Report of the Epoxidized Oils Subcommittee on Oxirane Oxygen, 1963

The Epoxidized Oils Subcommittee has recommended some modifications of AOCS Method Cd 9-57, Oxirane Oxygen. These modifications resulted from a collaborative study on three methods for oxirane oxygen analysis. The results of this study are shown in the tables below. The methods tested were as follows:

Method A—AOCS Tentative Method Cd 9-57, Oxirane Oxygen

Method B—AOCS Tentative Method Cd 9-57, Oxirane Oxygen, using an alternate method of hydrogen bromide-acetic acid reagent preparation.

Method C—A method of oxirane oxygen determination comprising addition of an excess of hydrogen bromide in acetic acid and back-titrating for unreacted hydrogen bromide.

The recommendations made by this Subcommittee received an affirmative vote by the Uniform Methods Committee. Amendments to the method and data from the study (Tables I, II and III) are shown below.

Amendments to AOCS Tentative Method Cd-9-63, Oxirane Oxygen

A. Apparatus:

1. Buret assembly of the Machlette type (gravity feed). Available from Scientific Glass Apparatus Co., Cat. No. J B6715 or equivalent. Provide a closed system for titration to avoid loss of hydrogen bromide by attaching the titration flask to the buret tip with a one-hole rubber stopper. The hole in the stopper should be formed so as to take the buret tip snugly with a small side opening to permit air to escape from the flask during titration.

B. Reagents:

2. Hydrogen bromide gas, anhydrous, available in cylinders from Matheson Co., Inc., Joliet, Ill., or 30–32% hydrogen bromide in acetic acid available from Eastman Kodak Co.

C. Solutions:

2. Hydrogen Bromide 0.1 N in acetic acid.
   b. Prepare by diluting 30–32% (ca. 4 N) hydrogen bromide in acetic acid with glacial acetic acid to approximately 0.1 N.

Standardization: Weigh accurately about 0.4 g dry acid potassium phthalate and dissolve, using a hot plate. Titrate solution at room temp with hydrogen bromide using no more than 0.1 ml (5 drops from a fine dropper) crystal violet indicator. Standardization should be in duplicate with a difference not to exceed 0.0004 N. Restandardize each day samples are analyzed.

TABLE I

Epoxidized Soybean Oil

Laboratory	Sample	Method A	Method B	Method C
1	A-1	6.70	6.71	6.84
	A-2	6.72	6.74	6.76
	B-1	6.68	6.71	6.77
	B-2	6.63	6.75	6.78
2	A-1	6.75	6.74	6.80
	A-2	6.73	6.73	6.76
3	A-1	6.72	6.70	6.84
	A-2	6.71	6.71	6.80
	B-1	6.77	6.74	6.83
	B-2	6.76	6.75	6.79
4	A-1	6.74	6.73	6.77
	A-2	6.71	6.71	6.72
	A-3	6.71	6.71	6.82
	A-4	6.71	6.73	6.78
5	A-1	6.66	6.68	6.81
	A-2	6.69	6.68	6.77
	B-1	6.67	6.69	6.81
	B-2	6.67	6.69	6.73
6	A-1	6.70	6.70	6.66
	A-2	6.69	6.70	6.68
	B-1	6.66	6.70	6.68
	B-2	6.70	6.72	6.69
7	A-1	6.59	6.62	6.86
	A-2	6.61	6.61	6.75
	B-1	6.63	6.52	6.75
	B-2	6.55	6.55	6.93
8	A-1	6.59	6.72	6.85
	A-2	6.58	6.82	6.79
	B-1	6.59	6.72	6.90
	B-2	6.62	6.78	6.91
Range		6.55	6.52	6.66
		6.77	6.82	6.93

TABLE II

2-Ethylhexyl Epoxy Tallate

Laboratory	Sample	Method A	Method B	Method C
1	A-1	4.79	4.78	4.96
	A-2	4.78	4.79	4.96
	B-1	4.81	4,78	4.93
	B-2	4.83	4.81	4.91
2	A-1	4.78	4.81	4.91
	A-2	4.78	4.80	4.90
3	A-1	4.78	4.78	4.94
	A-2	4.77	4.79	4.92
	B-1	4.78	4.80	4.95
	B-2	4.78	4.80	4.93
4	A-1	4.78	4.77	4.87
	A-2	4.77	4.77	4.92
	B-1	4.80	4.76	4.90
	B-2	4.79	4.78	4.94
5	A-1	4.72	4.71	4.94
	A-2	4.77	4.72	4.95
	B-1	4.73	4.72	4.96
	B-2	4.70	4.75	4.91
6	A-1	4.74	4.77	4.86
	A-2	4.76	4.76	4.82
	B-1	4.74	4.75	4.87
	B-2	4.78	4.77	4.77
7	A-1	4.71	4.65	4.90
	A-2	4.64	4.67	4.92
	B-1	4.69	4.68	4.97
	B-2	4.68	4.69	4.87
8	A-1	4.64	4.76	4.98
	A-2	4.67	4.76	4.92
	B-1	4.65	4.74	5.01
	B-2	4.64	4.73	5.00
Range		4.64	4.65	4.76
		4.83	4.81	5.01

TABLE III

Glycidyl Stearate

Laboratory	Sample	Method A	Method B	Method C
1	A-1	4.54	4.49	4.18
	A-2	4.52	4.52	4.10
	B-1	4.55	4.51	4.25
	B-2	4.54	4.52	4.24
2	A-1	4.48	4.50	4.09
	A-2	4.50	4.50	4.09
3	A-1	4.51	4.52	4.04
	A-2	4.52	4.53	4.03
	B-1	4.49	4.51	4.02
	B-2	4.51	4.48	4.01
4	A-1	4.50	4.49	3.74
	A-2	4.48	4.46	3.89
	B-1	4.50	4.48	3.89
	B-2	4.49	4.49	3.74
5	A-1	4.41	4.46	3.87
	A-2	4.48	4.49	3.78
	B-1	4.42	4.42	4.08
	B-2	4.42	4.47	4.08
6	A-1	4.42	4.48	4.42
	A-2	4.46	4.45	4.42
	B-1	4.47	4.48	4.43
	B-2	4.48	4.49	4.43
7	A-1	4.44	4.37	4.44
	A-2	4.46	4.40	4.25
	B-1	4.43	4.32	4.26
	B-2	4.44	4.35	4.31
8	A-1	4.42	4.31	4.02
	A-2	4.45	4.46	4.36
	B-1	4.41	4.39	4.39
	B-2	4.44	4.44	4.06
Range		4.41	4.31	3.78
		4.55	4.54	4.43

D. Procedure:

1. Wt 0.3–0.5 g (± 0.0001 g) of the sample into 50-ml Erlenmeyer flask. Dissolve the sample in 10 ml benzene or chlorobenze (in case of epoxy resins use chlorobenzene). Add stirring bar and crystal violet indicator (maximum 0.1 ml or 5 drops with a fine dropper).
3. Stir and titrate the sample (rapidly at first) with the 0.1 N hydrogen bromide solution to a bluish-green end point that persists for 30 sec. Control the rate of the magnetic stirrer so as to avoid splashing.

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• *Letters to the Editor*

A Rapid Semi-Micro Method for Preparation of Methyl Esters from Triglycerides Using Chloroform, Methanol, Sulphuric Acid.

THE PRESENT PROCEDURES of methyl ester preparation for subsequent gas chromatographic analysis have the disadvantages in the case of the older methods, such as refluxing with Sodium Methoxide or Sulphuric Acid catalysed Methanol of being time consuming and laborious, while the more recent rapid reagents such as Diazomethane and Boron Trifluoride are either hazardous or noxious in their use, or require fresh preparation. The present suggested method uses standard stable reagents and relies on a combination of increased heat and pressure, together with a solvent as a carrier for the sample to accelerate the esterification process.

Apparatus

Reaction Tube: 4″ x ¼″ I.D. Hard glass Test Tube, flared rim.

Pressure Sealing Device: This device may be simply constructed from commonly available laboratory materials as illustrated, or the design may be improved if engineering facilities are available. As shown, the tube holder consists of a metal cork borer plugged at the bottom, with two screw type tubing clamps fastened to the top. These can be tightened down on a small channel section steel plate which holds the seal. A necessary precaution, but not shown, is the inclusion of a small pad of asbestos in the bottom of the metal tube to cushion the glass tube against breakage under pressure and which also holds the flared rim above the metal surface.

The most important feature of the device is the selection of the material for the seal. Sheet neoprene has proved most satisfactory in withstanding the attack of solvent under high temperature and pressure. It gives very long service and seals well, using only moderate finger pressure.

The pressure sealing device also protects against shattering in the event of tube breakage. So far, this has never occurred except through overtightening.

Heating Block: The pressure sealing device should fit neatly into a hole in the heating block, which is preferably of aluminium or brass for rapid heat transfer, and is maintained at 170C.

Reagents: These should be analytical reagent grade. Chloroform—methanol—sulphuric acid: This is prepared volumetrically in the proportions 100:100:1.

Procedure

One drop of oil (approximately 30 mg) is placed in the test tube to which is added approximately 0.75 ml chloroform—methanol—sulphuric acid. The tube is placed in the pressure sealing device and heated in the block at 170C for five minutes. After rapid cooling under running water the test tube is removed from the device and the solvent boiled off in a hot water bath. A small piece of zinc is usually first added, which neutralises the sulphuric acid, avoiding charring of the esters. At this stage the esters have given satisfactory results in the gas chromatograph, but to avoid contamination of the esters by zinc products, it is preferable to wash and extract as follows: To the test tube is added 1 ml of water followed by 1 ml

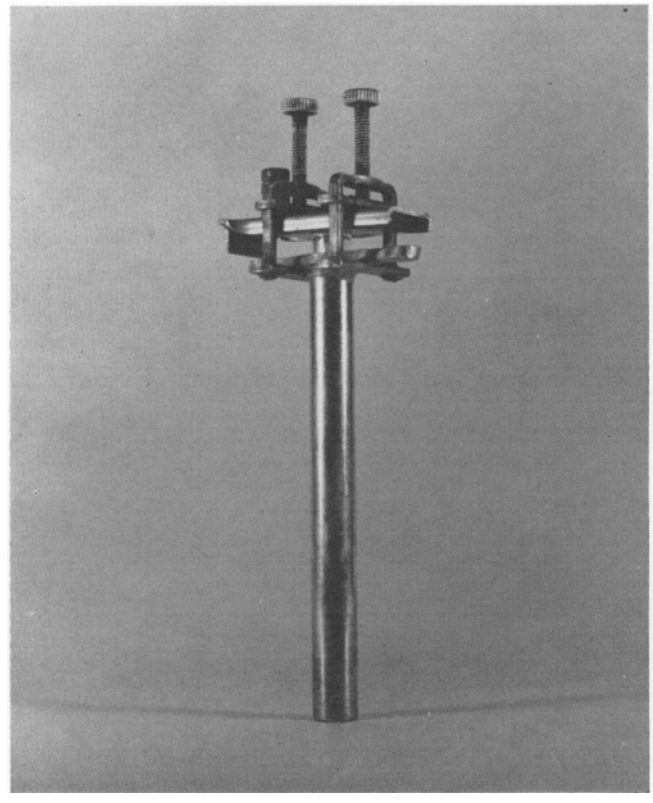

FIG. 1. Pressure sealing device.