completely precipitated with ammonium molybdate when treated in the manner described by the present A.O.C.S. method for phosphate. Phosphates of this type are hydrolyzed to the "ortho" form when boiled steadily for 15 minutes in a nitric acid solution.

2. Silicates interfere with the determination by occluding phosphates if during dehydration they are heated at too high a temperature.

3. The volumetric method for the estimation of phosphate is more rapid than the gravimetric method, and yields results which are reliable and reproducible to within 1.5%.

4. The method will determine total P_2O_5 but will not differentiate between the different types of phosphate. It is convenient where only one type of phosphate is present. For mixtures of phosphates additional specific analyses must be employed.

REFERENCES:

1. Cobbs, Soap, 14, No. 11, 24 (1938).
2. Gillet, Soap, 15, No. 1, 24 (1939).
3. Gerber and Miles, Ind. Eng. Chem., Anal. Ed. 10, 519, 1938.
4. Pemberton, Chem. News, 46, 4 (1882); J. Am. Chem. Soc., 16, 278 (1894). See also Methods of Analysis of the Ass'n. of Off. Agric. Chem., 3 ed., 16, (1930); Hildebrand and Lundell, Applied Inorganic Analysis, 567, (1929); Scott's Standard Methods of Analysis, 697 (1939).
5. Shimer, Chem., Eng. 6, 197 (1907); J. Am. Chem. Soc., 27, 287 (1909).

The Pharmacology of Soaps
The Irritant Action of Refined Oil Soaps on Human Skin

By BYRON E. EMERY and LEROY D. EDWARDS*

THIS laboratory undertook sometime ago the study of the irritant action of soaps on human skin. The first papers ([1]), dealing with the irritant action of soaps made from single fatty acids and single alkyl sulfates, were presented at the Atlanta meeting of the American Pharmaceutical Association (August 1939), and are to be published in the Journal of that organization. The same method of application of the soaps, as described in these earlier reports, has been used in this subsequent work on soaps of refined oils.

Sources of Refined Oils

The refined oils, sweet almond, castor, corn, linseed, palm, palm kernel (denatured), peanut, poppyseed, rapeseed, sesame, and soya were obtained from Eimer and Amend, New York. Cocoa butter, coconut, cod liver, cottonseed and olive oils were secured from the School of Pharmacy, W.R.U. Raisin seed oil was supplied by the California Products Co., Fresno, Calif. Avocado pear oil was purchased from the Mefford Chemical Co., Los Angeles, Calif. Beef suet was purchased from a meat market and the fat rendered.

TABLE I.
THE PHYSICAL-CHEMICAL PROPERTIES OF 5% SOAP SOLUTIONS OF SINGLE REFINED OILS

	State of 5% Soap Solution		pH at 28°C.	
Refined Oil	Na	K	Na	K
Almond	L	L	10.3	10.1
Avocado pear	L	L	9.3	9.4
Beef suet	G	G	10.5	10.7
Castor	L	L	9.5	9.7
Cocoa butter	G	G	10.8	11.1
Cocoanut	L	L	10.2	10.4
Cod liver	L	L	10.0	10.4
Corn	L	L	10.1	10.4
Cottonseed	L	L	10.0	10.5
Linseed	L	L	10.3	10.3
Olive	L	L	10.2	10.4
Palm	G	G	gel (too thick)	10.5
Palm kernel	L	L	10.3	10.4
Peanut	L	L	10.1	10.5
Poppyseed	L	L	10.0	10.3
Raisin seed	L	L	9.3	9.5
Rape seed	L	L	10.3	10.5
Sesame	L	L	10.3	10.5
Soya bean	L	L	10.3	10.4

L = Clear liquid G = Gel

The Preparation of Soaps of Refined Oils

The U.S.P. XI methods were used for the determination of the saponification value and the preparation of free fatty acids of the oils.

The following method was used for the preparation of the neutral soaps. Approximately 150 grams of an oil, accurately weighed, was added to one liter of 95% alcohol in a two-liter pyrex flask connected to a reflux condenser. The calculated amount of 6N NaOH was added to the boiling alcohol-oil mixture, and the whole allowed to reflux for one hour. At this point the mixture was tested for the completeness of saponification and for excess alkali. The saponification was considered complete when the soap from 5 cc. of the hot mixture produced a clear solution with 50 cc. of hot distilled H_2O. The soap formed was considered a neutral soap when 5 cc. of the hot mixture diluted with 50 cc. of previously neutralized alcohol, containing phenolphthalein, produced a pink color which was discharged by one drop of 0.05N HCl. The soap was dried in a pyrex flask at the temperature of a boiling water bath under the vacuum produced by a water aspirator. The soap, after it had reached a gel state due to the distillation of the alcohol, was transferred to a press which made ribbons of the soap approximately 0.5 mm. in thickness and 5 mm. in width. The soap was then dried for 5 hours under the above conditions. The potassium soaps were made in a similar manner. Some physical and chemical properties of the 5% soap solutions of the oils are given in Table I.

Skin Results of Soaps of Refined Oils

The results on human skin of the 5% solutions of neutral soap prepared from the refined oils are listed in Table II.

*From the Department of Pharmacology, School of Medicine and the School of Pharmacy, Western Reserve University, Cleveland, O.

TABLE II

Results of 5% Refined Oil Soap Solutions on Human Skin

(22 Males — 5 Females)

Sodium Soap of Refined Oils	Total + M.	Total + F.	Total ± M.	Total ± F.	Total + and ± Results M.	%	F.	%	Combined Results M & F	%
Almond	1	0	1	0	2	9.1	0	0	2	7.4
Avocado	0	0	2	0	2	9.1	0	0	2	7.4
Beef suet	1	0	0	0	1	4.5	0	0	1	3.7
Castor	3	3	11	1	14	63.5	4	80	18	66.6
Cocoa butter	0	1	1	0	1	4.5	1	20	2	7.4
Coconut	2	4	9	0	11	50.0	4	80	15	55.5
Cod liver	0	0	0	0	0	0	0	0	0	0
Corn	0	0	0	1	0	0	1	20	1	3.7
Cottonseed	0	2	2	1	2	9.1	3	60	5	18.5
Linseed	1	1	2	1	3	13.6	2	40	5	18.5
Olive	0	0	4	0	4	18.2	0	0	4	14.8
Palm	1	1	3	0	4	18.2	1	20	5	18.5
Palm kernel	5	2	5	1	10	45.4	3	60	13	48.1
Peanut	2	0	0	1	2	9.1	1	20	3	11.1
Poppyseed	0	1	0	0	0	0	1	20	1	3.7
Raisin	0	2	2	0	2	9.1	2	40	4	14.8
Rape seed	2	2	0	2	2	9.1	4	80	6	22.2
Sesame	1	1	1	0	2	9.1	1	20	3	11.1
Soya bean	0	1	1	0	1	4.5	1	20	2	7.4
Potassium Soap of Refined Oils										
Almond	0	1	1	0	1	4.5	1	20	2	7.4
Avocado	3	1	3	0	6	27.2	1	20	7	25.9
Beef suet	0	1	1	0	1	4.5	1	20	2	7.4
Castor	5	2	8	1	13	59.0	3	60	16	59.2
Cocoa butter	0	1	5	2	5	22.7	3	60	8	29.6
Cocoanut	9	2	2	1	11	50.0	3	60	14	51.8
Cod liver	1	3	2	0	3	13.6	3	60	6	22.2
Corn	0	0	0	0	0	0	0	0	0	0
Cottonseed	3	2	9	1	12	54.5	3	60	15	55.5
Linseed	1	1	4	1	5	22.7	2	40	7	25.9
Olive	2	0	2	1	4	18.2	1	20	5	18.5
Palm	0	0	4	2	4	18.2	2	40	6	22.2
Palm kernel	7	2	2	1	9	40.8	3	60	12	44.4
Peanut	0	1	4	1	4	18.2	2	40	6	22.2
Poppyseed	1	0	1	1	2	9.1	1	20	3	11.1
Raisin	2	1	5	0	7	31.8	1	20	8	29.6
Rape seed	0	0	0	1	0	0	1	20	1	3.7
Sesame	0	1	1	0	1	4.5	1	20	2	7.4
Soya bean	0	1	1	0	1	4.5	1	20	2	7.4

If there was irritation five minutes after the conclusion of the test and this irritation remained for more than two hours (irritation was determined by the presence of redness, itching, pain or any other damage to the epithelium layer), the result was recorded as "plus." "Plus-minus" if irritation was present but disappeared in two hours, and "minus" if no irritation was noted. These results were obtained on 22 males and 5 females. It is admitted that these numbers must be increased before any final conclusions can be drawn.

The oils, based on the present results, may be listed in order of decreasing irritant action as follows:

Sodium Soaps

Females: castor, coconut, rape, cottonseed, palm kernel, linseed, raisin, cocoa butter, corn, palm, peanut, poppyseed sesame, soya. (No reaction: almond, avocado, beef suet, cod liver and olive.)

Males: castor, coconut, palm kernel, olive, palm, linseed, almond, avocado, cottonseed, peanut, raisin seed, rape. sesame, beef suet, cocoa butter, soya. (No reaction: cod liver, corn, and poppyseed.)

Combined Males and Females: castor, coconut, palm kernel, rape, cottonseed, linseed, palm, olive, raisin seed, peanut, sesame, almond, avocado, cocoa butter, soya, beef suet, corn, poppyseed. (No reaction: cod liver.)

Potassium Soaps

Females: castor, cocoa butter, coconut, cod liver, cottonseed, palm kernel, linseed, palm, peanut, almond, avocado, beef suet, olive, poppyseed, raisin seed, rape, sesame, soya. (No reaction: corn.)

Males: castor, cottonseed, coconut, palm kernel, raisin seed, avocado, cocoa butter, linseed, olive, palm, peanut, cod liver, poppyseed, almond, beef suet, sesame, soya. (No reaction: corn and rape.)

Combined Males and Females: castor, cottonseed, coconut, palm kernel, cocoa butter, raisin seed, avocado, linseed, cod liver, palm, peanut, olive, poppyseed, almond, beef suet, sesame, soya, rape. (No reaction: corn.)

The Na and K soaps based on the combined results on males and females in their order of decreasing irritant action, are as follows: Na castor, K castor, Na coconut, K Cottonseed, K coconut, Na palm kernel, K palm kernel, K cocoa butter, K raisin seed, K avocado, K linseed, K peanut, Na rape, K cod liver, K palm, Na cottonseed, Na linseed, Na palm, K olive, Na olive, Na raisin seed, Na peanut, Na sesame, K poppyseed, Na almond, Na avocado, Na cocoa butter, Na soya, K almond, K beef suet, K sesame, K soya, Na beef suet, Na corn, Na poppyseed, K rape. (No reaction: Na cod liver and K corn.)

Discussion of Results and Conclusions

From the results of the irritant action of the soaps of pure fatty acids on skin ([1]), it would be expected that soaps of oils containing lauric and myristic acids or both of these acids should be more irritant than the soaps of oils not containing these acids. This was found to be true in the case of the oils of coconut, palm, palm kernel, cottonseed and avocado. These oils produced irritant soaps in an approximate order of their lauric and myristic acid content. The most striking observation is that castor oil soaps are the most irritant soaps of the soaps of refined oils studied. This oil, composed almost entirely of the mild ricinoleic acid, does not contain, based on present day methods, any of the more irritant soap acids. The irritant action of castor oil soaps is unexplainable at this time. Many unknown factors may be the cause of this difference in irritant action between ricinoleic and castor oil soaps, e.g., presence of unknown fatty acids, effect of one or more acids on the solubility and hydrion concentration of the resultant mixtures, double bond effects in the chain, effects of isomerism and double bond hydroxy effects. In general, the K soaps are more irritant than Na soaps, but there are exceptions in the work to date. Females for most soaps are more subject to irritation than males. As noted above, more work must be done on simpler mixtures of fatty acids before any final conclusions can be drawn as to the relative irritant action of these soaps of refined oils.

(1) Emery, B. E. and Edwards, L. D., Jour. A. Ph. A., to be published.

The Use of Standards in the Control of Soap Plant Operations

By W. A. PETERSON
COLGATE-PALMOLIVE-PEET CO., JERSEY CITY, N. J.

IN ESTABLISHING a system of controls over the operation of soap plant processes, the use of standards constitutes a most effective method for providing the plant superintendent with information vital to maintaining high efficiency of operation and minimizing wastages of materials.

The application of standards is not a new idea. Most plants, small or large, have some sort of operating controls. Many of these, however, have never been examined critically to determine whether they are based on adequate facts and sound reasoning and thus represent the best practice after all factors have been considered, or whether they are merely traditional; handed down "from father to son," with their original basis obscure. Arbitrary standards, which rest on nothing but an opinion, have little positive value. In many cases economic conditions, equipment and methods within a plant change so that what were good standards a few years ago may be economically unsound today.

Standards may be used to control many phases of plant operations, for example:

1. The output of processing units, such as soap kettles, soap dryers, glycerine evaporators, stills, etc.
2. The loss of materials, such as caustic soda, salt, fats and glycerine during processing.
3. The quality of products.
4. The efficiencies of packing units, such as soap presses, wrappers, chip filling machines, etc.
5. The labor and controllable burden costs of various unit operations.
6. The wastage of packing materials used in finishing operations, such as wrappers, cartons, containers, etc.
7. The amount of allowable scrap in operations such as bar soap cutting and pressing, spray soaps, etc.

A good standard should be a measure of the normal performance to be expected under good operation. It must never be set so high that it is rarely attained, for under such conditions foremen and operators soon get discouraged and lose interest. Rather, the standard should be designed so as to reveal losses of efficiency or materials that can definitely be traced to improper operating technique, time delays, poor mechanical equipment, poor materials, and other causes that should not exist, or at least should be tolerated only within known limits.

It is also obvious that standards should never be set by merely taking an average of past performance. Intelligent studies of each operation, by personnel thoroughly familiar with the processes and equipment involved, are required. It is sometimes necessary, when the person assigned to this work is inexperienced in the particular process he wishes to standardize, for him first to learn the operations by working on them long enough to get his basic information "first hand." He must avoid the danger of taking anything for granted. For example, an operation may have been done in a certain way for many years, but this could mean no more than that no one ever questioned it. A natural tendency among new operators is to accept what the former operator tells him. Perhaps this former operator did not understand the process as well as he should have and passes along this misinformation to the new-comer. The person seeking to examine the process for standardization purposes must have sufficient experience and judgment to sift the information so as to retain the facts and discard the rest.

To illustrate, let us consider a few of the standardizable operations listed above. Inasmuch as conditions may vary greatly from one plant to another, due to differences in types of equipment used and products made, there may be no universal standards applicable to all conditions. It would be misleading to assign numerical values to them in a general discussion such as this. Therefore, the examples given will illustrate principles and methods as being the most important part of the subject, and will be confined to considerations of the first two groups listed, as applied specifically to two of the important processing divisions of a soap plant, namely, the kettle room and the glycerine refinery.

Capacity Standards:

In the kettle room, the value of a standard for the output of a given number of kettles is two-fold; first, it establishes the maximum "normal" capacity of the plant and avoids the otherwise all too frequent differences of opinion on this point. Second, when the full plant capacity is not required, a steam economy may be gained by reducing the number of kettles in active use, thus decreasing radiation losses.

In setting a standard for the capacity of a kettle room, one must determine the fair minimum number of hours required to perform all of the boiling operations, eliminating from consideration all unnecessary delays, such as excess loss of time waiting for the delivery of raw materials from another department (fats, rosin, salt, caustic), failure of mechanical equipment (pumps, pipe lines, valves, etc.). To this must be added the minimum settling time necessary to yield kettle soap of the desired quality, and the fair minimum time necessary to deliver the settled soap to the next operation and prepare the kettle for