore, MD
Silica Gel *	Silica Gel 60	Baxter Scientific Products, Obetz, OH



Thin Layer Chromatography
0%
Separation
100%
Separation
Non-Polar Fraction
Polar Fraction
Non-Polar Fraction
Polar Fraction
Fresh Oil
Degraded Oil
Diatomaceous Earth
COLUMN
MAGNESOL®
COLUMN
Polar
Non-polar

TLC Results

- Diatomaceous Earth had no effect on the separation of polar and non-polar compounds
- Synthetic magnesium silicate yielded complete separation of the polar and non-polar fractions

HPSEC Results
Initial Used Frying Oil

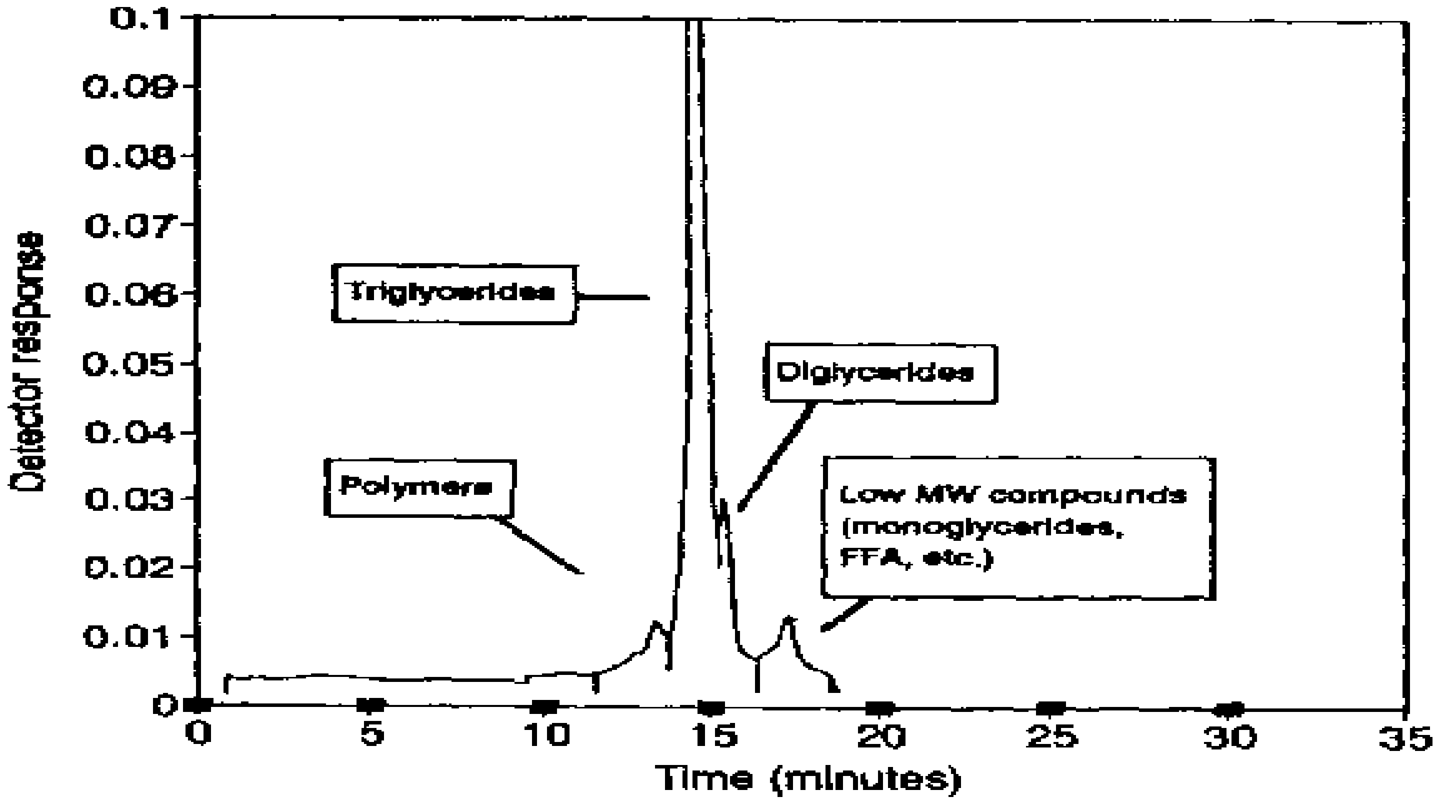


FIG. 1. HPSEC of the initial used frying oil. 25 cm SS columns; G2500HXL (500 angstrom) in series with G2000HXL (250 angstrom) 30°C; tetrahydrofuran at 1 mL/min; refractive index detection.

Quantitative Results of Polar Materials Adsorbed

Adsorbent	Polymers	Diglycerides	Low M.W.	Total Polars
Activated Carbon	1.5	17.4	19.6	38.5
Basic pH Alumina	8.6	13.9	71.5	94.0
Neutral pH 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

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

HPSEC Results

- Results verify that DE had no capacity to remove polar materials from the frying oil
- Synthetic magnesium silicate had the greatest capacity for removal of polar materials

Batch Treatment Procedure

- 1.3 gallons of used frying oil at 150 C were placed into a 1/4-scale commercial type re-circulation oil filter with 41g (1% by wt.) of filter media.
- The oil was re-circulated through the filter media cake for 5 minutes.
- The filter cake was removed from the filter for evaluation.
- Portions of each filter cake were weighed, placed in a Soxhlet extractor, and extracted with organic solvents to remove the residual used frying oil and adsorbed polar compounds.
  - Petroleum ether removed the residual used frying oil.
  - Diethyl ether, methanol, and methanol with NaOH were used to remove the adsorbed polar compounds.
- The residue from the extraction was weighed, dissolved in tetrahydrofuran, and analyzed by High Performance Size Exclusion Chromatography (HPSEC).

Laboratory Batch Treatments

Material	Trade Name	Manufacturer
Activated Carbon	Darco T-88	American Norit Co., Jacksonville, FL, USA
Acidic pH Alumina	Brockmann 1	Aldrich Chemical Co., Milwaukee, WI, USA
Neutral pH Alumina	ABA 6000	Selecto Inc., Kennesaw, GA, USA
Basic pH Alumina	A-2	LaRoche Chemicals, Baton Rouge, LA, USA
Bleaching Earth	Filtrol 105	Harshow Filtrol, Cleveland, OH, USA
Diatomaceous Earth	FW-18	Eagle Picher, Reno, NV, USA
Magnesium Silicate	Magnesol XL	The Dallas Group, Whitehouse, NJ, USA
Silica	Trisyl	Grace & Co., Baltimore, MD, USA

Filter Cake Extraction Results

Adsorbent	TAG (g)	Polymers (g)	DAG (g)	LMW (g)	Total Polar Compounds (g)	Adsorptivity (mg polars/g Adsorbent)
Activated Carbon	0.50	0.00	0.83	1.90	2.74	67
Alumina (Acidic)	0.07	0.06	0.10	3.09	3.25	79
Alumina (Neutral)	0.10	0.05	0.15	3.34	3.54	86
Alumina (Basic)	0.29	0.15	0.44	3.03	3.63	89
Bleaching Earth	0.72	1.43	0.87	2.27	4.47	109
Diatomaceous Earth	0.02	0.04	0.01	0.05	0.10	2
Magnesium Silicate	0.98	1.37	1.44	5.33	8.14	199
Silica	1.72	1.22	2.04	1.88	5.14	125

Batch Treatment Results

- DE had no capacity to remove polar materials from the frying oil
- Synthetic magnesium silicate had the greatest capacity for adsorption of polar compounds

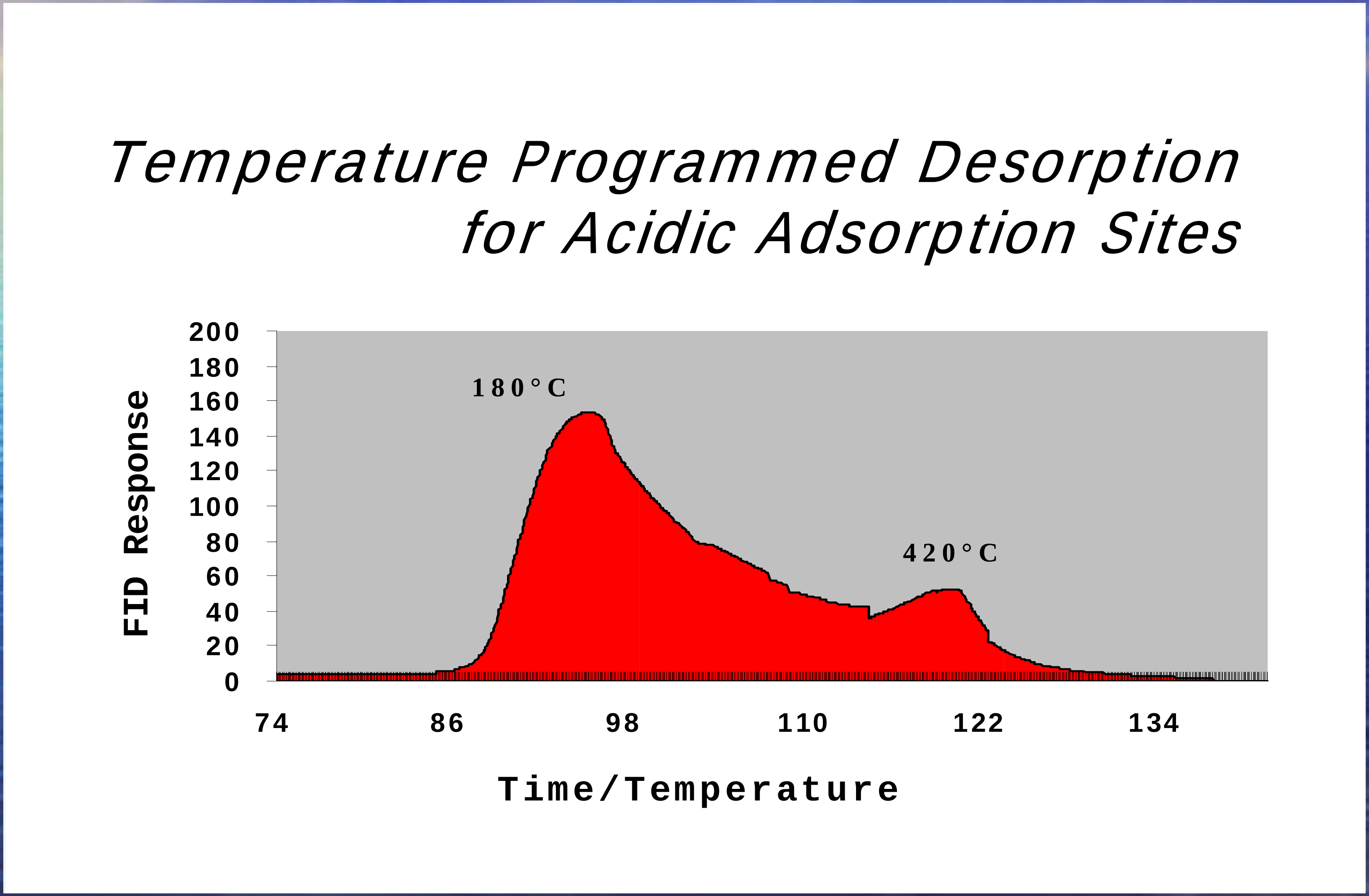
Determination of Active Filter Aid Adsorption Sites by TPD

- Adsorbents have charged sites on their surface which attract polar compounds and hold them for removal by filtration
- Adsorptive sites may have either acidic or basic character
- TPD uses special instrumentation and techniques to measure the number and strength of adsorptive sites

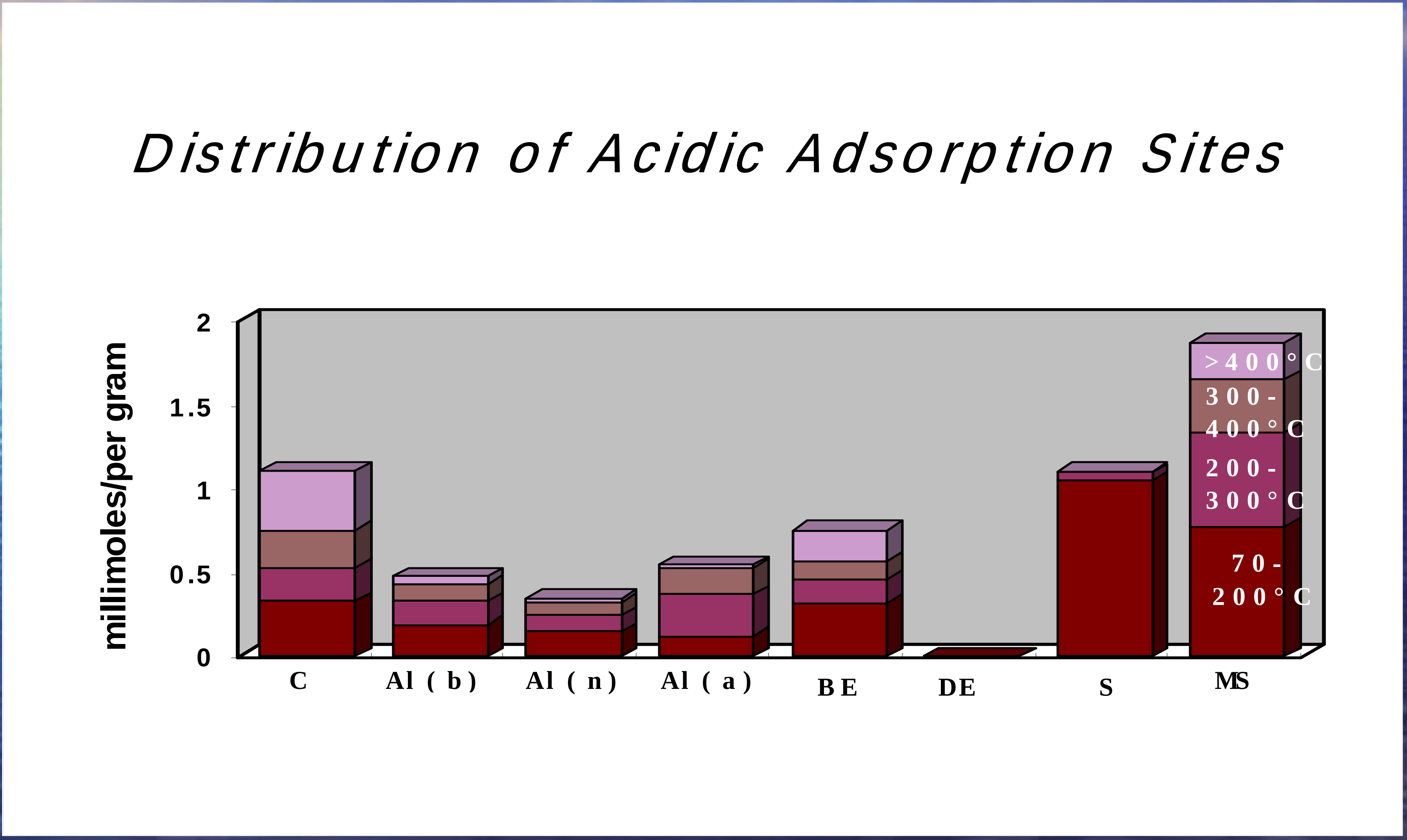
TPD Protocol

- Place a known weight of adsorbent in an empty gas chromatographic column
- Inject known quantities of a “probe” reagent until the material is saturated
  - Acidic sites: n-Butylamine
  - Basic sites: Trifluoroacetic acid
- Desorb “probe” reagent by temperature programming the GC to 420°C
  - The temperature at which the probe material is desorbed is an indication of the strength of the adsorptive site, and the height of the peak is a measure of the number of sites

TPD: Synthetic Magnesium Silicate



TPD: Comparison of Adsorbents



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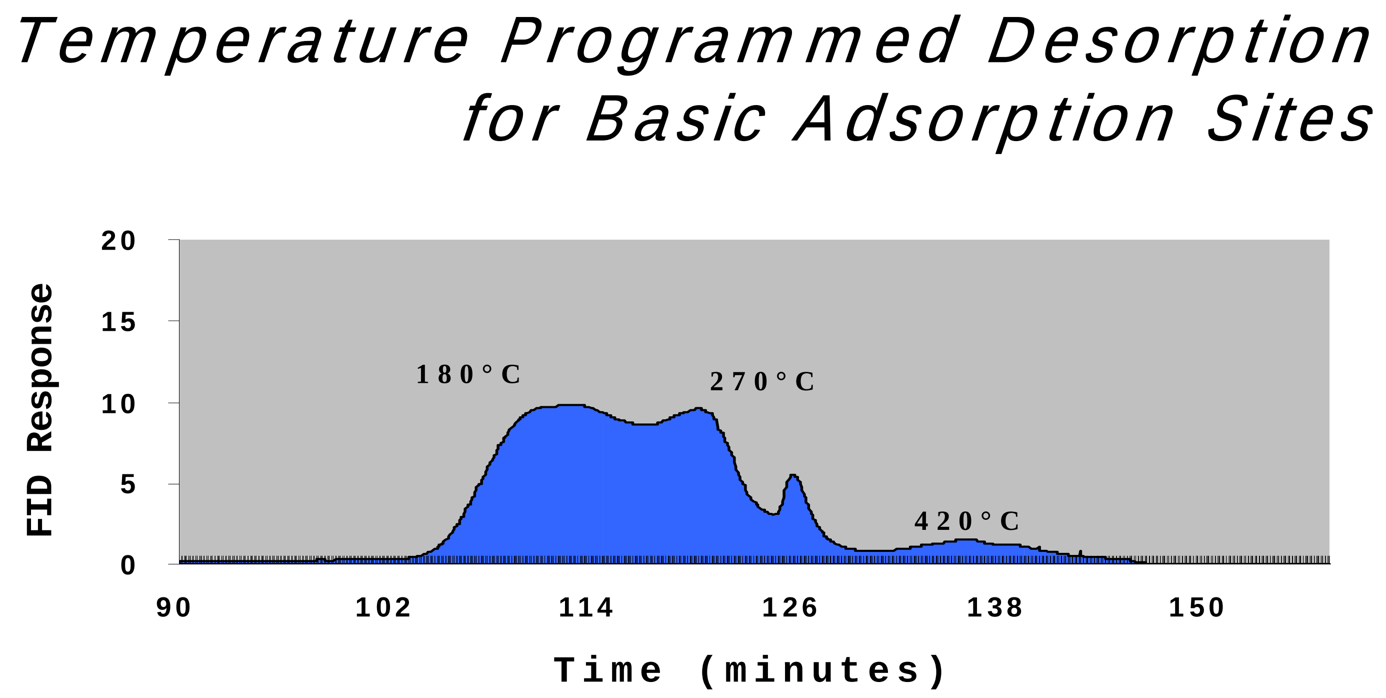
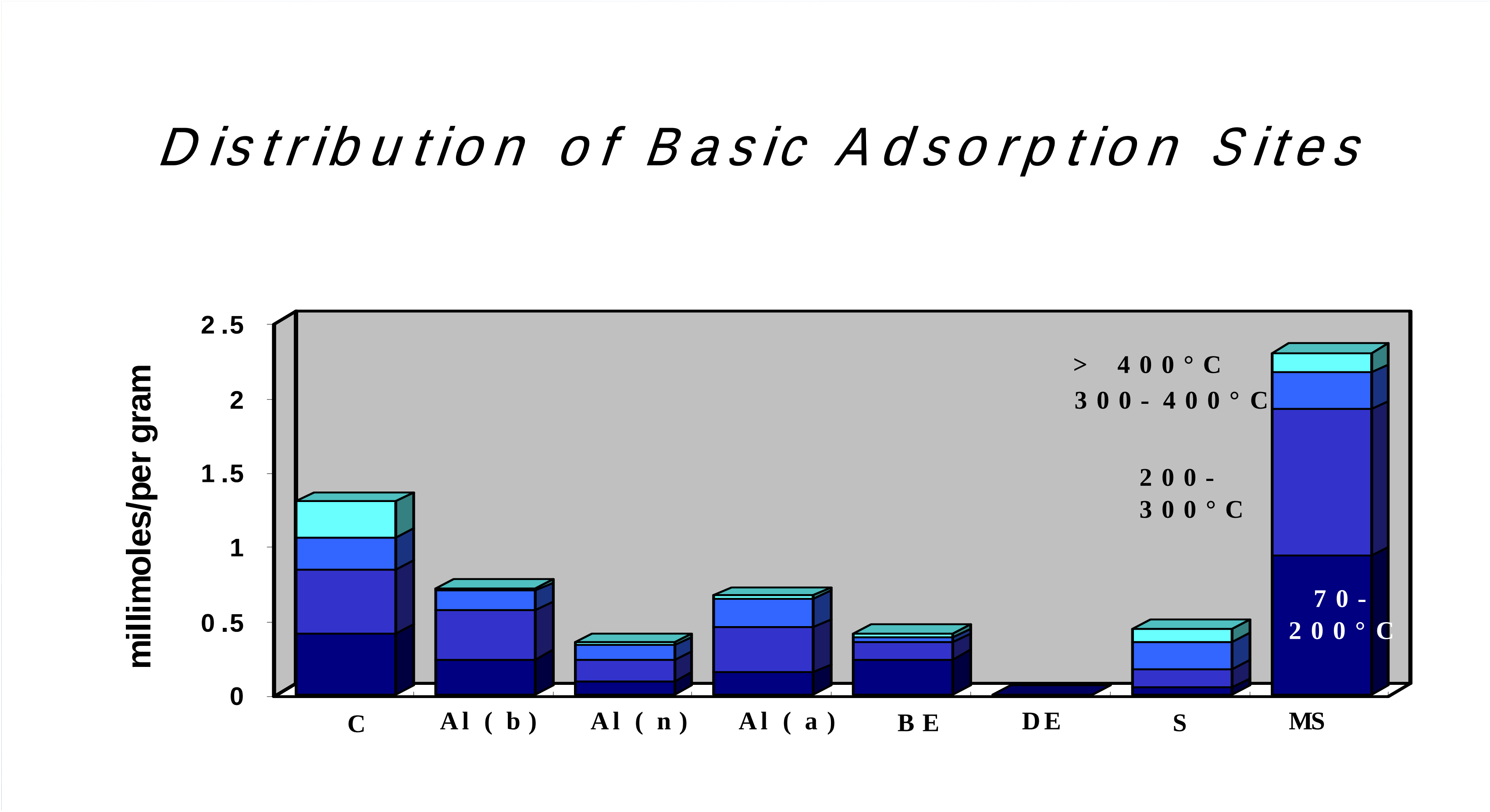


TPD: Comparison of Adsorbents



TPD Results

- DE had no acidic or basic adsorption sites
  - This supports the findings in column and batch tests that DE did not remove any polar material
- Synthetic Magnesium Silicate had the most acidic and basic adsorption sites
  - This supports the findings in column and batch tests that synthetic magnesium silicate had the greatest capacity to adsorb polar compounds

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Controlled Frying Study
French Fries

- The purpose of this study was to determine the useful life of frying oil when treated and filtered with synthetic magnesium silicate as compared to a control, which was filtered through diatomaceous earth (DE).
  - Criteria was 25% Total Polar Materials (TPM)

Controlled Frying Study French Fries

- Small Fry Kettles were filled with 4.35Kg (9.5lb) of a partially hydrogenated soybean oil.
- 14.5Kg of fresh potatoes were fried over a 12-hour period each day (3.33Kg food per Kg oil).
- 400g batches of freshly cut potatoes were fried at 177°C (350°F) for 8 minutes with 5 to 10 minutes between batches.
- The oil was filtered daily in a re-circulating filter machine for 5 minutes.
  - Oil from the control fryer was filtered with 1% by weight diatomaceous earth (DE).
  - Oil from a second fryer was treated and filtered daily with 1% by weight synthetic magnesium silicate.

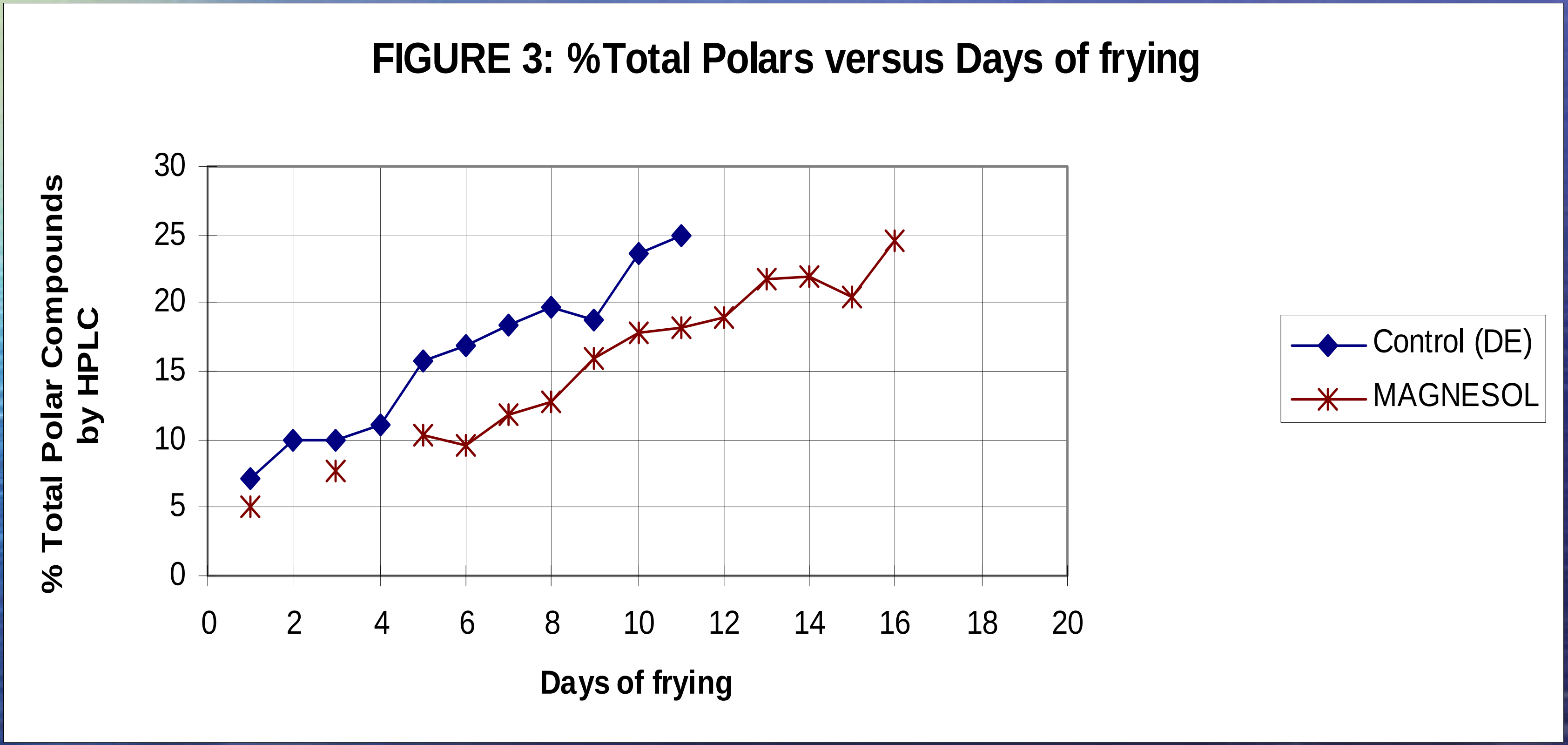
Controlled Frying Study
French Fries

Filter Media	Days of Frying	% FFA	Photometric Color	% Polymers	% Total Polars
Control (DE)	11	4.92	94.4	7.4	24.9
1% magnesium silicate	16	5.04	51.6	7.4	24.5

- Criteria to end frying study: 25% TPM

Filter Media	Days of Frying	Average daily make-up (g)	Food-to-oil ratio	Weight percent oil in fries
1% DE (Control)	11	999	11.04	8.42
1% magnesium silicate	16	1040	11.55	7.62

Controlled Frying Study French Fries



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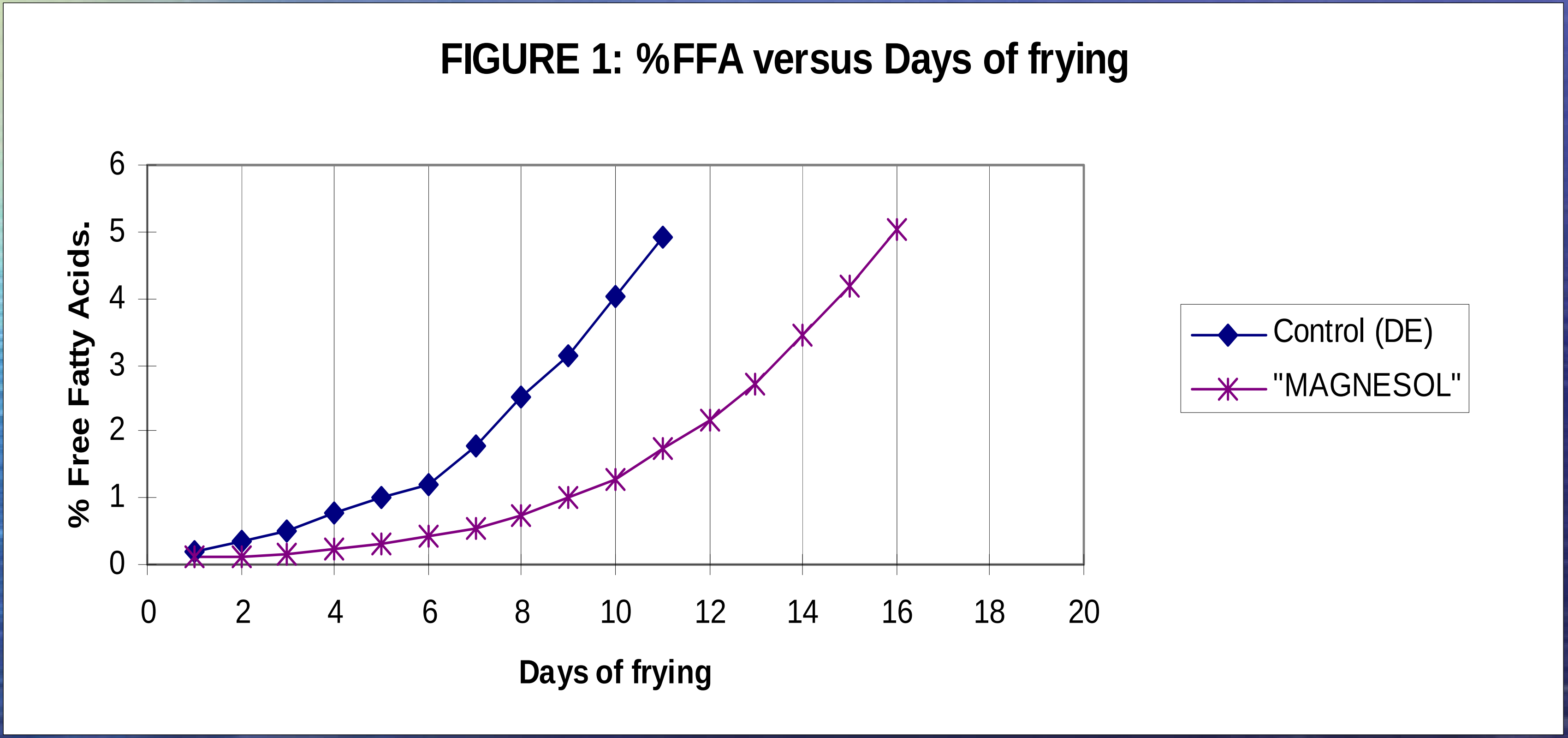
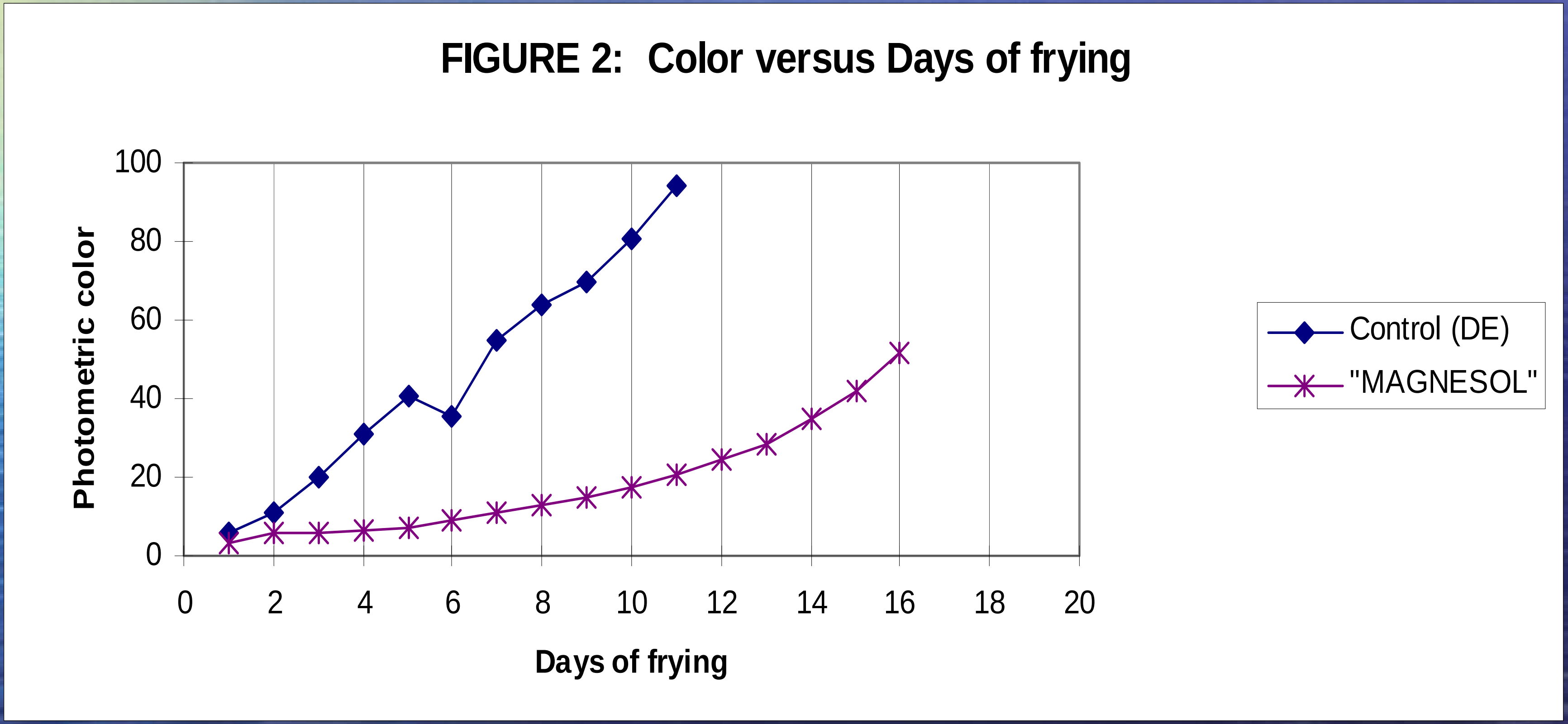


Controlled Frying Study
French Fries



Controlled Frying Study French Fries

- Synthetic Magnesium Silicate effectively extended the useful life of the frying oil by 31% when compared to the control
  – Criteria was 25% TPM maximum

Controlled Frying Study
Chicken

- The purpose of this study was to determine the useful life of frying oil when treated and filtered with synthetic magnesium silicate as compared to a control, which was filtered through diatomaceous earth (DE).
  - Criteria was 2.0% Free Fatty Acid (FFA)

Controlled Frying Study
Chicken

- Small Fry Kettles were filled with 9.5 lb of a partially hydrogenated soybean oil.
- 40 lb of fresh chicken was fried each day over a 14-hour period.
  - The chicken was coated with a mixture of flour and salt.
  - Chicken was fried in 1.5 lb batches for 14 minutes.
  - Batches were fried every 20 minutes.
- Oil was filtered and returned to the fryer each morning before frying.
  - 2% by weight of synthetic magnesium silicate was added to the oil and allowed to mix for 1 hour and then filtered.
  - 2% DE was used in a second fryer as a "control".

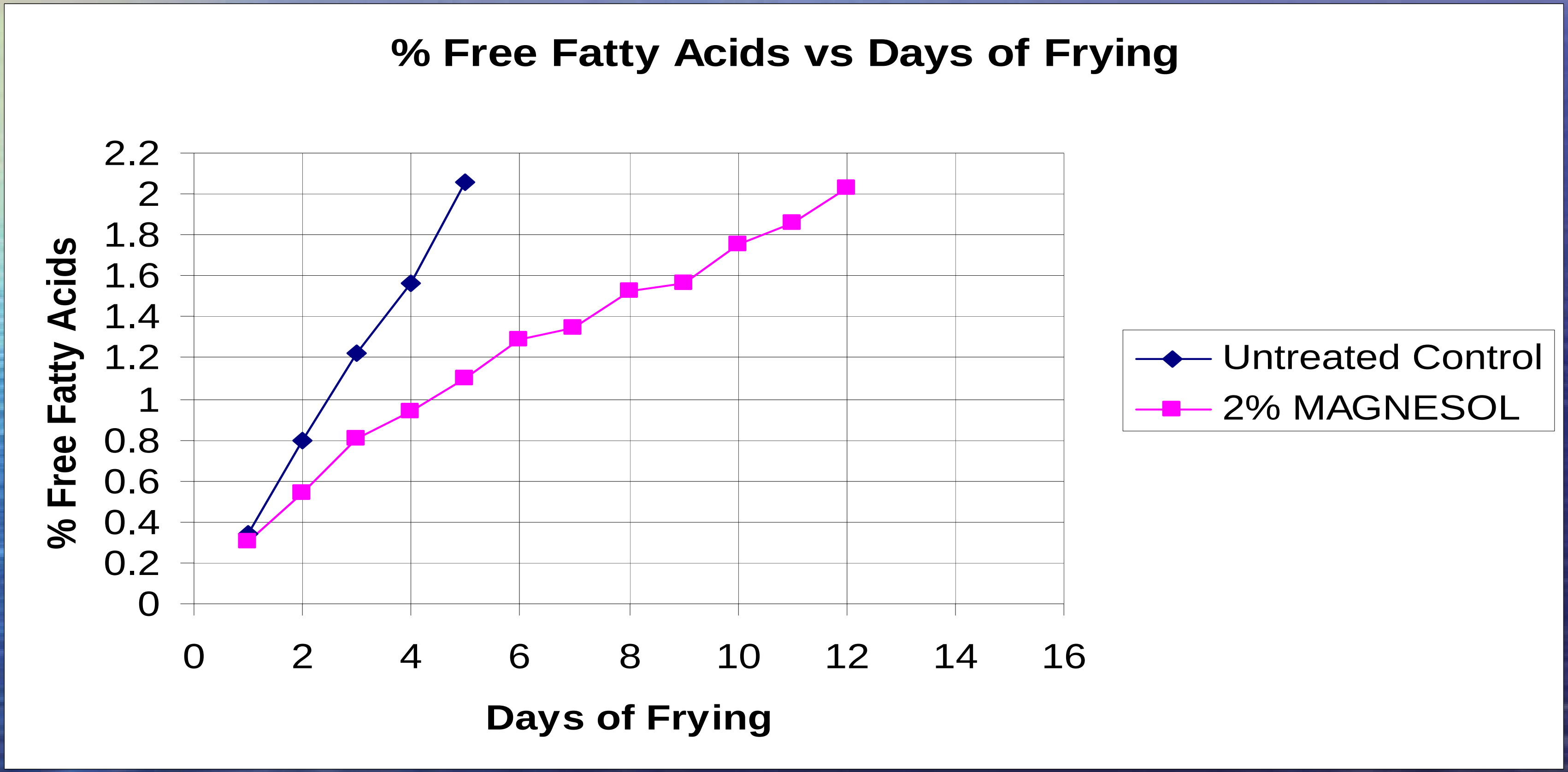
Controlled Frying Study
Chicken

Filter Media	Days of Frying	% FFA	Photometric Color
2% DE (Control)	5	2.06	137.4
2% magnesium silicate	12	2.03	93.2

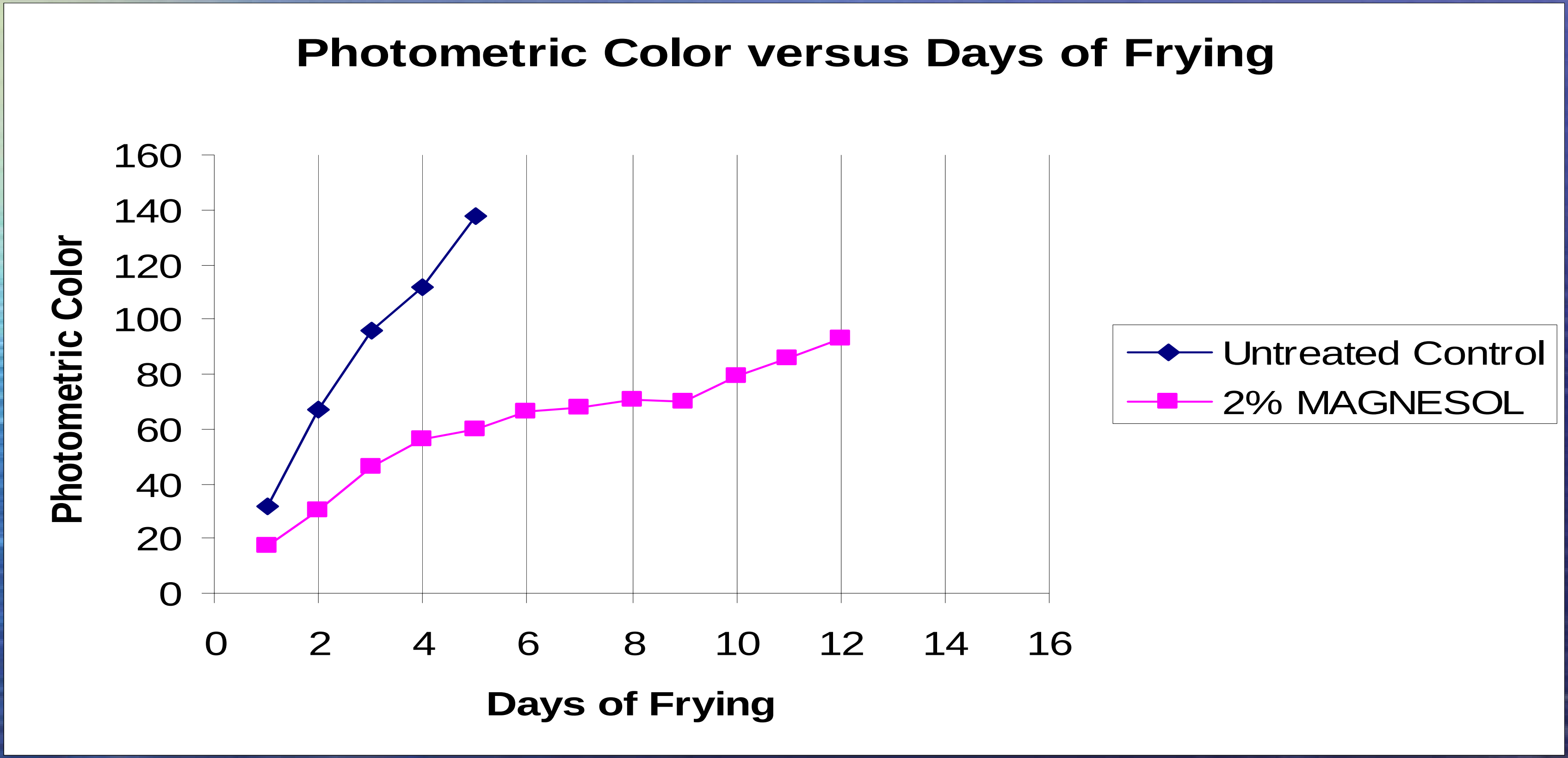
- Criteria to end frying study: 2% FFA

Filter Media	Days of Frying	Average daily make-up (g)	Food-to-oil ratio
2% DE (Control)	5	763	11.99
2% magnesium silicate	12	708	18.61

Controlled Frying Study
Chicken



Controlled Frying Study
Chicken



Controlled Frying Study
Chicken

- Synthetic Magnesium Silicate effectively extended the useful life of the frying oil by 58% when compared to the control
  - Criteria was 2% FFA maximum

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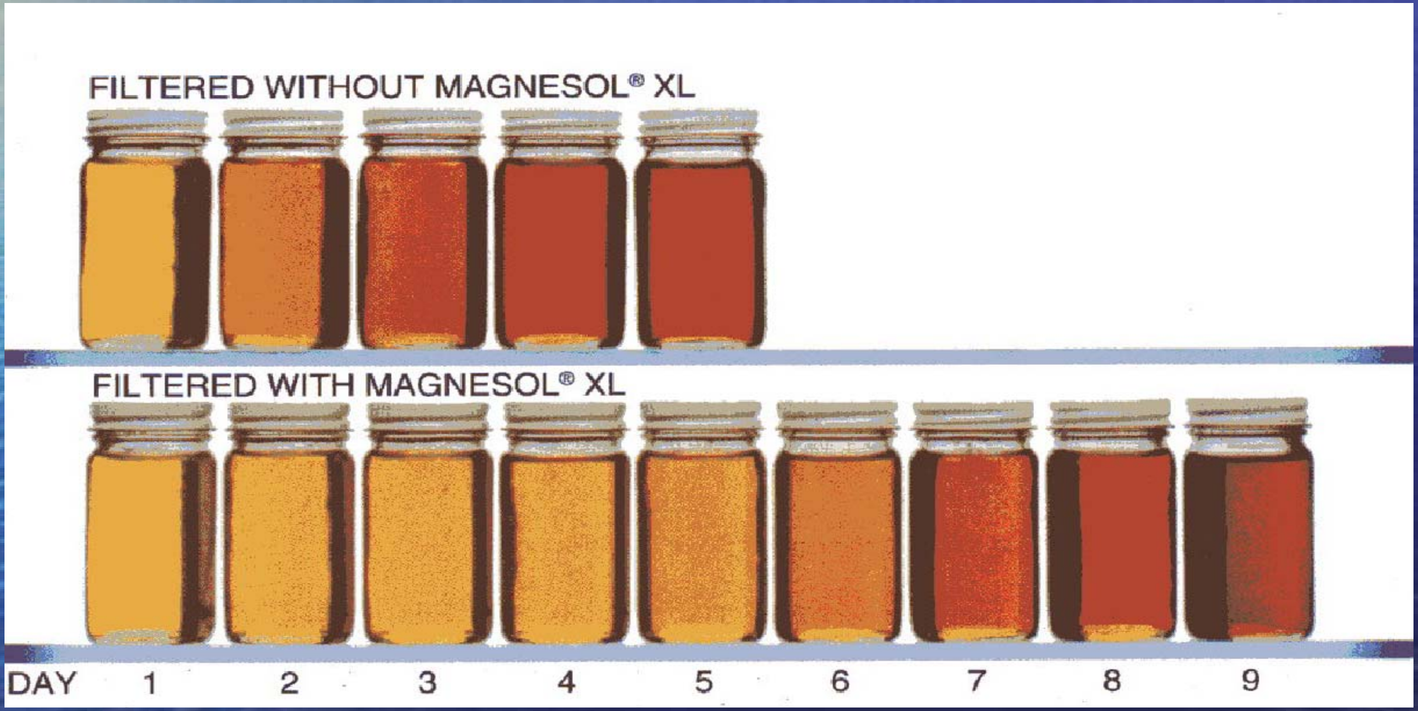
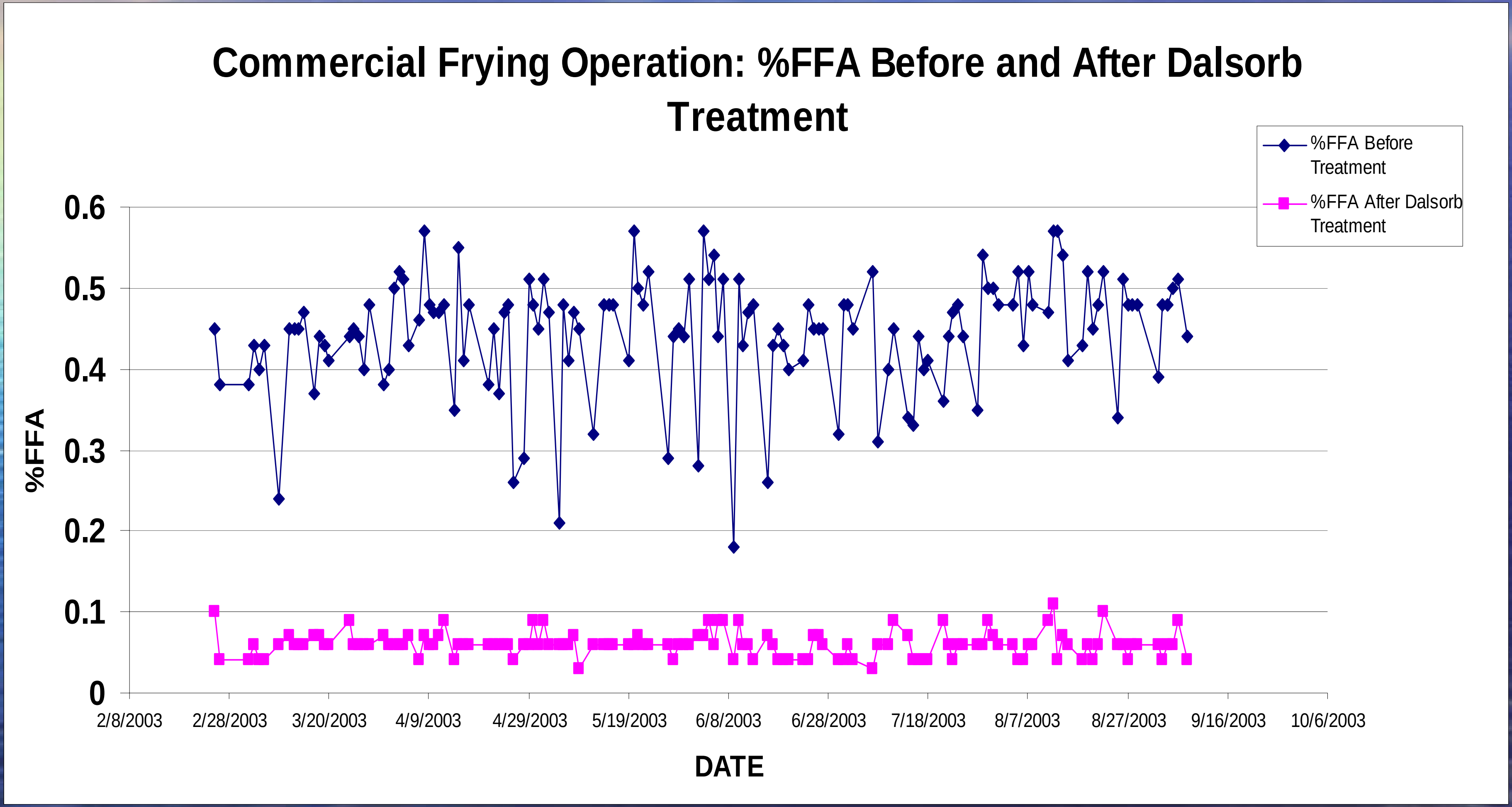
Restaurant Field Results



Commercial Field Results



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Treatment of Dietary Heated Fats

- Numerous studies report dietary heated fats contain harmful substances that may cause deleterious effects when fed to laboratory animals.
  - Adverse biological effects include enlargement or fatty necrosis of the liver, slowed growth, hair loss and dermatitis when such fats were fed to rats.

Procedure

- Frying oil which had been used for 7 days was split into two portions. One portion was treated with 10% by weight synthetic magnesium silicate.
- 30 male weanling rats were maintained on standard diet for one week then randomly split into three groups.
  - NH diet included fresh partially hydrogenated soybean oil
  - 7DH diet included the 7 day old used oil
  - T-7DH diet included the synthetic magnesium silicate treated oil
- The rats were fed the test diet for 10 weeks.
- After 10 weeks, the animals were randomly killed by Guillotine and blood and liver samples were collected for analysis.

Diet Compositions

	Virgin oil	7 day used oil	Treated 7 Day used oil
Casein	150	150	150
Dextrose	600	600	600
Cellulose	50	50	50
Vitamin Mix	10	10	10
Mineral Mix	40	40	40
PHSBO (NH)	150	0	0
PHSBO 7-DH	0	150	0
PHSBO T-7DH	0	0	150

Several Parameters in a Pair-Feeding Experiment

	Virgin oil	7 day used oil	Treated oil
Feed Efficiency, g gain/g feed	0.232	0.232	0.232
Liver weight/body weight ratio (mg/g)	2.75	2.95	2.894
Liver Protein (mg/g)	392.65	593.22	487.09
Microsomal protein (mg/g)	30.51	56.47	30.60
Liver Lipid (mg/g)	63.88	79.66	72.86
Lipid/Protein ratio	0.98	0.81	0.92
Liver glycogen (mg/g)	11.03	6.32	8.81

Hepatic Microsomal Cytochromes Content (Detoxification Enzymes)

	Virgin oil	7 Day used oil	Treated oil
Cytochrome b5 content (nmol/mg micr. Protein)	0.46	0.75	0.49
Cytochrome P450 content (nmol/mg micr. Protein)	1.04	1.68	1.15

Results

- Oils used for deep frying as well as the compounds generated in used oils caused a generalized increase in the content and activity of the liver detoxification enzymes when ingested.
- The non-treated oil group of rats developed enlarged livers while the treated oil group did not.

Results

- Treatment of the used oil with synthetic magnesium silicate improved the nutritional parameters of the oil
- Toxic components generated during the heating process of the oil were partially removed by adsorption