International Chemical Union

Minutes of Meeting of International Commission on Fats and Oils. Part III. London, England, July 1947

Translated by C. L. Hoffpauir of Southern Regional Research Laboratory,* New Orleans, Louisiana.

THIS translation gives the minutes of the meeting in London during July 1947, incorporating the decisions made on the unified international methods and the plans for collaborative work to be done before the next meeting of the Commission. Methods under discussion included those for the sampling and analysis for moisture and oil specified for several oil-bearing seeds. They also included those for alkalis and rosin in soaps and those for soluble and insoluble volatile acids and sterols in fats and oil, also for the determination of thiocyanogen and peroxide numbers in fats and oil. The organization of and representation on the present International Commission on Fats and Oils are also given.

SUPPLEMENT II_6

Preparation of Lead Thiocyanate

Dissolve 250 grams of C. P. lead acetate [$Pb(C_2H_3O_2)_2 \cdot 3H_2O$] in 500 ml. of distilled water. In another vessel dissolve 250 grams of potassium thiocyanate. The lead thiocyanate is precipitated and collected on a Buechner funnel. It is washed with distilled water, alcohol, and finally with ethyl ether. The thiocyanate is dried as completely as possible by drawing air through the mass and finally is transferred to a porcelain dish and kept in a desiccator over P_2O_5 for 8-10 days. The lead thiocyanate so prepared is greenish or yellowish white. If it is highly colored it is rejected. The reagent precipitated under these conditions should not be kept more than two months.

Preparation of Anhydrous Acetic Acid

Acetic acid is best dehydrated by boiling with acetic anhydride under a reflux condenser. Two liters of pure acetic acid (99.5-100%) and 100 ml. of acetic anhydride (99-100%) are placed in a 3-liter flask, in the neck of which is suspended a large test tube through which cold water circulates and which serves as a condenser. This mixture is heated for 3 hours at approximately 135°C. by use of an oil bath and with reflux cooling. After the anhydrous acid has cooled to room temperature it is poured into well dried bottles having glass stoppers.

SUPPLEMENT II_7

Preparation of Lead Thiocyanate

A solution of 25 grams of lead acetate in 50 ml. of water is filtered and poured with stirring into a filtered solution of 25 grams of ammonium thiocyanate (or potassium thiocyanate) in 50 ml. of water. The precipitate is filtered, dried by suction, and then washed with a little glacial acetic acid and a little acetic anhydride. The lead thiocyanate is placed in a glass-stoppered bottle along with 450 ml. of acetic acid. The flask is kept in the dark for at least 6 days with occasional shaking.

Note: The acetic acid used is glacial acetic acid mixed with about 2% of acetic anhydride and distilled, rejecting the first fraction. The acetic anhydride is a recently distilled pure product.

*One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

SUPPLEMENT II_{8a}

Thiocyanogen Number

Reagents:

1. Acetic Acid. Commercial glacial acetic acid is purified by boiling under reflux for 3 hours with 10% acetic anhydride and then by distillation over phosphoric anhydride.
2. Lead Thiocyanate. Preparation is given in Supplement II_6.
3. Bromine. Dry by agitation with concentrated sulfuric acid.

Preparation of N/5 Thiocyanogen Solution: To prepare 1 liter of solution, 50 grams of dry lead thiocyanate is suspended in 500 ml. of anhydrous acetic acid and 5.1 ml. of bromine is added to another 500-ml. portion of dry acetic acid. Two ground glass-stoppered flasks of 2- to 3-liter capacity are well cleaned and dried for containing these solutions. The solution of bromine is slowly poured in small portions into the suspended lead thiocyanate. The mixture is shaken vigorously after each addition until completely decolorized. After all the bromine is added, allow the precipitate to settle and immediately filter as rapidly as possible. A Buechner funnel (13 cm. diameter), qualitative filter paper, and two suction flasks which have been dried in an oven at 105°C., are used for the filtration. The whole solution is first filtered by suction into the first flask. The funnel is then placed in the second flask, and the solution is filtered again. After the second filtration the solution should be perfectly clear. The solution is then poured into a colored flask having a ground glass stopper and stored in a cool place at 15-21°C.

Determination of Thiocyanogen Number: A sample of 1.0 to 0.3 gram of oil is weighed into a well dried ground glass-stoppered 125-ml. Erlenmeyer flask. Add 25 ml. of the thiocyanogen solution with a pipette and allow to stand in the dark for 24 hours. The temperature of the room in which the flask is kept should be 18 to 21°C. The weight of sample taken depends on the thiocyanogen number to be obtained. The excess of thiocyanogen must be at least equal to 100% and at most equal to 150% of the weight of the oil though a larger excess does little harm. After 24 hours one gram of dry powdered potassium iodide is added and the flask shaken for 2 minutes. It may be desirable to shake the test for 3 minutes. A mechanical shaker as used with iodine numbers is very convenient. Then add 30 ml. of distilled water and titrate with N/10

solution of thiosulfate using starch as an indicator.

At least three analyses should be made on each sample. The solution should also be titrated after 24 hours. If the difference in titration is more than 0.2 ml. for the blank test, the solution decomposed too fast and the values obtained are too low.

SUPPLEMENT II_{7a}

Thiocyanogen Number

Reagents:

Acetic acid
Acetic anhydride
Lead thiocyanate

See Supplement II_7.

Bromine, analytical reagent.

Preparation of Thiocyanogen Solution: The quantity of lead thiocyanate resulting from the preparation in Supplement II_7, placed in 450 ml. of acetic acid and 50 ml. of acetic anhydride, is usable after about six days. Then add 1.8 ml. of bromine drop by drop, agitating until the liquid is decolorized after each addition. The solution is filtered on a dry double filter into a dry glass-stoppered flask. It can be used for 10 to 14 days.

Determination of Thiocyanogen Number: Accurately weigh 110-500 mg. of the fatty material into a dry ground glass-stoppered flask. Add 25 or 50 ml. of the thiocyanogen solution and shake until the fat has completely dissolved. Store in the dark for 24 hours at a temperature of 15-20°C. Run a blank determination, omitting the sample, at the same time. After 24 hours add 10 ml. of a solution of potassium iodide (approximately 16.5%) and titrate the liberated iodine with N/10 solution of thiosulfate.

Letting: P=weight of fat sample,
a=ml. of thiosulfate for blank,
b=ml. of thiosulfate for sample, and
N=normality of thiosulfate.

The thiocyanogen number is $\frac{a - b}{P} \times N \times 126.9$

SUPPLEMENT II_8

Thiocyanogen Number

Reagents:

As in Supplement II_{8a}.

Carbon Tetrachloride. Shake carbon tetrachloride twice with concentrated sulfuric acid (5% by volume for each operation). Wash it with water and follow with a washing with a 50% solution of potassium hydroxide (5% by volume for each washing). Dry with solid potassium hydroxide and distill from phosphoric anhydride.

Preparation of Thiocyanogen Solution: Suspend 50 grams of lead thiocyanate in 500 ml. of a mixture of equal volumes of acetic acid and carbon tetrachloride. Dissolve 5 ml. of bromine in another 500 ml. of the same mixture and add this solution a little at a time to the first solution with vigorous agitation until the color disappears. Filter rapidly on a Buechner. Make two filtrations on the same filter. The solution should then be clear and colorless. It can be kept for several days in ordinary ground glass-stoppered flasks stored in the dark.

Determination of Thiocyanogen Number. Same procedure as given in Supplement II_{8a}.

SUPPLEMENT II_9

Peroxide Number—Cold Method

Pass a current of pure dry carbon dioxide through 10 ml. of chloroform in a 250-ml. ground glass-stoppered flask for several minutes. Without interrupting the current of carbon dioxide, introduce the accurately weighed analytical sample of the fatty material (about 1 g.). After the sample has dissolved, add 15 ml. of glacial acetic acid and 1 ml. of a saturated solution of pure potassium iodide. The current of carbon dioxide is then interrupted, the flask stoppered and left for 5 minutes. At the end of this period add 75 ml. of water, shake vigorously and titrate the liberated iodine with N/100 solution of thiosulfate.

SUPPLEMENT II_{9a}

Peroxide Number—Cold Method

Conduct the operations as in Supplement II_9 but allow the flask to stand for one hour instead of for 5 minutes before the final titration is made.

SUPPLEMENT II_{10}

Peroxide Number

Place 10 ml. of chloroform containing approximately 1 gram of fat in a test tube. Immediately add 15 ml. of glacial acetic acid and approximately 1 g. of finely powdered pure potassium iodide. Bring to boil immediately and continue boiling for 3 minutes. Cool rapidly in a stream of water. The contents of the tube are poured into a flask containing 75 ml. of distilled water. Shake vigorously and titrate the liberated iodine with a N/100 solution of thiosulfate.

SUPPLEMENT II_{11}

Determination of Percentage of Neutral Oil

1. Determine the average molecular weight of the fatty acids of the oil by preparing the insoluble fatty acids (see Unified International Methods) and then by titrating an analytical sample of 5 grams dissolved in neutral alcohol with N/1 alkali.
2. Determine the acidity of the fatty material to be analyzed.
3. Then calculate the true acidity and subtract from 100 to obtain the percentage of neutral oil (+ unsaponifiable).

SUPPLEMENT II_{12}

1. Determine the acid number. Call it I_A.
2. Determine the saponification number. Call it I_S.
3. Calculation:

$$\frac{I_S - I_A}{I_S} = \text{Neutral oil} + \text{unsaponifiable (approximately)}$$

SUPPLEMENT II_{13}

Dissolve 5 g. of fatty material in 50 ml. of 95% ethyl alcohol in a separatory funnel. It is exactly neutralized in the presence of phenolphthalein with N/1 alcoholic potassium hydroxide. Taking into account the volume of alcohol, add to the separatory funnel enough water to reduce the alcohol concen-

tration to 50%. Extract both neutral oil and unsaponifiable with petroleum ether as in the method for the determination of unsaponifiables (see Unified International Methods).

SUPPLEMENT II_{14}

Determination of Neutral Fatty Material Mixed with Fatty Acids

The solution of the fatty material in ethyl ether is passed through a column of aluminum oxide. All the neutral fatty material and the unsaponifiables pass through the column. The fatty acids are adsorbed. The neutral fats and the unsaponifiables are recovered.

Apparatus: A glass tube, approximately 1.8 cm. in diameter and 30 to 40 cm. long, is drawn at one end to a diameter of 0.6 cm. The tube is mounted vertically on a support, with the drawn out end at the bottom. Place a small plug of defatted cotton in the neck of the drawn out end to serve as a support of the column of alumina. Fill the column within 10 cm. of the top of the tube. This upper portion of the tube serves as a reservoir which is filled by means of a funnel. The cotton plug can be replaced by a fritted glass disk. The liquid passing through the column is received in a flask.

Aluminum Oxide: Aluminum oxide suitable for adsorption chromatographic analysis is used. It can be obtained from Savory and Moore Ltd. or from the British Drug House Ltd. in England. The oxide is previously colored blue with bromothymol blue in order to locate the position of the region of adsorption of the fatty acids on the column. In this region the blue turns yellow. The preparation is obtained by impregnating aluminum oxide with a 3% alcoholic solution of bromothymol blue. The excess liquid is removed by drainage. The powder is then spread out on a hot plate. The drying is terminated at about 100°C. Mix a sufficient quantity of this strongly colored oxide with colorless oxide to obtain a faint but distinct blue tint.

Method: Aluminum oxide so prepared is suspended in ethyl ether and poured into the tube with care, preferably with the aid of a funnel. The oxide distributes itself uniformly and is packed gently. The column should be about 20 cm. high. It is necessary that it be covered with solvent at all times so that the upper surface is not exposed to the air. Approximately one gram of the fatty material is accurately weighed and dissolved in 50 to 80 ml. of ether. When the ether which initially covers the alumina has been drained to about 3 cm. above the free surface of the column, the solution of fatty material is added and passes through the alumina. When the level of the solution is not more than 3 cm. above the free surface of the column, add in portions, preferably numerous, 150 c.c. of ether to wash the column. About 5 cm. at the lower end of the column of alumina must not have changed color at the end of the washings.

The ether solution is concentrated by distilling the major portion of the solvent and then drying and weighing to obtain the weight of neutral oil and unsaponifiable matter contained in the analytical sample. The aluminum oxide can be reactivated in a satisfactory manner after use by evaporating the solvent with which it is impregnated and heating at 500°C. for three hours. After several reactivations part of the alumina is powdered too fine for good percolation through a column. It can be separated from this part by screening on a 325-mesh sieve. The alumina retained on the sieve can then be re-used. Chloroform can be used as a solvent instead of ethyl ether.

Styrenated Drying Oils

H. M. SCHROEDER and R. L. TERRILL, Spencer Kellogg and Sons inc., Buffalo, N. Y.

STYRENE, first isolated over 100 years ago, has now become a readily available industrial chemical. The synthetic rubber program made necessary by World War II involved styrene production on the order of 400 million pounds per year. While large quantities will be consumed in the synthetic rubber and plastics industries, it is evident that styrene will be available for other purposes. One interesting application of the compound has been in the production of styrenated drying oils.

There are many references in the literature to reactions of drying oils with unsaturated hydrocarbons, including styrene and other vinyl compounds. Some of these references are very old, and most of the proposed methods yielded heterogenous products. About 1930 the possible reactions of styrene with drying oils began to attract considerable attention. Polystyrene was already well known but had been demonstrated to have serious deficiencies as a coating material, principally poor adhesion, brittleness, and incompatibility with other ingredients.

One of the first methods proposed for reacting styrene with a drying oil comprised polymerization of an aqueous emulsion of styrene and tung oil with hydrogen peroxide as a catalyst (1); the products were similar to factice. The next development was the disclosure of methods for polymerizing styrene with film-forming materials (including drying oils) in the presence of inert solvents (2). This principle of reaction in solvents was extended in several British patents (3) to include copolymerization of styrene with partially polymerized oils, frosting drying oils (tung and oiticica), and dehydrated castor oil. The function of solvents was presumably to establish reaction control in order to obtain useful clear copolymers.

When copolymerizing in the presence of solvents, the residual styrene odor was found to be very pronounced, and further processing of copolymers was not possible without removing the bulk of the solvent. The possibility of reacting styrene with drying oils by the mass or bulk polymerization method was in-