Alkaline Contaminant Materials in Used Frying Oils: A New Quick Test

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ABSTRACT

The AOCS recommended practice Cc 17-79 measures titratable alkalinity (soaps) at the low parts per million level in fresh, alkali-refined vegetable oils. This method indicated that titratable alkalinity is present at levels equivalent to many parts per million of "soap" in used frying oils. A colorimetric quick test was developed to show the presence and semi-quantitative concentration of alkaline contaminant materials (ACM), such as soap, in two types of fresh and used frying oils. The quick test works with fresh and used vegetable and animal/vegetable oil blends where it is not possible to use Cc 17-79.

INTRODUCTION

The deterioration of cooking properties of a frying oil is marked by the formation of a variety of non-volatile chemicals in the oil. Typical degradation routes of frying oils were described by Fritsch (1). Much of the traditional study of used frying oil non-volatiles has addressed the degradation of fatty acids and other contributors to titratable acidity.

Testing with non-aqueous pH indicators showed that fresh frying oils have a relative pH of approximately 3, while well-used oils have a pH of 6.5 or higher. Alkaline contaminant materials (ACM) raise the pH of the oils. The ACM originate from oil processing residues, foods and oil degradation products. The primary alkalinity in used frying oils arises from the interaction of food materials with oil degradation products.

Nelson (2) developed a titrimetric method for measuring residual alkali (calculated as % soap) in soybean and palm oils. The AOCS Recommended Practice Cc 17-79 (3) offered an improved technique for measuring parts per million (ppm) of soaps in refined vegetable oils. The methodology of Zarins, White and Feuge (4) cannot rapidly measure soap or alkalinity levels in used frying oils. These methods, and others cited by Zarins et al., require laboratory skills to measure soaps or alkalinity in oils. The AOCS recommended practice (RP) Cc 17-79, "Soap in Oil-Titrimetric Method," was selected for further work.

RP Cc 17-79 was used to survey fresh and used frying oils and oil carried on frozen, preblanched foods from a variety of sources. The frying of foods in well used oils had generated up to about 100 ppm of soaps (titratable alkalinity) in both vegetable and animal/vegetable oil blends. Also, some fresh coconut oils contained large amounts of soaps. Many dark colored fresh and used oils, such as palm oil, precluded a sharp end-point to the titration. We used a model system of sodium oleate in fresh corn oil to determine that RP Cc 17-79 could be used to measure from zero to about 5 ppm soap under ideal conditions in a laboratory.

A colorimetric quick test kit was devised (5) which could determine "soap" (ACM) at the level of zero to about 200 ppm, by improving upon the AOCS RP Cc 17-79 precedent. This simple quick test also was used to determine the ACM levels in restaurant frying oils. Results were rapid and semi-quantitative, and the test could be used easily with dark colored and heavily contaminated oil, where Cc 17-79 was marginal or failed.

The quick test was then used to determine soap, or ACM, levels in two different restaurant frying oils. The oils were used to prepare similar food mixes in a restaurant where we could tightly monitor and sample from the operation over a period of weeks. The accumulation of ACM in both frying oils increased with usage and was diminished by dilution with the addition of fresh oil to the fryer.

EXPERIMENTAL

Restaurant Frying Oils

A premium cost vegetable oil (Fry-Max, Proctor & Gamble) or an economy, hardened animal/vegetable oil (Fri-al, Continental) were heated in an 8-l gas-fired fryer operated at 180 ± 15 C for 12 hr/day, six days/week. Foods fried were potatoes (75%) and breaded chicken, fish, vegetables, meat and sausages (25%) for a daily total of about 7 kg. Laboratory samples were 5% or less of oil volume per day taken after the hot oil was filtered through a MirOil (Allentown, Pennsylvania) plastic oil filter assembly. Polypropylene containers were used for the oil samples because glass introduced measureable alkaline substances into the oils, both with brief room-temperature contact, or with longer contact at freezer temperatures.

Quick Test Kit for ACM

A preferred embodiment of the quick test kit (solution and containers) (5) follows. To make 1 l of test kit solution: add 0.04 gm ACS reagent grade bromophenol blue to 750-800 ml of reagent grade acetone and stir to get a pale yellow solution. Add 75.0 ml distilled or deionized water to above, to obtain a gold colored solution.

Add 0.10 N reagent grade sodium hydroxide to above, to obtain a greenish tinge to the solution. This may require about 1.10 ml of NaOH solution. Wash the alkali traces into the solution with minimum acetone. Add 0.01 N reagent grade hydrochloric acid to the above solution to restore a pure yellow color. This can require about 5 drops of the acid solution. When prepared with due caution against accidental contamination, the test solution is stable for months in a darkened container.

The test kit solution can be used to extract and examine warm oils (approx. 70 C) in the ratio of 5 ml solution to 6 ml oil to be tested. After 30 seconds of shaking the oil and test solution together in a ½-in. diameter polypropylene test tube, the solution is left to settle. The oil quickly forms a lower layer. The transparent upper layer assumes a color directly correlated to the amount of soaps or ACM extracted from the oil. The test usually is not inferfered with by emulsion formation, or by pigment materials from the oil.

Calibration of Test Kit for ACM

The quick test solution color ranges were compared to the values found by RP Cc 17-79 for a serial dilution of sodium oleate or sodium stearate in fresh corn oil. The corn oil (Mazola, Best Foods) had a starting concentration of zero ppm soaps as determined with RP Cc 17-79. The non-linearity of soaps added to the model corn oil systems vs. the amounts found by RP Cc 17-79 (Table I) suggests that the RP Cc 17-79 is not useful for measuring alkalinity above a few parts per million (which was the original intent of that method).

The color ranges developed by the quick test solution with respect to the model system of sodium oleate in fresh corn oil are shown in Table II. The Table II values were

TABLE I

Titration of Soaps Added to Refined Corn Oil: AOCS Recommended Practice Cc 17-79

PPM added sodium oleate to corn oil	PPM found sodium oleate by Cc 17-79	Color of quick test
0	0	Yellow
5.0	6.1	Yellow
10.0	7.8	Yellow-green
11.6	12.8	Lt-green
21.0	21.3	Lt-green
40.0	27.0	Greenish-blue
54.6	22.6	Lt. blue
79.3	27.4	Blue
106.0	34.0	Dark blue
222.1	54.4	Violet

PPM added sodium stearate to corn oil	PPM found sodium stearate by Cc 17-79	Color of quick test
0	0	Yellow
6.2	2.7	Yellowish-green
13.0	4.8	Lt-green
24.8	7.9	Lt-green
63.0	26.1	Blue
93.8	36.2	Dark blue
127.1	44.7	Dark blue
249.3	68.9	Violet

accepted as the basis for calibrating the response of the quick test for use with the restaurant samples.

RESULTS

The analyses of the restaurant oil samples for ACM were performed with the newly developed quick test. Table III shows the soap (ACM) values indicated by the quick test kit colors.

The quick test kit showed the accumulation of ACM increasing with the useage of the oil regardless of replenishment of oil to make up for the oil carried out on the food. Note the presence of a small amount of ACM in the fresh economy oil. We suspect the ACM to be at least partially responsible for the soakage of well-used oil into food. We have established that the ACM materials are found among the polar material fraction of used oils and will report on that separately.

ACKNOWLEDGMENT

This work was funded by a grant from the MirOil Filter Division of Oil Process Systems, Inc., of Allentown, Pennsylvania.

TABLE II

Color Ranges for ACM Quick Test

PPM sodium oleate added to corn oil	Color developed in Libra quick test
0	Yellow
6	Yellow
7	Yellow-green
10	Light green
35	Green
40	Green-blue
55	Light blue
65	Blue
80	Dark blue
150	Blue-violet
180	Violet

TABLE III

Restaurant Study: Oil Samples Filtered at End of 12-Hr Day

Premium oil		Economy oil	
	PPM soap quick test		PPM soap quick test
Start	0	Start	6
Day 1	7	Day 1	6
Day 2	10	Day 2	10
Day 3	10	Day 3	30
Day 4	20	Day 4	30
Day 5	20	Day 5	10*
Day 6	40	Day 6	20
Day 7	40	Day 7	30
Day 8	40		
Day 9	55		
Day 10	55		

*Heavily diluted with fresh oil before sample taken from fryer.

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[Received December 12, 1984]