Use of Experimental Design in Detergency Tests With a Natural Soil[1]

JAMES R. TROWBRIDGE, Colgate-Palmolive Research Center,
909 River Road, Piscataway, New Jersey 08854

ABSTRACT

A balanced incomplete block design is used to obtain detergency data in a test where cloth swatches are soiled by rubbing against the skin. The design provides increased precision in the data by adjusting for differences among soilers. The wash treatments are part of a second order rotatable design in three variables: the ratio of sodium nitrilotriacetate to sodium tripolyphosphate builder, pH of the wash solution, and temperature. The effect of builder ratio was not highly significant. Soil removal increased with higher pH and went through a maximum with increase in wash temperature. Redeposition was also measured by reflectance values obtained for unsoiled areas of the swatches. Redeposition increased with increase in wash temperature.

INTRODUCTION

The application of experimental design principles offers great advantages to those concerned with the study of detergency under a variety of conditions. In some cases the experimenter is concerned with unwanted variation such as differences among several preparations of soiled cloth. These differences are often isolated and prevented from obscuring the significance of the desired treatment comparisons by choosing an appropriate experimental plan from a wide variety available in the literature (1).

In other cases the investigator is concerned with the effects of several continuous variables on detergent performance. It is generally quite unsatisfactory to investigate one varible at a time, while holding the others constant since this approach ignores the possibility of interactions between variables. It is also frequently not possible to carry out the large number of experimental trials which would be required to explore completely the detergency response over the entire range of each of the chosen variables. However it is possible to obtain a very good estimate of the effects of the variables and their interactions over a limited region with a comparatively modest number of experimental trials by employing an efficient design of a type developed by Box, et al. (2). These designs are known as rotatable composite designs and are particularly effective when the center point of the design is in a region of special interest. For example, if one of the variables is water hardness, a good choice for the center point might be a hardness level corresponding to the average level of hardness encountered in home water supplies.

The chief purpose of this publication is to illustrate the use of an incomplete block design to isolate differences in skin soil obtained from different individuals and to give an example of a response surface in which detergency was determined as a function of three variables (builder ratio of sodium nitrilotriacetate (NaNTA) to sodium tripolyphosphate (NaTPP), wash solution pH and temperature).

A previous publication describes a technique for soiling test swatches by rubbing them over the surface of the skin (3). These swatches may be resoiled after washing and thus carried through a number of soil wash cycles. In addition to simulating the history of a typical laundered item, this process provides an increasing accumulation of unremoved soil and increases the power of the test procedure to discriminate among different wash treatments.

Two significant sources of variability in the soiling procedure are differences in the degree of soiling of swatches soiled by the same individual and differences in the ease of soil removal from swatches soiled by different individuals. The first source is reduced by expressing the response as the per cent regain of a reflectance as a result of washing based on the loss of reflectance due to soiling. The second source is reduced by assigning panelists to blocks of treatments in a designed experiment in which variance due to blocks is separated from the residual error variance.

EXPERIMENTAL PROCEDURE

A total of 105 cotton test swatches (Test Fabrics, Inc., Style No. 400 MW) were selected at random and assigned, 5 apiece, to each of 21 soilers. The assignment of swatches to 21 wash treatments and 21 panel members (soilers) was in the form of a balanced incomplete block experimental design as shown in Table I.

Swatches were soiled in the manner described previously (3) and resoiled after washing for a total of three soil-wash cycles. The per cent soil removal values for each swatch were calculated as follows:

$$Y = \frac{[(W_1 - S_1) + (W_2 - S_2) + (W_3 - S_3)] \times 100}{[(91 - S_1) + (W_1 - S_2) + (W_2 - S_3)]}$$

Where Y is per cent soil removal, S_n is the per cent reflectance (R_d) of the soiled portion of the swatch after the nth soiling and W_n is the per cent reflectance after the nth washing. The value, 91, is a maximum reflectance value for an unsoiled swatch. Per cent soil removal values for each swatch are also listed in Table I.

The data of Table I was analyzed as described by Cochran and Cox (4) to provide the means and adjusted means of Table II. The means of the five swatch values for each treatment have been adjusted to the values which would have been expected if all swatches had received the same mean degree of soiling as provided by an average of the 21 panelists.

An analysis of variance for the balanced incomplete block data is presented in Table III.

Second Order Rotatable Design

The first 20 wash treatments listed in Table II are part of a second order design in three variables (5). The variables and coded levels are described in Table IV.

The variables are X_1, the ratio of sodium nitrilotriacetate (NaNTA) to sodium tripolyphosphate (NaTPP); X_2, the pH of the wash solution; and X_3, the wash temperature. The pH of the prepared wash solution was adjusted at room temperature with a small amount of either sodium hydroxide or sulfuric acid as required. Washing was done in a Terg-O-Tometer for 10 min in 150 ppm hardness water with five 4 x 6 swatches in 500 ml solution and 100 cpm agitation speed. After washing swatches were rinsed for 5 min at the same temperature used for washing. The composition of the wash solution is 0.015 sodium paraffin

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[1] One of five papers presented at the Symposium, "Basic Aspects of Detergency," AOCS-ISF World Congress, Chicago, September 1970.

TABLE I

Balanced Incomplete Block Design and Experimental Soil Removals

Block[a]	Wash[b] treatment	Soil removal, %	Wash[b] treatment	Soil removal, %	Wash[b] treatment	Soil removal, %	Wash[b] treatment	Soil removal, %	Wash[b] treatment	Soil removal, %
I	21	64.9	1	69.3	4	74.4	14	58.3	16	71.0
II	1	69.3	2	60.9	5	50.8	15	53.8	17	62.6
III	2	70.9	3	72.0	6	61.5	16	72.9	18	68.8
IV	3	75.8	4	78.6	7	68.1	17	60.0	19	74.0
V	4	73.1	5	62.2	8	68.4	18	69.0	20	66.2
VI	5	70.1	6	71.4	9	76.2	19	74.7	21	66.3
VII	6	65.4	7	67.5	10	77.2	20	71.9	1	67.8
VIII	7	72.6	8	74.5	11	77.3	21	73.4	2	77.0
IX	8	67.3	9	69.9	12	73.0	1	64.8	3	73.0
X	9	65.4	10	75.5	13	52.8	2	62.3	4	73.2
XI	10	75.6	11	78.2	14	62.7	3	71.5	5	63.1
XII	11	68.8	12	64.4	15	65.1	4	75.8	6	71.4
XIII	12	74.2	13	64.4	16	71.0	5	69.7	7	70.7
XIV	13	54.3	14	70.9	17	71.2	6	67.1	8	61.7
XV	14	67.6	15	75.4	18	71.1	7	70.1	9	72.0
XVI	15	76.8	16	79.7	19	72.2	8	75.4	10	74.8
XVII	16	67.2	17	72.6	20	77.7	9	74.7	11	64.9
XVIII	17	73.4	18	78.4	21	71.8	10	81.8	12	77.8
XIX	18	77.0	19	75.6	1	74.1	11	77.4	13	69.0
XX	19	57.4	20	66.9	2	66.1	12	72.4	14	65.1
XXI	20	71.0	21	62.5	3	67.4	13	64.0	15	67.1

[a] Panel members (soilers) used to soil the test swatches. [b] Assignment of swatches to 21 wash treatments.

sulfonate (essentially C_{14}-C_{17} linear hydrocarbon with random substitution at 2 C atoms); 0.030% builder (specified mixture of NaNTA and NaTPP); 0.030% sodium sulfate; 150 ppm water hardness (3:2, Ca/Mg ratio).

The experimental design plan, observed and calculated response are listed in Table V. The observed responses were fitted to a complete second order equation by the method of least squares (5).

$$\hat{Y} = b_0 + b_1x_1 + b_2x_2 + b_3x + b_{11}x_1{}^2 + b_{22}x_2{}^2 + b_{33}x_3{}^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3$$

The values of the fitted coefficients and the significance level based on the pure experimental error (six replicate center points) are given in Table VI.

An analysis of variance for the fitted equation is shown in Table VII.

DISCUSSION OF RESULTS

From the coefficients in Table VI, the following response equation can be used to predict per cent soil removal:

$$Y\ (\%\ \text{soil removal}) = 70.2 + 0.65X_1 + 1.65X_2 - 0.93X_3 + .62X_1{}^2 + 1.32X_2^2 - 2.44X_3^2 + 0.23X_1X_2 + 0.04X_1X_3 - 0.58X_2X_3$$

where X_1, X_2 and X_3 are the coded values of the variables listed in Table IV. For example, the predicted soil removal at the center point of the experiment, where all variables have a coded value of 0, is 70.2%.

TABLE II

Percentage Soil Removal Values

Treatment no.	Mean	Adjusted mean
1	69.1	70.3
2	67.4	69.6
3	71.9	72.6
4	75.0	77.1
5	63.2	63.9
6	67.4	67.7
7	69.8	68.2
8	69.5	68.5
9	71.6	71.7
10	77.0	76.2
11	73.3	71.7
12	72.4	72.3
13	60.9	60.8
14	64.9	65.9
15	67.6	68.5
16	72.4	71.7
17	68.0	68.6
18	72.9	71.3
19	70.8	69.0
20	70.7	72.2
21	67.8	65.9

TABLE III

Analysis of Variance
(Soil Removal) Balanced Incomplete Block[a]

Source	DF	SS	MS
Treatments (unadj.)	20	1472	
Blocks (adj.)	20	1408	70.4
Intrablock error	64	1031	16.1
Total	104	3911	

[a] Effective error variance (single swatch), 18.46; effective error variance *treatment mean*, 3.69.

TABLE IV

Rotatable Second Order
Design in Three Variables

	Coded level				
	-1.682	-1	0	1	1.682
X_1, NaNTA/NaTPP	8:92	25:75	50:50	75:25	92:8
X_2, pH	7.8	8.5	9.5	10.5	11.2
X_3, deg F	50	70	100	130	150

TABLE VII

Analysis of Variance for Fitted Second Order Equation

Source	DF[a]	SS[a]	MS[a]
First order terms	3	54.9	18.3
Second order terms	6	131.9	22.0
Lack of fit	5	69.2	13.8
Experimental error	5	14.7	2.94

[a] Abbreviations: DF, degrees of freedom; SS, sum of squares; MS, mean squares.

The most significant term in Table VII is the second order square term for temperature which has a large negative coefficient. This unexpected result means that soil removal as measured by reflectance goes through a maximum value as wash temperature is increased. We have also observed the soil removal to go through a maximum as temperature is increased for other detergent systems in the skin soil test. Usually we observe maximum soil removal in the range of 100-120 F. Other significant terms are the linear and square term for the pH variable. Soil removal becomes increasingly better as pH increases. Soil removal is slightly better when the builder ratio is in the direction of more NaNTA and less NaTPP but the effect is not highly significant. There are no significant interactions as indicated by the relatively small values of the crossproduct coefficients.

The effect of the significant variables, pH and temperature, is shown in Figure 1. Here the location of contour lines of equal per cent soil removal has been plotted at a time sharing computer terminal based on the fitted equation for a composition containing a 50:50 mixture of the two builders (coded variable $X_1=0$).

The two digit numbers plotted in Figure 1 represent the per cent soil removal at the indicated level of temperature and pH. The plotting routine can be programmed for any desired contour interval (an interval of 2 for Figure 1) and the approximate points at which contours cross a horizontal line are shown for each line of printing.

A circle has been drawn in Figure 1 at a coded radius of 1 unit. Within this circle the standard error of the predicted value is about 1.5% soil removal. Predictions outside of this region become less reliable as the radius is increased and the standard error is about ±4% at a radius of 2 units.

The lack of fit mean square in Table VII is large compared to the error mean square and indicates that a second order model is inadequate to properly represent the data. The nature of the inadequacy becomes apparent from an inspection of the residuals in Table V. The sign of the residuals is strongly correlated with the value of the temperature variable, X_3. All residuals are positive when X_3 = -1

TABLE V

Per Cent Soil Removal
Second Order Rotatable Design

Observed response	Calculated response	Residual	X_1	X_2	S_3
70.3	68.0	2.3	-1	-1	-1
69.6	68.8	0.8	1	-1	-1
72.6	72.1	0.5	-1	1	-1
77.1	73.7	3.4	1	1	-1
63.9	67.3	-3.4	-1	-1	1
67.7	68.2	-0.5	1	-1	1
68.2	68.9	-0.7	-1	1	1
68.6	70.8	-2.2	1	1	1
71.7	70.9	0.8	-1.682	0	0
72.3	73.1	-0.8	1.682	0	0
71.7	71.2	0.5	0	-1.682	0
76.2	76.7	-0.5	0	1.682	0
60.8	64.9	-4.1	0	0	-1.682
65.9	61.8	4.1	0	0	1.682
68.5	70.2	-1.7	0	0	0
71.7	70.2	1.5	0	0	0
68.6	70.2	-1.6	0	0	0
71.3	70.2	1.1	0	0	0
69.0	70.2	-1.2	0	0	0
72.2	70.2	2.0	0	0	0

TABLE VI

Fitted Coefficients—Soil Removal[a]

Term	Coefficient	Student's t
b_1	0.65	0.93
b_2	1.65	2.36[b]
b_3	-0.93	1.33
b_{11}	0.62	1.38
b_{22}	1.32	2.92[c]
b_{33}	-2.44	5.41[d]
b_{12}	0.23	0.37
b_{13}	0.04	0.07
b_{23}	-0.58	0.96

[a] Constant term (b_0) = 70.2.
[b] Significant at <0.10 P.
[c] Significant at <0.05 P.
[d] Significant at <0.01 P.

TABLE VIII

Analysis of Variance (Redeposition) Balanced Incomplete Block

	DF[a]	SS[a]	MS[a]
Treatments (unadj.)	20	6.41	
Blocks (adj.)	20	2.58	.129
Intrablock error	64	1.55	.024
Total	104	10.54	

[a] Abbreviations: see Table VII.

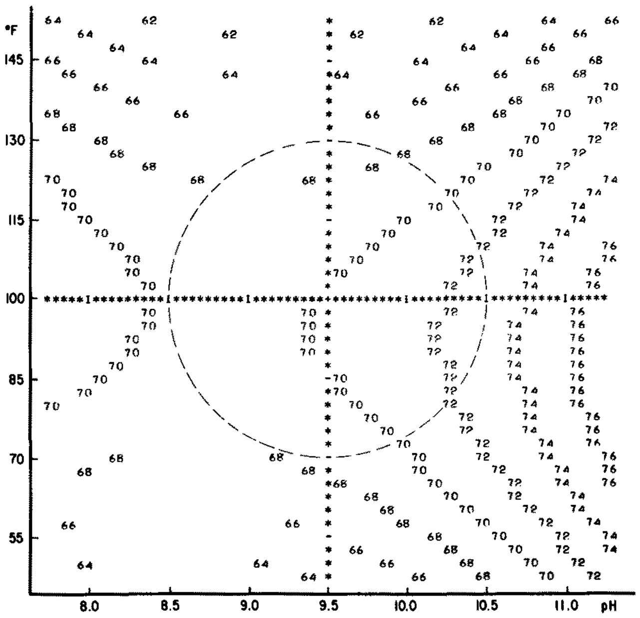

FIG. 1. Effect of temperature and pH on soil removal at 50:50 NaNTA/NaTPP ratio.

TABLE IX

Fitted Coefficients–Redeposition[a]

Term	Coefficient	Student's t
b_1	0.034	1.46
b_2	0.029	1.24
b_3	-0.265	11.28[d]
b_{11}	0.023	1.52
b_{22}	-0.041	2.70[c]
b_{33}	-0.098	6.47[e]
b_{12}	-0.035	1.70
b_{13}	0.020	0.99
b_{23}	0.052	2.55[b]

[a] Constant term b_0 = 88.41.
[b] Significant at <0.10 P.
[c] Significant at <0.05 P.
[d] Significant at <0.01 P.

and negative when $X_3 = +1$. The largest residuals occur when X_3 has extreme values of ±1.682. When a third order term, $b_{333}x_3{}^3$, is introduced into the model equation, the mean square for lack of fit (4 DF) is reduced from 13.8 to 3.6 and the fit is much improved. New fitted values for the coefficients of the temperature terms are $b_3 = -4.9$, $b_{33} = -2.47$ and $b_{333} = 2.27$. The values of the other coefficients remain essentially unchanged.

Redeposition

Reflectance readings were also obtained on an unsoiled area of each swatch. These provide a measure of the extent of redeposition of soil back onto the fabric during the wash. Since the extent of redeposition is also dependent on the soil load, the per cent reflectance readings after the third wash for the unsoiled areas were adjusted for block effects as described previously for soil removal. An analysis of variance is presented in Table VIII. The fitted coefficients of the prediction equation for redeposition are shown in Table IX. The observed and calculated responses are in Table X.

The precision of the reflectance readings on the outside area of the swatch which were reproducible within 0.1 R_d unit is close to the theoretical limit of the instrument. Observed values in Table X are again based on the adjusted mean of five individual swatches. The effects of the treatment variables on reflectance are small but in some cases show great statistical significance. These effects may also be of considerable practical significance when observed as a cumulative effect from a large number of washings. By far the largest coefficient involves the first order effect of temperature. As observed in a number of detergency studies, redeposition increases with increasing wash temperature. The effect of temperature and pH on redeposition at $X_1 = 0$ is shown in Figure 2. The computer plotted numbers represent the units and tenths digits of the per cent reflectance readings minus 80 (86 = 88.6%).

ACKNOWLEDGMENTS

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TABLE X

Redeposition Values Second Order Rotatable Design

Observed response	Calculated response	Residual	Coded level X_1	X_2	X_3
88.48	88.54	-0.06	-1	-1	-1
88.64	88.64	0.00	1	-1	-1
88.55	88.56	-0.01	-1	1	-1
88.52	88.52	0.00	1	1	-1
87.84	87.86	-0.02	-1	-1	1
88.03	88.04	-0.01	1	-1	1
88.07	88.10	-0.03	-1	1	1
88.17	88.14	0.03	1	1	1
88.48	88.42	0.06	-1.682	0	0
88.52	88.54	-0.02	1.682	0	0
88.29	88.25	0.04	0	-1.682	0
88.34	88.35	-0.01	0	1.682	0
88.62	88.59	0.03	0	0	-1.682
87.70	87.69	0.01	0	0	1.682
88.48	88.42	0.06	0	0	0
88.37	88.42	-0.05	0	0	0
88.44	88.42	0.02	0	0	0
88.40	88.42	-0.02	0	0	0
88.33	88.42	-0.08	0	0	0
88.47	88.42	0.05	0	0	0

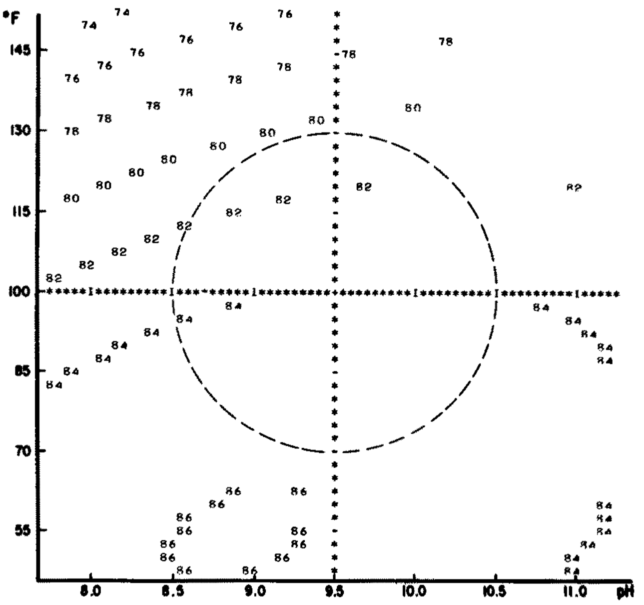

FIG. 2. Effect of temperature and pH on soil redeposition at 50:50 NaNTA/NaTPP ratio.

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