at 40C this difference is still more significant. In this particular case we are, therefore, able to distinguish between two parallel running homologous series. The alternation effect is, therefore, also noted in the CH_2 increment.

Unsaturation. Although the van Elk relation has not been specifically derived for general applicability to all types of structures we were interested in the influence of unsaturation on E_m. The results are listed in Table V. Comparative saturated esters have been included to facilitate comparison. Their E_m values have been obtained from the regression equations using the data in Table IV.

The increment of the double bond apparently shows a more than proportional increase with increasing unsaturation in the same chain. This behavior has been noted earlier in other physical properties. The influence of the *trans*-modification in methyl linolenate is markedly discernible, as shown by the small difference with methyl linoleate. This might be expected as ϵ is strongly dependent on the spatial structures.

Limiting Value

The ϵ of the limiting fatty acid methyl ester may also be obtained from the following equations:

$$E_m = E_{sp} \cdot M = (\epsilon - 1)^{3/4} M/d = A + n E_{CH_2} \quad [11]$$

$$\lim_{n \to \infty} E_{sp} = \lim_{n \to \infty} (A + n E_{CH_2})/(46.026 + n\,14.026) = E_{CH_2}/14.026 = (\epsilon_\infty - 1)^{3/4}/d_\infty \quad [12]$$

Substitution of the limiting densities obtained earlier (6), i.e. 0.85407 at 20C and 0.84225 at 40C yields limiting dielectric constants of 2.15 at 20C and 2.14 at 40C. These values are slightly higher than those computed from the Smittenberg relation, but in view of the large amounts of extrapolation involved in both methods the fit may be considered to be reasonably close.

REFERENCES

1. Allen, R. R., JAOCS *32*, 671 (1955).
2. Bogdanov, L. I., and N. N. Stepanenko., Zhurn. Fiz. Khim. *26*, 1477 (1952); *27*, 1481 (1953).
3. Buchanan, T. J., J. Chem. Phys. *22*, 578 (1954).
4. Dobrosserdov, Dm., Chem. Zentr. *I*, 953 (1911).
5. Elk, J. van, Thesis Delft (1962).
6. Gouw, T. H., and J. C. Vlugter, JAOCS *41*, 142–145 (1964).
7. Gouw, T. H., and J. C. Vlugter, *Ibid.* 426–429 (1964).
8. Gouw, T. H., and J. C. Vlugter, *Ibid.* 514–515 (1964).
9. Gouw, T. H., and J. C. Vlugter, *Ibid.* 524–526 (1964).
10. Jackson, L. C., Phil. Mag. *43*, 481 (1922).
11. Jatkar, S. K. K., B. R. Y. Iyengar and N. V. Sathe, J. Indian Inst. Sci. *28A*, Part II, 1 (1946).
12. Kauffmann, H., "Beziehungen zwischen physikalischen Eigenschaften und chemischer Konstitution," Ferdinand Enke, Stuttgart, (1920).
13. Lüdde, K. H., Fette Seifen Anstrichm. *61*, 1156 (1959).
14. Maryott, A. A., and E. R. Smith, "Table of Dielectric Constants of Pure Liquids." National Bureau of Standards, Circular 514, (1951).
15. Mecke, R., R. Joeckle, G. Klingenberg and W. Mecke, Z. Elektrochem. *66*, 239 (1962); *66*, 514 (1962).
16. Mecke, R., and K. Rosswog, *60*, 47 (1956); *62*, 500 (1958).
17. Oehme, F., J. Electroanal. Chem. *1*, 181 (1960).
18. Oehme, F., Chem. Ztg. Chem. Apparatur *83*, 330 (1959).
19. Oehme, F., and H. Wirth, "Die Bestimmung des molekularen Dipolmomentes," Wiss.-techn. Werkstätten GmbH, Weilheim, Oberbayern.
20. Phadke, S. R., J. Indian Inst. Sci. *34A*, 293 (1952); *35A*, 123 (1953).
21. Singleton, W. S., in "Fatty Acids," Editor K. S. Markley. Part I. Interscience, New York, 1960.
22. Smittenberg, J., and D. Mulder, Rec. Trav. Chim. *67*, 813 (1948).
23. Smyth, C. P., "Dielectric Behavior and Structure." McGraw Hill, New York 1955.
24. Thwing, Ch.B., Z. Phys. Chem. *14*, 286 (1894).
25. Volarovich, M. P., and N. N. Stepanenko, J. Expt Theor. Phys. USSR *10*, 817 (1940); *14*, 313 (1944).
26. Walden, P., Z. Phys Chem. *70*, 584 (1910).

[Received October 8, 1963—Accepted July 6, 1964]

A Neutron Activation Method for Soil Removal Measurements: A Comparison of the Reflectance Method and the Neutron Activation Method[1]

D. A. NETZEL, C. W. STANLEY and D. W. RATHBURN,[2]
Midwest Research Institute, Kansas City, Missouri

Abstract

A nondestructive neutron activation analysis technique has been developed to determine the amt of particulate kaolinite clay soil removed from cotton fibers during a wash cycle.

Neutron bombardment of aluminum, present as a constituent of the kaolinite lattice structure, produces short-lived aluminum-28. The amt of particulate soil present on a piece of cotton cloth before and after the wash cycle is determined by γ scintillation counting of the aluminum-28, thus providing an absolute method for the determination of the percentage of soil removed. A comparison of this method with the reflectance method has been made, and equations relating reflectance to clay concn for washed and unwashed soiled cloths have been developed for a given surfactant. It was found that the relationship of the concn of the soil on the test cloths and the measured reflectance depends upon whether the cloth has been washed or unwashed.

The validity of the applicability of the Kubelka-Munk equation relating reflectance to soil content on cotton fabric has been experimentally confirmed for soiled cloths have high reflectivity.

Introduction

THERE HAS BEEN A large amt of work devoted to developing methods for measuring and evaluating detergency (1–3). Any true evaluation procedure for determining the detergent effectiveness of a surfactant must include a means for determing the absolute soil content on test cloths both before and after cleaning.

The method for measuring the amt of soil on a piece of cloth depends upon the type of soil being used during an investigation. Reflectance methods have been used for carbon (4), clay (5), soiled cloths and iron analyses have been used for cloth soiled with ferric oxides (2). Transmittance measurements (6) on the wash liquor have been made to determine the amt of soil removed from a cotton test swatch. With the advent of radiotracers, tagged soils of many different types have been prepared and used in the evaluation of the detergency process (7,8).

[1] Presented in part at the AOCS Meeting, Minneapolis, 1963, and at the 15th Annual Chemistry Conference, Kansas City Sec., ACS.
[2] Kansas State University, Manhattan, Kan.

TABLE I

Possible Nuclear Reactions in Irradiated Clay

Type of reaction	Isotopic abundance of reactant (%)	Half-life of product (min)	Cross-section (millibarns)	Type of radiation and energy (mev)
$Al^{27}(n_{th}, \gamma)Al^{28}$	100	2.3	212	β^- 2.865 γ 1.782
$Al^{27}(n_{1\,mev}, \gamma)Al^{28}$	100	2.3	0.41	β^- 2.865 γ 1.782
$Al^{27}(n_{1\,mev}, p)Mg^{27}$	100	9 4	2.80	β^- 1 75, 1 59 γ 0.87, 1.02
$Al^{27}(n_{1\,mev}, \alpha)Na^{24}$	100	900	0.60	β^- 1 39 γ 1.368, 2.754
$Si^{30}(n_{th}, \gamma)Si^{31}$	3.05	162	120	β^- 1.47
$Si^{30}(n_{1\,mev}, \gamma)Si^{31}$	3.05	162	1.1	β^- 1.47
$Si^{28}(n_{1\,mev}, p)Al^{28}$	92.27	2.3	3.0	β^- 2.865 γ 1.782
$Si^{28}(n_{1\,mev}, p)Al^{29}$	4.68	6 7	2.7	β^- 2.5, 1.4 γ 1.28, 2.43
$Na^{23}(n_{th}, \gamma)Na^{24}$	100	900	540	β^- 1.390 γ 1.368, 2 754
$Cl^{37}(n_{th}, \gamma)Cl^{38}$	24.6	37.3	600	β^- 4.81, 1.11, 2.77 γ 2.15, 1.60
Other possible reactions which may be encountered:				
$M^{55}(n_{th}, \gamma)Mn^{56}$	100	156	13,400	β^- 2.81, 1.04, 0.65 γ 0.82, 1.81, 2.13
$S^{36}(n_{th}, \gamma)S^{37}$ [a]	0.016	5.0	140	β^- 1.6, 4.3 γ 2.7

[a] Possible if sulfur-containing surfactants are absorbed on the test cloths.

None of the artificial soils used today represents natural soil. Attempts have been made to compound various single components of natural soil (9). Powe found that natural particulate soil consists largely of clay, not carbon, and Martin and Davis (5) developed a procedure whereby cotton cloth can be soiled with kaolinite clay.

Neutron activation analysis was used in the present work to provide an absolute measure of the clay soil present on test cloths. The activity of a test cloth after neutron bombardment was used to determine the quantity of material present. The clay which is chiefly aluminum silicate, may be represented by the empirical formula $[Al_2(Si_2O_5)(OH)_4]$. Neutron irradiation of the clay results in the activation of the aluminum atoms within the lattice structure of the clay. Therefore, a measure of the amt of aluminum removed from a test cloth is a measure of the amt of soil removed.

The advantages of neutron activation analysis are: 1) nondestructive nature of the analysis, 2) insensitivity to chemical form of the element and 3) high sensitivity. The sensitivity depends upon a high neutron flux, the cross-section (probability of the nuclear reaction occurring), the isotopic abundance of the isotope giving rise to the reaction, the half-life of the nuclide measured and the detection efficiency of the measuring equipment. To achieve a high neutron flux, a nuclear reactor is usually employed.

Table I summarizes the numerous nuclear reactions which can occur in clay when irradiated by both fast and thermal neutrons from the reactor. Given in Table I are: 1) the reactions which can occur, 2) the isotopic abundance of the reactant isotope, 3) the half-life of the product, 4) the cross section for the reaction and 5) the type and energy of the radiation emitted by the product.

Of the possible reactions which may occur in the irradiation of clay, the thermal neutron irradiation of aluminum-27 is the most feasible reaction to monitor because of the large isotopic abundance of the reactant and the relatively large cross section for the nuclear reaction. Because of the short half-life of aluminum-28, there is no appreciable residual activity

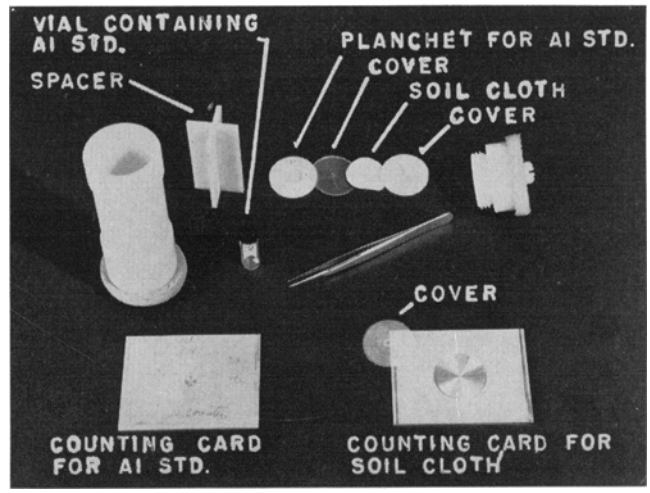

FIG. 1. Construction view of sample carrier used in the pneumatic tube assembly.

of the soiled cloth during the wash cycle. Also the short half-life of aluminum-28 allows short irradiation times, thereby minimizing the build-up of the longer half-life activities of the clay and cloth components.

To measure the absolute amt of soil removed from a soiled cloth, it is necessary that the cloth remain intact during three main phases: 1) the irradiation of the cloth, 2) the counting of the activity on the cloth and 3) the washing of the test cloth. No difficulties in the design of the facilities to maintain the cloth intact for irradiation and counting were encountered. However, if the soiled cloth was washed by the normal procedure (11), excessive fraying at the edges of the cloth would result. The soil loss by fraying of the cloth would defeat the purpose of the absolute soil removal determination. Therefore, it was necessary to modify the wash procedure to prevent fraying of the test cloths.

Experimental

Clay-Soiled Cloth. The kaolinite clay-soiled cloth used in this investigation was supplied by the Whirlpool Corp. The reflectivity as measured with a Hunter multipurpose reflectometer ranged from 50–80 reflectance units.

To determine by the reflectance method the amt of soil removed, the reflectance of washed 3 x 6 in. pieces of clay-soiled cloth was measured and compared to the reflectance of the unwashed soil cloth.

A die 1⅛ in. in diam was used to cut pieces of soiled cloth to be used in the activation analysis method. Each unsoiled cloth disc had an avg wt of 0.1015 g.

Irradiation and Counting. The reactor facilities used were located at the University of Kansas, Lawrence, Kan. A pneumatic tube assembly was used to irradiate the cloth samples. The sample irradiation time of 2.5 min was controlled using an automatic timer on the pneumatic tube system.

The sample carrier which was placed in the pneumatic tube for the irradiation experiments is shown in Figure 1. The carrier, constructed from high-density polyethylene, has end caps with coarse threads to permit rapid removal of the sample from the carrier after irradiation. Planchets of high density polyethylene were used to hold the soiled cloth and the aluminum standard in place during irradiation.

After irradiation in a neutron flux of ca. 10^{10} neutrons/cm^2/sec, the soiled cloth and the aluminum standard were removed from the carrier and placed

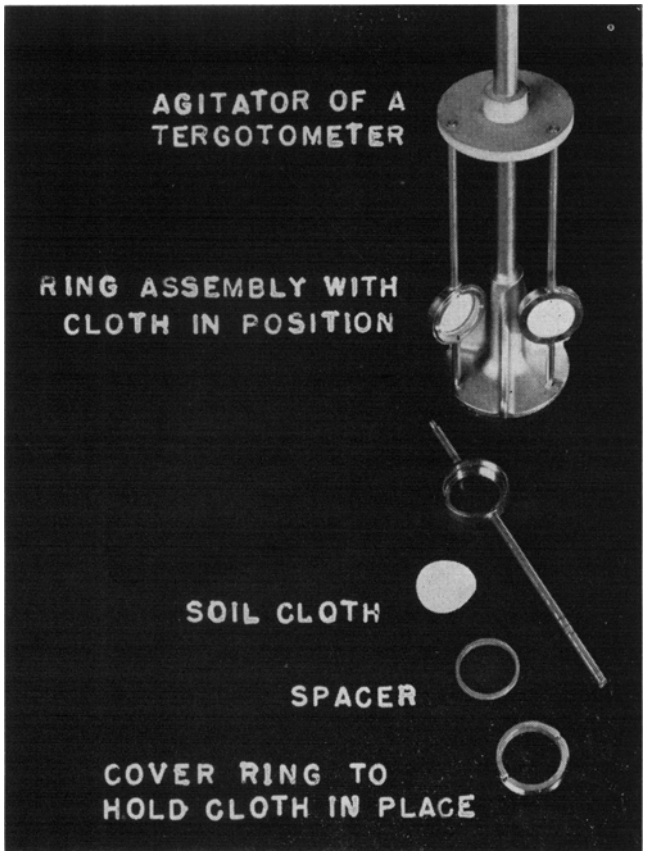

FIG. 2. Agitator assembly for soil cloths used for activation analysis.

on their respective counting cards in holes milled out to 0.5 the total thickness of the cards. The sample was covered with a Lucite disc $\frac{1}{32}$ in. thick to hold the cloth flat on the counting card.

The counting equipment consisted of a high voltage supply, a linear amplifier, a single channel differential analyzer and a scaler unit. Two γ scintillation detectors were connected to the same high voltage supply, with a switch to connect the scaler with one or the other detector. Each detector consisted of a 1 x $1\frac{1}{2}$ in. scintillation crystal and an RCA 6655-A photomultiplier tube. Each scintillation detector was mounted on a standard lucite counting platform.

Differential counting was used to determine the activities of the soiled cloth samples and the aluminum standard after irradiation. With differential counting, activities which have energies either greater or less than the γ energy of aluminum-28 will not be counted. Thus, it was possible to exclude the activities due to the other components in the clay.

The half-lives of the activity on the cloth and aluminum standard were determined by alternately counting the samples. Any large deviation of the measured half-life from the literature value of 2.3 min for aluminum-28 would indicate the presence of other decaying species. The decay curves for the irradiated soiled cloths indicated very small amt of contaminates having a γ energy of ca. 1.78 mev.

Wash Procedure for Reflectance Method. Six clay-soiled cloth swatches (3 x 6 in.) and six U.S. Testing redeposition cloth swatches (3 x 6 in.) were washed in 1 liter surfactant solution contained in a Terg-O-tometer unit with a water-to-cloth ratio of 40:1. The wash conditions used were:

Temperature, 140F
Wash time, 10 min

TABLE II
Reflectance and Activity Ratios of Unwashed Clay-Soiled Cloths

Series	Reflectance	Ratio of activity on cloth to activity of aluminum std
A	50.2	1.537
		1 594
	68.8	0.567
		0.499
	69.9	0.312
		0.372
	70.8	0.328
		0.260
	71.8	0.274
		0.289
	72.3	0.312
		0.372
	73.3	0.306
		0.181
	78.2	0.242
		0.187
B	50.2	1.588
		1.355
	68.8	0.532
		0.558
	69.9	0 157
		0.346
	70.8	0.296
	71.8	0.298
	72.3	0.211
		0.410
	73.3	0.318
	78.2	0.197
		0.177

Agitation, 90 rpm
Rotation of agitator, ~330 degrees

The conditions for the rinse cycle were:

Rinse volume, 1 liter distilled water
Rinse temperature, 120F
Rinse time, 2 min

Before the rinse cycle, the cloth swatches were passed through a hand wringer. For the rinse cycle, the cloth swatches were agitated mildly by hand. After 2 min, the cloth swatches were removed and again passed through the hand wringer and allowed to air dry. A Hunter reflectometer was used to determine the reflectivity of the cloth swatches both before and after the wash cycle.

Figure 2 shows the special holding assembly used for the soiled cloths during a wash cycle. The holding arrangement for the soiled cloth had to be flexible enough to allow for the normal tumbling action that a piece of cloth receives during a wash cycle. The soiled cloth disc, which was positioned between two rings, had an exposed diam of 1 in. Two support rods attached the ring assembly to the agitator of a Terg-O-tometer in such a way as to allow free rotation of the ring around the axis of the rods. During agitation, the ring containing the soiled cloth turned first in one direction and then back in the other direction, thus simulating the tumbling effects a piece of cloth would receive during the wash cycle. Three stainless-steel holding assemblies for the soiled cloths were attached to one agitator of the Terg-O-tometer.

Early experiments showed that if 3 x 6 in. soiled cloths were washed with the test soiled cloths within the ring assemblies to maintain a 40:1 ratio of water-to-cloth, the large swatches of cloth would bind the rotation of the rings during the wash cycle and so prevent agitation of the small pieces of cloth. Therefore, the wash procedure was modified to maintain a 40:1 ratio of water-to-cloth, 12.5 g soiled cloth and 12.5 g redeposition cloth cut into $1\frac{1}{8}$ in. circles were added to the surfactant solution being studied in place of the 3 x 6 in. cloth swatches. The washing conditions were the same as with the 3 x 6 in. cloths.

For the rinse cycle, the agitator assembly containing the three rings and soiled cloths was removed from the surfactant solution, placed into another Terg-O-tometer beaker containing 1 liter of distilled

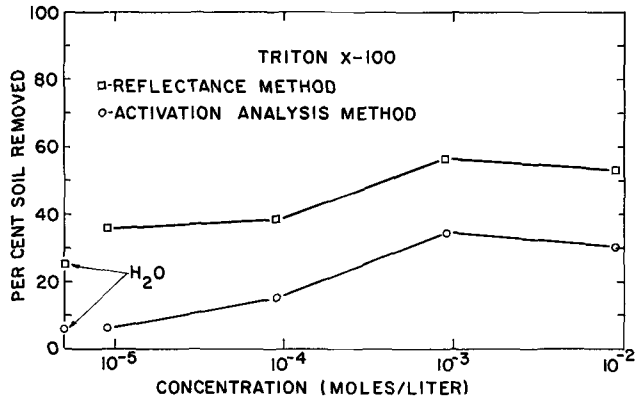

FIG. 3. Comparison of the percentage of soil removed as determined by activation analysis and by the reflectance method.

water at 125F, and agitated at 90 rpm for 1 min. After the rinse, the soiled cloths were removed from the ring assemblies and placed on a glass plate. The excess water was removed by blotting each side of the cloth and the soiled cloths allowed to air dry on the glass plate. After drying, the soiled cloths were reirradiated and the activity measured.

Surfactant Solutions. Triton X-100 (Rohm & Haas Co., Philadelphia, Pa.) solutions of 0.009, 0.09, 0.9 and 9.0 mM concn were prepared, using distilled water. Specially washed Triton X-100 was used as received from Rohm & Haas.

Calculations. The reflectance values measured for the soiled cloth swatches were converted to the Kubelka-Munk K/S values (12) and the actual percentage soil removed (SR) was calculated from the following equation:

$$\% \text{ SR} = \left[\frac{(K/S)_{S_o} - (K/S)_{S_f} + (K/S)_{R_f} - (K/S)_{\bar{R}_o}}{(K/S)_{S_o} - (K/S)_{\bar{R}_o}}\right] \times 100 \qquad [1]$$

where subscripts of the K/S values refer to the type of cloth:

S_o = soiled cloth before wash
S_f = soiled cloth after wash
R_f = redeposition cloth after wash
$\bar{R}_o$ = avg of the redeposition cloth before wash

The activity data for the activation analysis work were recorded in terms of counts/min. To facilitate the correlation of activity data, all data were corrected back to end of bombardment (EOB) activities. When more than one count was made, the EOB activity was computed for each count and then averaged.

Because the neutron flux was not constant with time, the EOB activities of the soiled cloths were divided by the EOB activities of their respective internal aluminum standards. All aluminum pieces weighed nearly the same (0.32 mg) and, therefore, the ratio of the activity of the soiled cloth to the activity of the standard determined on any one day could be compared to the activity ratio determined on another day. This procedure was used to determine the amt of soil removed from a piece of cloth, since the soil content of the cloth before and after a wash cycle was measured on different days.

Because the exposed area of the cloth for washing was less than the total area, a soil ring remained on the cloth where it had been clamped during the wash cycle; therefore, the activities measured on the cloth before and after washing had to be corrected. Since the wash area was 79% of the total area of the cloth, the initial activity ratio (A_I') used in calculating the

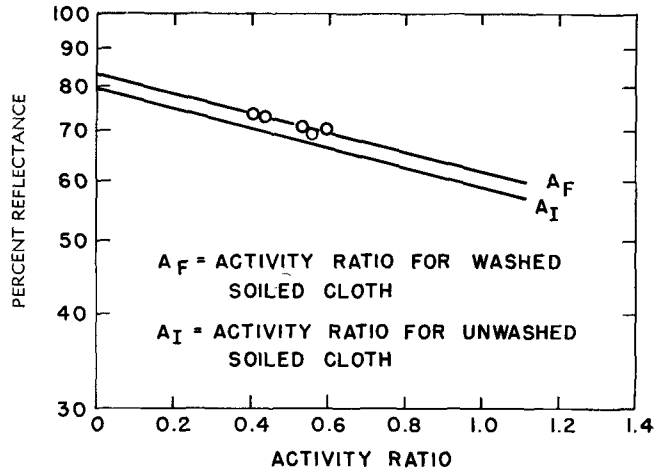

FIG. 4. Reflectance of washed clay soiled cloth as a function of the soil content (in terms of activity ratios).

percentage of soil removed was 79% of the total initial activity ratio (A_I^C/A_I^{Al}), where A_I^C = initial activity on cloth and A_I^{Al} = initial activity of the aluminum standard. The activity ratio of this ring of soil is 21% of the total initial activity. Thus, to compute the amt of activity due to the soil remaining on the washed area of the cloth (A_F'), 21% of the total initial activity ratio was subtracted from the total final activity ratio measured (A_F^C/A_F^{Al}). The percentage of soil removed was determined from the following equation:

$$\% \text{ SR} = \left[1 - \frac{A_F'}{A_I'}\right] \times 100 = \left[1 - \frac{A_F^C/A_F^{Al} - 0.21\, A_I^C/A_I^{Al}}{0.79\, A_I^C/A_I^{Al}}\right] \times 100 \qquad [2]$$

The actual amt of clay on each cloth disc can be computed from the activity ratios since the activity and the wt of each aluminum standard were known. Independent analytical laboratories had determined the aluminum content of the clay to be 14.5%. Thus, the activity ratios given in Table II and those plotted in Figure 4 need only to be multipled by a factor of 2.21 (0.32/0.145) to obtain the wt of clay in mg/cloth disc.

The lines of regression for the data reported were computed by the "least squares" method using an IBM 1620 computer.

Discussion

A comparison of the percentage of soil removed for various concn of Triton X-100, as determined by neutron activation analysis and by the reflectance method, is shown in Figure 3. Each point represents the average of six or more determinations. The inflection of the curves between the concn of 10^{-4} and 10^{-3} moles/liter corresponds to the concn range in which critical micelle concn of Triton X-100 (13) occurs. The decrease in detergent effectiveness as the surfactant concn is increased is not an uncommon effect (14). However, most important is the similarity of the curves obtained by the two methods and the displacement from one another.

To explain the displacement it was necessary first to relate the reflectance of clay-soiled cloth to the actual amt of clay present on the soiled cloth and second to determine the validity of the Kubelka-Munk equation used to compute the percentage of soil re-

TABLE III

Reflectance Values and Activity Ratios for Unwashed and Washed Clay-Soiled Cloths

Triton X-100 concn of (mM)	Reflectance of unwashed soiled cloths	Total activity ratio A_I	Reflectance of washed soiled cloths	Total activity ratio A_F	% Soil removed from activity ratios	% Soil removed from reflectance values
0	66 5	0.591	69.15	0.459	22.3	25.0
0.009	65.7	0.632	70.4	0.398	37.0	35.6
0.090	65.9	0.621	71.0	0.369	40.6	38.4
0.900	65 4	0.647	72.95	0.278	57.0	56.5
9.000	66.9	0.570	72.85	0.236	58.3	53.0

moved for soiled cloths of high reflectance values. Table II lists the total activity ratios (A_I^C/A_i^{A1}) of the unwashed soiled cloths and the reflection values (R_I) for the soiled cloths for two series of experiments. The reflectance values given in the table are average values for large pieces of soiled cloth. The reflectance values of the individual pieces of cloth used in the activation analysis method were not determined because of mechanical difficulties encountered in measuring the reflectance values of the small pieces of cloth. The use of these average reflectance values may account for the discrepancies in activity ratios for a given average reflectance value. If the logarithms of the reflectance values are plotted against the values of the activity ratios of the unwashed soiled cloths, a straight line results. This resulting line can be represented by the following equation:

$$\log R_I = \log R_O + \lambda A_I \qquad [3]$$

where R_I = reflectance value of the unwashed soiled cloth
R_O = reflectance value of the unwashed, unsoiled cloth
λ = slope of the line
A_I = the total initial activity of the cloth divided by the activity of the aluminum standard

The values of R_O and λ were found to be 1.90 and −0.128, respectively.

In a similar study, using graphite as a soil, Harris et al. (1) found that the reflectance of the soiled cloth was related to the log of the amt of graphite on the cloth:

$$R = -A \log G + B \qquad [4]$$

where R = reflectance
G = concn of graphite on the cotton fabric, and A and B are dependent upon experimental conditions

His investigation supported the work of Utermohlen and Wallace (2).

In regions of high reflectivity the log of the reflectance is related directly to the concn of the soil on the cloth, whereas, in the region of low reflectivity, the reflectance is related to the log of the concn of the soil on the cloth as found by Harris et al. Though the authors have no experimental evidence, it can be assumed that in the study of soil redeposition, the reflectance ought to be related to the concn of the soil on the cloth by Equation 3 rather than 4, because of the high reflectivity region of the redeposition cloth.

TABLE IV

Reflectance of Clay Soiled Cloths Washed with Various Concentrations of Triton X-100

Trition X-100 concn (mM)	Reflectance of unwashed soiled cloth	Activity ratio for unwashed soiled cloth (A_I)[a]	Reflectance of washed soiled cloth	% Soil removed[b]	Calculated activity ratio for washed soiled cloth (A_F)
0	66.5	0.591	69 15	6	0.556
0.009	65.7	0.632	70.4	6	0.594
0 090	65.9	0.621	71.0	15	0.528
0.900	65 4	0 647	72.95	34	0.427
9.000	66.9	0.570	73.85	30	0.399

[a] Computed from Equation 3 for known reflectance reading.
[b] Determined directly by activation analysis using Equation 2.

The Kubelka-Munk (12) equation which is generally used to calculate a value proportional to soil content from the reflectance values (R) is:

$$K/S = \frac{(1-R)^2}{2R} \qquad [5]$$

Bacon and Smith (15) were the first investigators to use this equation to measure the soil content on test cloths and many other investigators (1–3) have found that the equation is valid if the range of reflectance of the soiled cloth is from 20–60 reflectance units. Martin and Davis (5) have confirmed the application of the Kubelka-Munk equation in the region of high reflectivity, using clay soiled cloth.

The validity of the Kubelka-Munk equation for soils of high reflectivity can also be demonstrated with our data using Equation 3 with the constants given and the reflectance data used to calculate the percentage of soil removed for various concn of Triton X-100 solutions (see Table III). The reflectance data for the soiled cloth both before and after washing were converted to activity ratios using Equations 3. The ratios were then used to calculate the percentage of soil removed (Equation 2). The percentage of soil removed calculated by transforming the reflectance values to activity ratios and the percentage of soil removed computed from reflectance values, using Equation 1, are also given in Table III. It can be seen that agreement is good and that the applicability of the Kubelka-Munk equation in regions of high reflectivity is confirmed.

Therefore, to explain the difference in the percentage of soil removed as measured by the two methods, one must assume that the relationship between the reflectance and the amt of soil on the cloth depends upon whether the cloth was unwashed or washed.

Using the percentage of soil removed as determined directly by activation analysis, since this method gives the absolute amt of soil removed, it was possible to calculate the activity ratio (A_F) which would correspond to the measured reflectance values of the washed soiled cloths.

Table IV lists the reflectance data and their corresponding activity ratios for various concn of Triton X-100. The upper line in Figure 4 is a plot of the log of the reflectance of the washed soiled cloth (R_F) as a function of the calculated activity ratio. The lower line represents the relationship between reflectance and the concn of the soil on the cloth before washing. The equation for the top line is:

$$\log R_F = 1.92 - 0.127\, A_F \qquad [6]$$

The assumption that washed soiled cloths give higher reflectance readings than unwashed soiled cloths for a given amt of soil on the cloth is supported by the work of Harris et al. (1). They had found that the relationship between the reflectance of a graphite-soiled cloth and the absolute amt of graphite on the cloth varied depending upon whether the cloth was washed or unwashed. Higher reflectance readings were obtained for the same amt of graphite on the cloth after the cloth had been washed than before the cloth was washed, in agreement with our study on clay-soiled cloths.

A comparison of two absolute methods (neutron ac-

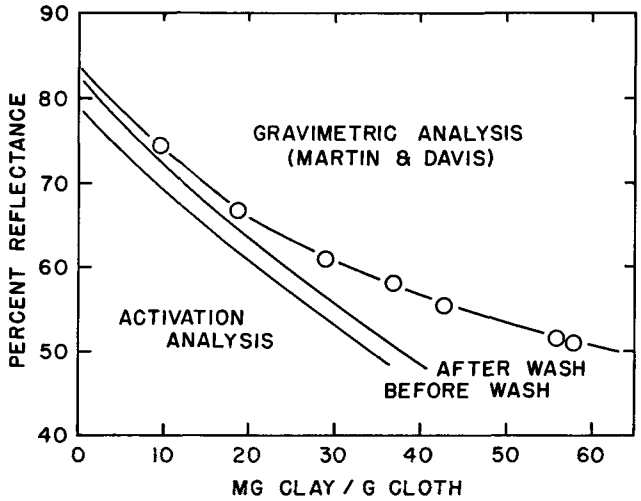

FIG. 5. Comparison of two absolute methods for relating reflectance to soil content of clay soiled cloth.

tivation and gravimetric analysis) for relating the percentage of reflectance to the soil content of clay soiled cloth is given in Figure 5. The soil content expressed as mg of clay/g cloth was determined from activity ratio data of clay soiled cloths and the known wt of the cloth disc used in the activation analysis method. The gravimetric analyses of the soil content of clay soiled cloths are the data of Martin and Davis (5).

Fairly good agreement is obtained for the two absolute methods at high reflectance reading or low clay-soil content on the soiled cloth. The discrepancies noted between the two methods in the range of 50 reflectance units have not been completely resolved.

ACKNOWLEDGMENT

Assistance from Russell Mesler, University of Kansas, and G. J. Hennon. This work carried out with the financial support of the Whirlpool Corp.

REFERENCES

1. Harris, J. C., M. R. Sullivan and L. E. Weeks, Ind. Eng. Chem. *46*, 1942 (1954).
2. Utermohlen, W. P., and F. L. Wallace, Tex. Res. J. *17*, 670 (1947).
3. Bacon, O. C., and J. E. Smith, Amer. Dyestuff Reporter *43*, 619 (1954).
4. Linfield, W. M., E. Jungermann and J. C. Sherrill, JAOCS *39*, 47 (1962).
5. Martin, A. L., and R. C. Davis, Soap Chem. Spec., April and May, 1961.
6. Barker, G. E., and C. R. Kern, JAOCS *27*, 113 (1950).
7. Hensley, J. W., M. G. Kramer, R. D. Ring and H. R. Suter, *Ibid.* *32*, 138 (1955).
8. Diamond, W. J., and H. Levin, Tex. Res. J. *27*, 787 (1957).
9. Shelberg, W. E., J. L. Mackin and R. K. Fuller, Ind. Eng. Chem. *46*, 2572 (1954).
10. Powe, W. C., Tex. Res. J. *29*, 879 (1959).
11. Harris, J. C., "Detergency Evaluation and Testing," Interscience Publishers, Inc., New York, 1954.
12. Kubelka, P., and F. Munk, Z. Tech. Physik. *12*, 593 (1931).
13. Crook, E. H., D. B. Fordyce and G. F. Trebbi, J. Phys. Chem. *67*, 39 (1963).
14. Tachikana, T., A. Yube and M. Tsubomura, J. Coll. Sci. *15*, 278 (1960).
15. Bacon, O. C., and J. E. Smith, Ind. Eng. Chem. *40*, 2361 (1948).

[Received December 11, 1963—Accepted June 4, 1964]

Continuous Production of Cyclic Fatty Acids[1]

R. E. BEAL, R. A. EISENHAUER and E. L. GRIFFIN, JR., Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

Kinetic studies of a batch treatment of linseed oil to produce cyclic acids indicated that of a continuous process conducted in a flow-through reactor and involving rapid heat-up of reactants, followed by a short reaction time, might be feasible. Tests were conducted in a continuous system to examine the effects of flow rate (retention time), reaction temp, reaction system pressure and reagents on product yields. The reactant solution (linseed oil-ethylene glycol-sodium hydroxide) was pumped through an externally heated tube and discharged through a back-pressure valve. Maximum cyclic acid yields based on wt of oil were 37% by the continuous method and 40.4% by the batch process when the feed was saturated with nitrogen, and 39.5% and 46.1% for the respective methods when the feed was saturated with ethylene. These differences may be offset by the advantages inherent in a continuous process.

Introduction

THE CHEMISTRY of cyclic monomeric fatty acids prepared from linseed oil, and details of their production in batch reaction using the oil and an alkali catalyst in a suitable solvent system, have been described in previous papers from the Northern Laboratory (3,4,6,7).

Unsaturated cyclic acids have been given a preliminary evaluation in alkyd resin formulations and found to impart good color stability properties to the resin with respect to yellowing tendency (6). The low-melting point of the completely saturated cyclic fatty acids suggests that other valuable uses also may be developed in the fields of lubricants, plasticizers and other products.

Extensive studies of the relation of processing conditions to yield of product suggested the production of these cyclic fatty acids by a continuous process. Details of such a process for producing cyclic fatty acids are described here, and a comparison is made of some product yields obtained by the batch and continuous methods.

Equipment and Procedure

Figure 1 is a diagram of the continuous apparatus used. It consists of a supply container, positive displacement pump, steam preheater, both a preheater coil and a reactor coil immersed in a molten solder bath, an aftercooler, a variable back-pressure valve and a product collector. The entire flow system is constructed of 3/8-in. type 316 stainless-steel tubing. The internal volumes of the bath preheater coil (28 ml) and the reactor coil (136 ml) were determined by displacement measurements with water. The reactants consisting of linseed oil, sodium hydroxide and ethylene glycol were mixed and heated in another vessel, not shown, to effect saponification of the oil and solution of the soaps and excess sodium hydroxide in the solvent. This solution was deaerated under vacuum to

[1] Presented in part at the AOCS Meeting, New Orleans, 1962.
[2] A laboratory of the No. Utiliz. Res. & Dev. Div., ARS, USDA.