NOTICE

Standard Crude Glycerin Samples

In 1929 the Soap Section undertook the preparation and analysis of a Standard Crude Glycerin to be used as a check on the accuracy of such analyses in commercial transactions. Sixteen laboratories participated in the analytical work in which an almost unbelievable accuracy was attained. A four-ounce bottle of this Standard Crude Glycerin, with its accepted analysis by International Standard Methods printed on the label, may be obtained from Mr. J. C. P. Helm, 509 Tchoupitoulas Street, New Orleans, Louisiana, at a cost of only one dollar.

This notice is to emphasize the availability of these Standard Crude Glycerin samples, and even if your laboratory has had no difficulty in check analyses, the Standard should be on hand for check purposes in the event of controversies. Also, for those who are striking glycerol balances in the operations of their crude and refinery plants, such a standard should be of inestimable value.

ABSTRACTS

Oils and Fats

Edited by

M. M. PISKUR and RUTH LINDAHL

The spoilage of fats and oils. The Kreis reaction and its carrier. Richard Neu. *Chem.-Ztg.* 73, 733-36 (1937).—Neu reviews the literature on the subject of rancidity of fats, giving a bibliography of 36 references. He presents a new method for carrying out the Kreis test which yields a clear solution of the epihydrin-aldehyde-phloroglucinol condensation product. This solution, it is claimed, can be used directly for spectrographic analyses. The method is as follows: "Two cc. of the fat to be examined are placed, drop by drop, on 10-12 grams of granular silica gel contained in a porcelain dish about 5 cm. in diameter. (Standard Gel of the Silica Gel G.M.B.H., Berlin was used.) The fat is added in such a manner that absorption of the gel takes place immediately without wetting the walls of dish more than necessary. When this has been carried out correctly (which can be done with ease) one obtains a granular material which is then placed in a calcium chloride tube, a piece of glass wool having previously been placed in the base of the bulb. The upper part of the tube is then closed with a cork containing a glass tube of 1-2 mm. diameter, bent at right angles to the tube containing the sample. The bottom of this tube, which is drawn out to a fine capillary, dips in a 0.2% solution of phloroglucinol (prepared by dissolving 0.2 gm. pure phloroglucinol in 100 ml. of alcohol or of 20% HCl). The tube containing the sample may be cooled with cold water. The amount of phloroglucinol solution used is varied according to the degree of decomposition of the sample under examination, the volume being varied so that a color of sufficient depth for spectrographic examination is obtained (that is, the absorption band must be visible). In general, cells of sufficient width and permitting lengthwise examination are used, or one may use the absorption vessels recommended by Baly or Pulfrich. A vigorous stream of moist hydrochloric acid vapor is then passed down through the tube. The moist HCl stream is obtained by passing a stream of CO_2 which has been dried by conc. H_2SO_4 through a wash flask containing 25 cc. of conc. HCl (sp. gr. 1.18) and through a drying tower containing pumice stone which has been soaked in conc. HCl. Shortly after the stream has begun to pass through the tube, the solution at the bottom becomes more or less colored, depending upon the degree of decomposition of the sample. It is well to cool the absorption flask with ice water. The solution will be absolutely clear and show no traces of fat droplets even after bubbling the gas through for 1½ hours. The colored solutions can be examined directly in a spectroscope. The colors are stable for 1 hour. It is important, however, that the specified amounts of HCl be adhered to strictly, as otherwise stability of color is adversely influenced and the condensation may not be complete." Neu points out that the merit of this method lies in the large surface of fat which is exposed by adsorption on silica gel. He calls attention to the fact that no photographs of the adsorption bands of rancid oils have been published and fills the gap in the literature by supplying two spectral photographs covering rancid olive oil, C_6—C_{10} fatty acids, and epihydrin aldehyde.

Cooked butter. W. Ritter. *To be published in Deutsche Lebensm. Rundschau.* Ritter discusses several phases of the manufacture of cooked butter in Switzerland. (1) *Methods of Manufacture:* The usual process for preparation of cooked butter consists in removing the water by evaporation; in this process the buttermilk constituents settle out in insoluble form and the fat can be easily separated. Other processes separate the fat at temperatures below 50°C. by allowing product to stand and then separating the fat. In the first process, a fat insoluble residue which can be used for feed preparation is obtained. In the latter process, a watery layer which is useless is obtained. (2) *Changes During Cooking:* The butter first melts and a cloudy system is produced. When boiling begins a strong foam usually forms, later giving way to quiet boiling. The mixture soon clarifies with temp. rising to 105-110°C. A second foam develops which in some instances turns brown. The residue which separates is sometimes coarse and flocculent and at other times fine and crystalline. (3) *Lecithin in Cooked Butter:* Cooked butterfats, which have been obtained by separation at low temp. (below 50°C.), contain no lecithin, while those obtained by boiling contain lecithin. It appears that the lecithin at first goes into the insoluble residue from which it is later dissolved into the fat at the higher temperatures and toward the end of the process. (4) *Water Content of Cooked Butter:* Due to solubility of water in butterfat, it is practically impossible to reduce moisture below 0.1%. Moisture is an important consideration in rust which develops in tin cans containing the cooked butter, and in autoxidation of the fat. (5) *Differences Between Melted and Cooked Butter:* "Melted" butter is fat removed at low temperature and "cooked" butter is that removed by boiling or evaporation of water. Melted butter usually has the odor of the raw material

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from which it is derived, while cooked butter has the typical odor of this product. Cooked butter, due to its lecithin content, browns on heating while melted butter becomes white. Cooked butter has better keeping qualities due to removal of the watery phase and its content of food materials for bacteria. (6) *Cooling the Liquid Fat:* Ritter discusses graininess of fat and the conditions which give rise to fine-grain and coarse-grain products. Following method is suggested for obtaining a fine-grain fat: First cooling to 30-33°C., then inoculating with solid fat and stirring vigorously at this temp. for some time. After this the product can be cooled further. A fat of this character will remain plastic at ordinary temps. and will not melt down. (7) *Experience with Market Samples:* Ritter states this product has met with favorable acceptance in Switzerland. Most complaints have concerned themselves with tallowy flavors and have most frequently been associated with corrosion of the tin container in which the product is packed.

Rendering economy. *Natl. Prov.* **97**, 23, 41 (No. 16), (1937). A description of the plant of the Joplin Rendering Co., Joplin, Mo.

Refining fats. H. Schmalfuss. *Fette u. Seifen* **44**, 292-6 (1937). Several methods are recommended for refining various oils. Several limiting characteristics are suggested for food oils and fats.

Report on the problem of disclosing new German oil sources. 1. Grape oil. H. P. Kaufmann and H. Fiedler. *Fette und Seifen* **44**, 286-9 (1937). A brief monograph on grape seed is given. The oil content of grape marc was 14.2-14.8. The oil characteristics were: acid no. 0.83-2.01, sapon. no. 198-195.9, I no. 103.6-137.8, (SCN) no. 61.2-76.1 and (OH) no. 3.3-12.2. Various treatments of marc were attempted to increase the oil content of the seeds.

Oat flour improves keeping quality of fatty fish. J. M. Lemon, M. E. Stansby and C. E. Swift. *Food Indus.* **9**, 576-7, 583 (1937). The authors pointed out that oxidative rancidity of the oil in salt mackerel is a problem concerning the keeping quality of the fish. Several tests on oat flour treatment of salt mackerel were carried out with favorable results. This work parallels similar work previously reported, on lard, bacon, potato chips, nuts, salad dressing and packing materials for fat contg. foods.

Report on the colorimetry of fatty oils. VI. H. Heller. *Angew. Chem.* **50**, 752-3 (1937). Polemic. The author did not obtain the various color reactions as described by Jesser and Thomae on soybean oil by treatment with acetic acid anhydride or the treatment with arsenic trichloride. Heller reports a color reaction of bright green changing to an emerald green then to deep green for acetic anhydride test and an olive green to violet to deep red for the arsenic trichloride test. Jesser and Thomae reported there was blue to a dirty deep greenish brown for the acetic acid anhydride test and red to green to black for the other. Heller maintained that the test does not definitely distinguish soybean oil from several other oils. **Reply to the report of Dr. Heller.** H. Jesser and E. Thomae. *Ibid.* 753 (1937). Jesser and Thomae repeated the test on several com. soybean oil samples and samples of oil which according to Heller gave similar color reactions. They reaffirmed the results in their first report stating that soybean oil can be detected by color reaction with acetic acid anhydride and H_2SO_4.

Shortening properties of plastic fats. A. W. Harvey. *Ind. Eng. Chem.* **29**, 1155-9 (1937). The shortening values of com. plastic fats as well as some shortening products prepd. in the laboratory were compared by the use of the Bailey shortometer and by subjective eating tests on pastry specimens and by appearance of cakes made with the fats.

The fatty oil from the seeds of Valerianella Olitorea. Poll. Alph. Steger and J. Van Loon. *J. Soc. Chem. Ind.* **58**, 298-300T. (1937). Seed kernels of *Valerianella olitorea,* Poll. contain 38.7% oil, shell, 4%; the kernel is 29.4% of the seed. The characteristics of the kernel oil are n^{70}/d 1.4582, iodine value, Wijs 144.9, thiocyanogen value 84.2, sapon. value 190.5, acid value 3.7 and $d^{78}/4$ .8800, unsapon. 1.2. Compn. of the oil is unsapon. 1.2, glycerol as C_3H_2 4.2, volatile and insol. products 1.8, saturated acids 11.5, oleic acid 18.0, linoleic acid 52.7, and linolenic acid 10.6.

Vitamin A content of cod liver oil. A comparison of spectrophotometric and chemical methods. A. D. Holmes, F. Tripp and G. H. Satterfield. *Ind. Eng. Chem., Analyt. Ed.* **29**, 456-7 (1937). The vitamin A potency of thirty-two samples of cod liver oils was detd. by the Hilger vitameter E value and the antimony trichloride Blue value methods. A comparison of the results obtained by the 2 methods indicated that in general they were of the same order. The oils that gave high E values also gave the lowest Blue values. The Blue value: E value ratio was between 9.0:1 and 11.0:1 for the majority of the samples under consideration. The fatty acid content of an oil has no direct relationship to the amt. of red color or yellow color produced by the action of the antimony trichloride soln. of the oil. The results obtained for free fatty acid and unsaponifiable material showed that the amt. of free fatty acid and unsapon. material present in an oil is not correlated with its E value or Blue value; there is no consistent relationship between the vitamin A potency and the free fatty acid or unsapon. material present in cod liver oils.

The composition of the liver fats of some New Zealand farm animals. T. P. Hilditch and F. B. Shorland. *Biochem. J.* **31**, 1499-1515 (1937). The phosphatide and "glyceride" constituents of the liver lipoids of ox, cow, pig and sheep have been studied in detail. Survey of the available data together with the results of the present investigation establishes that liver phosphatides are characterized by the presence of increased proportions of stearic, C_{20} and C_{22} unsatd. acids together with diminished proportions of hexadecenoic acid, as compared with the corresponding liver "glycerides." A marked tendency of liver phosphatides as compared with liver glycerides to contain acids of higher mol. wt. is also shown. Bromination studies established that linoleic acid is not present in detectable amt. in cow and ox liver fatty acids resp., although traces of this acid are found in the pig and sheep liver

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fatty acids. The presence of linolenic acid in sheep liver fatty acids is also recorded.

Molecular distillation. State of the vitamins in certain fish liver oils. K. G. D. Nickman. *Ind. & Eng. Chem.* **29**, 1107-11 (1937). Fish oils are composed chiefly of fatty triglycerides which evaporate in the mol. still between 190° and 250°C. The small fraction which distills below 190°C. contains some hydrocarbons, the free fatty acids, and the uncombined portions of the sterols and vitamins. The fraction is relatively larger from oils rich in vitamins and sterols; and crude oils yield more of low-boiling distillate than do refined oils. A single distillation of a fish oil can effect a concn. of the vitamins varying from 5 to 50 times.

Methods for the production of oils from fish livers of low oil content. II. A note on a modified digestion process. H. N. Brocklesby and K. Green. *Prog. Rpts. of Pacific Biol. Sta. and Pacific Fisheries Exptl. Sta.* 1937, No. 33, 7. It was disclosed that the bulk of com. halibut livers landed at Pacific Coast ports undergoes considerable autolysis with subsequent developments of free fat acids in the oil. Analysis of the wash water used in refining showed that a certain amt. of vitamin A was retained either by the soapy water itself or by small traces of emulsified oil. The wash waters were extd. by mixing with a quantity of cod liver or similar oil equal to half the original oil. By using the counter current principle, wherein the first extn. is carried out with oil already fortified with vitamin A from previous extns., practically all the vitamin A remaining in the wash liquors may be economically recovered. Oils contg. 40,000 International units or more of vitamin A may be produced.

Fish as a source of vitamins A and D—herring, brisling, and their products. G. Lunde, v. Aschehoug and H. Kringstad. *Ind. Eng. Chem.* **29**, 1171-5 (1937). Fresh, smoked and canned brisling (*Clupea sprattus*) and herring caught in different localities in different yrs. were tested for their vitamins A and D potency. Data on brisling, herring body and herring liver oils were resp., 8-64, 2-38, and 3,600-11,000 International units (I. U.) vitamin A per g. and 70-140, 90-150 and—— I. U. of vitamin D per g. Data on canned brisling and canned kippered herring are 90-960 and 50-60 I. U. vitamin A per 100 g. with 1,000-3,000 and 840-2,000 I. U. vitamin D per 100 g. With brisling no loss of vitamins A and D resulted from the smoking, canning processes or storage of canned product. With herring body oil vitamin A is not affected by the smoking process but is decreased by the canning process; the vitamin D content was unchanged by the processes.

Fatty livers in the goose produced by overfeeding. E. Flock, J. L. Bollman, H. R. Hester and F. C. Mann. *J. Biol. Chem.* **121**, 117-29 (1937). Very large and fatty livers and a greatly increased amt. of depot fat may be produced in the goose by forced feeding of a high carbohydrate diet. This fat is definitely more satd. than normal, the liver fat being even more satd. than the depot fat. The increased saturation is not due to a shift in the usual proportions of liquid and solid fatty acids. Fatty livers may develop spontaneously in geese when the marked increase in blood fats associated with the egg-laying season occurs. Though very fatty, these livers remain approx. normal in size. The I nos. of the fatty acids in the liver were lower than those of the depot fat, but the difference in saturation was not as marked as in the vigorously stuffed birds.

The liver lipids in normal dogs on different types of fat, with and without added lecithin. S. H. Rubin, C. H. Present, and E. P. Ralli. *J. Biol. Chem.* **121**, 19-26. The results of lipid analyses of the livers of 33 normal dogs by a microgravimetric technique are reported. When divided into 5 classes, according to the type of fat added to the basal diet, the total lipids and the individual lipid fractions, except for the I nos. of the total fatty acids, show no statistically significant differences among the classes.

In vitro digestion of fats. N. N. Dastur and K. V. Giri. *Proc. Soc. Biol. Chem. India* **1**, 40-1 (1937). The rates of hydrolysis of various substrates by castorseed lipase are in the decreasing order: butterfat (I) (cow and buffalo), coconut (II), sesame (III), and groundnut oils (IV). With pancreatic lipase (pH 12.6) I was the most slowly hydrolyzed substrate, but at pH 9.3 it was rapidly digested. The rates of hydrolysis of I and II but not of III or IV are markedly accelerated in presence of Na taurocholate. The kinetics of the hydrolysis of I and other oils have been examd. (*Chem. Abs.*)

An effect of choline on the vitamin B—sparing action of fats. E. W. McHenry. *Biochem. J.* **31**, 1616-21 (1937). The increase in wt. of young rats is influenced by the amts. of vitamin B_1, choline and fat in the diet and the effects of these three dietary factors are probably interrelated. When a diet deficient in vitamin B_1 is fed the inclusion of more than 26% fat prevents a serious loss in wt. The effect of the fat is augmented by the addn. of choline to the diet. Under the latter conditions, the optimum amt. of dietary fat has been found to be about 40%. When vitamin B_1 is supplied and choline is deficient in the diet the amt. of dietary fat optimum for wt. increase ranges between 10 and 26%.

Research on the polymerization of fat. 1. The heat polymerization of drying fat. H. P. Kaufmann, J. Baltes and H. Buter. *Fette u. Seifen* **44**, 289-92 (1937). Data presented give the changes in characteristics (I no., SCN no., and diene no.) of wood oil, oiticica oil and linseed oil with time of polymerization.

Swelling of drying oil films in water. J. Rinse and W. H. G. Wiebols. *Ind. Eng. Chem.* **29**, 1149-54 (1937). A method is described for measuring the swelling of thin coating films in water with an accuracy of 1 to 2%. The superiority of tung oil over linseed oil for underwater application is confirmed quantitatively. Linseed oil films (raw and bodied) absorb more water when Pb driers are present, less when Mn is present, and least with Co. The influence of the driers on tung, oiticica, and Synourin oil films is just the opposite—i. e., Pb films show the least and Co films the greatest swelling. A possible explanation of this phenomenon may be based on the 2 principal processes during film formation—i. e., polymerization and oxidation. Polymerization dominates when conjugated

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double bonds are present, as in tung, oiticica and Synourin oil, and probably Pb is the best catalyst. Oxidation is more important in the film formation of linseed oil and is probably speeded up most by Co. When only Pb is present, which does not promote oxidation so rapidly, the linseed oil film dries slowly and remains more hydrophilic.

PATENTS

Flesh or fish meal. H. Wielrath. Ger. 646,922, Cl. 53g 4.02. Drying and rendering of flesh and fish is carried out in the vapors of a solvent having a b.p. greater than water and immiscible in water as halogenated hydrocarbons. The material and solvent are boiled together until the b.p. rises to that of the solvent.

Fatty oils and fats. K. Ludecke. Ger. 647,219. Cl. 53h 1.01. The fat or oil content of green seeds can be increased by grinding the seeds, mixing with carbohydrates (sugar) with or without some salts ($MgSO_4$, Na_2CO_3, etc.), and allowed to stand 15-50 days. The material is then dried and the fat extd. The fat obtained is appreciably greater than that contained in the original seeds and is acid free.

Antioxidant. D. P. Grettie (to Industrial Patents Corp.). U. S. 2,095,740. Lard is stabilized by addn. and incorporation therewith of a quantity of a distillate secured by the deodorization of hydrogenated sesame seed oil.

Fats and oils. J. McKee. U. S. 2,083,572. Oleaginous oils and fats of a sp. gr. of less than .970 are heated under diminished pressure without access to air to raise the sp. gr. to about .975 and then ozone is passed there through to ozonize the oils. The oils are used for medicinal purposes.

ABSTRACTS

soap

Edited **by M. L. SHEELY**

Modern views on the washing of textiles and the constitution of the new washing agents. A. Chwala. *Monatsh. Seide Kunstseide* 42, 268-9 (1937). In dil. solns. soaps exhibit a linear dependence of elec. cond. upon concn. At a certain concn. a sudden break occurs and the cond. decreases. This characteristic behavior of soaps and similar substances is due to the formation of micelles. Various washing agents affect differently the establishment of equil. in the 4 stages: (1) complete dissocn. of soaps into large colloid anions and small cations, (2) aggregation of the large ions to preliminary micelles, with simultaneous mach. and electrostatic union of the small ions, (3) further aggreation with the formation of ion micelles of higher stability, and (4) absorption of dissociated soap particles by the neutral particles and elec. charging of the latter. (*Chem. Abs.*)

Spraying Technic. Bert Thomas. *Seifensieder-Ztg.* 64, 466-7 (1937). A no. of practical suggestions as to the proper technic of spraying-drying washing agents are given. (*Chem. Abs.*)

Visible Action of Sodium Lauryl Sulfate on Microorganisms. Milward Bayliss. *J. Lab. Clin. Med.* 22, 700-4 (1937). Na lauryl sulfate in a diln. of 1:320 clears cultures of Gram-neg. organisms grown in liquid media in 1 hr. Vibrios are cleared by dilns. up to 1:2560 and pneumococci by dilns. of 1:5120. Streptococci and most other Gram-pos. bacteria remain unchanged. The clearing is accompd. by a marked increase in the viscosity of the media, indicating that parts of the bacterial cells have become dispersed. (*Chem. Abs.*)

Separating Petroleum Emulsions. *Chemical Industries,* 41, 264 (1937). The separation of water-in-oil emulsions, such as are produced by oil wells, has been the subject of extensive investigation, and among the numerous methods proposed, the addition of chemical dehydration compounds seems to be most attractive. The following summary of an article, "Chemical Methods for Separating Petroleum Emulsions," by Ir. G. W. Baron Van Dedem M. I., page 65, August 12, 1937, Oil and Gas Journal, lists his conclusions:

1. It is necessary to possess analysis of the edgewater of every separate drilling project in an oil field, indicating the quantities of carbonate, bicarbonate, weak organic acids, sulfate, the total hardness and the pH value.

2. It is necessary to know the titration curve and the pH value of optimum, emulsion breaking effects of the dehydration compounds to be considered. This optimum value must be in line with the pH of the salt water.

3. For Alkaline water with high pH, which ordinarily also contains little alkaline earth salts, the neutral soaps of oleic acid, solid fatty acids, liquid saturated fatty acids, linoleic acid, etc., depending upon the pH and the alkaline earth content of the salt water, should be applied.

4. For alkaline water with lower pH, preferably buffered with bicarbonate, neutral or weakly acid ricinoleate, as pure as possible, has to be considered (eventually also other oxyacids, and perhaps also resin soaps). Instead of ricinoleate, either subject to a purification process or not, more economical results can often be obtained with ordinary Turkey-red oil with the sulfonate group esterified and loosely linked.

5. For more acid water, one should consider the soaps of naphthenic acids, preferably having a low sulfate content, and the more stable fatty acid, alcoholic, or aromatic sulfonates and the petroleum sulfonates, having a higher sulfate content, provided these are