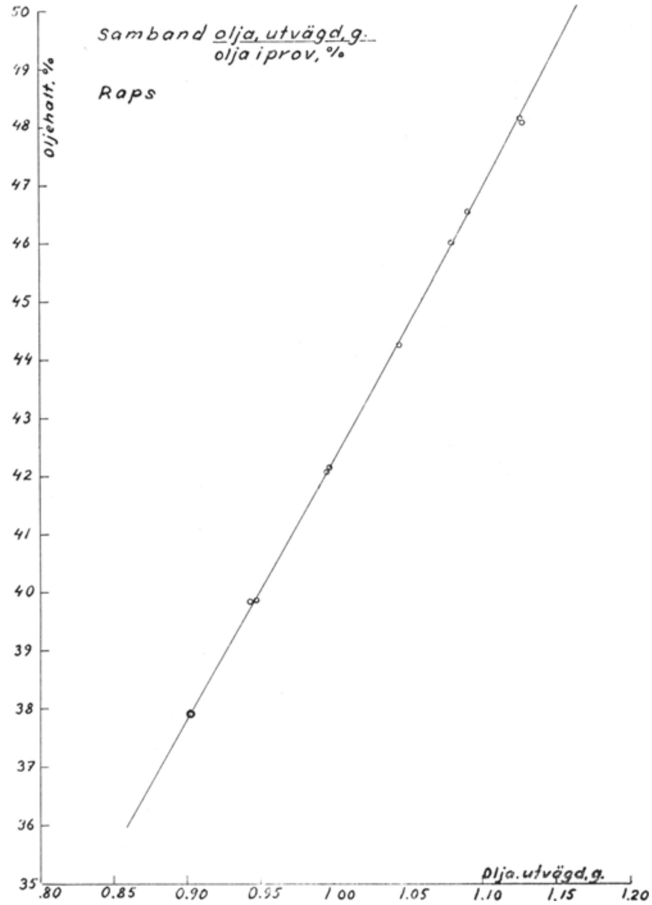

FIG. 1. Diagram for calculating percentage of oil from weight of oil.

Summary

A new method for the determination of oil on long series of oilseed is presented. It is a gravimetric method which reduces the hand labor to a minimum.

TABLE III

Analyses of Rapeseed Performed With and Without Addition of Quartzite. Oil in Dry Substance. Averages of Two Parallels.

Sample no.	The new method with quartzite		The new method without quartzite		Extraction analysis (Butt)
	Oil %	Difference from standard method	Oil %	Difference from standard method	
16,154	46.0	—0.4	46.3	—0.1	46.4
16,179	46.0	—0.3	46.3	±0	46.3
16,209	44.8	—0.6	45.2	—0.2	45.4
16,236	45.6	+0.4	46.0	—0.2	46.2
16,242	47.3	—0.6	47.4	—0.5	47.9
16,264	45.4	—0.5	45.5	—0.4	45.9
16,267	49.1	—0.3	49.0	—0.4	49.4
16,268	45.9	±0	46.0	+0.1	45.9
16,269	46.5	—0.4	46.8	—0.1	46.9
16,270	47.7	—0.1	47.7	—0.1	47.8
16,705[a]	48.2	—0.3	48.3	—0.2	48.5
Averages		—0.3		—0.2	

[a] Turnip rape also.

Testing this method on a series of pure samples of oilseed, which were analyzed for five days with two analyses on each sample every day, the standard deviation for a single analysis lay within 0.30% and for the average of two duplicates within 0.27% of oil. The difference between averages for the new method and averages of extraction analyses made with continuous extractors did not exceed 0.28% of oil.

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Measurement of Calcium Ion Suppression by Protection of Foam of Sodium Cetyl Sulfate Solutions

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BUILDERS as protective agents in the form of phosphates are being used with synthetic detergents in greater proportion and greater tonnage than they ever were with fatty acid soaps. The protection they afford enables a reasonable detersive action to be accomplished in hard water by a relatively smaller proportion of the more expensive synthetic detergent.

The measurement of the suppresion of calcium ions is important in any examination of detergency. It can also be used to evaluate technical phosphates or other builders as well as new materials for which the virtue of sequestration or calcium ion suppression is claimed.

In the following work the foam height is used as an indicator that the concentration of sodium cetyl sulfate is undiminished or, in other words, that the solution is effectively free from calcium ions. Although the foam of many synthetic detergents is not as seriously affected by the presence of calcium ion as is the foam of pure sodium cetyl sulfate, it must be remembered that builders are used for many purposes where the efficiency is affected to varying degrees by the presence of calcium ion (1, 2).

Several methods for estimating the removal of calcium ions have been previously described. Andress and Wust (3) and later Hafford *et al.* (4) used a turbidimetric titration. In the latter procedure the indicator which precipitates as calcium salt was apparently present in the phosphate tested, and both the concentration and type of phosphate which forms

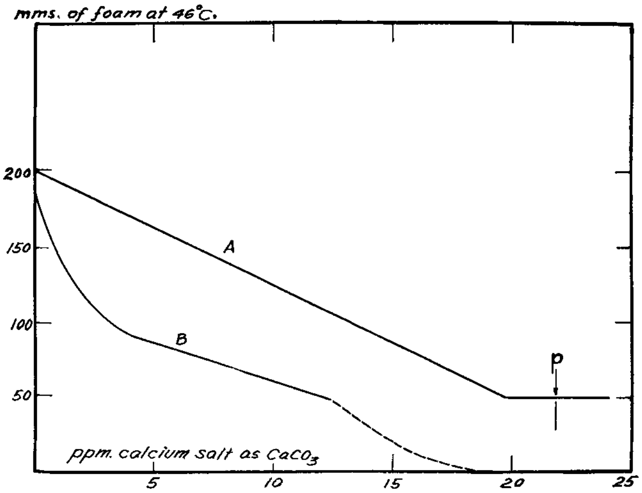

Figure 1.

FIG. 1. Effect of adding calcium chloride solution on the foam height of 0.015% sodium cetyl sulfate.

A. Solution with 0.0375 M NaCl
p = Concentration of calcium salt equivalent to sodium cetyl sulfate.
B. Solution without NaCl.

insoluble calcium salts were variable. The addition of a small amount of oxalate or fatty acid soap as an indicator has also been used for similar turbidimetric tests (5).

Calcium ions may be removed by the formation of soluble complex anions or by the precipitation of insoluble calcium salts. Turbidimetric procedures appear to be suitable only for the estimation of removal of calcium by complex anion formation but not by precipitation or when both precipitation and soluble complex formation are involved.

These limitations were largely overcome by Miles and Ross by using the foaming properties of fatty acid soaps for the determination of the minimum amount of salts required to prevent the precipitation of calcium soaps (6). However these tests required adjustments of pH to correspond to the optimum foam volume for the soap (7). In order to avoid these restrictions of soap with regard to pH changes, it is desirable to use a material as indicator whose foaming properties are not affected by changes in pH. Furthermore the calcium salt of this indicator should have a sufficiently low solubility at the temperature examined to compete with the precipitation of the calcium salt or the formation of complex ions of the compound tested so as to permit comparative evaluation of protection in hard water. Pure sodium cetyl sulfate meets both of these requirements.

Procedure

The 0.06 g. of pure sodium cetyl sulfate prepared by the procedure previously described (8) was dissolved in 384 cc. water at 46-49°C., and to this solution 8 cc. of calcium chloride solution were added, which contained 5,000 p.p.m. calcium hardness (expressed as $CaCO_3$). The solution was aged at least 10 min. and then 8 cc. of a 0.1% phosphate or other solution tested were added. After 5 min. a pour-foam test was made and the initial foam height noted (9). The water in the jacket of the apparatus was kept at 49°C.

The 1-cc. portions of the protective solution to be tested were then added until the pour-foam test gave a foam height of 180-200 mm., which is the end-point for complete protection. When the total final volume was 400 cc., it contained 100 p.p.m. calcium salts (expressed as $CaCO_3$), which is equal to 4×10^{-4} moles of calcium salts in 400 cc. The amount of phosphate or other protective agent required is determined. The mole and weight ratios given in Table I are calculated from these data. Other concentrations of calcium salts were obtained by adding the necessary amounts of calcium chloride solution.

TABLE I

Protection of Sodium Cetyl Sulfate in Calcium Hard Water

Compound tested	Calcium hardness, p.p.m.	pH	Mole ratio, compound tested/ calcium	Weight ratio, compound tested/ $CaCO_3$
Sodium orthophosphate (Na_3PO_4)	20	11.0	20.0	32.5
	100	11.2	8.0	13.0
Tetrasodium pyrophosphate ($Na_4P_2O_7$)	20	9.5	2.6	6.9
	100	9.5	2.4	6.4
	360	8.0	1.7	......
	360	9.6	1.2	......
Sodium tripolyphosphate ($Na_5P_3O_{10}$)	20	8.0	1.6	5.9
	20	9.5	1.1	4.1
	100	8.0	1.7	6.3
	100	8.5	1.4	5.2
	100	9.0	1.2	4.4
	100	9.5	1.1	4.1
	100	10.1	1.0	3.8
	100	11.0	1.0	3.8
	360	8.0	1.3	4.8
	360	8.5	1.15	4.2
	360	9.0	1.1	4.1
	360	9.5	1.0	3.7
Sodium metaphosphate (Calgon)	20	6.6-9.5	......	3.7
	100	6.7	......	5.8
	100	8.0	......	4.6
	360	6.3	......	5.5
	360	8.0-9.5	......	4.6
Tetrasodium salt of ethylene diamine tetra-acetic acid	100	6.8-11.0	1.0	3.8
	360	8.8	1.0	3.8

The pH of the solution was adjusted with NaOH or HCl solution. A Beckman Model G glass electrode assembly was used for all pH measurements.

Results and Discussion

A concentration of 0.015% sodium cetyl sulfate corresponds to the break in foam height *vs.* concentration curve (8) for aqueous solutions. Addition of sodium chloride to the solutions decreases the concentration at which a sharp break in the curve appears.

The sensitivity of the protection test is indicated by the effect of adding calcium chloride solution on the foam height of solutions of sodium cetyl sulfate containing 0.0375 molar (0.219%) sodium chloride, Figure 1 (A). The end-point corresponds to about two parts per million of calcium salt (expressed as $CaCO_3$) for concentrations of sodium chloride about 50% greater than the largest amount present in any of the protection tests reported.

The ratios given in Table I show the relative quantities of the compounds necessary to reduce the calcium ion (Ca^{++}) concentration to a value which no longer produces depressing effects on the foam (less than 2 p.p.m. or 2×10^{-5} molar calcium salt).

For the phosphates at a particular pH, higher total calcium salt concentrations gives smaller ratios of the compound tested to the calcium salts required for protection. For any particular total calcium salt concentration an increase in pH for the range studied requires smaller ratios.

Precise values are difficult to obtain for sodium orthophosphate and tetrasodium pyrophosphate at various pH values. This behavior is probably due to changes in equilibria in ortho and pyrophosphoric acids and may also be due to variations in composition and adsorption effects of the calcium phosphate precipitates. When calcium phosphate precipitates are not formed, the values necessary for protection are much more easily obtained.

The protection obtained with changes in pH apparently reflects shifts in equilibria for the various phosphates. It should be emphasized that the values are significant only on a relative basis and for a particular pH of the solution.

For sodium triphosphate, protection is obtained in the pH range 9.5-11 at a mole ratio of 1.1 to 1.0. At lower pH (values) a larger mole ratio is required.

For tetra sodium salt of ethylene diamine tetra acetic acid, at pH above 6.8, the mole ratio for protection is 1.0 for 100 p.p.m. as well as for 360 p.p.m. calcium hardness. At 100 p.p.m. calcium hardness at pH less than 6.8, larger mole ratios are required for protection for this compound.

Some of the data with sodium cetyl sulfate have been compared with the protection obtained with sodium oleate as the foam indicator (6). For a solution with total hardness of 100 p.p.m. calcium salt, tetrasodium pyrophosphate, sodium triphosphate, and sodium metaphosphate (Calgon) show the same order of protection for the two tests, but the ratios of the protection values are different. For the sodium oleate test greater difficulty was experienced in estimating the end-point than with the cetyl sulfate. In order to operate in the region of optimum foam height, the pH was maintained at 10.5. Such a restriction is not required in the cetyl sulfate measurements.[1]

The test for protection of foam of sodium cetyl sulfate may be considered from the point of view of a competition for calcium ion (Ca^{++}) by the cetyl sulfate anion to precipitate calcium cetyl sulfate and by the compound tested to precipitate a calcium salt or to form a complex calcium ion.

For example, for the tetrasodium salt of ethylene diamine tetra-acetic acid the following equilibria may be considered, where parentheses represent thermodynamic activities:

$$K = \frac{(\text{Ca Y}^{-2})}{(\text{Ca}^{++})\ (\text{Y}^{-4})} \tag{1}$$

where Y^{-4} is ethylene diamine tetra-acetate anion.

$$(\text{Ca}^{++}) \text{ at end point} = \frac{(\text{Ca Y}^{-2})}{K\ (\text{Y}^{-4})} \tag{2}$$

when the foam height is 180-200 mm.

$$K^1 = \frac{(\text{H}_3\text{O}^+)\ (\text{Y}^{-4})}{(\text{HY}^{-3})} \tag{3}$$

$$K_{sp} = \text{solubility product of calcium cetyl sulfate} = (\text{Ca}^{++})\ (\text{D}^-)^2 \tag{4}$$

where (D^-) represents the cetyl sulfate anion concentration: K and K^1 are available from the work of Schwarzenbach and coworkers (10). Using these values, the calculated solubility of calcium cetyl sulfate is approximately 2 mg. per 100 cc. This is the solubility in a solution containing about 0.015 M sodium chloride.

Measurements of the electrolytic conductivity of a saturated solution of calcium cetyl sulfate at 45°C. indicate a solubility in water of about 1 mg. per 100 cc. This estimate was made on the basis of the equivalent conductance of calcium (Ca^{++}) and of cetyl sulfate anion.

It appears that the solubility of calcium cetyl sulfate is greater when other salts are present than in distilled water. This is in accord with the difference between curves A and B in Figure 1. Curve A (with NaCl) is always above B (without NaCl), and some foam is still obtained after the equivalence point p.

Summary

Relative protection of various compounds against calcium salts was determined by a pour-foam test, using sodium cetyl sulfate as a foam-producing indicator. The sensitivity of the test corresponds to less than 2 p.p.m. of calcium salt.

Some of the data are compared with similar tests, using sodium oleate as an indicator, and advantages of the cetyl sulfate test are noted.

The test is discussed from the point of view of a competition for calcium ion by the cetyl sulfate anion to precipitate calcium cetyl sulfate and by the compound tested to precipitate a calcium salt or form complex calcium ions.

On the basis of the equilibria involved an estimate is made of the approximate solubility of calcium cetyl sulfate in the salt solutions tested.

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[1] It has been drawn to our attention by A. F. Rutkiewic that due to the low solubility of potassium cetyl sulfate this procedure cannot be applied in the presence of potassium salts.