chlorophyll fluorescence with the absorption coefficients of the constituents of the mixture and with its thickness.

Summary

1.) Difficulties in applying the "chlorophyll value" test to fat samples has led us to investigate the apparent "quenching" of chlorophyll fluorescence in mineral oil solution when cottonseed oil or lard is added to it. The disappearance of chlorophyll fluorescence in ultraviolet light caused by the addition of cottonseed oil appears to be due to the absorption of the light by the cottonseed oil and to the intense white fluorescence of the oil itself rather than to a chemical reaction of some constituent of the oil with the excited chlorophyll.

2.) There was no evidence of a stoichiometric quenching reaction between chlorophyll and acceptor substances in the fats used in this study and, in consequence, no "endpoint" was observed in any of the titrations.

3.) A lack of correlation between either the peroxide value or the stabilities measured in conventional ways and the amount of chlorophyll fluorescence of several fats makes the "chlorophyll value" test appear to have doubtful value as a generally applicable test for fat rancidity or stability.

4.) The crude absorption curves here presented suggest that the greater absorption of near ultraviolet light by oxidized fats may be related to their content of fat peroxides.

Qualitative Test for Bicarbonate Ion In Soap Products

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The usual qualitative tests available for ascertaining the presence of bicarbonate in a mixture of carbonate and bicarbonate yield ambiguous results in the presence of alkaline salts such as sodium pyrophosphate, silicate and others.

Mellor (1) suggests four tests for detecting the bicarbonate ion, one of which gave promising results in preliminary experiments. The test described in this paper is based upon the fact that bicarbonates will liberate hypochlorous acid from hypochlorites. In the presence of potassium bromide, bromine will be liberated by the hypochlorous acid and can be extracted by chloroform or carbon tetrachloride. The depth of color obtained gives an approximation of the amount of bicarbonate present.

Reagents

(a) *Hypochlorite Solution.* Dissolve 50 grams of chlorinated lime, U. S.P. XII reagent grade, in 500 ml. of water. An appreciable residue will remain. Stir vigorously at intervals and after an hour or longer filter into a 1000-ml. volumetric flask. Make to volume with water at room temperature, and mix. This solution keeps well if stored in a cool, dark place.

Instead of the above, 20 to 25 grams of true calcium hypochlorite may be dissolved directly in water in a 1000-ml. flask, made up to volume at room temperature, and mixed.

(b) *Potassium Bromide Solution.* Dissolve 75 grams of potassium bromide in 500 ml. of water. Filter into a 1000-ml. volumetric flask and bring to volume with water at room temperature.

Procedure

The test should be run on alcohol-insoluble material obtained in the usual manner (2) except that the alcohol-insoluble material need only be air dried by drawing air through the filter.

Transfer 25 ml. of the hypochlorite solution and 25 ml. of the potassium bromide solution to a 60 ml. cylindrical separatory funnel. Add 5 ml. of carbon tetrachloride. Add 0.5 to 5 grams of the alcohol-insoluble material (depending upon the amount of $NaHCO_3$ expected to be present) in small quantities at a time.

Stopper the separatory funnel and shake vigorously. Allow the carbon tetrachloride to settle and observe for any brown or pink coloration. View against white paper as a background.

Liberation of bromine with subsequent coloration of the carbon tetrachloride layer indicates the presence of sodium bicarbonate.

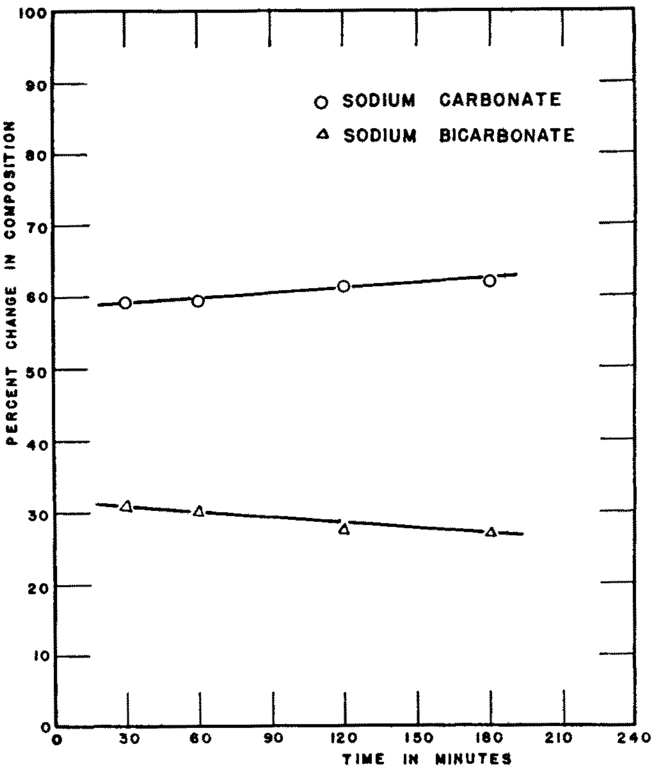

FIG. 1. Change in composition of a mixture of sodium bicarbonate and sodium carbonate in ethyl alcohol at the boiling point.

If very small amounts of sodium bicarbonate are present the test should be compared with a blank run in the same manner but omitting addition of the sample.

Experience with the method will enable one to estimate the amount of bicarbonate present.

Experimental and Discussion

Some loss of bicarbonate was anticipated during the preparation of the alcohol-insoluble material prior to making the test. To determine the magnitude of the loss, 1-gram portions of a mixture of sodium carbonate and sodium bicarbonate were heated in 100 ml. volumes of boiling ethyl alcohol for periods varying from 30 minutes to 3 hours, filtered, and titrated to phenolphthalein and methyl orange. The sodium carbonate content increased slightly and the sodium bicarbonate content decreased somewhat more rapidly. The values have been plotted and are shown in Figure 1. The original mixture contained 58.20% of sodium carbonate and 35.32% of sodium bicarbonate. Inspection of the plot indicates that unless the sample is kept in contact with ethyl alcohol at the boiling point for an excessive length of time, the loss of bicarbonate ion is not sufficiently serious to vitiate the test.

Unknowns were prepared by adding sodium bicarbonate in increasing amounts to a mixture of equal parts of sodium carbonate, pyrophosphate and silicate. In each case, the mixtures were treated with hot ethyl alcohol as in the determination of alcohol-insoluble. As a result of experimental work with the unknowns, it appears that the limit of sensitivity is about 0.1 gram of sodium bicarbonate in the presence of 1 gram of the mixture of carbonate, pyrophosphate and silicate. Using 5 grams of sample for the test about 0.02 gram of sodium bicarbonate can be detected. This is the extreme limit of sensitivity of the test.

The presence of trisodium phosphate does not affect the sensitivity of the test. Sodium tetraborate (borax) produces a positive reaction if present in large amounts. If the test is run on borax by itself, the amount of bromine liberated is roughly equivalent to that encountered when working at or close to the limits of sensitivity of the test. Thus, unless very large amounts of borax are present, the indications of the test are still valid. "Calgon" ($Na_6P_6O_{18}$) interferes seriously with the test. Sodium perborate and trisodium phosphate do not interfere.

The presence of wetting agents and sodium sulfate likewise do not influence the test. Care must be taken, however, in the presence of wetting agents not to shake the contents of the funnel too vigorously, otherwise the carbon tetrachloride will emulsify.

A series of soap samples which were known to contain sodium bicarbonate by the carbon dioxide evolution method (3) gave positive results when tested in accordance with the above described procedure.

Acknowledgments

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Abstracts

Oils and Fats

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M. M. PISKUR and SARAH HICKS

DETECTION OF OLIVE OIL IN EDIBLE OIL MIXTURES. J. Fitelson. *J. Assoc. Off. Agr. Chem. 26,* 499-506 (1943). A simple method of detg. the "squalene" content is proposed as an aid in the detection of olive oil in mixt. of the common, edible, vegetable oils. The squalene is concd. in a fraction obtained by the selective adsorption treatment of the unsaponifiable matter. The unadsorbed residues from olive oil consist almost entirely of squalene and the unsatd. material in the much smaller residues from other oils consists largely of squalene. The unsatn. of these residues is assumed to be due to squalene, and the quantity of this hydrocarbon present in oils is calculated from the total halogen absorption. The results obtained by this method show good reproducibility. Although all of the vegetable oils examined contained squalene, olive oil is characterized by its much higher squalene content. However, the wide range found in olive oil, together with the small quantites of squalene present in other oils must be considered in applying the proposed method.

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UNSATURATED SYNTHETIC GLYCERIDES. I. UNSYMMETRICAL MONOÖLEO-DISATURATED TRIGLYCERIDES. B. F. Daubert, H. H. Fricke, and H. E. Longnecker. *J. Am. Chem. Soc. 65,* 2142-4 (1943). Data are reported for a series of monoöleodisaturated triglycerides, 1-oleo-2,3-dicaprin, 1-oleo-2,3-dilaurin, 1-oleo-2,3-dimyristin, 1-oleo-2,3-dipalmitin, and 1-oleo-2,3-distearin. UNSATURATED SYNTHETIC GLYCERIDES. II. UNSYMMETRICAL DIOLEO-MONOSATURATED TRIGLYCERIDES. B. F. Daubert, C. J. Spiegl, and H. E. Longnecker. *Ibid.,* 2144-5. The melting points of the unsymmetrical dioleo-monosaturated triglycerides increase with increasing length of the carbon chain of the saturated fatty acid. The av. change in refractive index with change in temp. (dn/dt) for the compds. prepd. is 0.00037. Hydrogenation of the dioleo-monosaturated triglycerides gave 1-acyl-2,3-distearins comparable of those prepd. previously by other methods.

THE INFLUENCE OF PREVIOUS DIET ON THE PREFERENTIAL UTILIZATION OF FOODSTUFFS. I. FASTING KETOSIS AND NITROGEN EXCRETION AS RELATED TO THE