

1954

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Lionel K. Arnold  
*Iowa State College*

George Burnett Jr.  
*Iowa State College*

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### Recommended Citation

Arnold, Lionel K. and Burnett, George Jr. (1954) "The Determination of Small Amounts of Trichloroethylene in Soybean Oil Meal," *Proceedings of the Iowa Academy of Science*, 61(1), 210-216. Available at: <https://scholarworks.uni.edu/pias/vol61/iss1/24>

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## The Determination of Small Amounts of Trichloroethylene in Soybean Oil Meal

By LIONEL K. ARNOLD AND GEORGE BURNETT, JR.

In a previous paper before the Academy (1) Hollowell and the senior author presented a method for determining small amounts of trichloroethylene in soybean oil and soybean oil meal based on the reaction of Fujiwara (5) and Ross (8) and previous work by Gilchrist at Iowa State College (7). The method is based on the observation that pyridine and certain halogenated hydrocarbons react in the presence of sodium or potassium hydroxide to produce a characteristic pink to red color. The intensity of color, between certain limits, is proportional to the concentration of the chlorinated hydrocarbon, all other variables held constant.

Since the color developed in this reaction is not stable, standards made from inorganic colored solutions were used. Another development was the use in the duPont method of colored glass standards. This method is more complicated since the trichloroethylene is stripped from the oil by steam distillation and collected in toluene before applying the pyridine and sodium hydroxide. A similar method is described by Snell and Snell (9).

All of the above procedures are limited in accuracy since they depend upon the accuracy of the color standards used and the ability of the investigator to compare the unknown with these standards. An obvious improvement would be to determine the color intensity by means of a colorimetric instrument such as a photoelectric colorimeter or a spectrophotometer and convert the instrument readings directly to percent trichloroethylene by suitable calibration curves. A modification of the duPont method for trichloroethylene in oil in which the color is determined by a spectrophotometer has been developed by Eisdorfer and Mehlenbacher (4).

### COLOR DEVELOPMENT

The work reported in this paper was the development of a method for the determination of trichloroethylene in soybean oil meal in which the intensity of the color developed by the pyridine-sodium hydroxide was determined by a colorimeter.

Little similarity existed between the methods used by the previous investigators to develop the pyridine-sodium hydroxide color.

All agreed, however, that a period of heating was required to fully develop the color and, with two exceptions (1, 7), that the reaction should be slowed by rapid cooling prior to making the color reading. This same pattern of heating and cooling was followed in the photoelectric method.

Gilchrist (7) found in his work that pyridine-sodium hydroxide stock solution could be prepared by thoroughly mixing together at room temperature 10 grams of sodium hydroxide dissolved in 100 ml. of distilled water and 100 ml. of pyridine. When this is done, the upper pyridine layer increases in volume to approximately 135 ml. and after a 24-hour stabilization period, can be used alone to produce the Fujiwara color reaction. The two layers should not be separated so long as the reagent is being used. In the procedure actually used by Gilchrist, as in all previous investigations, the aqueous alkali solution and the pyridine were added separately. A procedure using the single reagent was found to be more convenient and to give more reproducible results.

To insure uniform heating, the method first used by Cole (2)

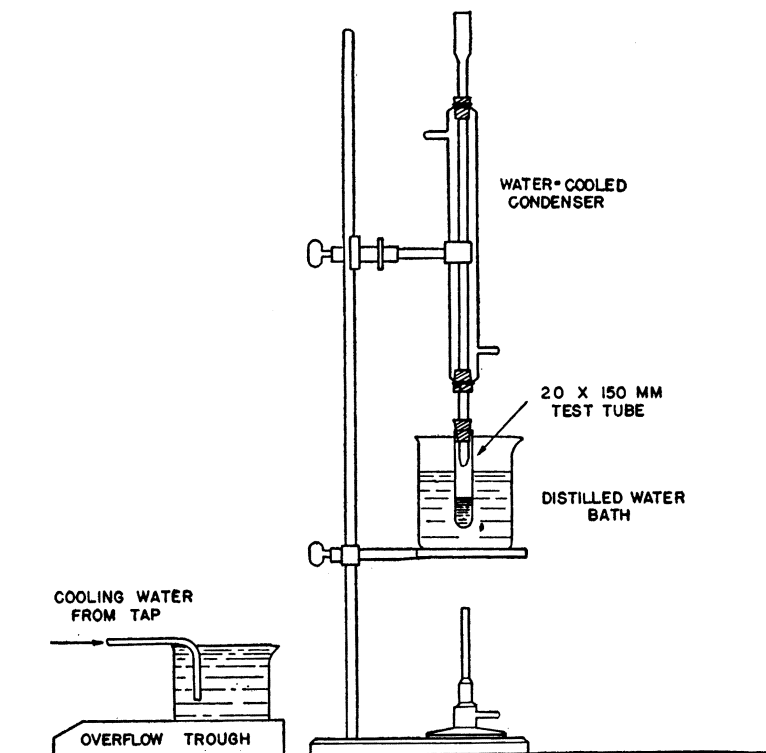


Figure 1. Pyridine-Sodium Hydroxide Test Apparatus.

of heating the reagents and unknown in a test tube in a bath of boiling water was adopted. Losses from the tube to the atmosphere during the heating period were prevented by immediately attaching the tube to the lower end of a small vertical water-cooled condenser. At the end of the heating period, the tube, still attached to the condenser, was rapidly removed from the hot water bath and lowered into a beaker into which tap water was continuously flowing. A uniform cooling period of 1 minute was early found to be adequate to slow the color reaction. The arrangement of the equipment is shown in Figure 1.

Four different periods of heating were investigated, viz., 60, 90, 120 and 150 seconds. It was found that the amount of color developed increased with the time of heating, approaching a maximum very slowly. A plot of color development vs. time gave a pattern approximating that of a first-order reaction. As a result of these tests, a heating period of 120 seconds, or two minutes, was selected as giving a nearly maximum amount of color development in the range of concentrations for which the test remains sensitive.

#### CALIBRATION CURVE

In photometric methods, results can be obtained with a minimum of calculation if a calibration curve is constructed in which the concentration of the unknown is plotted against some function of the transmittance as measured by the instrument being used. If this is done on rectangular coordinates using the logarithm of the transmittance, and Beer's Law holds, the result will be a straight line. On some colorimeters, such as the Klett-Summerson photoelectric colorimeter (Model 900.3) used in this work, a logarithmic scale is used which gives readings that are directly proportional to the concentration of the substance being determined.

Figure 2 is the calibration curve developed for trichloroethylene in which the net scale reading was plotted directly against concentration. Beer's Law was observed to hold up to concentrations of approximately  $230 \times 10^{-6}$  grams trichloroethylene per ml. The curve was determined using standard trichloroethylene solutions, a filter with a transmission range between 400 and 450 millimicrons, and the analytical procedure described later. The solutions were prepared by dissolving known amounts of the solvent in ethyl alcohol and diluting to solutions of lesser concentration. The trichloroethylene was weighed in a sealed glass capillary which was broken beneath the surface of a known volume of ethyl alcohol. The resulting curve is accurate only for the instrument for which it was prepared.

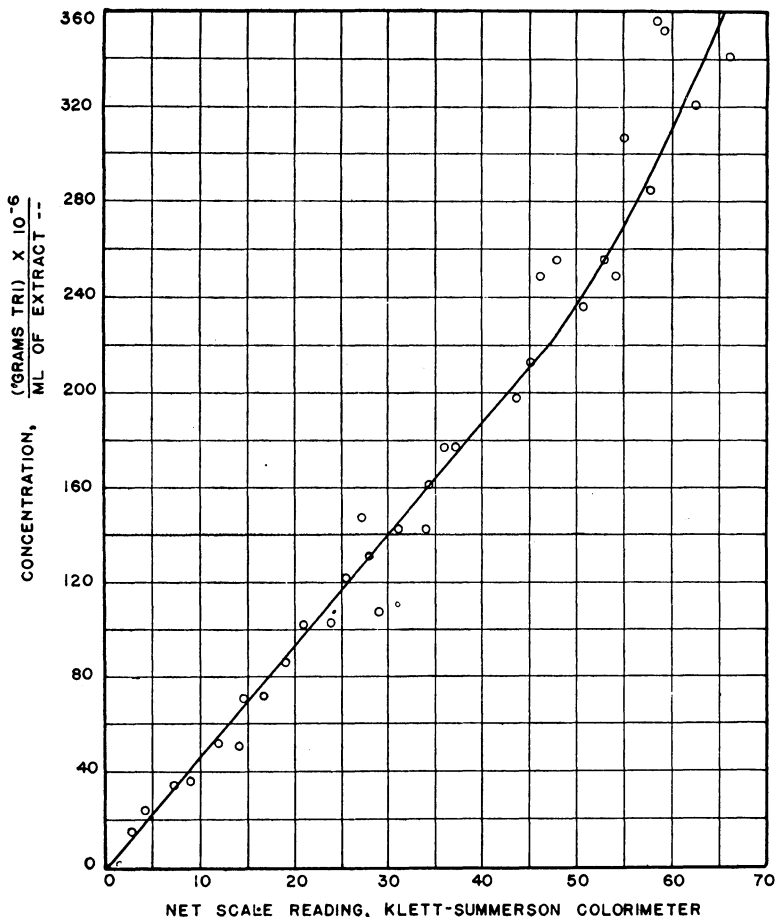


Figure 2. Calibration Curve Trichloroethylene in Ethyl Alcohol (Blue Filter Used).

PROCEDURE

The following method was adopted for the colorimetric determination of trichloroethylene in soybean oil meal. Ethyl alcohol was used as the extracting solvent to recover the residual trichloroethylene from the meal.

1. Weigh out approximately a 5 gram sample of meal in a 50 ml. glass stoppered bottle. Immediately after weighing, add 25 ml. of ethyl alcohol.
2. Allow 1 hour with occasional shaking for complete extraction of the trichloroethylene from the meal. This time may vary with the condition of the meal and should be verified by rechecking until a constant value is obtained.
3. Add 1 ml. of the ethyl alcohol extract to 5 ml. of the pyridine-sodium hydroxide reagent in a 20x150mm. test tube. Immediately attach to the lower end of a small vertical water-cooled condenser and immerse in a bath of boiling water.

4. Exactly 2 minutes after adding the extract, remove the tube from the boiling water and lower it into a bath of running tap water (approximately 20°C) while still attached to the condenser. The time of heating is very critical.
5. Allow 1 minute in the cold water bath for cooling. During this time pour 7 ml. of pure ethyl alcohol down the condenser to dilute the color developed in the tube and to wash out the condenser.
6. At the end of the cooling period, remove the test tube from the condenser and pour its contents into a standard Klett-Summerson colorimeter tube. Mix the contents thoroughly by inverting the tube several times and read immediately in the colorimeter with the instrument zeroed on distilled water. Record this value as the total reading.
7. Prepare a reagent blank in exactly the same manner as the unknown except that 1 ml. of pure ethyl alcohol is added in place of the extract.
8. Determine the color throw from the soybean oil meal by adding 12 ml. of pure alcohol to 1 ml. of extract in a third colorimeter tube. Mix and read in the colorimeter. Subtract the instrument reading for pure ethyl alcohol to obtain the color throw.
9. Subtract the value of both the reagent blank and the color throw from the total reading to obtain the net reading. This corresponds to the color actually developed by the pyridine-sodium hydroxide reagent reacting with the trichloroethylene in the extract.
10. Read the concentration in grams trichloroethylene per ml. of extract from the calibration curve for the net reading obtained. Multiply this value by 25 and divide by the sample weight in grams to obtain the p. p. m. of trichloroethylene in the original meal sample.

The above procedure can be greatly simplified if the color throw reading does not vary significantly from sample to sample and thus can be assigned a constant value. The colorimeter can then be zeroed on the reagent blank and the total reading obtained in step 6 will represent the net reading plus the constant color throw value. Subtracting the latter value, one can then go directly to the calibration curve and read off the corresponding trichloroethylene concentration.

When commercial hexane was tried as the extracting solvent, not all of the residual trichloroethylene present was recovered. This was verified by the fact that when a standard solution of trichloroethylene in hexane was added to meal which had been extracted with a non-chlorinated solvent, a portion of the trichloroethylene present appeared to react in some manner with the meal, the amount thus unaccounted for increasing with time. This did not occur when similar tests were carried out using standard solutions of trichloroethylene in ethyl alcohol.

#### OTHER APPLICATIONS

When compounds other than trichloroethylene were subjected to the pyridine-sodium hydroxide test, it was discovered that the color reaction occurred with a much wider variety of materials

than those first reported by Ross (8). Table I contains a list of those compounds found to produce the characteristic pink to red color. The compounds are arranged in order of decreasing activity, those at the lower end of the table producing color only when the pure compound is used.

**Table I**

Halogenated Hydrocarbons Sensitive to the Pyridine-Sodium Hydroxide Test

<i>Number</i>	<i>Compound</i>
1	Trichloroacetic Acid
2	Monochloroacetic Acid
3	Chloroform
4	Trichloroethylene
5	Tetrachloroethane
6	Bromoform
7	Carbon Tetrachloride
8	Bromobenzene
9	Dichloroethylene
10	Methylene Chloride
11	Perchloroethylene
12	Iodoform
13	Methylene Bromide
14	Pentachloroethane
15	Monoiodobenzene
16	Benzene Chloride

The following compounds when subjected to the test gave, instead of red, shades of yellow to brown: benzal chloride, methyl iodide, methyl bromide, ethylene bromide, methylene iodide, and ethylene chloride. The following gave no color: ethylene chlorohydrin, flourobenezene, methyl chloroform, hexachloroethane, methylamine hydrochloride, and dimethylamine hydrochloride.

The test may also be applied to other carrier materials than soybean oil meal. An example is the determination of residual trichloroethylene in soybean oil. In this application, the oil is dissolved in the extracting solvent (ethyl alcohol is satisfactory) along with the trichloroethylene and carried through the color reaction. A necessary precaution is that the oil be free of fatty acids which will saponify in the alkaline pyridine reagent and contaminate the color solution.

#### SUMMARY

An improved method for the determination by the Fujiwara reaction of amounts of trichloroethylene in soybean oil meal from about five parts per million upward has been developed. It involves the following: extraction of the meal by ethyl alcohol, addi-

tion of pyridine-sodium hydroxide reagent to the extract, heating to develop color, cooling, and reading color intensity in a photoelectric colorimeter. This method is also adaptable to certain other chlorinated hydrocarbons and other carrier materials.

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CHEMICAL ENGINEERING DEPARTMENT

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