

A Modified Liquid-Liquid Extractor for Routine Oil Analysis

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THE Official A.O.C.S. Methods (1, 2) for determining the percentage of total fatty acids and unsaponifiable matter involve a series of cumbersome, batchwise extractions of these materials, using separatory funnels or extraction cylinders. The shortcomings inherent in this procedure have been the subject of considerable discussion. In general, the official procedures are laborious and time-consuming; consequently a rather high degree of skill is required to obtain reproducible results. In an attempt to minimize or eliminate these various faults, continuous liquid-liquid extractors were investigated.

Liquid-liquid extractors have become common laboratory tools, and the initial approach to the problem involved examination of available commercial equipment.¹ In 1938 Wood and Roschen (3) published an excellent paper on the use of liquid-liquid extractors for routine oil analyses and presented numerous data correlating their procedure with the Official A.O.C.S. Methods of the day. Although these investigators made a good case for extractors, their work apparently was not widely accepted by the soapstock processing industries.

In the analysis of unsaponifiable matter no particular difficulties were encountered in the use of the several simplified extractors examined. Total fatty acids, on the other hand, presented numerous problems. Upon acidification of the saponified sample, fatty acids along with undefined insoluble impurities precipitate. These acids in the presence of water have a rather high adhesion for glass and stick tenaciously to the surface of the apparatus. Consequently the fatty acids are not quantitatively washed from extractors as the solvent has a tendency to channel through the liquid and does not adequately contact material adhering to the extractor walls. A number of devices for improving solvent dispersion were tried including extractors designed with inner tubes, utilizing fritted glass discs. Except for the high initial cost no objections were found to the use of fritted glass inner tubes for unsaponifiable matter analysis. In the case of total fatty acid extractions however the heterogeneous nature of the acidulated sample frequently caused the discs to become plugged, thus reducing their efficiency. Those soapstocks containing large amounts of insoluble impurities, *i.e.* cottonseed, gave the most difficulty in clogging the openings in fritted glass discs. This, of course, hindered solvent dispersion and usually resulted in incomplete extractions.

After a number of exploratory experiments it became apparent that some mechanical means of agitation and solvent dispersion must be devised. Although there is considerable literature on liquid-liquid extractors incorporating various mechanical agitators, most of these are too cumbersome for routine control analysis. The magnetic stirring motor was chosen as

the simplest and most efficient type of agitator for this work. Kaye and Burlant (4) recently described a continuous liquid-liquid extractor that utilized a magnetic agitator. Their apparatus is made with interchangeable parts designed to accommodate volumes from 50 ml. to 10 liters. No examination was made of the Kaye-Burlant design since it was felt that this device was too elaborate for use in routine analysis.

The prerequisites used as a guide in developing the apparatus were as follows: a) the extractor should be simple to construct and easy to maintain; b) it should be low in cost; c) the extractor should lend itself to a wide variety of applications; and d) it should eliminate emulsion problems often encountered in manual procedures.

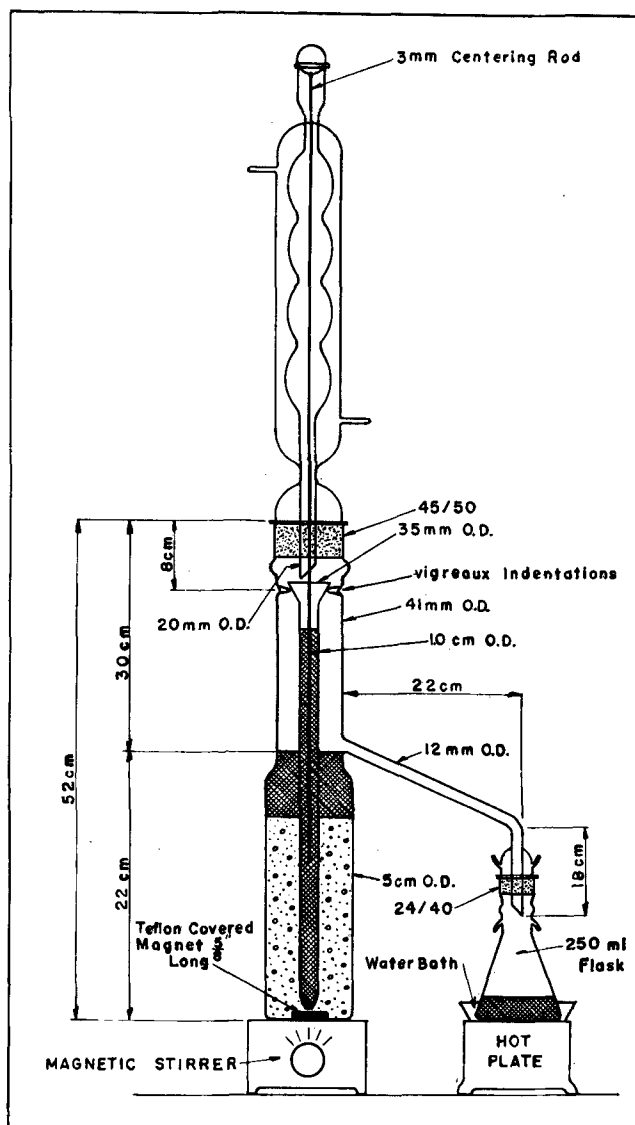


FIG. 1. Liquid-liquid extractor.

¹ Only simplified extractors were examined, that is, extractors without mechanical agitators. Since this paper was written, extractors with devices for agitation have become available commercially.

The Extractor

The apparatus illustrated in Figure 1² is self-explanatory; however it has been the authors' experience that difficulties are often encountered in making the proper initial adjustment of the inner tube. Despite the apparent simplicity of the inner tube, it is the most critical part of the apparatus. It is advisable therefore individually to fit each extractor with its own particular inner tube.

The optimum conditions for the most efficient extraction require a balance between minimum agitation and maximum solvent dispersion. Vigorous agitation may lead to the excessive carry-over of insoluble impurities in the total fatty acid analysis and may give emulsions in some unsaponifiable matter determinations. Optimum conditions are best achieved by use of an inner tube with an orifice approximately 1.0 mm. I.D. with the tip suspended as close as possible and directly above the magnetic bar. A magnetic bar approximately $\frac{5}{8}$ in. in length will efficiently disperse the solvent without setting up a vigorous agitation at the solvent inter-face. Actual operating conditions and experience will determine the correct orifice size for most efficient operation. If the orifice is too large, the solvent leaves the tube as a large drop and will not be properly dispersed. On the other hand, an orifice that is too small will result in a flooded column. When an extractor is functioning properly, the dispersed solvent phase is composed of a multitude of tiny bubbles uniformly distributed and quite regular in size. Time spent to achieve proper dispersion of solvent will be rewarded with rapid, efficient, and quantitatively accurate extractions.

Total Fatty Acid and Oxidized Acids Determinations

A. TOTAL FATTY ACID PROCEDURE.

The proposed methods have been adapted for liquid-liquid extractors from the Official A.O.C.S. Methods. To determine total fatty acids, follow the procedure in A.O.C.S. G 3-39 from C-1 through C-3, and then proceed as indicated below.

1. Place the magnetic bar in the extractor before transferring the sample. In order to prevent losses during the transfer, clamp the extractor to a ringstand so that the side arm outlet is inclined slightly upward.
2. Dissolve the saponified sample in 100 ml. of distilled water and heat until the soap has completely dissolved. Wash the contents into the extraction cylinder with hot distilled water, taking care not to use excessive amounts of water.
3. Add 3 to 5 drops of indicator and a small but definite excess of dilute HCl. Agitate the contents with a magnetic stirrer.
4. Cool the contents of the extractor to 35°C. or below. Add cold distilled water to bring the level of the liquid up to a point 7-8 cm. below the side arm.
5. Add from 175 ml. to 200 ml. of petroleum ether to the 250-ml. reflux flask.
6. Put reflux flask in place, fill the inner tube with petroleum ether; and while the solvent is running from the orifice, slide it into position. The solvent escaping from the inner tube prevents the orifice from becoming plugged with insoluble impurities.
7. Set up the extractor and start the solvent refluxing.
8. Adjust the speed of the magnet to obtain maximum solvent dispersion and minimum agitation.
9. Let the extractor run for at least 3 hours.

10. Carefully wash the 24/40 ground glass joint with Skellysolve F, remove the reflux flask, and with the aid of a small funnel wash the contents of the flask into the 250 ml. separatory funnel.

NOTE: Because of its tendency to "creep," petroleum ether is a difficult liquid to pour without losses. Therefore the fatty acid solution is transferred to a 250-ml. separatory funnel and dispensed gradually into the filter. This minimizes "creeping" and greatly simplifies the filtration.

11. Filter the extract into a previously desiccated, tared, rubber extraction flask. Care should be exercised in washing the filter paper and separatory funnel. This can best be accomplished with a small syringe or a wash bottle containing solvent.
12. Complete the analysis and calculation according to A.O.C.S. Official Method G 3-39.

B. OXIDIZED ACID PROCEDURE.

The method for determining oxidized acids can be described briefly as follows: After the total fatty acids have been removed, the residual petroleum ether is siphoned from the extractor; and the last traces of petroleum solvent are removed with a stream of clean, dry air.

The extraction of oxidized acids is then carried out in the same manner as the total fatty acid extraction except that anhydrous ethyl ether is used in place of petroleum ether.

The extraction is completed when the solvent phase becomes colorless. This is normally accomplished in an hour or less. Upon completion of the extraction the extract solution is treated in accordance with the procedure for total fatty acids.

Results of Total Fatty Acids and Oxidized Acids Determinations

Limited solvent requirements represent a distinct advantage of liquid-liquid extractors. The total fatty acid procedure uses approximately 100 ml. of solvent, less than $\frac{1}{3}$ the solvent required in the A.O.C.S. procedure. In addition to a saving in solvent, considerable time is saved in the filtration step and in evaporation.

The following tables present data verifying the accuracy of this method:

TABLE I
Duplicate Runs on One Sample of Acidulated Soya Soapstock,
Using Liquid-Liquid Extractor

	T.F.A.
	%
1.....	96.11
2.....	96.21
3.....	96.13
4.....	95.92
5.....	96.16
Mean.....	96.11
Standard Deviation.....	0.12

NOTE: Sample (5) was extracted for 6 hours. Samples 1-4 were extracted for 3 hours.

In Table II columns (a) and (b) show excellent agreement for T. F. A., indicating that 3 hours is sufficient for complete extraction. Columns (e) and (f) correlate well with (a) and (b), indicating that the several methods are in good agreement if a sufficient number of manual extractions are made. An outside laboratory reported 95.0% T.F.A. on this sample.

The acid values were obtained by dissolving the extracted fatty acids in previously neutralized 95.0% ethanol, diluting to 100 ml., and titrating an aliquot with N/10 KOH solution. Although columns (e) and

² The basic extractor was obtained from the Ace Glass Company, Vineland, N. J.

TABLE II
Comparison of Several Extraction Methods. One Sample of Acidulated Soya Soapstock. Run in Duplicate.

Analysis	L-L Extractor		A.O.C.S. G 3-39			A.O.C.S. Modified ^a
	(a) 3 Hr.	(b) 6 Hr.	(c) 4 Ext.	(d) 6 Ext.	(e) 8 Ext.	(f) 7 Ext.
T.F.A.	95.4 95.4	95.2 95.4	94.1 93.8	94.6 94.8	95.4 95.6	95.3 95.3
Oxi. Acids	1.58 1.65	1.95 1.93		1.75 1.83	0.58 0.67	1.64 1.69
Acid Value on T.F.A.		181.0 181.5		181.0 182.0	175.0 176.0	177.5 178.0

^a The modified A.O.C.S. Method is essentially the same as the Official A.O.C.S. Method, using a separatory funnel in place of the extraction cylinder.

(f) show excellent agreement with respect to percentage of T.F.A., the acid values of their extracted fatty acids are somewhat lower than those obtained by using the liquid-liquid extractors. This indicates that materials other than fatty acids are carried over into the extract when using the A.O.C.S. Method. Physical appearance of the extracted fatty acids further substantiates this. In general, acids obtained by the liquid-liquid extractors are clear and clean while the A.O.C.S. Method produces grayish, cloudy acids. Table III shows similar results in the analysis of a group of samples submitted by the A.O.C.S. Soapstock Analysis Committee. In this case comparison was made with Tentative A.O.C.S. Method G 3-53, a modification of G 3-39.

The oxidized acid data in columns (a) and (b) of Table II were obtained by making 1-hr. extractions with ethyl ether after the total fatty acids were removed. In columns (d), (e), and (f) the oxidized acids were obtained by making 3 or more extractions to give a colorless solvent phase.

A limited number of oxidized acid analyses have been run; therefore only generalized observations can be made on the results at this time. In the case of the A.O.C.S. Method, the percentage of oxidized acids varies inversely with the number of extractions made in the T.F.A. analysis. This would indicate that prolonged extraction with petroleum ether tends to solubilize the oxidized acids, carrying them along with the fatty acids. The lower acid values of these fatty acids also show that more impurities are extracted when the number of extractions is increased. When the liquid-liquid extractor is used, prolonged extraction apparently does not carry the oxidized acids or other impurities into the fatty acids. This is shown by both the oxidized acid results and acid values of the fatty acids.

The data in Table IV are representative of analyses made in this laboratory over the past year. Correlation between the two methods has always been well within the accepted limits of error. In general, the

TABLE III
Comparison of Liquid-Liquid Extractor with A.O.C.S. Tentative Methods

Sample A.O.C.S. Cooperative	Percentage of T.F.A.		Acid Value		Percentage of Unsaponifiable	
	A.O.C.S. G 3-53	L-L	A.O.C.S.	L-L	A.O.C.S. Ca 6b-53	L-L
No. 13	93.1 93.0	93.2 93.1	186.8 187.2	189.0 188.0	4.66 4.88	4.98 4.86
No. 14	83.0 83.4	83.6 83.3	188.4 191.0	191.6 191.9	4.04	3.95 3.99
No. 15	42.4 42.4	42.3 42.4	187.0 186.7	188.6	2.81 2.68	2.69

TABLE IV
Comparison of Liquid-Liquid Extractor with A.O.C.S. G 3-39

Sample	% T. F. A.	
	A.O.C.S. G 3-39	L-L Extractor
1.....	92.4%	92.9%
2.....	91.3%	92.0%
3.....	90.2%	91.0%
4.....	90.9%	90.9%
5.....	92.5%	93.0%
6.....	94.6%	95.0%

liquid-liquid extraction results in slightly higher percentages of T.F.A. of slightly higher acidity, indicating more efficient extraction with less removal of non-fatty acid impurities.

Unsaponifiable Matter Determination

A. PROCEDURE.

Follow the A.O.C.S. Official Method Ca 6a-40 up to and including C-1. Then proceed as indicated below:

1. Place the magnetic bar in the extraction cylinder. Clamp the extraction cylinder to a ringstand so the side arm is tilted slightly upward. Carefully wash the contents of the flask into the cylinder with hot water up to the 80-ml. mark. It should be noted that this step adjusts the alcohol-water ratio approximately 3 to 5 or 37½% alcohol by volume; in order to prevent emulsion formation it is necessary that this ratio be maintained. This can be done by using a 37½% aqueous alcohol solution to adjust the liquid level in the extractor to a point 7-8 cm. below the side arm.
2. Cool the extractor to slightly below room temperature. Fill the inner tube with petroleum ether and lower it into position. Add approximately 200 ml. of petroleum ether to the reflux flask. Reflux for 6 hours or until extraction is complete.
3. Carefully transfer the extract solution to a 250-ml. separatory funnel.
4. Complete the analysis and calculation according to A.O.C.S. Ca 6a-40.

Results of Unsaponifiable Matter Determinations

Table V illustrates analysis of a group of materials with a broad range of unsaponifiable matter. Severe emulsions made it impossible to extract No. 8 by the A.O.C.S. (1) Method. Correlation between the two methods is well within the accepted limits of error on all the materials investigated. Additional data are presented in Table III.

In general, it has been found that more time is necessary to extract unsaponifiable matter than is required for total fatty acid extraction. This will

TABLE V
Comparison of Unsaponified Determinations Using A.O.C.S. and Liquid-Liquid Extraction Procedures

Sample	A.O.C.S. Ca 6a-40 7 Ext.	L-L Extractor 6 Hours
1. Deodorized Soya Oil.....	{ 0.52 0.52
2. Degummed Linseed.....	1.15	{ 1.16 1.06
3. Lecithin.....	0.83	0.86
4. Fatty Acids No. 1.....	1.01	0.96
5. Fatty Acids No. 2.....	3.10	3.01
6. Fatty Acids No. 3.....	4.42	4.36
7. Fatty Acids No. 4.....	8.31	8.21
8. Cotton-Soya Still Pitch.....	{ 28.49 28.38
All answers are corrected for titratable acids.		

vary with the nature of the substance being analyzed. In the work done 6-hour extractions have been more than sufficient for the wide variety of substances examined. It is believed that the 6-hour figure can be safely reduced for many types of materials; however the method as proposed is designed to analyze a wide range of products (See Table V).

No emulsion difficulties were encountered during the extraction of unsaponifiable matter from any of the samples examined. Although with some substances, still pitches for example, slight emulsion will tend to form if the agitator is rotating too fast or if the solvent is refluxing too rapidly. This difficulty can be corrected by making appropriate adjustments in agitation.

Washing of the final extract solution with 10% aqueous alcohol as required in the A.O.C.S. procedure can be eliminated since no soap is entrained in the solvent if the extractors are operating properly. However one alcohol wash is recommended as a precautionary measure. The A.O.C.S. Method (1) requires correction for traces of fatty acids. This correction is included in the method proposed here; however for most purposes the correction is so insignificant that it could be eliminated. A similar conclusion was reached by Wood and Roschen (3).

Summary

1. A continuous liquid-liquid extractor was designed and procedures were devised for the determination of total fatty acids, oxidized acids, and unsaponifiable matter. These procedures give results that are in agreement with the present A.O.C.S. Methods.

2. The continuous liquid-liquid extractor has the following advantages:

- a) It is simple in design, easy to operate and keep clean. The inner tube which gives better solvent dispersion than standard commercial pieces can be made out of ordinary glass tubing at relatively low cost.
- b) The operation is automatic. Once a bank of these extractors is set up, the operator is free to do other work.
- c) The extractions are made rapidly without troublesome emulsions.
- d) Greater accuracy is possible because of limited handling.
- e) The enclosed system minimizes health and fire hazards inherent in the present A.O.C.S. Methods.

REFERENCES

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A New Batch Solvent-Extraction Pilot Plant¹

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AN all-stainless steel, batch solvent-extraction pilot plant has been designed, constructed, and test-operated at the Southern Regional Research Laboratory. The plant is illustrated in Figure 1. It is an improvement over an earlier plant (4), which was used for more than 200 extractions. Its stainless steel construction makes it particularly useful as a research tool for the extraction of a variety of vegetable and other materials, either native or specially prepared, with suitable solvents for the production of meals, oils, pigments, and other constituents, of essentially unmodified quality and purity or with special qualities. Features of the plant are an improved batch extractor, a high-velocity rising-film type evaporator with its vacuum and other auxiliary equipment, and pneumatic control and mechanical recording instrumentation.

Design and Installation

The plant is located outdoors to minimize dangers when solvents, such as ethyl ether are used, and is installed on a structural steel frame mounted on reinforced concrete pedestals, which are monolithic with a reinforced concrete slab. Figure 2 is a flow chart which defines the major equipment units and their positions in the process. Designed for versatile and labor-saving operations, and in accordance with the ASME Code for Unfired Pressure Vessels, one of the existing extraction units with a capacity of 5 cubic

feet is shown at the center of Figure 1. Although the extractors have capacities of 3.5 and 5.0 cu. ft., found during the past 8 years to be the most practical sizes for the extraction of small lots of new and established materials, extractors of this design with other capacities can be made and used by increasing or decreasing the length of the unit. Figure 3 illustrates the detail of the extractor. It is made of 14-in. 304 stainless steel pipe and is jacketed with 18-in. carbon steel pipe. Its accessories are of 316 stainless steel construction. Hot water can be circulated through the jacket when extractions are to be made at other than ambient temperatures, and the extractor is provided with an agitator which is manually operated at intervals to reduce channeling and at the same time not create too many fines. The agitator shaft has two sections to permit removal of the upper section along with the top head when charging flakes into the extractor. Two filter frames covered with cloth are mounted in the top head for filtering the miscella as it leaves the extractor on its way to the evaporator. For easy discharge of the extracted meal into a large can, the bottom head is hinged to the body with silicon-bronze hinges. Immediately above the bottom flange on the interior of the extractor body is a retaining screen which restrains the meal from discharging while the bottom head is swung down and the collector is slid beneath the extractor. Since tilting of the extractor is not required for discharging, it is bolted rigidly to the steel through two support lugs. There is a solid baffle above the solvent inlet in the bottom head to reduce the channeling of the solvent.

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