A Colorimetric Method for Determining Small Amounts of Trichloroethylene in Vegetable Oils

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RECENTLY considerable attention has been focussed on the use of trichloroethylene (TCE) as a solvent in the commercial extraction of vegetable oils. One of the most important requirements of a successful TCE-extraction process is that of satisfactory solvent removal. An efficient process should produce an oil containing an utter minimum of residual solvent. In this connection it is important to be able to determine accurately small amounts (0.001-0.5%) of TCE in extracted crude and refined oils. Since none of the methods available for this purpose was entirely satisfactory from the point of view of accuracy, precision, and sensitivity, the development of a suitable method was undertaken.

Methods for determining trichloroethylene in a variety of materials have been described by a number of investigators (8, 9, 10, 11). The most generally used method for detecting or estimating traces of TCE is the Fujiwara pyridine-caustic soda color test (7). Adaptations of this method have been used in determining traces of TCE in blood, tissues, respired air, and other materials (2, 3, 4, 6).

Recently this color reaction has been applied to the determination of TCE in vegetable oils. Arnold and Hollowell (1) employed a modification of this test for estimating traces of TCE in soybean oil. Unfortunately their procedure is capable of giving only approximate results since the color is developed directly in the oil and it is evaluated by visual comparison with artificial standards. Furthermore the method is not applicable to dark oils, such as crude cottonseed oils, and it is only partially successful with many medium-colored oils. A procedure for the same purpose developed by the duPont Company (5), also employing a modification of the Fujiwara color test for TCE, overcomes some, but not all, of the disadvantages of the previously described method. In this procedure the TCE is separated from the oil by steam distillation and the TCE content of the distillate is determined colorimetrically. This method is not entirely satisfactory for work of high precision because it employs visual comparison with artificial color standards as a means of color evaluation instead of employing an objective instrumental procedure. Also the color development procedure is not sufficiently flexible to compensate for occasional unexplained variations in extinction values.

The procedure presented in this paper employs a combination of a continuous-return steam distillation and a codistillation with xylene to separate the TCE from the oil. The TCE content of the distillate is determined by spectrophotometrically measuring the color produced when a portion of the solution is heated with pyridine and sodium hydroxide solution. In operation, the sample is weighed into a flask and a measured amount of xylene and excess water is added. During the distillation some of the water and all of the xylene and TCE are carried over into the continuous-return receiver. There the layers separate, the xylene-TCE solution remains on top, and the excess water returns to the flask to be redistilled. After the distillation is complete, some of the xylene is removed from the receiver arm and its TCE content determined colorimetrically.

Experimental

Since the success of the method is dependent upon a satisfactory color development procedure, the details of this procedure were worked out first. All of the color measurements were made with a Coleman Model 6B spectrophotometer. The following are the more important of the color development test conditions that were investigated:

a) Optimum wavelength for color measurement.
b) Effect of variations in reagent concentrations.
c) Effect of variations in heating time and temperature.
d) Applicability of Beer's law.
e) Color stability with time.

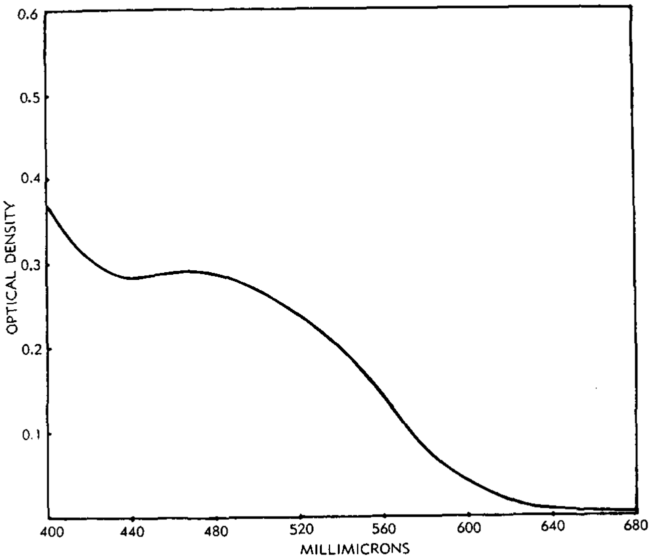

FIG. 1. Absorption spectrum of color produced in reaction.

Figure 1 is a graph of the absorption curve for the color produced in this reaction. From this graph it is apparent that any wavelength from 440 to 480 would be satisfactory for color measurement. The wavelength chosen for use in this method is 475 mμ.

In order to determine the effect of different amounts and concentrations of reagents, a series of test determinations were made, using fixed amounts of a xylene solution of TCE and pyridine (1 and 10 ml. respectively) and various amounts of caustic soda solutions of different strength. The results indicate that strong caustic soda solutions (e.g. 50%) were unsatisfactory because they failed to develop the color completely within a reasonable length of time (e.g., 1 hour). This can probably be attributed to the low solubility of strong caustic soda in the pyridine reaction medium. Weak caustic soda solutions (e.g. 1%) developed the color rapidly, but unfortunately these colors did not follow Beer's law; that is, they did not show a proportionality between optical density and concentration. Furthermore the color intensity-concentration relationships did not exhibit a satisfactory day-to-day reproducibility. Medium strength caustic soda solutions (10-30%) showed the most satisfactory characteristics of any tested. The concentration chosen for all further work was 5 ml. of 20% sodium hydroxide solution to 10 ml. of pyridine and 1 ml. of xylene-TCE solution.

A study of the effect of variations in heating time and temperature on the color intensity produced showed that the best and at the same time the most convenient set of time and temperature conditions were 4½ ± ½ minutes at the temperature of boiling water. This temperature was chosen because it was the easiest to reproduce and keep constant. This heating time was chosen because it represents the time at which the maximum color intensity is produced at 475 mμ. and at which there is a minimum of variation of color intensity with heating time. This can be seen in Figure 2, a graph of color intensity vs. heating time.

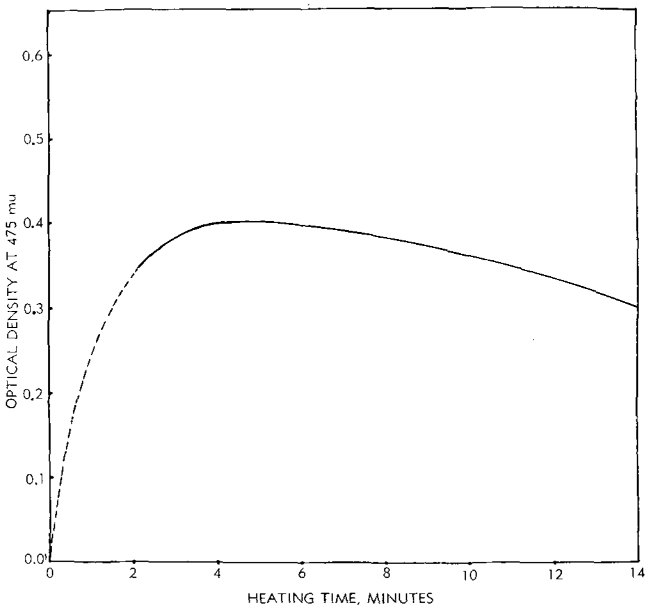

FIG. 2. Rate of color development with heating.

To compensate for possible variations in color produced due to small variations in heating time, temperature, or other minor conditions, a side-by-side standard is run with each group of unknowns developed and read. The TCE contents of the unknowns can then be calculated by direct proportionation of optical densities, provided that Beer's law applies. Figure 3 shows that Beer's law does apply in this reaction.

Figure 4 shows that the color produced in this reaction is stable for at least 10 minutes. This is sufficient time to measure the absorption of a number of samples. The color fades rapidly on contact with acid gases (CO_2, SO_2, etc.), and it is also somewhat light-sensitive so it is important to store the filtered solution in a clean, dry, stoppered cuvette, away from the direct light. The use of side-by-side standards serves to compensate for possible errors caused by fading since the fading rate is approximately constant.

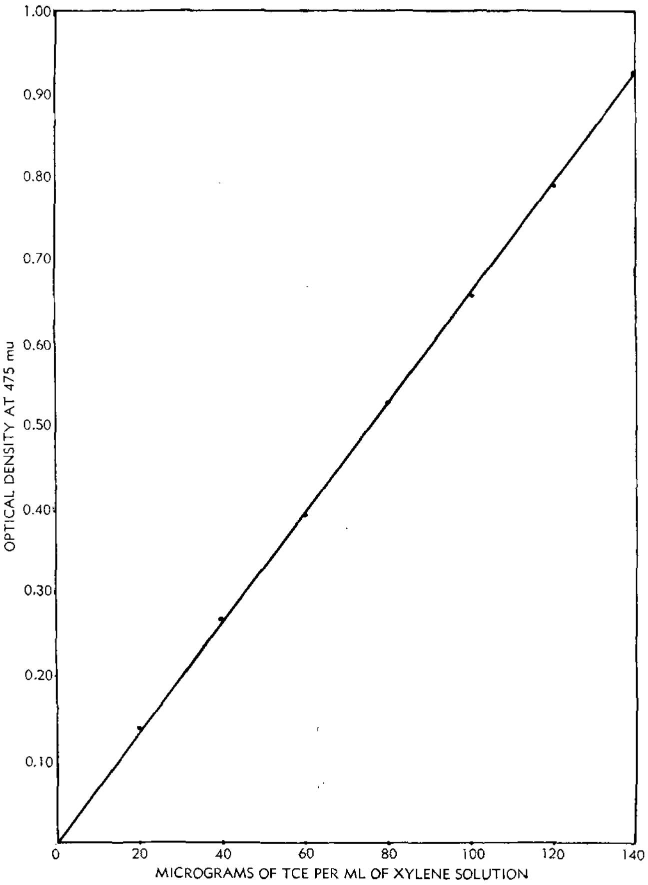

FIG. 3. Optical density—TCE concentration graph.

To complete the method an investigation was made of distilling rates and times. This investigation indicated that quantitative recoveries of added TCE could be obtained in one hour at a distillation rate of 20-30 drops per minute. To insure an adequate safety factor a minimum distillation time of 1.5 hours at the above rate was chosen for use in this method. These conditions were employed in all the subsequent work.

Table I lists the results found when a series of expressed and extracted (hexane) crude and refined oils, to which known amounts of pure TCE were added, were analyzed by the described method. Table II

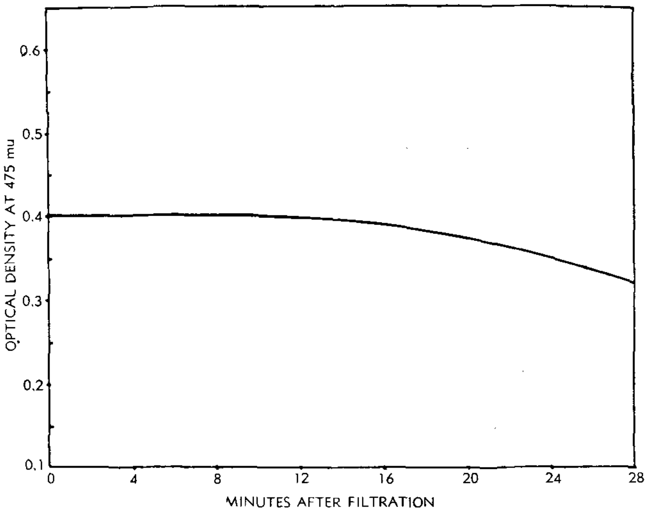

FIG. 4. Color fading with time.

TABLE I

Analysis of Cottonseed and Soybean Oils Containing Added TCE

Oil Sample	TCE Added, %	TCE Found, %
C/S Hydraulic—Crude	....	0.0002
C/S Hydraulic—Crude	0.0009	0.0010
C/S Hydraulic—Crude	0.0037	0.0037, 0.0038
C/S Hydraulic—Crude	0.146	0.147, 0.147, 0.153
C/S Hydraulic—Refined and Bleached	0.292	0.288, 0.285
C/S Hexane Extracted—Crude	0.073	0.074
C/S Hexane Extracted—Crude	0.583	0.60, 0.60
S/B Hexane Extracted—Crude	0.037	0.034, 0.035
S/B Hexane Extracted—Crude	0.073	0.070
S/B Hexane Extracted—Refined and Bleached	0.0073	0.0072
S/B Hydraulic—Crude	0.146	0.139

lists the results found when some TCE extracted oils were analyzed before and after the addition of known amounts of TCE.

Method

A. Apparatus:

1. All glass distilling apparatus consisting of
   a. Flask, Erlenmeyer, 500-ml. glass-stoppered.
   b. Distillation receiver, continuous return, 12.5 ml. capacity with 24/40 standard taper joints, Kimble No. 22009 or equivalent.
   c. Condenser, water cooled, with 24/40 standard taper, Allihn type preferred.
2. Hot plate, electrically heated and thermostatically controlled.
3. Buret, 50-ml.
4. Pipets, volumetric, 1-ml., 2-ml., 5-ml., and 10-ml.
5. Pipet, Mohr type, 10-ml.
6. Flasks, glass-stoppered, 25-ml., 50-ml., and 100-ml.
7. Test tube, 150 x 22 mm., glass-stoppered.
8. Graduated cylinder, 50-ml.
9. Funnel, 50 mm. diameter, short stem.
10. Filter paper, Whatman No. 41, 9.0 cm. diameter. Do not substitute.
11. Spectrophotometer, Coleman Model 6B. Set up, calibrate, and operate according to the manufacturer's instructions.
12. Cuvettes, round, 19 x 105 mm. matched, for use with Model 6B spectrophotometer.
13. Rubber stoppers to fit cuvettes.
14. Glass boiling beads.
15. Stopwatch.

B. Reagents:

1. Sodium hydroxide, A.C.S. grade.
2. Xylene, A.C.S. grade.
3. Pyridine, reagent grade. This reagent must be purified in the following manner before use to prevent high and erratic blanks. Reflux the reagent with about 2-3% of solid sodium hydroxide pellets in an all-glass apparatus for at least 1 hour, then distill into a clean, dry amber colored bottle, discarding about 5% at the beginning and at the end.
4. Trichloroethylene, reagent grade.
5. Sodium sulfate, anhydrous, A.C.S. grade.
6. Defoamer, Dow Corning Silicone Antifoamer "A."

C. Solutions:

1. Sodium hydroxide, 20% by weight.

D. Procedure:

1. Weigh 10 ± 0.05 g. of the sample into a 500-ml. Erlenmeyer flask. Add to this 10.0 ml. of xylene with a volumetric pipet. Finally add ca. 75 ml. of distilled water, 15-20 glass boiling beads and a small amount (ca. 10-20 mg.) of silicone defoamer.
2. Connect the flask to the distilling apparatus. Heat the contents of the flask to boiling on a hot plate and adjust the heating rate to maintain a distillation rate of 20-30 drops per minute. At this rate all of the xylene should distill into the side arm of the receiver in less than 30 minutes.
3. After about 30 minutes rinse down the inside of the condenser with five 1-ml. portions of distilled water added through the top.
4. After 90 minutes discontinue the distillation. Allow the distillate to cool to room temperature and transfer as much as possible of the xylene layer to a clean, dry test tube with the aid of a pipet.
5. Add ca. 0.5 gm. of sodium sulfate to the contents of the tube, stopper and shake vigorously until the xylene solution becomes clear. If it does not become clear after shaking for 2 minutes, add more Na_2SO_4 and repeat the shaking.
6. Transfer 1.00 ml. of the clear xylene solution to a clean, dry test tube with the aid of a volumetric pipet. If the trichloroethylene content of the sample is more than 0.012%, the color developed in D, 9 will be too dark to be measured. The xylene solution should then be diluted in the following manner before use. When the sample contains more than 0.012%, but less than 0.15%, dilute 2.00 ml. of the xylene solution to 25 ml. with reagent xylene. For samples containing up to 0.3%, 2.00 ml. should be diluted to 50 ml.; for those containing up to 0.6%, 2 ml. should be diluted to 100 ml. Treat 1.00 ml. of the diluted solution as if it were the original clarified xylene solution.
7. Transfer 1.00 ml. of one of the standard solutions of trichloroethylene in xylene, prepared as directed in F, 3, into another clean, dry test tube. The trichloroethylene concentration of the standard chosen should approximate that of the solution being tested as closely as possible.
8. Prepare a reagent blank by transferring 1.00 ml. of reagent xylene to another test tube.
9. With the aid of a buret, add 10.0 ml. of pyridine to each of the tubes prepared above. With a rapid delivery buret or pipet, add 5.0 ml. of sodium hydroxide solution to the contents of each of the test tubes. Stopper each and shake the set vigorously for about 15 seconds. Loosen the stoppers and place all of the tubes in a vigorously boiling water bath.
10. After 4½ ± ½ minutes, remove the tubes from the bath, loosen the stoppers and cool the solutions in an ice bath to below 25°C.
11. Remove and discard the lower (aqueous) layer from each of the tubes with a 10-ml. measuring pipet. It is not important if some of the upper layer is discarded as long as at least 7 ml. remain in the tube.
12. Immediately filter the colored (pyridine) solution remaining in the tube through a sheet of dry Whatman No. 41 filter paper. Catch the filtrate in a clean, dry 19-mm. cuvette. Stopper each with a clean, dry rubber stopper.
13. Measure the optical density of each solution, within 10 minutes after filtration, at 475 millimicrons with the instrument previously adjusted to read zero with a cuvette containing distilled water.

TABLE II

Analyses of TCE-Extracted Oils Before and After Addition of Known Amounts of TCE

Oil Sample	TCE, %		Recovered (net)
	Added	Total Found	
Crude S/B—"A"	....	0.0014	....
Crude S/B—"A"	0.0017	0.0030	0.0016
Crude S/B—"B"	....	0.0192	....
Crude S/B—"B"	0.0292	0.0487	0.0295
Crude C/S—"C"	....	0.071	....
Crude C/S—"C"	0.146	0.213	0.142
Crude C/S—"D"	....	0.074	....
Crude C/S—"D"	0.015	0.090	0.016

E. Calculations:

$$\text{Trichloroethylene, \%} = \frac{D \times E\,(A - B)}{20 \times (C - B)}$$

A = Optical density of the sample solution as determined in D, 13.

B = Optical density of the reagent blank solution, as determined in D, 13.

C = Optical density of the standard solution, as determined in D, 13.

D = Milligrams of trichloroethylene per ml. of standard solution.

E = Volume in ml. to which 2-ml. portion is diluted in D, 6. E = 2 when no dilutions are made.

F. Standard Solutions:

1. Weigh 5.000 ± 0.001 g. of trichloroethylene into a 100-ml. volumetric flask. Dilute to volume with xylene and mix thoroughly.
2. Pipet 5.00 ml. of solution F, 1 into a 100-ml. volumetric flask. Dilute to volume with xylene and mix thoroughly.

This solution contains 2.5 mg. of trichloroethylene per ml.

3. Pipet 1.00, 2.00, 3.00, 4.00, and 5.00 ml. of solution F, 2 into a series of 100-ml. volumetric flasks. Dilute each to volume with xylene and mix thoroughly. These standard solutions contain 0.025, 0.050, 0.075, 0.100, and 0.125 mg. of trichloroethylene per ml. respectively.

General Remarks

The addition of a defoamer to the distillation mixture has been found necessary because certain of the oils, especially crude soybean oils, foam excessively during the distillation. Silicone Antifoamer "A" proved to be the best of the defoamers tested for this purpose.

Some filter papers have been found to bleach the orange colored pyridine solution to a yellow. This is thought to be due to the presence of free acid in the paper. A number of lots of Whatman No. 41 filter paper have been tested to date, and all have been found to be quite satisfactory.

While this method has been written for the use of a Coleman Model 6B spectrophotometer, it is thought likely that any colorimeter might be used satisfactorily. A modified form of this method, employing a Cenco-Sheard-Sanford photelometer, has been in operation for more than a year now.

It is thought probable that this method could be modified to cover the determination of TCE in many other materials beside oil, such as meals, tissues, air, etc.

Summary

An accurate method for determining small amounts of trichloroethylene in vegetable oils has been presented. The method employs a distillation procedure to separate the trichloroethylene from the oil and a colorimetric procedure based on the Fujiwara reaction to determine the trichloroethylene in the distillate. The method has been tested on known samples of crude and refined soybean and cottonseed oils varying in trichloroethylene content from 0.001% to 0.6% with excellent results.

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Solvent Extraction for the Oil Mill Superintendent[1]

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BEING directly in charge of operations, the oil mill superintendent is usually held accountable for operating results. Success or failure is easily, and continuously, measurable; since he is held responsible, the esteem with which the superintendent is held by his management is a reflection of his mill's record. Accordingly, in operating a process, or in selecting one for future operation, decisions are usually made by taking the course believed to provide the most favorable answer to the question "How will it affect my results?" Theoretical aspects are given consideration only when they would appear to have immediate bearing on this question.

The success of a solvent extraction mill superintendent may be measured by the degrees to which he attains the following goals:

1. Maintain continuous seven-day operation at full capacity.
2. Manufacture and ship finished products of uniform quality, a quality which is at least acceptable, and preferably superior to that of competing products.
3. Obtain optimum yields of oil and meal.
4. Operate with minimum solvent loss and utility requirements.
5. Operate safely.

It will be seen that these goals are not at all peculiar to the superintendent of an oil mill. If, instead of the words oil and meal, we use the term finished products; and if, instead of solvent loss and utility requirements, we use the term operating costs or direct costs, then these same five goals could be, and are, used by the superintendent of almost any process plant. In the same way the general methods for reaching these goals are similar in all cases.

This paper will be confined to an extraction plant of the standard type. The seed enters the process, is prepared by cracking, adjustment of temperature, and moisture content, and is flaked. Oil may or may not be removed by prepressing. After preparation the flakes are extracted, and the solvent removed from the extracted oil and the spent flakes.

The oil mill superintendent is then concerned with the five goals as they apply to this process.

1. *Maintaining continuous seven-day operation.* In particular, the procedure for maintaining continuous seven-day operation is similar for any type of plant. The superintendent who does not yet have a plant should be given the opportunity by his management to examine the available processes very critically. Common sense and general operating experience will enable the superintendent to determine the points of greatest stress. He should insist that bearing loads are acceptable, that conveyors are adequately designed, and that the equipment selected is rugged and well constructed. The superintendent who is now operating a plant can do much to reduce down time and achieve 24-hour, seven-day operation by systematic study of the causes of breakdowns. It often will be found that a comparatively few weak points in the plant are responsible for a large percentage of the down time.

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