Use of Dried Air in the Active Oxygen Method of Determining Relative Stabilities of Fats

JULIUS J. NAGY, B. W. BEADLE, and H. R. KRAYBILL
Research Laboratory, American Meat Institute, University of Chicago

THE recent and current widespread interest in the use of antioxidants in fats has greatly stimulated interest in accelerated stability tests for it is only through the use of such methods that rapid progress may be made. It is extremely important that the laboratory test be reliably indicative of the results which would be obtained in shelf storage experiments in kitchen or warehouse over a much longer period of time.

The Barcroft-Warburg apparatus (1, 10) has recently been applied to studies on the stability of fats (6). During extensive studies on fat stability conducted in this laboratory (9), it was observed that the method employing the Barcroft-Warburg apparatus yielded results which gave good positive correlation with those obtained by the active oxygen method (AOM) (7) when the lard used contained no added antioxidant and when lecithin was added. However, when d-isoascorbyl palmitate or stearate was added to the lard in concentrations between 0.001 and 0.10 per cent, the two methods no longer yielded comparable data. The higher concentrations of the esters, which were antioxidants according to the active oxygen method, actually decreased the stability as determined in the Barcroft-Warburg apparatus. Stabilities determined organoleptically during storage at room temperature showed much better correlation with values obtained by use of the Barcroft-Warburg apparatus than with those obtained by the active oxygen method.

Because the Barcroft-Warburg apparatus was supplied with dry oxygen from a tank, while the AOM apparatus was supplied with compressed air which was scrubbed in a series of aqueous solutions (7), it was thought that the presence or absence of water vapor might be a factor in explaining the anomalous results.

There are a few references in the literature to the effect of moisture on the development of rancidity, but these statements are not entirely in agreement, and do not apply specifically to the present problem. Lea (8) pointed out that early writers believed that the presence of water accelerated the development of rancidity, and even was essential to the process. Holm, Wright and Greenbank (5) reported that dry milk powder became rancid more quickly than when moisture was present. Triebold and Bailey (11) reported that crackers became rancid in dry atmosphere more quickly than in conditions of high humidity. Lea (8) stated that the influence of moisture on the rate of oxidation of a pure fat is not known definitely. Water has been said to increase the stability of butter at 95° C. (4) but to have no effect on the stability of lard at 50° C. (3). Ewbank and Gould (2) found that drying the air by passing through sulfuric acid in the active oxygen method reduced the induction period of butter oil by 15 to 20 per cent.

Observations on the effects of moisture on stabilities as determined by means of the AOM and storage tests are reported in this paper.

Experimental

AS A preliminary experiment, samples of lard containing 0.10% ascorbyl esters were studied on both types of apparatus and in storage at room temperature. It was found with the active oxygen method that the stability of the treated lard was much greater in the presence of wet air than in air which was dry; the same results were obtained with the Barcroft-Warburg apparatus, using oxygen. Similarly, the samples stored at room temperature in dry oxygen became very rancid in 30 days, while the samples in moist oxygen remained "fresh." This was evidence that the presence or absence of water is an important factor in a study of antioxidants, and indicated a need for further work. Table 1 shows storage data obtained on two lard samples containing d-isoascorbyl palmitate and one sample to which no antioxidant had been added. The samples over moist oxygen remained fresh much longer than did the samples over dry oxygen when d-isoascorbyl palmitate was present. The presence or absence of water had no effect on the stability of the lard to which no antioxidant was added. The stability of Lard 2 was actually decreased by d-isoascorbyl palmitate in dry oxygen.

A number of antioxidants were then studied as to their effects on the stability of lard as determined by the active oxygen method, using the apparatus as described (7), both with washed air, and with air that was dried after being washed. Two drying towers 3 inches in diameter and 18 inches tall were used, the first being packed with anhydrous calcium chloride, the second with glass wool and phosphorus pentoxide (it was determined that these drying towers did not reduce the flow of air significantly). Similar data were obtained on lard to which no antioxidant had been added. The results which were obtained in these studies are shown in Table 2.

TABLE 1

Storage Tests of Lard in Presence of Water and Absence of Water
(Room Temperature in Oxygen)

Lard*	Method of Storage	Time	Antioxidant	Peroxide Milliequivalents Per 1,000 gms.	Condition of Sample
No. 1	In dry jar	30 days	0.1% d-isoascorbyl palmitate	380	Very rancid
No. 1	In jar over water	30 days	0.1% d-isoascorbyl palmitate	16	Not rancid
No. 2	In dry jar	43 days	None	11	Not rancid
No. 2	In jar over water	43 days	None	10	Not rancid
No. 2	In dry jar	43 days	0.1% d-isoascorbyl palmitate	300	Very rancid
No. 2	In jar over water	43 days	0.1% d-isoascorbyl palmitate	10	Not rancid

* No. 1, 5 hours stability and No. 2, 7 hours stability by AOM.

TABLE 2

The Effect of Moisture on Stability Determinations, Using the Active Oxygen Method

Sample	Antioxidant Added	Stability of Untreated Sample (Hours) A.O.M.		Stability of Treated Sample (Hours)	
		Wet Air	Dried Air	Wet Air	Dried Air
Lard*	None	7	7	....	....
Lard*	None	8	8	....	....
Lard*	None	4	4	....	....
Lard*	None	9	9	....	....
Lard*	None	10	10	....	....
Hydrogenated Lard	None	21	21	....	....
Lard*	0.1% d-isoascorbyl palmitate	4	4	10	7
Lard*	0.1% d-isoascorbyl palmitate	7	7	12	7
Lard*	0.1% d-isoascorbyl palmitate	8	8	17	12
Lard*	0.1% l-ascorbyl palmitate	7	7	21	10
Lard*	0.1% l-ascorbyl palmitate	8	8	25	17
Lard*	0.1% d-isoascorbyl stearate	7	7	9	3
Lard*	0.1% d-isoascorbyl stearate	8	8	15	10
Lard*	0.1% l-ascorbic acid	8	8	18	13
Lard*	0.05% l-ascorbic acid	10	10	26	22
Lard*	0.10% l-ascorbic acid	10	10	32	22
Lard*	0.20% l-ascorbic acid	10	10	35	22
Lard*	0.1% gum guaiac	3	3	15	15
Lard*	0.1% gum guaiac	7	7	19	19
Lard*	0.1% gum guaiac	8	8	24	24
Lard*	0.1% lecithin	4	4	10	9
Lard*	0.1% lecithin	7	7	12	9
Lard*	0.1% lecithin	8	8	14	10
Lard*	0.05% mixed tocopherols	4	4	15	15
Unrefined lard	0.05% mixed tocopherols	7	7	17	17
Unrefined lard	0.05% mixed tocopherols	7	7	30	30
Lard*	0.05% mixed tocopherols	8	8	18	18
Lard*	0.05% mixed tocopherols	7	7	24	23
Hydrogenated Lard	0.05% mixed tocopherols	21	21	55	54
Unrefined lard	0.05% alpha-tocopherol	7	7	24	23
Lard*	0.05% Age-Rite Resin	7	7	21	21
Lard*	0.02% hydroquinone	7	7	87	87
Lard*	0.01% nordihydroguaiaretic acid	7	7	69	66
Lard*	0.01% nordihydroguaiaretic acid	8	8	86	89
Lard*	0.05% thiourea	7	7	21	14
Lard*	0.05% thiourea	8	8	27	16
Lard*	0.05% citric acid	8	8	11	10
Lard*	0.10% citric acid	10	10	13	12
Lard*	0.05% triethanolamine	8	8	17	9
Lard*	0.05% vanillin	8	8	9	9

* Steam rendered, earth bleached lard was used.

Discussion

FROM an inspection of Table 2 it will be noted that the samples of lard to which no antioxidant had been added showed the same stability with either the wet air or the dried air. Some, but not all, of the antioxidant-treated samples showed about the same stability in wet air as in dried air. Certain of the antioxidant-containing samples, notably those treated with ascorbic acid, its esters, thiourea, or triethanolamine showed definite differences in their stabilities, depending on whether the air used was wet or dry. In some cases these differences were rather large. For example, one of the samples of 7-hour lard containing 0.1% l-ascorbyl palmitate possessed a stability of 21 hours when tested with wet air, as compared with 10 hours when tested with dry air.

It thus seems quite clear that the presence or absence of water in the air used for the active oxygen method is a very important factor to be considered when this method is used for the study of antioxidants. The data obtained to date indicate that, when certain antioxidants are present, the accelerated test as obtained with dried air shows better positive correlation with storage data than it does in the customary procedure. The antioxidants which are thus affected by moisture do not seem to be closely enough related to allow for generalization at the present time.

The safest procedure in the use of accelerated stability tests seems to lie in the recognition of the possible effect of moisture on the results obtained in the presence of antioxidant materials. It should be established in any given instance that the data may be projected to storage conditions, and it should be remembered that the conditions which may be safely used in the study of one antioxidant may yield results which are entirely misleading during the study of another antioxidant.

Summary

The active oxygen method, when used for the study of lards to which no antioxidant has been added, yields essentially the same stability figures whether or not the air stream is passed through a drying tower after being scrubbed. This is not always true when antioxidants have been added to the lard. Among the antioxidants whose effects have been found to be essentially unaffected by moisture under the conditions used are gum guaiac, tocopherols, Age-Rite resin, and nordihydroguaiaretic acid. Lard to which d-isoascorbyl palmitate, ascorbic acid, triethanolamine, or certain other materials have been added shows a much higher stability in the presence of moist air than in the presence of dry air. Preliminary storage tests indicate that the data obtained through the use of dried air are more reliable as an indication of storage behavior than are the data obtained by the use of the moist air commonly used in the active oxygen method. A recognition of this effect of moisture is of great importance in the study of the effects of various antioxidant materials on the stability of lard.

REFERENCES

1. Dixon, M. "Manometric Methods," MacMillan Co., New York (1934).

2. Ewbank, F. C., and Gould, I. A., Oil & Soap *19*, 205-209 (1942).

3. French, R. B., Olcott, H. S., and Mattill, H. A. Ind. Eng. Chem. *27*, 724 (1935).

4. Greenbank, G. R., and Holm, G. E. Ind. Eng. Chem. *16*, 598 (1924).

5. Holm, G. E., Wright, P. A., and Greenbank, G. R. J. Dairy Sci. *10*, 33 (1927).

6. Johnston, W. R., and Frey, C. N. Ind. Eng. Chem., Anal. Ed. *13*, 479 (1941).

7. King, A. E., Roschen, H. L., and Irwin, W. H. Oil & Soap *10*, 105 (1933).

8. Lea, C. H. "Rancidity in Edible Fats"; Food Investigation Special Report No. 46, London (page 181) (1938).

9. Nagy, J. J., Vibrans, F. C., and Kraybill, H. R. Oil & Soap *21*, 349 (1944).

10. Perkins, J. J. Ind. Eng. Chem., Anal. Ed. *15*, 61 (1943).

11. Triebold, H. O., and Bailey, C. H. Cereal Chem. *9*, 91 (1932).