Refractive Index as an Objective Method for Evaluation of Rancidity in Edible Oils and Fats

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Abstract

Common edible oils and fats (refined peanut oil, sesame oil, safflower oil, and butter oil, ghee) were exposed to direct sunlight, fluorescent light and Schaal Test. Data collected on refractive indices (N_D^{25}) show an increase of the order of 0.001 ± 0.0003 at the stage of development of perceptible rancid odor. The pattern of changes in refractive indices and peroxide values of these edible oils, autoxidized at 100 ± 5 C, show that refractive indices indicate more precisely the termination of the induction periods than peroxide values.

Introduction

The common edible oils and fats of commercial importance in this country include peanut oil, sesame oil, butter oil (ghee), safflower oil, mustard oil, coconut oil and hydrogenated vegetable oil (vanaspati). A minimum shelf-life of six months for these oils and fats under the varied operational climatic conditions, ranging from tropical to subarctic climates, is a primary requirement of the Indian Defense Services.

The most commonly used methods of assessing the stability of fats and oils are the active oxygen method (1) and Schaal test (2). In these tests peroxide value is correlated with the organoleptic evaluation of rancidity. However it is reported (3–6) that peroxide value has its inherent limitations and that it does not precisely indicate the exact termination of the induction period.

Refractive indices of fats and oils have been reported (4,5) to increase on autoxidation. A rapid refractometric method for the determination of light stability of fats has also been reported (7). This paper describes the pattern of changes in the refractive indices of fats and oils on autoxidation in relation to rancid odor development.

Experimental Procedures

One hundred grams each of commercially refined samples of safflower oil, peanut oil, sesame oil and butter oil (ghee) were exposed to direct sunlight and fluorescent light (8) in uncovered pyrex glass beakers. The period of exposure varied from 3–36 hr depending on development of rancidity. These were also similarly subjected to the Schaal test at 60 C (2) and 70 C (9). The periods of incubation in the Schaal test varied from 96–696 hr at 60 C and 48–384 hr at 70 C.

Both the light exposed and oven-incubated samples were periodically assessed, along with the unexposed control samples, by a panel of six judges, for the development of perceptible rancid odor. Every time at predetermined intervals one sample of each oil or fat was used for the determination of peroxide value by the AOCS method (10) and refractive index (N_D^{25}) in a Pulfrich refractometer (11). The results are presented in Table I.

One hundred grams each of commercially pure samples of coconut oil and mustard oil in addition to the above oils and fats were heated in uncovered pyrex beakers in an air oven maintained at 100 ± 5 C. The periods of exposure varied from 4–268 hr depending on development of rancidity. These were periodically assessed by the same panel of judges and similarly analyzed for the respective peroxide values and refractive indices (N_D^{25}). The patterns of changes in peroxide values and refractive indices (N_D^{25}) are given in Figures 1 and 2, respectively. The relationship between peroxide value and refractive index in one instance (safflower oil) is shown in Figure 3.

Results and Discussion

Exposure to light and heat caused significant increase in the refractive indices and peroxide values of the oils and fats (Table I). However the patterns

TABLE I
Light Exposure Tests and Schaal Tests on Some Edible Oils and Fats

Condition of exposure	Safflower oil			Peanut oil			Sesame oil			Butter oil (ghee)		
	Period (hr)	PV[b]	Refractive index (N_D^{25})	Period (hr)	PV[b]	Refractive index (N_D^{25})	Period (hr)	PV[b]	Refractive index (N_D^{25})	Period (hr)	PV[b]	Refractive index (N_D^{25})
	0	5.8	1.4775	0	5.6	1.4708	0	5.2	1.4732	0	2.2	1.4600
Sunlight	6	31.8	1.4777	6	24.2	1.4708	6	18.5	1.4732	3	6.5	1.4601
	12	46.9	1.4778	12	35.7	1.4710	12	27.8	1.4734	9	8.7	1.4601
(34–39 C)	18[a]	74.3	1.4786	18[a]	55.7	1.4718	18[a]	50.1	1.4741	15[a]	13.8	1.4607
	24	120.5	1.4791	24	92.4	1.4726	24	80.7	1.4749	21	25.6	1.4613
Fluorescent	6	20.6	1.4776	6	15.6	1.4708	6	11.5	1.4732	6	4.3	1.4600
light	12	25.6	1.4776	12	18.6	1.4708	12	14.3	1.4732	12	5.1	1.4600
(Light	18	36.1	1.4778	18	21.3	1.4709	18	19.2	1.4733	18	7.5	1.4601
Exposure	24	44.3	1.4778	24	29.2	1.4709	24	25.7	1.4734	24[a]	12.9	1.4607
Apparatus)	30[a]	60.8	1.4785	30	32.6	1.4710	30	28.3	1.4734	30	18.4	1.4611
(32–37 C)	36	67.9	1.4788	36[a]	55.8	1.4718	36[a]	47.6	1.4741	36	34.4	1.4616
	96	50.4	1.4778	96	20.4	1.4708	96	8.0	1.4732	96	3.8	1.4600
Schaal Test	144	60.5	1.4779	192	46.5	1.4710	264	35.2	1.4734	480	5.7	1.4601
(60 ± 2 C)				240	60.3	1.4712	432	51.3	1.4735	600	9.8	1.4602
	192[a]	131.4	1.4790	264[a]	73.0	1.4719	528[a]	68.1	1.4744	696[a]	16.9	1.4610
	48	59.2	1.4778	48	38.6	1.4709	96	16.2	1.4732	96	4.2	1.4600
Schaal Test	96[a]	113.4	1.4787	96	51.0	1.4712	216	47.4	1.4734	216	6.5	1.4601
(70 ± 2 C)	120	152.4	1.4792	120[a]	99.4	1.4721	264[a]	71.6	1.4743	360[a]	15.4	1.4608
	216	322.7	1.4802	216	180.4	1.4729	312	95.8	1.4750	384	23.6	1.4613

[a] Stage of perceptible rancid odor development reported by the panel of judges.
[b] PV = Peroxide value (milli equivalents of oxygen/kg).

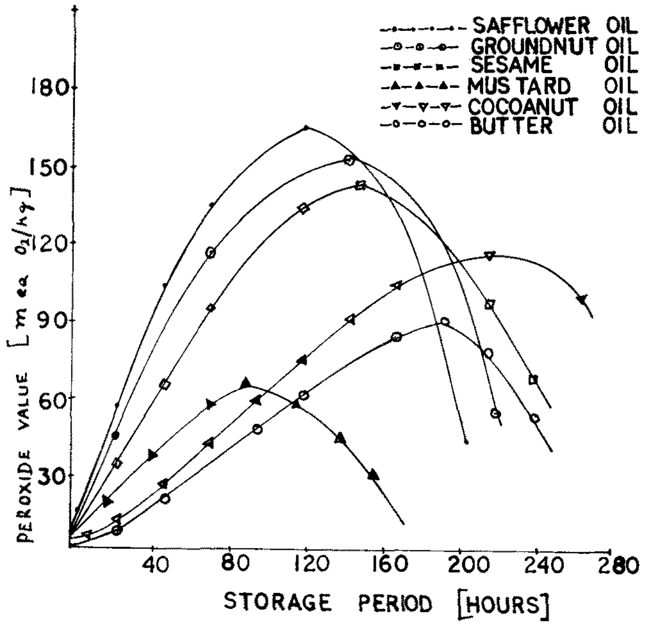

FIG. 1. Peroxide value of oils and fats stored at 100 ± 5 C.

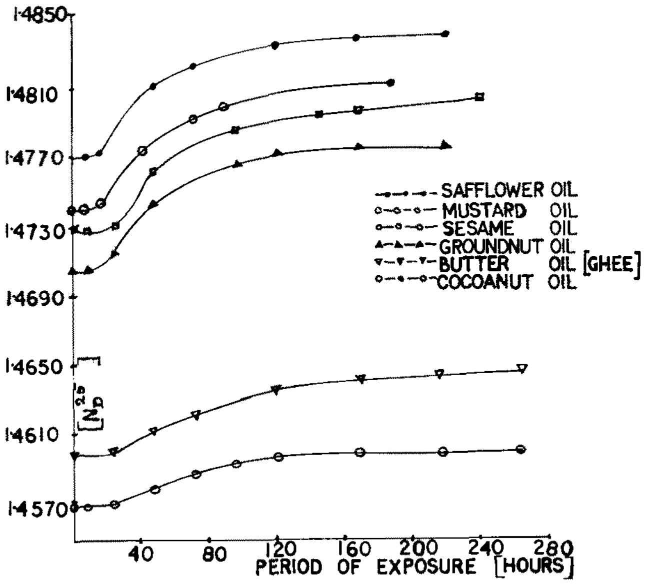

FIG. 2. Refractive indices of oils and fats autoxidized at 100 ± 5 C.

of changes in refractive indices and peroxide values were different. Peroxide values increased at a steady rate over the primary induction period and, after the onset of rancidity, the rate was slightly higher.

Comparatively changes in refractive indices (N_D^{25}) were not significant (not more than +0.0004) during the induction periods. Thereafter in all the samples there was a sharp increase, of the order of 0.001 ± 0.0003, which invariably coincided with the detection of perceptible rancid odor. It is observed (Table I) that the sharp increase in refractive indices precisely indicate the termination of the respective induction periods. The application of "t" test to the increase in refractive indices of the oils and fats before and after the perception of rancid odor (termination of induction periods) show that these results are statistically significant.

Direct sunlight had more deleterious effect than fluorescent light or Schaal test. Butter oil (ghee) had the least light stability and the most heat stability.

Peroxide values in the samples stored at 100 ± 5 C increased steadily in the early heating periods, reached a maximum, and then registered a gradual drop (Fig. 1). However, peroxide value curves did not indicate the exact end of the induction periods under these conditions of storage. Safflower oil showed the maximum peroxide development, while mustard oil had the least.

The pattern of changes in refractive indices (Fig. 2) was similar to that of light exposure and Schaal tests. Refractive indices remained unchanged during the primary induction period, registered a sharp increase at the termination of the induction periods and then continued to increase gradually. In all the cases the sharp inflection in the refractive index curve invariably coincided with the termination of the induction period and the onset of perceptible rancid odor.

The refractive index curve, based on the above data, indicates the end of the induction period more precisely than the peroxide value curve. Besides, determination of refractive index is subject to less error than peroxide value.

However, there appears to be some relationship between the pattern of peroxide development and changes in refractive indices of the autoxidized oils or fats, safflower oil (Fig. 3) being an example. Refractive index changes according to the three known stages of autoxidation of fats and oils (4). Over the primary induction period, when peroxide formation is less, refractive index remained constant; thereafter during the secondary stage of relatively more peroxide formation refractive index registers a sharp increase until the peroxide value reaches the maximum; in the tertiary stage of peroxide decomposition, however, when the peroxide value curve registers a drop, the refractive index continues to increase further, at a steady rate, the curve being less sharp than in the secondary stage. This pattern is observed in other cases as well (Fig. 1 and 2).

The increase in refractive index with autoxidation is possibly attributable to conjugation known to precede hydroperoxide formation in the secondary stage, and polymerization of partially oxidized fats in the tertiary state of autoxidation, since both conjugation and polymerization are reported to result in increased refractive indices of oils and fats (12,13).

Our work on the correlation of peroxide values and refractive indices of autoxidized oils and fats, con-

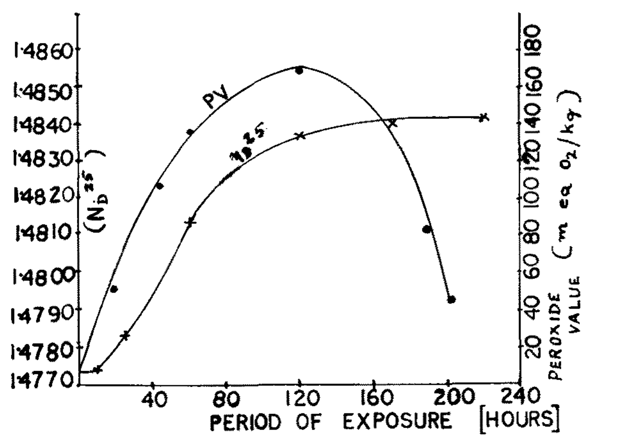

FIG. 3. Relation between peroxide value and refractive index (safflower oil autoxidized at 100 ± 5 C).

firms the results reported previously by Czechoslavakian workers (4,5).

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REFERENCES

1. King, A. E., H. L. Roschen and W. H. Irwin, Oil and Soap *10*, 105 (1933).
2. Joyner, N. T., and J. E. McIntyre, Ibid. *15*, 184–186 (1938).
3. Dugan, L. R., Jr., JAOCS *32*, 605–609 (1955).
4. Janicek, G., and J. Pokorny, Inst. of Chem. Tech. Prague *4-1*, 157–83 (1960); Abstract, JAOCS *40*, 28A (1963).
5. Pokorny, J., F. Ginzelova and G. Janicek, J. Inst. Chem. Tech., Prague *7–2*, 285–92 (1963); Abstract, JAOCS *41*, 34 (1964).
6. Morton, I. D., Food Process. Market. *36*, 303–308 (1967).
7. Popov, A., M. Gardev, St. Ivanov and T. Petkova, Nahrung *10*, 45–48 (1966); Abstract, J. Sci. Food Agr. *18*, i–26 (1967).
8. Moser, Helen A., C. D. Evans, J. C. Cowan and W. F. Kwolek, JAOCS *42*, 30–33 (1965).
9. Mehlenbacher, V. C., "The Analysis of Fats and Oils," The Garrard Press Publishers, Champaign, Illinois, 1960, p. 195.
10. AOCS Official Method, 1960, Cd 8–53.
11. AOCS Official Method, corrected 1951, Cc 7–25.
12. Eckey, E. W., "Vegetable Fats and Oils," Reinhold Publishing Corp., New York, 1954, p. 73.
13. H. W. Schultz, E. A. Day and R. O. Sinnhuber, ed., "Symposium on Foods: Lipids and Their Oxidation," The Avi Publishing Company, Westport, Connecticut, 1962, p. 297.

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