However nickel added as a finely divided metal (as in the form of hydrogenation catalyst) to soybean oil just prior to deodorization of the oil has shown greater detrimental effects on oxidative stability of the liquid oil than has the addition of an equivalent amount of nickel in the form of its chloride salt. The effect of surface area on catalytic activity is well known and a similar effect on the rate of oxidation could logically be expected.

Both zinc and lead are detrimental, but it is doubtful if they are likely to occur in concentrations which would produce effects that could be detected organoleptically. Concentration effects that can be detected organoleptically are probably near the toxic level and for this reason further care is warranted in avoiding contamination. It has been stated that zinc is not detrimental to butter (2); however this does not hold true for soybean oil.

The effects of the alkaline-earth metals offer another problem primarily connected with refining and removal of soaps. Such metals are detrimental, and although investigation of their influence was not extensive, it is believed the effects are sufficiently important to warrant further studies.

Summary

The concentration of iron as determined spectroscopically in commercial soybean oils showed almost a hundred-fold variation. Values from 0.003 p.p.m. to a high of 2.50 p.p.m. of iron were obtained. The average for 12 edible oils was 0.90 p.p.m. of iron. Commercial undeodorized oils had an average iron content of only 0.19 p.p.m., and laboratory-refined samples had an average iron content of 0.12 p.p.m.

No correlation was found between the metal content and the stability of commercial edible soybean oil. This lack of correlation is attributed to the use of metal deactivators by some processors. A high correlation between stability and metal content has been shown in studies on both laboratory-refined soybean oils and oils containing added iron and other metals.

Iron added to soybean oil in concentrations of 0.3 p.p.m. was very detrimental to the oxidative and flavor stability. A.O.M. values for the sample containing 0.03 p.p.m. of added iron were higher than the control. Organoleptically however no difference between the two samples was discernible after three days of storage at 60°C. Taste panel flavor responses showed that soybean oil containing added iron developed off-flavor responses very quickly while the oil containing no added iron first became predominantly rancid and later developed the off-flavors so typical of aged soybean oil.

Iron is a high temperature catalyst and at deodorization temperatures is very detrimental to soybean oil. Iron contamination also promotes the development of high peroxide values, in contrast to chromium, cobalt, and zinc. These last metals when present in relatively low concentrations do not produce high peroxide levels but promoted the formation of off-flavors.

Under similar conditions the effects of iron contamination on cottonseed and soybean oil showed that little change was produced in the cottonseed oil sample containing 0.3 p.p.m. of added iron, but very drastic changes, such as high peroxide values and low flavor scores, were produced in the soybean oil containing added iron.

Different concentrations of copper in soybean oil showed copper to be at least 10 times, but probably less than 100 times, more detrimental than iron. In soybean salad oil iron was more detrimental than copper when evaluated on the basis of actual amount of metal present in the oil. This was especially true for the oils containing the higher amounts of iron. The copper content was rather consistent in all oils examined regardless of the source or method of processing. This indicated little contamination from copper-containing equipment, and perhaps the amount of copper present was native to the bean and the oil.

All metal contamination is probably detrimental to the stability and quality of soybean oil and the less the contamination, the better the oil. Since oil must be processed in metallic equipment, the amount of contamination that cannot be avoided can be counteracted by the judicious use of metal deactivators.

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Improved Procedure for Cleaning Glassware Used in Determining the Stability of Fats and Oils by the Active Oxygen Method

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EXPERIENCE with the active oxygen method or accelerated stability test of King, Roschen, and Irwin (1) for determining the keeping quality or stability of fats and oils led various workers to the realization that rigid cleanliness of the glassware used in the test, and particularly the aeration and sample tubes, was essential in obtaining reproducible results with replicated samples. In recognition of this fact the Committee on Analysis of Commercial Fats and Oils (2), in preparing for the Quartermaster Corps a standard method for determining the stability of fats and oils "incorporating the best technique known at the time," included specific directions for the preparation of a cleaning solution and

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

exact details for cleaning the aeration and sample tubes.

The method specified that the glassware be cleaned with strong chromic-sulfuric acid followed by rinsing at least 4 times with warm tap water, soaking in tap water for at least 2 hours, rinsing 6 times with distilled water, and drying in an air oven at 105°C. Even when the prescribed procedure is rigidly followed, numerous anomalous stability values have been observed by the authors and others at this laboratory who have had occasion to determine the stability of a wide variety of fats and oils. In general, the number of anomalous results have been observed to increase with increasing age or repeated use of the sample tubes. The following may be cited as typical examples of these anomalous results.

The stability of a refined and deodorized rice bran oil was determined in which tubes were used after the following treatments: a) old tube which had been cleaned several times with chromic-sulfuric acid as prescribed, b) new tube washed with distilled water only, c) old tube cleaned a number of times as prescribed and finally washed with a synthetic detergent, d) new tube washed with synthetic detergent. The stability of the oil in AOM hours under the four conditions were a) 20, b) 26, c) 28, d) 28. By contrast with these results duplicate determinations of the stability of a refined and deodorized cottonseed oil using a) two new tubes washed only with water, and b) two new tubes cleaned with synthetic detergent gave stability values of 19.5, 19.5, 19.0, and 19.0 AOM hours.

Laug (3) in 1934 pointed out that the use of sulfuric acid-potassium dichromate mixtures for cleaning glassware was a recognized source of trouble in biological work. Media stored in such glassware became contaminated by dichromate which had not merely adhered to the surface but had actually penetrated the glassware. He demonstrated that seven rinsings with tap water, followed by three others with distilled water, was sufficient for the removal of the dichromate from the surface but that such treatment was ineffectual in removing the "absorbed" materials. He further demonstrated that the rate of diffusion of the dichromate out of the glass into hot distilled water is not a linear function of time. Even after long soaking in several wash waters, dichromate was still observed to diffuse out of the glass. In short, it appears that it is virtually impossible to remove the dichromate by soaking and rinsing glassware with water.

The authors have found that washing stability tubes which had been previously cleaned several times with chromic-sulfuric acid with a detergent appears to restore them to their original condition; that reproducible results can be obtained in replicated tests; and that the same stability values can be obtained with old tubes cleansed with a synthetic detergent as with new tubes.

The procedure employing detergents for cleaning the aeration and sample tubes has been used by the authors for more than a year during which time failures to obtain reproducible results have been reduced from approximately 30% to about 3%.[2] Furthermore various operators, using several different but standardized stability baths, have likewise obtained satisfactory reproducibility in the "keeping time"[2] of identical oils.

The cleansing procedure is as follows: Oil sample tubes are rinsed once or twice with acetone to remove most of the adhering fat or oil. They are then partially filled with a warm solution of Dreft[3] (50 g. in 4 l. of water) and thoroughly scrubbed with a brush. The tubes are drained and the scrubbing repeated with fresh solution. The tubes are then allowed to stand over night in the detergent solution after which they are rinsed six times with distilled water and dried in the oven at 110°C. Old aeration tubes may be handled in a similar way, using a miniature brush, or new tubes may be used for each determination after having been treated in the same manner.

Summary

Glassware cleaned with a synthetic detergent instead of hot or cold chromic-sulfuric acid leads to improved reproducibility of the stability of fats and oils determined by the active oxygen method. When the glassware used in this method is cleaned with hot chromic-sulfuric acid, chromium compounds are absorbed within the glass walls and subsequently diffuse into the oil or fat thereby leading to erratic results. A method is described for cleaning the glassware used with the fat stability method which has given reliable results in the hands of the authors for more than a year, during which it has been in almost daily use.

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[2] Only those stability values (expressed as AOM hours) which agree within 10% or less for any pair of samples are considered to be reproducible.

[3] Dreft is merely cited as a part of the experimental conditions, and this does not constitute a recommendation of Dreft over any other product having similar properties.

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