SCIENTIFIC SERVICES S/D, INC.
42 MAIN STREET
P. O. BOX 778
SPARROW BUSH, N.Y. 12780

EVALUATION

OF

THE

EFFECT OF

WATER HARDNESS ON

PERFORMANCE OF

AUTOMATIC DISHWASHER DETERGENTS

AND SAVINGS POSSIBLE

BY

SOFTENING WATER

FOR

THE

WATER QUALITY RESEARCH FOUNDATION

JANUARY 14, 2011

PROJECT:

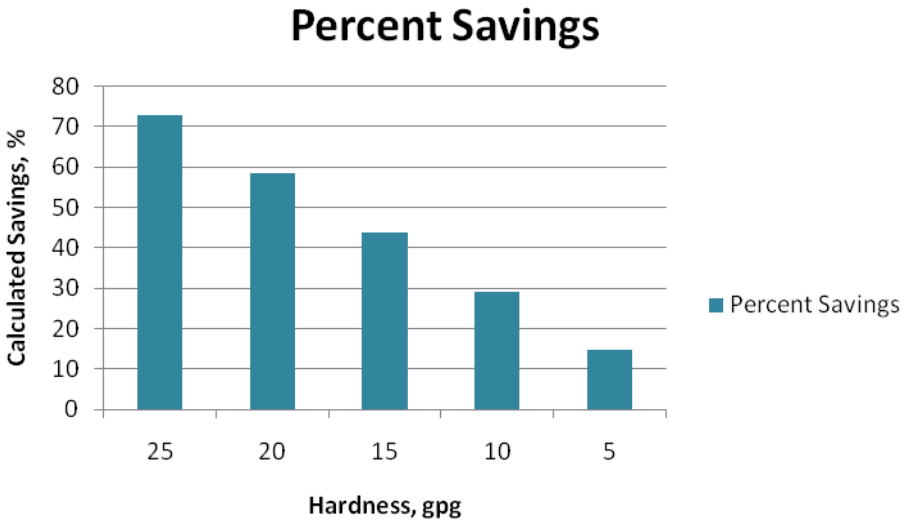
To carry out a designed experiment using ASTM D 3556 to quantify the relative effects of hardness and detergent dosage to show savings possible by softening hard water. Include tests for removing difficult soils in addition to the usual spot and film evaluation.
Determine the relative dose/hardness relationship with three non phosphate automatic dishwashing detergents with two consecutive wash-dry cycles for spot and film. With one detergent run five cycles to ensure that effects do not change with number of cycles.

Repeat the tests with a private label detergent submitted by the Water Quality Association.

Confirm the hardness/dose relationships with fixed use tablet detergents and demonstrate the ability to save energy by air drying.

SUMMARY:

Less automatic dish detergent can be used if hard water is softened. The dose necessary to maintain the response at the midpoint or average condition of the experiment was calculated. For the average response, the dose necessary for each hardness level to produce that level of performance was calculated. The difference between the dose needed when water is soft and the dose needed at the various levels of hardness gives the possible savings from softening the water. Of course, if detergent use is not reduced or reduced only partially, better soil removal and appearance will result. The results are shown in the Graph below.



INTRODUCTION:

When this project was conceived, it was apparent that the automatic dishwashing industry was in flux. The 40 year saga of phosphate replacement was coming to an end. The pressure to remove phosphates from detergents has resulted in the industry trade association announcing removal of phosphates by July 2010. The US Department of Energy has mandated machine design changes that are being introduced to reduce water and energy use.

Demands on the detergent formulation to clean dishes and deliver spot and film free glassware are difficult to meet. With the aid of vigorous wash action cleaning was relatively easy to achieve. But trace amounts of proteins, fats and starches collect on glassy surfaces and form unsightly films or cause water to bead up and form visible spots. Formulations were developed with alkalies to facilitate cleaning. Special surfactants were invented to control foam and survive until the final rinse to cause water to sheet off surfaces rather than coalesce into droplets that evaporate and produce spots. Chlorine bleaches were added to oxidize films of starch and protein. Silicates were included to prevent corrosion of the washware and machine parts. Polyphosphate water softeners mitigated the bad effects of hard water and were essential for producing detergents safe for household use.

It took a monumental research program to meet all the conflicting requirements and produce products which meet all modern demands. The ASTM test method that was standard for decades had to be revised to provide a better evaluation of spots and film build up as well as to provide a more realistic soil. Removal of difficult soils was also added. The new formulations which have been on the market since July 2010 utilize enzymes and non chlorine bleaches along with other innovations to produce satisfactory results.

Machine design changes are ongoing. Less water is used but hot water is still a requirement. One big change is the use of sensors to make the machines smarter in handling the different soils encountered in the process. In Europe many machines have built in water softeners.

SAMPLES TESTED:

	SS#	Batch Code
Finish Automatic Dishwasher Detergent Gel	8039	S0043 0912
Cascade Shine Shield w/ Dawn	8040	9364173141338
Palmolive Eco+	8041	0008US582790
Trader Joe's Automatic Dishwasher Detergent	8044	9292G
Finish Powerball Tabs	8051	0238690
Cascade Complete Gels Tablets	8052	02326252A3 2234

PROCEDURE:

Equipment used:

2 GE dishwashers GSD4000JWW
2 light boxes
Culligan Medalist 10X49 Metered Water Softener
Brainweigh B 300 D – 3 place top loading scale
Pipette
12 - 30ml beakers (6 per machine)
Spoon
Thermometer
pH meter
Mettler 4400 top loading scale
HP Photosmart M415 digital camera
Samsung 600Watt Microwave Oven
Dimco-Gray Timer

Prepare 2 GE dishwashers GSD4000JWW with the specified dummy load. Prepare glasses by scrubbing with soft abrasive and surfactant followed by rinsing and soaking in a citric acid bath and finally rinsing with distilled water. Test glasses for sheeting to ensure absolute cleanliness. Calculate the tap water hardness and the amount of hardness to add to each part of the cycle to achieve 0, 513 & 256.5ppm. Since the original water is soft (30 ppm), sodium chloride and sodium bicarbonate were added to simulate natural hard water being softened. Make the soils; Oatmeal, Dry Milk, and Grease, to be applied to the saucers. The guidelines of ASTM D 3556 were followed for the tests. Evaluations of the glasses and saucers were performed at the end of each cycle after cooling and ageing. At least three trained evaluators were used.

The dishwashers used were models without sensors and automatic dosing. This allowed us to set the dose and hardness. The smart machines would not allow setting the conditions for the study.

Conditions:

Water Hardness – 0, 513, 256.5 ppm (3:1 Ca/Mg)
Detergent Dosage – 30 grams in small cup, 55 grams in large cup, 80 grams both cups
Temperature – 130 - 135ºF
Dishwasher Load – 10 dinner plates, 6 Forks, 6 Knives, 6 Spoons, 12 glasses, 11 filler saucers & 12soiled saucers
Soils: Oatmeal, **cooked prepared fresh semi daily** – 24 grams
Dry Milk – 10 grams
Grease, 1/3 each lard, tallow and margarine – 10 grams
Soiled Saucers – 3 each of:
Egg Yolk – 0.5g cooked for 1 minute
Pizza Sauce – 0.5g sauce + 1g cheese cooked for 30 seconds
Spinach,canned – 2g cooked for 2 minutes
Brownie Mix – 1g cooked for 1 minute
Fish, Bread Crumbs & Olive Oil – 1g each cooked for 5 minutes

Evaluation data was recorded on log sheets and transferred to computer spread sheets. Results were then arranged for statistical analysis by JMP Statistical Software.

RESULTS:

The main experiment was designed to produce data that could be analyzed by JMP Statistical Software. A full factorial design with a center point was used.

Dose, g detergent	Water Hardness, ppm
30	0
30	513
80	0
80	513
55	256.5

These five runs were repeated with Cascade, Finish and Palmolive liquid non phosphate detergents. Two consecutive wash-dry cycles were made with evaluation for spots and film on the 10 glasses and soil removal from three saucers with each soil.

A minimum of three trained panelists evaluated each glass and saucer. The evaluation ratings were assembled in spreadsheets for analysis. The data fit linear equations for effects of hardness and dosage. The analysis included tests for statistical significance. Graphs were produced to illustrate the effects.

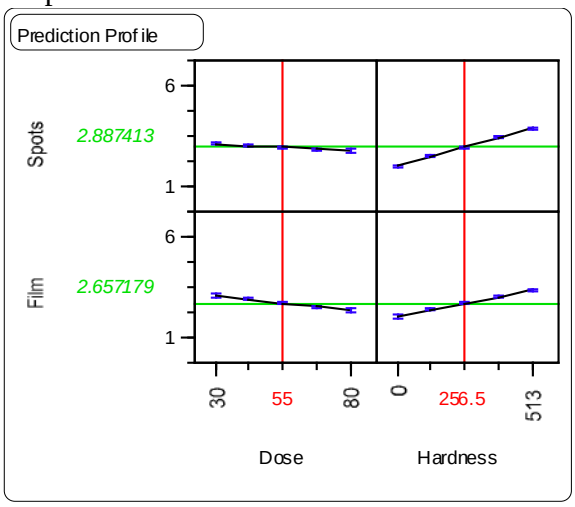
This experiment was repeated with Trader Joe's Detergent to show that a private label product reacted the same to hardness and detergent level.

Cascade Detergent was run for an additional three cycles to show that the hardness/dose performance relationship would persist.

Finally, a short demonstration of air drying to save electrical energy of the heated dry cycle showed that equal or better results were obtained for spots and film with soft water when compared to hard water.

Evaluation of Relative Hardness and Dose Effects on Average of Three Detergents

Effect of Dose and Hardness on Spotting and Filming
Scale 1 no spots or film, 5 unacceptable spots and film
Graphs



The graph shows that hardness is much more effective than detergent use level for preventing spots and film on glassware.

Spot Statistics
Average Three Detergents
Effect of Dose and Hardness on Spotting and Filming

Screening Fit

Spots

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	2.3094195	0.069912	33.03	<.0001
Dose	-0.006731	0.001087	-6.19	<.0001
Hardness	0.0036968	0.000106	34.90	<.0001

Effect Test

Effect Equations
Dose effect = 0.00673 X 50 = 0.337

Hardness Effect = 0.00370 X 513 = 1.90

Film Statistics

Film

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	2.8639751	0.085964	33.32	<.0001
Dose	-0.015307	0.001336	-11.46	<.0001
Hardness	0.0024761	0.00013	19.01	<.0001

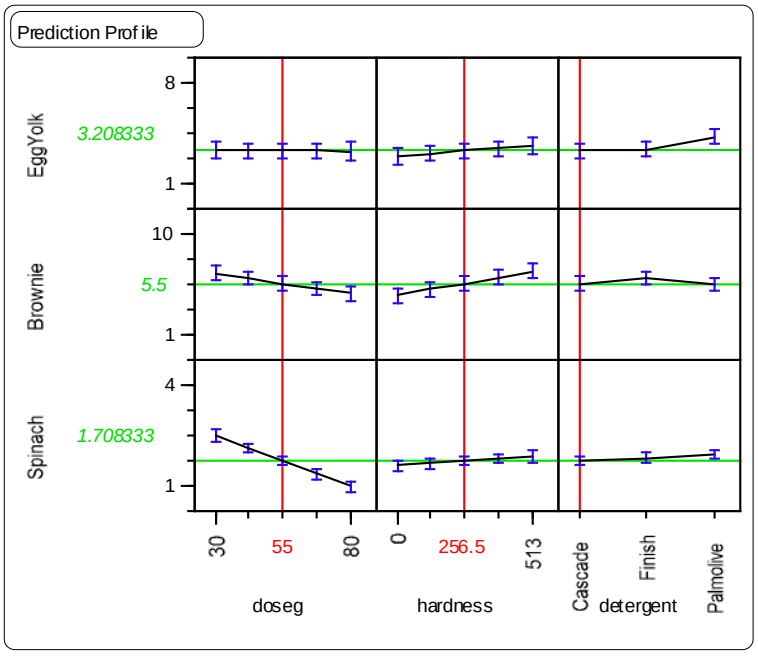
Effect Test

Effect Equations
Dose Effect = 0.0153 X 50 = 0.765

Hardness Effect = 0.00248 X 513 = 1.27

The statistical calculations confirm the graphical depictions of the effects of dose and hardness on spotting and filming. All of the effects are highly significant. For spot intensity the softening of water produces about six times the effect as increasing dose from 30 to 80 g. Film formation is affected about twice as much by hardness as by the dose.

Evaluation of Relative Hardness and Dose Effects
Soil Removal Results with Three Detergents
Scale 10 no removal – 1 total removal
Graphs of Results



The graph shows that the three detergents are different but the trends about the same. Removal of the three soils is affected differently by hardness and detergent level, but more detergent and lower hardness results in more soil removal.

Statistics

Egg Yolk Removal

Screening Fit

EggYolk

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	3.2902778	0.390583	8.42	<.0001
doseg	-0.001111	0.005974	-0.19	0.8527
hardness	0.0013537	0.000582	2.32	0.0215
detergen[Cascade-Palmoli]	-0.368056	0.211203	-1.74	0.0836
detergen[Finish-Palmoli]	-0.243056	0.211203	-1.15	0.2518

Effect Test

Effect Equations

Egg Dose

0.001111X50 = 0.055 not significant

Egg Hardness = 0.001354 X 513 = 0.69

Brownie Removal

Brownie

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	6.5416667	0.440385	14.85	<.0001
doseg	-0.036111	0.006735	-5.36	<.0001
hardness	0.0041694	0.000656	6.35	<.0001
detergen[Cascade-Palmoli]	-0.125	0.238133	-0.52	0.6005
detergen[Finish-Palmoli]	0.2916667	0.238133	1.22	0.2227

Effect Test

Effect Equations

Dose Effect = 0.0361 X 50 = 1.81

Hardness Effect = 0.00417 X 513 = 2.14
Spinach Removal

Spinach

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	3.3326389	0.109491	30.44	<.0001
doseg	-0.030417	0.001675	-18.16	<.0001
hardness	0.000555	0.000163	3.40	0.0009
detergen[Cascade-Palmoli]	-0.09375	0.059206	-1.58	0.1156
detergen[Finish-Palmoli]	0	0.059206	0.00	1.0000

Effect Test

Effect Equations
Dose Effect = 0.0304 X 50 = 1.52

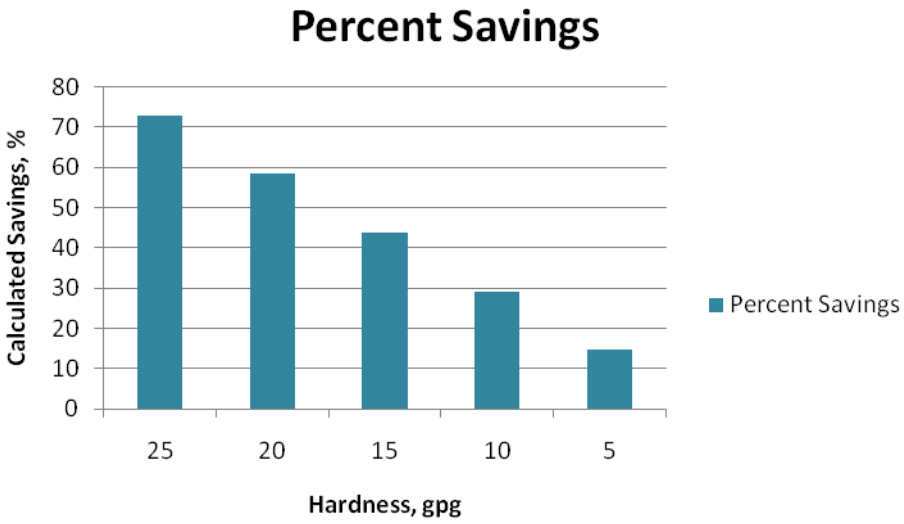
Hardness Effect = 0.000555 X 513 = 0.284

CALCULATION OF POSSIBLE SAVINGS:

The equations for response of spotting, filming and soil removal to water hardness and detergent dosage with the three liquid detergents were averaged. The dose necessary to maintain the response at the midpoint or average condition of the experiment was calculated. For the average response, the dose necessary for each hardness level in g to produce that level of performance was calculated. The difference between the dose needed when water is soft and the dose needed at the various levels of hardness gives the possible savings from softening the water. Of course, if detergent use is not reduced or reduced only partially, better soil removal and appearance will result. The calculations are in the Table below and the results are shown in the Graph.

Maintain avg. at midpoint		**Coefficients**	
	Intercept	**Dose**	**Hardness**
Spot	2.30942	-0.006731	0.003697
Film	2.86398	-0.015307	0.002476
Egg	3.2903	-0.00111	0.001354
Brownie	6.5417	-0.036111	0.004169
Spinach	3.33264	-0.03042	0.000555
Average	3.667608	-0.017936	0.00245
Ave Response		3.3120655	

Hardness, gpg	Hardness, ppm	Calc Dose, g	Savings, g	Savings, %
30	513	89.874582	70.05853	87.57316
25	427.5	78.198161	58.38211	72.97763
20	342	66.521739	46.70569	58.38211
15	256.5	54.845318	35.02926	43.78658
10	171	43.168896	23.35284	29.19105
5	85.5	31.492475	11.67642	14.59553
0	0	19.816054	0	0

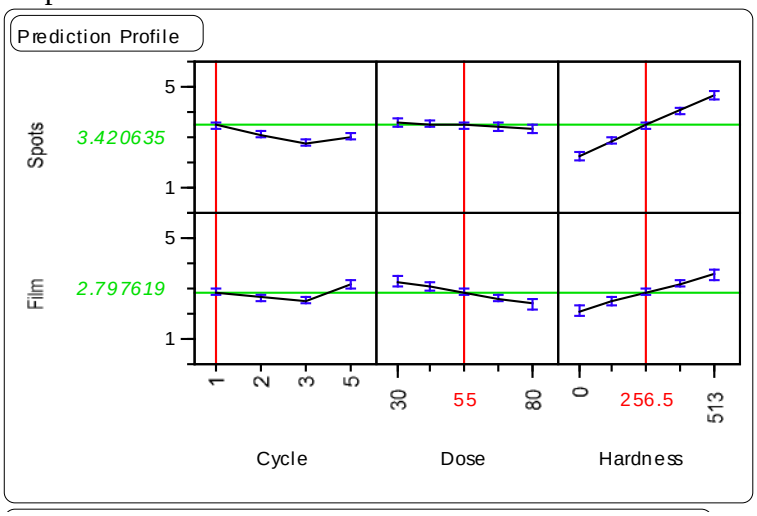


Evaluation of Additional Cycles:

Cascade with 1 – 5 Cycles

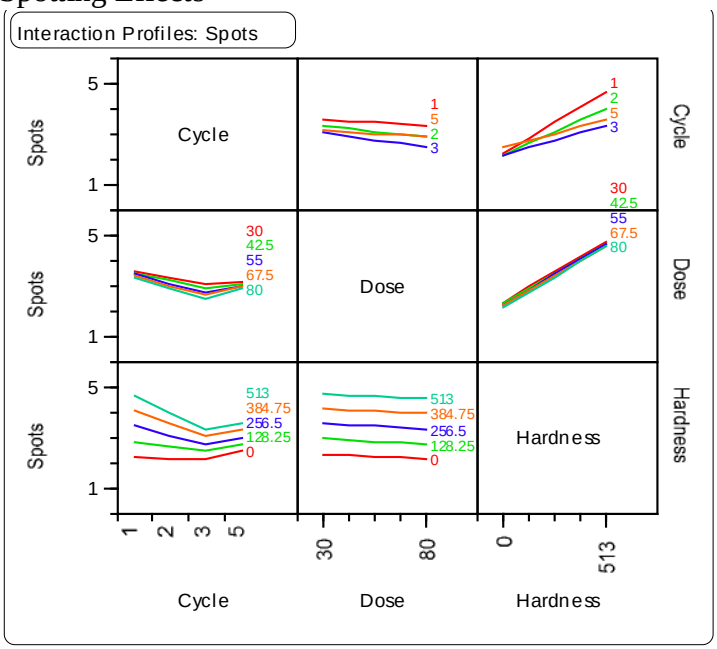
Evaluation of Relative Hardness and Dose Effects

Graphs of Main Effects

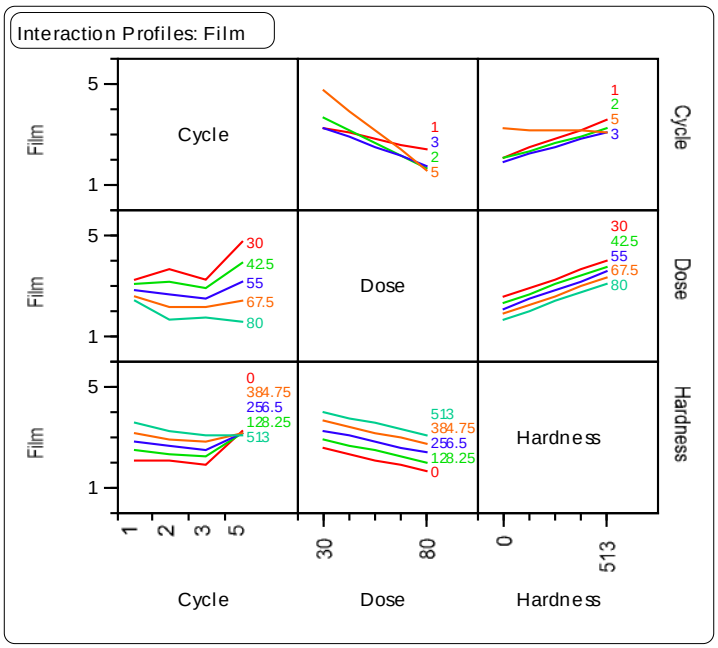


Interactions of No. of Cycles with variables

Spotting Effects



Filming Effects



Spotting Statistics

Screening Fit

Spots

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	2.68754	0.085154	31.56	<.0001
Cycle[1-5]	-0.241905	0.14854	-1.63	0.1037
Cycle[2-5]	-0.083904	0.142314	-0.59	0.5556
Cycle[3-5]	0.16446	0.146811	1.12	0.2629
Dose	-0.007751	0.001323	-5.86	<.0001
Hardness	0.0031115	0.000129	24.13	<.0001
Cycle[1-5]*Dose	0.0037924	0.002311	1.64	0.1011
Cycle[2-5]*Dose	-0.000249	0.00221	-0.11	0.9102
Cycle[3-5]*Dose	-0.004849	0.00228	-2.13	0.0336
Cycle[1-5]*Hardness	0.0015385	0.000225	6.83	<.0001
Cycle[2-5]*Hardness	0.0004328	0.000215	2.01	0.0448
Cycle[3-5]*Hardness	-0.000831	0.000222	-3.74	0.0002

Effect Test

Filming Statistics

Film

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

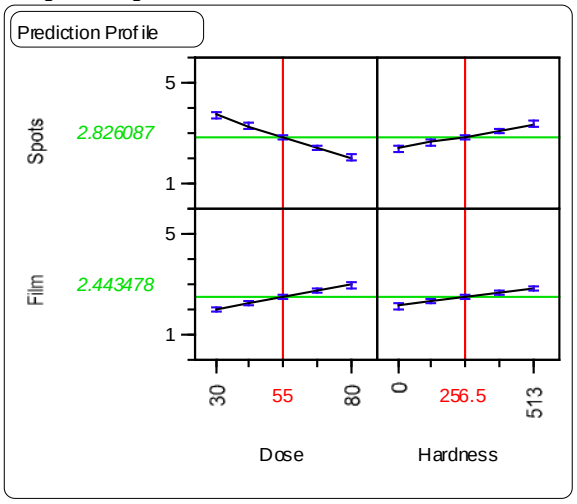
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	4.342425	0.097099	44.72	<.0001
Cycle[1-5]	-1.278139	0.169377	-7.55	<.0001
Cycle[2-5]	-0.138789	0.162278	-0.86	0.3926
Cycle[3-5]	-0.838425	0.167406	-5.01	<.0001
Dose	-0.037253	0.001508	-24.70	<.0001
Hardness	0.0017805	0.000147	12.11	<.0001
Cycle[1-5]*Dose	0.0193362	0.002635	7.34	<.0001
Cycle[2-5]*Dose	-0.00202	0.00252	-0.80	0.4230
Cycle[3-5]*Dose	0.0076529	0.002599	2.94	0.0033
Cycle[1-5]*Hardness	0.0010216	0.000257	3.98	<.0001
Cycle[2-5]*Hardness	0.0004169	0.000246	1.70	0.0899
Cycle[3-5]*Hardness	0.0005586	0.000253	2.21	0.0277

Effect Test

There is an interaction of the effect of detergent use level on spot and film ratings. The same is true for film ratings. Through three cycles there is a gradual improvement in the ratings but with cycle five, there is a reversal. Although the effects are statistically significant, the inflection in the trend is suspicious and more cycles would be needed to see if there would be a problem at the low dosage. Furthermore, the trends of effects of hardness and dose on spot and film results are in the same direction, i.e., better results at higher detergent dosage and lower water hardness. So it was concludes that the hardness and dose effects can be considered without the effect of number of wash-dry cycles.

Evaluation of Relative Hardness and Dose Effects
Trader Joe's Detergent

Graph of spot and film



Statistics Spot and Film Effects

Screening Fit

Spots

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	4.2086957	0.122312	34.41	<.0001
Dose	-0.033913	0.001899	-17.86	<.0001
Hardness	0.0018815	0.000185	10.17	<.0001

Effect Test

Film

Summary of Fit

Analysis of Variance

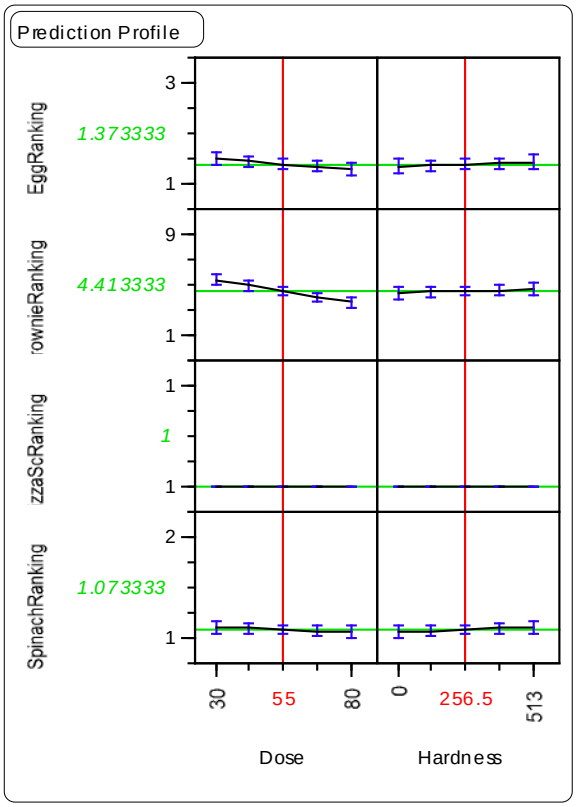
Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1.0321739	0.103681	9.96	<.0001
Dose	0.0192174	0.001609	11.94	<.0001
Hardness	0.0013815	0.000157	8.81	<.0001

Effect Test

Effect Equations
Dose
0.01922X50 = 0.961
Hardness
0.001882 X 513 = 0.965
Graphs of Soil Removal Trader Joe's



Statistics Trader Joe's

Egg Soil

Screening Fit

EggRanking

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1.57	0.130837	12.00	<.0001
Dose	-0.004333	0.002031	-2.13	0.0345
Hardness	0.0001624	0.000198	0.82	0.4132

Effect Test

Brownie Soil

BrownieRanking

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	6.2433333	0.465018	13.43	<.0001
Dose	-0.036	0.007218	-4.99	<.0001
Hardness	0.0005848	0.000704	0.83	0.4072

Effect Test

Pizza Sauce Soil

PizzaScRanking

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1	0	?	?
Dose	0	0	?	?
Hardness	0	0	?	?

Effect Test

Spinach Soil

SpinachRanking

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1.1033333	0.061486	17.94	<.0001
Dose	-0.001	0.000954	-1.05	0.2965
Hardness	0.0000975	0.000093	1.05	0.2965

Effect Test

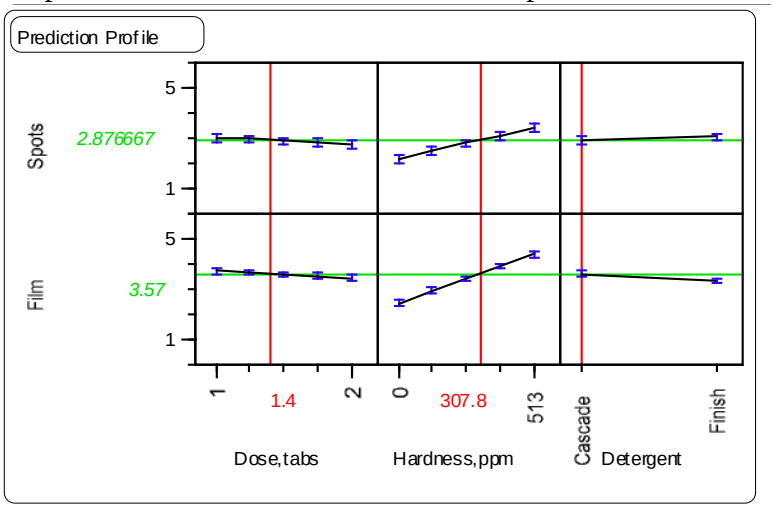
Trader Joe's detergent was very effective at removing soils. Pizza Sauce was completely removed in all runs so there were no differences in data to analyze. The other three soils were not affected by hardness levels.

Spot and film performance with Trader Joe's detergent performance was statistically significant for dose and hardness differences. With increasing dosage filming got worse, although within an acceptable range. More cycles would be necessary to see whether the filming leveled off. The polymer additive in dishwashing formulations sometimes does leave a visible film that aids in sheeting and builds up to an equilibrium level. Spotting decreased with increasing dose. The hardness effect was uniformly better at lower hardnesses.

Tests with Detergent Tablets

Water Hardness Effects on Performance with one and two tablets

Graph of Effects with Tablets Film and Spots



Statistics of Spotting Performance with Tablets

Screening Fit

Spots

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	2.6	0.1811	14.36	<.0001
Dose,tabs	-0.283333	0.10759	-2.63	0.0087
Hardness,ppm	0.0024204	0.00021	11.54	<.0001
Detergen[Cascade-Finish]	-0.071667	0.051971	-1.38	0.1684

Effect Test

Effect Equations
Spots
Dose = 0.2833 X 1 = 0.283
Hardness = 0.00242 X 513 = 1.24

With both tablet detergents the beneficial effect of softening the wash water is much greater than the use of two tablets rather than one. A caveat is that tablets are formulated to work well with a single tablet, so it is not surprising that use of a second tablet gave decent results. Note however, the excellent results attained with softened water.

Statistics of Filming Performance with Tablets

Film

Summary of Fit

Analysis of Variance

Lack of Fit

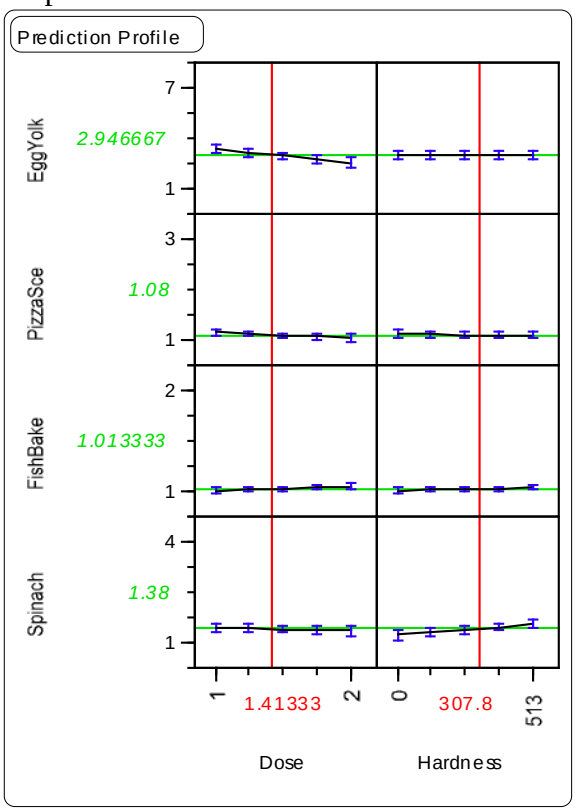
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	2.6321429	0.130369	20.19	<.0001
Dose,tabs	-0.263095	0.077451	-3.40	0.0007
Hardness,ppm	0.0037617	0.000151	24.92	<.0001
Detergen[Cascade-Finish]	0.1483333	0.037412	3.96	<.0001

Effect Test

Effect Equations
Film
Dose = 0.263 X 1 = 0.263
Hardness = 0.003762 X 513 = 1.92

Graph of Soil Removal Performance with Tablets



Statistics of Soil Removal Performance with Tablets
Egg Soil

Screening Fit

EggYolk

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	4.0878145	0.340364	12.01	<.0001
Dose	-0.814099	0.201837	-4.03	<.0001
Hardness	0.0000307	0.000395	0.08	0.9383

Effect Test

Statistics of Soil Removal Performance with Tablets
Pizza Sauce and Cheese

Pizza Sauce was completely removed in all runs so there were no differences in data to analyze.

Statistics of Soil Removal Performance with Tablets
Baked Fish

FishBake

Summary of Fit

Analysis of Variance

Lack of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.9457268	0.032197	29.37	<.0001
Dose	0.0361822	0.019093	1.90	0.0600
Hardness	0.0000535	0.000037	1.43	0.1548

Effect Test

Statistics of Soil Removal Performance with Tablets
Spinach Soil

Spinach

Summary of Fit

Analysis of Variance

Lack of Fit

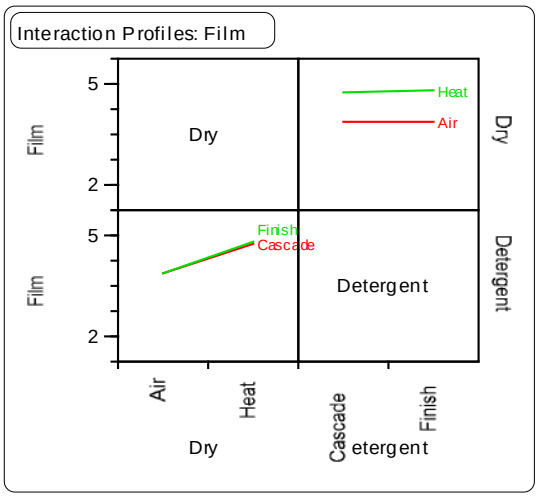
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1.3456852	0.17291	7.78	<.0001
Dose	-0.108235	0.102537	-1.06	0.2929
Hardness	0.0006085	0.000201	3.03	0.0029

Effect Test

Evaluation of Air Drying vs Heated Drying with Tablets

Film Performance



Statistics

Air Drying vs Heated Drying with Tablets

Screening Fit

Spots

Summary of Fit

Analysis of Variance

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	3.725	0.077017	48.37	<.0001
Dry [Air-Heat]	-0.375	0.077017	-4.87	<.0001
Detergen[Cascade-Finish]	-0.316667	0.077017	-4.11	<.0001
Dry [Air-Heat]*Detergen[Cascade-Finish]	-0.183333	0.077017	-2.38	0.0181

Effect Test

Film

Summary of Fit

Analysis of Variance

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	4.3	0.056368	76.28	<.0001
Dry [Air-Heat]	-0.458333	0.056368	-8.13	<.0001
Detergen[Cascade-Finish]	0	0.056368	0.00	1.0000
Dry [Air-Heat]*Detergen[Cascade-Finish]	0.0083333	0.056368	0.15	0.8826

Effect Test

From this brief experiment, it is shown that saving energy by air drying results in equal or better spot and film performance so it would be expected that the advantage of softened water would be maintained.

CONCLUSIONS:

Statistically significant improvements by reducing water hardness in spotting and filming performance as well as in better soil removal in automatic dishwashing were quantified in comparison to decreasing detergent dosage. From the main experiment, it can be calculated how hardness reduction is better at maintaining performance than is use of more detergent. A graph showing the savings in detergent possible was generated.

The effect of hardness in comparison to detergent dose was confirmed with Trader Joe's detergent.

Additional wash/dry cycles up to five in general showed no film build up for soft or hard water but as many as 30 cycles would be required to make sure that buildup did not occur.

Air drying as a way to save electrical energy is promising and may give better results when soft water is used rather than hard water.

George C. Feighner

President
Scientific Services S/D, Inc.