The proposed new methods and method changes outlined above constitute the greatest number of additions and revisions to be presented to a business session of this Society since our last general revision of Methods in 1945. They are a barometer of the activity of our technical committees.

We wish to thank the committee members and chairmen whose unselfish labors have made these new methods and revisions possible.

J. J. GANUCHEAU R. J. HOULE
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Report of the F.A.C. Subcommittee on Oxirane Oxygen, 1956

THE SUBCOMMITTEE on the determination of oxirane oxygen of the Fat Analysis Committee, of the American Oil Chemists' Society is recommending a new procedure based on a direct titration with acetic acid-hydrogen bromide. Data and statistical analysis of the results of the collaborative study are attached. The recommendation is made because the new method is a direct titration and therefore more convenient; the proposed procedure eliminates the necessity for determining and correcting for the acid value; and the precision of the acetic acid-hydrogen bromide method is somewhat better than the current method.

REFERENCE

Durbetaki, A. J., Analytical Chemistry, *28*, 2,000 (1956).

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W. O. LUNDBERG J. G. WALLACE
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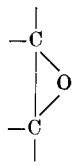
A.O.C.S. Tentative Method Cd 9-56

Oxirane Oxygen

Definition. This method determines oxirane oxygen, which is the oxygen contained in the following grouping:



Under the prescribed conditions of this method the oxygen is titrated directly with HBr in acetic acid.

Laboratory	Sample	Method A Hydrogen Chloride-Acetic Acid	Method B Acetic Acid-Hydrogen Bromide	Method C Pyridinium Chloride-Pyridine
1	Epoxidized soybean oil			
	A–1	6.06–6.10	6.36–6.36	6.08–6.07
	A–2	6.02–6.04	6.34–6.35	6.09–6.09
	B–1	6.03–5.99	6.35–6.34	6.12–6.13
	B–2	6.04–6.04	6.35–6.37	6.10–6.13
2	A–1	5.86–5.92	6.24–6.21	6.01–6.05
	A–2	5.84–5.82	6.27–6.24	6.01–6.19
	B–1	5.98–5.99	6.20–6.19	6.07–6.01
	B–2	6.01–6.07	6.22–6.20	5.93–5.93
3	A–1	5.95–5.98	6.17–6.19	5.95–5.94
	A–2	6.02–6.01	6.18–6.19	5.92–5.93
	B–1	6.03–6.01	6.19–6.15	5.94–5.95
	B–2	5.99–6.00	6.16–6.19	5.95–6.00
4	A–1	5.87–5.87	6.17–6.29	6.53–6.28
	A–2	6.02–6.17	6.16–6.15	6.30–6.27
5	A–1	5.90–5.90	6.27–6.26	6.14–6.11
	A–2	5.87–5.87	6.18–6.18	6.14–6.15
	B–1	5.92–5.93	6.23–6.24	6.10–6.10
	B–2	5.94–5.93	6.22–6.14	6.10–6.12
Range		5.82 6.17	6.14 6.37	5.92 6.53
Std. Dev.		.0797	.07281	.1393

Scope. This is applicable to epoxidized fatty materials and epoxy compounds in general.

A. Apparatus

1. Buret and bottle assembly (or other convenient arrangement) protected with drying tubes to maintain the standard solution free from contamination with moisture either through the atmosphere or otherwise. It is important that the titration be performed in a closed

Laboratory	Sample	Method A Hydrogen Chloride-Acetic Acid	Method B Acetic Acid-Hydrogen Bromide	Method C Pyridinium Chloride-Pyridine
1	Epoxidized butyl stearate			
	A–1	4.17–4.14	4.22–4.22	4.04–4.05
	A–2	4.10–4.09	4.21–4.22	4.05–4.06
	B–1	4.10–4.17	4.19–4.18	4.33–4.35
	B–2	4.13–4.16	4.20–4.20	4.33–4.29
2	A–1	3.98–3.91	4.12–4.10	3.95–3.97
	A–2	4.00–4.01	4.15–4.09	3.98–4.04
	B–1	3.96–4.05	4.08–4.13	3.99–4.02
	B–2	3.95–3.97	4.09–4.10	3.96–3.95
3	A–1	4.07–4.07	4.10–4.10	4.06–4.03
	A–2	4.10–4.09	4.09–4.10	4.04–4.01
	B–1	4.07–4.06	4.10–4.09	4.10–4.09
	B–2	4.08–4.03	4.10–4.09	4.10–4.09
4	A–1	3.95–3.97	4.05–4.08	3.99–4.11
	A–2	4.10–4.10	4.12–4.12	4.23–4.19
5	A–1	3.95–3.96	4.08–4.14	4.09–4.09
	A–2	3.97–4.00	4.07–4.09	4.09–4.08
	B–1	3.99–4.07	4.11–4.14	4.10–4.08
	B–2	4.04–4.02	4.09–4.09	4.10–4.09
Range		3.91 4.17	4.05 4.22	3.95 4.35
Std. Dev.		.0705	.0487	.1039

Laboratory	Sample	Method A Hydrogen Chloride-Acetic Acid	Method B Acetic Acid-Hydrogen Bromide	Method C Pyridinium Chloride-Pyridine
1	Cis-9,10-epoxystearic acid			
	A–1	5.24–5.26	5.33–5.33	5.28–5.28
	A–2	5.25–5.28	5.31–5.31	5.26–5.25
	B–1	5.31–5.28	5.33–5.32	5.28–5.28
	B–2	5.27–5.29	5.35–5.34	5.26–5.25
2	A–1	5.00–5.14	5.25–5.24	5.48–5.43
	A–2	5.07–5.13	5.22–5.21	5.37–5.72
	B–1	5.51–5.32	5.20–5.18	5.40–5.36
	B–2	5.08–5.09	5.22–5.20	5.46–5.50
3	A–1	5.22–5.26	5.21–5.23	5.25–5.22
	A–2	5.24–5.25	5.24–5.22	5.22–5.24
	B–1	5.26–5.26	5.23–5.21	5.23–5.21
	B–2	5.21–5.25	5.25–5.24	5.25–5.24
4	A–1	5.13–5.07	5.08–5.27	5.36–5.36
	A–2	5.31–5.17	5.08–5.10	5.36–5.36
5	A–1	5.05–5.05	5.22–5.20	5.27–5.28
	A–2	5.06–5.06	5.13–5.15	5.27–5.28
	B–1	5.05–5.03	5.24–5.23	5.28–5.26
	B–2	5.12–5.10	5.13–5.11	5.26–5.26
Range		5.00 5.51	5.08 5.35	5.21 5.72
Std. Dev.		.1135	.102	.103

system to avoid the loss of HBr. Provide a closed system by attaching the titration flask to the buret tip with a 1-hole rubber stopper. The hole in the stopper should be spherical so as to take the buret tip snugly with a small side-opening to permit the air to escape from the flask during titration.

2. Flasks, Erlenmeyer, 50-ml.
3. A magnetic stirrer of any suitable type with round magnetic stirring bars covered with Teflon or equivalent protective covering.

B. Reagents

1. Glacial acetic acid, A.C.S. grade.
2. HBr gas, anhydrous, available in cylinders from Matheson Company Inc.
3. Crystal violet (gentian violet), Eastman Kodak No. 1350 or equivalent.
4. Crystal violet indicator soln.; dissolve 0.1 g. of crystal violet in 100 ml. of glacial acetic acid.
5. Benzene, A.C.S. grade, or Chlorobenzene, analytical reagent grade.

C. Solutions

1. Sodium carbonate, anhydrous, analytical-reagent grade, MCW No. 7528 or equivalent. This serves as a primary standard. Be sure it is finely powdered and dried at 120°C. for 3 hrs. before using. Maintain in a desiccator over an efficient desiccant. (See Specification H 9-45.)
2. Glacial acetic acid—HBr 0.1 *N*. Prepare by bubbling HBr gas through glacial acetic acid to approximately 0.1 normal. A torsion-type of balance may be used to estimate the amount of HBr to be added.
Standardization. Weigh sufficient dry sodium carbonate to give a titration of *ca.* 20 ml., which is about 0.1 g. Dissolve in *ca.* 5 ml. of glacial acetic acid and titrate, using 5 drops of the crystal violet indicator. Sandardize daily. Calculate the normality of the HBr solution as follows:

$$\text{Normality} = \frac{\text{Weight of } Na_2CO_3}{0.053 \times \text{titration in ml.}}$$

D. Procedure

1. Weigh 0.3 to 0.5 g. (±0.0001 g.) of the sample into a 50-ml. Erlenmeyer flask. Dissolve the sample in 5 ml. of benzene or chlorobenzene (in case of epoxy resins, use chlorobenzene). Add 5 drops of the crystal violet indicator and a stirring bar.
2. Place the rubber stopper in position and lower the tip of the buret until it discharges just above the solution. This is important to avoid loss of HBr.
3. Stir and titrate the sample (rapidly at first) with the 0.1 *N* glacial acetic acid-HBr solution to a bluish-green end-point. Control the rate of the magnetic stirrer so as to avoid splashing.

E. Calculation

$$\text{Oxirane oxygen, } \% = \frac{\text{Titration} \times N \times 1.60}{\text{Weight of sample}}$$

F. Reproducibility

The average variance of components calculated from the collaborative data obtained by the investigating committee indicate the following 95% probability limits:

1. The difference between duplicate determinations made within a laboratory should not exceed 0.08.
2. The difference between the average of duplicate determinations made in different laboratories should not exceed 0.19.

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Fatty Acids of Asparagus Seed Oil[1]

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THE CONSTANTS of asparagus seed oil *(Asparagus officinalis L.)* were recorded in 1916 (6), but the fatty acids of the oil have not been investigated hitherto. The plant belongs to the family *Liliaceae*. Some information is available regarding the seed oils of two species of this family (4), *viz.*, *Veratrum nigrum,* a drug plant, and *Allium cepa,* the common onion (also classed under *Amaryllidaceae*). Their oils are reported to consist chiefly of glycerides of oleic and linoleic acids.

Asparagus is grown extensively in North America, and the possibility of utilizing the seed for its oil has been reviewed (1, 5). Some thousands of tons of seed could be harvested annually from the present plantings (5).

Experimental

Seed of *Asparagus officinalis L.,* Mary Washington variety, was obtained from a commercial seed house. It was ground in a Wiley mill. The seed is quite hard and tough and consequently is difficult to grind. Unless it is finely ground, the oil yield is reduced considerably.

The moisture content of the meal was determined, and the oil was extracted with petroleum ether. The oil content was 14.7% on a 10% moisture basis. Constants of the oil are given in Table I. The yield of glycerol from the oil, determined by the method of Colson (3), was in the normal range.

TABLE I

Constants of Asparagus Seed Oil

Iodine value	135.1
Saponification value	185.5
Unsaponifiable matter, %	1.46
Acid value	1.9
Peroxide value	3.2
Glycerol yield, %	9.9
Refractive index, $n_D^{25°}$	1.4750

The oil-free meal contained 21% protein and 11% fiber on a 10% moisture basis. A preliminary feeding trial with albino rats did not establish the feeding value of the meal conclusively.

Two samples of seed of the Eden variety were also examined with the following results: oil content, %, 12.8, 13.6; iodine value 130.0, 136.7; acid value 1.4, 0.4; saponification value 186.5.

The oil from the Mary Washington variety was examined in detail. The ultraviolet absorption spectra of its mixed fatty acids (before and after alkali isomerization) were typical of those of a nonconjugated oil with high diene and low triene acid content.

Examination of the Methyl Esters. The main portion of the oil was converted to methyl esters by methanolysis with acid catalyst. The esters (200 g.) were fractionally distilled at a pressure of 0.5 mm. through a Podbielniak Heli-Grid column. The residue was distilled further through a spinning band column. It was evident from the distillation curves that the fatty acids were mainly in the C_{18} series

[1] Presented at the meeting of the American Oil Chemists' Society, Philadelphia, Pa., October 10–12, 1955. Issued as N.R.C. No. 4426.