A Rapid Oxygen Bomb Method for Evaluating the Stability of Fats and Shortenings

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Abstract

A modification of the A.S.T.M. oxygen bomb method for evaluating the stability of any fat within a period of six hours or less has been developed. It is based upon the addition of selected levels of a copper catalyst, operating under the conditions previously used without catalyst. The precision of this bomb method has been characterized and the contributions of several factors to the overall variation have been estimated. The research indicates that it will not be possible to express bomb data in terms of AOM values by employing a factor.

On the basis of precision obtained by this procedure, it is concluded that it should be readily adaptable to industrial control applications.

Introduction

THE A.S.T.M. Oxygen Bomb method modified by Gearhart, Stuckey, and Austin (1) for predicting the relative stability of fats has been shown to be more rapid than the Active Oxygen Method (AOM) (2), and to possess good precision (3). While it is a relatively rapid procedure, analyses by their method (1) on more stable products still required a 20–40 hr interval for completion. Although the modified A.S.T.M. Oxygen Bomb method (1) is satisfactory for research purposes, present demands in commercial operations require a shorter method for control applications. Preferably this time should be as short as practicable; we set a maximum of 6 hr for the more stable products as our objective.

We hoped to reduce the elapsed time requirement for the bomb method without changing other factors, including sample size, dispersant, oxygen pressure, and bath temperature. If this objective could be realized, a flexible analytical technique would result where rapid determinations could be applied for control purposes, and longer but more precise determinations utilized for research considerations. The basic apparatus would remain unchanged.

Experimental

Of several approaches investigated, the most appropriate appeared to be the addition of an internal catalyst that could be added accurately in small amounts and be soluble in, or miscible with, the sample. Copper was selected because of its known catalytic effect in fat oxidation. The selection of a copper compound with appropriate solubility characteristics proved to be a problem. It was decided to introduce the catalyst in solution to effect mutual solubility and make it possible to add small amounts accurately. Copper salts of stearic, palmitic, and lauric acids were found to have poor solubility characteristics. However, a copper salt of coconut oil acids was shown to be sufficiently soluble in chloroform, so that small increments of less than 1 ml, when added to the sample, contained enough copper to reduce the time required for completion of a determination to almost any selected level.

The copper catalyst selected was prepared from coconut oil fatty acids of average molecular weight of 210. The potassium salt of the fatty acids was prepared first by dissolving 10 g of fatty acids in 150 ml of U.S.S.D. No. 30 alcohol and neutralizing to the phenolphthalein endpoint with 50% aqueous KOH. The theoretical amount of copper in the form of cupric chloride ($CuCl_2 \cdot 2H_2O$) amounting to 4 g was dissolved in 100 ml of water and added slowly with stirring to the fatty acid salt solution. The solution was filtered through a Buchner funnel and the precipitate washed with water. The final wash was made with No. 30 alcohol to remove most of the water to facilitate final drying. The resulting precipitate was then dried and finely ground. This preparation was analyzed for copper by standard chemical techniques. A solution was prepared which contained 374 μg of copper per ml of chloroform solution for catalytic studies.

The bomb procedure was as follows: 7.5 g of sample was weighed into a 50 ml beaker, melted on a steam bath, and the desired amount of catalyst added from a 1 ml measuring pipette, graduated in 0.01 ml and mixed. Immediately, a quantity equivalent to 6 g of fat was weighed onto a 2 × 3¾ × ¼ in. sheet of Kimpak dispersant, No. K-21, obtained from Kimberly-Clark Corporation. The weighing was carried out by placing the Kimpak on a watch glass which was tared on a torsion balance sensitive to 0.01 g. The appropriate weights were added and the liquid sample, with catalyst already incorporated, was poured evenly over the Kimpak until the balance point was restored. The Kimpak, now impregnated with sample, was placed in the glass bomb liner, covered, and the assembly inserted into the bomb which was then closed by tightening the threads with a wrench until the Teflon gasket was properly seated. Oxygen from a regulated cylinder was admitted to the bomb through the valve system until 50 lb pressure was reached, then released to atmosphere and refilled to 50 lb and the valve closed. The bomb assembly was checked for leaks by immersing in a cylinder of water and finally placed in a boiling water bath. A flexible tube connection from the bomb to a pneumatic pressure recorder provided a means of measuring and recording continuously, changes in pressure with time. The chart was set in motion when the loaded bomb was immersed in the holding bath to

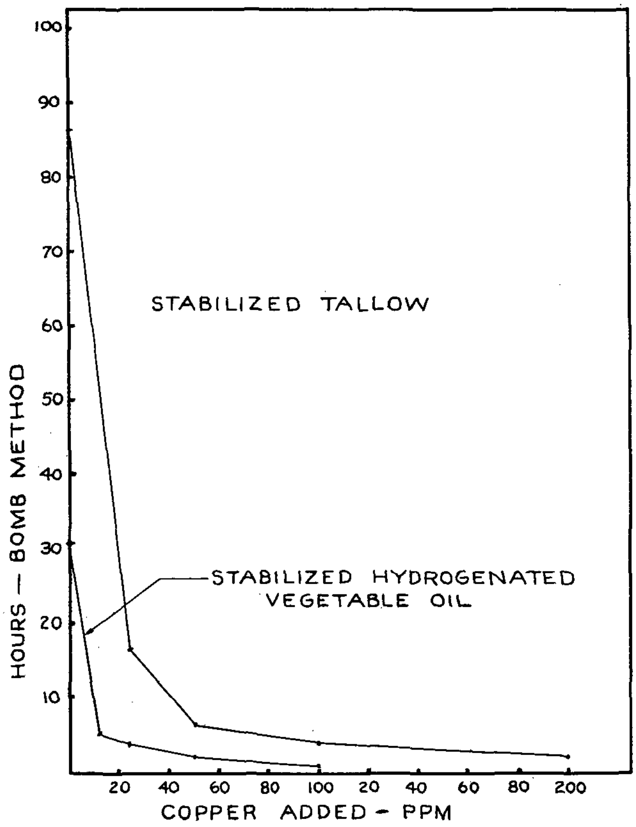

FIG. 1. Effect of copper catalyst on time required for bomb test.

initiate the run. The endpoint for a determination was selected as the end of the first 60 min period during which the drop in oxygen pressure was 2 lb. The total time from the inception of the run to this point was recorded as the sample value.

Results and Discussion

Figure 1 is a graphic representation of the effect of increasing levels of added catalyst on the time required to complete a determination with two different fats. The relationship is nonlinear over the range studied, with greatest acceleration of reaction rate realized at levels below 100 ppm. To bring about the extent of time reduction sought and to obtain precision within acceptable limits, 25 ppm was selected for all products except stabilized tallow where 100 ppm was considered appropriate. The basis for selecting these quantities was to operate in that region of catalyst concentration where slight deviations in amounts of catalyst would not have a pronounced effect on sample times.

TABLE I

Mean Values for the Different Factors

	Lower stability	Higher stability
	hours	*hours*
Bombs		
1	1.48	6.32
2	1.58	6.75
3	1.25	5.98
4	1.25	6.05
Kimpak		
1	1.35	6.36
2	1.42	6.29
Catalyst		
1	1.35	6.26
2	1.42	6.29
Catalyst level		
20 ppm	1.52	6.58
25 ppm	1.38	5.98
Overall standard deviation for single determination	0.18	0.40
Coefficient of variation	13%	6.4%

TABLE II

Summary of Data for Oxygen Absorption Method, Bomb Method With and Without Catalyst

Type of Fat	A.O.M. (A)	Bomb		Ratio		
		Without Catalyst (B)	With Catalyst 25 ppm Cu (C)	A/B	A/C	B/C
Meat fat ^{c}	41	19.7	1.2	2.1	34	16
Meat fat ^{b,c}	28	14.2	1.5	2.0	19	9
Meat fat ^{b,c}	40	11.7	1.5	3.4	27	8
Meat fat ^{b,c}	45	12.0	1.5	3.7	30	8
Meat fat ^{b,c}	50	23.4	2.2	2.1	23	11
Meat fat ^{c,d}	87	30.2	2.4	2.9	36	13
Meat Vegetable fat ^{b,c}	44	19.2	2.2	2.3	20	9
Meat fat ^{a,b,c}	......	15.7	1.7	....	....	9
Meat Vegetable fat ^{b,c,d}	148	38.6	5.8	3.8	26	7
Vegetable fat ^{d}	52	20.7	2.1	2.5	25	10
Vegetable fat ^{d}	56	14.4	1.8	3.9	31	8
Vegetable fat ^{d}	107	27.0	2.4	4.0	45	11
Vegetable fat ^{d}	138	39.9	2.9	3.5	48	14
Meat Vegetable fat ^{b,c}	98	42.2	3.7	2.3	26	11
Meat Vegetable fat ^{b}	12	14.2	1.2	0.8	10	12
Meat Vegetable fat ^{b,c}	98	29.6	2.8	3.3	35	11
Meat Vegetable fat ^{b,c}	103	32.3	3.2	3.2	32	10

[a] Foamed out of tube
[b] Blends
[c] Stabilizer
[d] All hydrogenated

An experiment was designed to compare two supplies of Kimpak and two catalyst preparations, at two catalyst levels on fats of two stability levels in four different bombs The mean values for the various factors are shown in Table I. These fats when measured by the bomb technique without catalyst yielded 14.8 hr for the lower stability and 38.6 hr for the higher stability.

Statistical analyses of the data revealed that there was a significant difference at the 5% level among the bombs and that this source contributed more to the overall variation than the other factors studied. The differences in Kimpak and catalyst sources were not

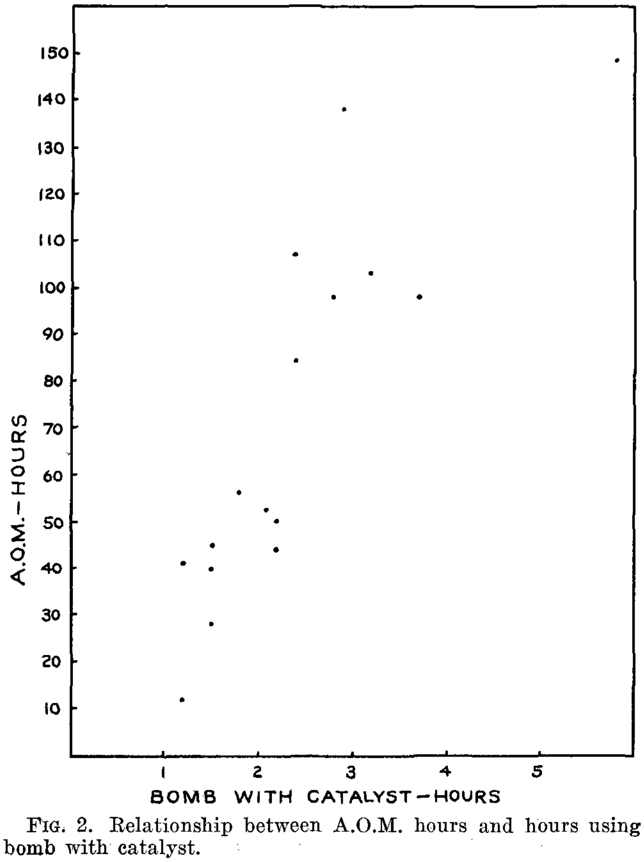

FIG. 2. Relationship between A.O.M. hours and hours using bomb with catalyst.

quite significant at the 10% level. These findings indicate that supplies of Kimpak and preparations of catalyst need not be problems in the performance of the rapid method. The variation due to bombs represents a random variable and is included in the overall precision estimate for the method.

Since the effect of varying the amount of catalyst in the region of 25 ppm was small, possible errors associated with addition of catalyst will not be of serious magnitude in the routine performance of the method.

It should be noted that while the standard deviation for samples of longer stability is twice that of the shorter stability samples, the coefficient of variation is about half.

Results obtained by application of the AOM method, the bomb method without catalyst and the bomb method with catalyst to commercially available fats and shortenings are tabulated in Table II and shown graphically in Figure 2.

It is evident from these data that an overall general correlation exists between the AOM and bomb methods, but that it is not possible to relate bomb values directly to AOM. This is not surprising when one considers the complex nature of the makeup of shortenings, not only with respect to type and extent of modification of the fatty portions, but also because of the varying response of such formulations to the array of possible antioxidant combinations.

All of the methods for measuring stability are basically empirical, so that the ultimate selection is made in light of the specific application. As previously suggested, some of the distinction in stability normally required for research applications can logically be sacrificed in control situations where speed is a primary consideration.

The rapid oxygen bomb method has the following advantages for control purpose:

1) The time required for evaluating the stability of any shortening can be adjusted to between 1 and 6 hr by proper selection of the level of catalyst.

2) Samples can be tested at different accelerated rates in the same bath at the same time. This is not possible when acceleration of the test is accomplished by increasing the temperature.

3) Tests on samples of different stability can be completed in about the same time in the same equipment by proper selection of the amount of catalyst to be used with the different types.

4) The equipment has been standardized by the A.S.T.M. and can be purchased complete from supply houses and can be used without modification.

REFERENCES

1. Gearhart, W. M., B. N. Stuckey, and J. J. Austin, JAOCS, *34* 427, (1957).
2. AOCS Official and Tentative Method, Cd 12–57.
3. Pohle, W. D., R. L. Gregory, and J. R. Taylor, JAOCS, *39* 226, (1962).

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Report on Activities of Industrial Oils and Derivatives Committee, 1963

FOUR OF THE Industrial Oils & Derivatives Subcommittees which met during the Society meetings in Atlanta, April 22–24, 1963, have been very active since the last meeting of the Society. Below is a brief summary of these activities, by K. E. Holt, Chairman.

Epoxidized Oil Subcommittee, Dave Barlow, Chairman

Two modifications to AOCS Tentative Method Cd 9-57, Oxirane Oxygen, were submitted to the Epoxidized Oil Subcommittee for consideration. The first involved an alternate method for the preparation of the HBr acetic acid reagent; the second modification proposed the addition of an excess of HBr – acetic acid reagent to the sample and back titrating for the unreacted HBr.

A study was set up, with eight collaborators participating, to study the effect of these modifications to method Cd 9-57. Samples of epoxy soybean oil, 2-ethyl hexyl epoxytallate and glycidyl stearate were selected for this study. The AOCS statistical design as outlined in Method M 1-59 was followed. All of the collaborators completed their part of the program and the results were studied at the meeting of the Subcommittee in Atlanta. It was concluded that modifying the method of preparation of the HBr – acetic acid reagent did not affect the results obtained by the method. The addition of an excess of HBr – acetic acid reagent, allowing the reaction to stand for 30 min and back titrating the excess HBr, produced results that were slightly higher than those produced by the present method. The Subcommittee was in agreement that the higher results were due to hydrolysis or side reactions with the excess HBr and an accurate measurement of true oxirane not being made.

Some minor modifications were recommended for method Cd 9-57 which the Subcommittee believes will improve the precision, but not change the numerical values obtained by the method. These recommendations were passed on to the Uniform Methods Committee and will appear in the next issue of the method.

Requests have been received for a method that will measure hydroxyl value on epoxidized oils. The subcommittee will undertake to review the current methods now being used and solicit ideas or methods from AOCS members.

The Drying Oils Subcommittee, Don Bolley, Chairman

The Drying Oils Subcommittee completed a study of the Color and Viscosity Methods and are recommending revisions of these methods to the Uniform Methods Committee.

Method Ka 3-58, Gardner Color, is revised to make the primary standards from glass with liquids as secondary standards. Glass standards presented to the Subcommittee by two different manufacturers were checked out and found to be satisfactory. Glass standards have the advantage of permanency which