Improvements in Detergency Precision with Radioactive Soil

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Abstract

Recent work on the use of seven-component, doubly labeled radioactive soil to evaluate detergency has depended on the analyses of the fabric for residual soil. Because of the variation of soil concentration within and between fabric swatches, considerable replication was required to lower the standard deviations to ±10%.

A method for the analysis of wash water has been developed which requires much less replication and achieves higher precision (<±2%). The method is based on the use of an inhomogeneous scintillator, which can emulsify, or at least suspend, large volumes of water in a liquid scintillator while maintaining good counting efficiency. Studies of closure, i.e., amount of soil recovered in wash water plus fabric compared with soil introduced into the Tergotometer, have demonstrated that the method is reasonably accurate and quite precise.

Introduction

A RECENT SERIES of publications has been concerned with developing a more precise analytical method to measure the effectiveness of detergents (1,2). This method, based on the use of a doubly labeled radioactive artificial soil, employs liquid scintillation counting of the soiled fabric before and after laundering. Liquid scintillation counting, in general, is precise to ±2% relative standard deviation and, with reasonable care in sample preparation, can be made precise to <±1%.

In the development of this method of radioassay applied to fabric surfaces, it soon became apparent that when the fabric is carefully soiled with the radioactive soil and promptly analyzed or is impregnated with a known amount of labeled surfactant, recovery of the added material was accurate and precise to predicted values.

It was therefore somewhat disconcerting, when this precise analytical tool was applied to studies in detergency, to find that precision of the final detergency data rarely was better than ±5% relative standard deviation and was usually ±10% with occasional excursions to ±30–50% (1). It seemed a great pity indeed not to be able to take advantage of the capabilities of the analytical method developed for detergency testing so an investigation was launched to determine the causes of variation in detergency data when a radioactive soil was used on various fabrics which were washed in a Tergotometer.

The study was developed around the Tergotometer as the laundering instrument and the requirement that the soil introduced into the system had to be quantitatively accounted for. This required analysis of both the wash water and fabric. Thus the project had three phases, analytical development, mass-balance study of the wash-dry steps, and the study of Tergotometer precision.

Experimental Procedures

Analytical Method Development

The analysis of the wash water is somewhat of a problem compared with the analysis of the fabric. First, there is the matter of sensitivity. The concentration of labeled soil on the fabric (approximately 20 mg per g of fabric) is considerably higher than in the water (approximately 20 mg per 500 g). Second, the problem of compatibility of the wash water containing the various builders plus calcium and magnesium salts with the scintillation counting solution caused some concern. Therefore, before the laundering experiments were initiated, a method for the analysis of single and double label soil in wash water was sought.

TABLE I

Comparison of Dioxane and Triton/Toluene Efficiencies

	Dioxane			Triton X-100		
Isotope	Volume, V	Counting efficiency, E	V × E	Volume, V	Counting efficiency, E	V × E
^{3}H	3	0.1	0.3	5	0.13	0.65
^{14}C	3	0.25	0.75	5	0.40	2.00

Because of the high dilution of soil the largest possible aliquots had to be analyzed. Only two solvent systems appeared practical. The first was a dioxane solution, 17 ml of which could accommodate 3 ml of water. The formula of this scintillator was 4 g of PPO,[1] 0.1 g of dimethyl POPOP,[1] 80 g of naphthalene in one liter of spectroscopic grade dioxane. This solvent has been found to be satisfactory for surfactant analysis (3).

The second solvent was that of Patterson and Greene (4), which could accommodate 5 ml of water. This consisted of 6 g of PPO, 0.1 g of dimethyl POPOP per liter of toluene, mixed with 500 ml of Triton X-100[1] emulsifier, a nonionic surfactant.

The third scintillator, for reference, was the toluene scintillator without Triton X-100. This was used to standardize the labeled soil, all components of which were toluene-soluble as has been shown in fabric analysis, and to analyze the fabrics directly for residual soil (2).

Since sensitivity appeared to be the main consideration in the choice of the proper scintillation solvent for wash water, that solvent was chosen for which the product of efficiency and sample volume would be greatest. Table I shows the comparison between the two systems used with counter settings for double-label analysis. The counter was a Packard Tri-Carb Model 3003.

Triton X-100/toluene scintillator was two to three times more sensitive for this analysis. Therefore this system (T-T) was further studied. It was essential that the counting efficiency for each sample be determined automatically for reasons advanced previously (1,2). The external standard method (ESM) described recently (2) was investigated for the T-T emulsion. Benson (5) has pointed out that T-T systems are unstable if temperature, water content, or method of preparation of the emulsions vary.

Thus the use of T-T scintillator was standardized in the following way. A 5 ml aliquot of wash water was first added to a counting vial, followed by 17 ml of T-T. The mixture was vigorously shaken by hand, heated to 35C in a water bath for 30 min, allowed to

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[1] Obtained from Packard Instrument Company, Downers Grove, Ill.

cool for one hour at ambient temperature before insertion into the counter at 4C. At least 30 min of cooling in the counter were required to bring the sample to a constant count rate. Along with each set of samples, two sets of sealed standards with the same solutions as the samples but with known amounts of carbon-14 in one set and tritium in the other were treated in the same way to minimize the difference in phase between standards and unknowns.

It was important to know whether the wash-water samples had to be taken for counting immediately or if they could be stored until a screening study had been completed and sampled at the same time. A time study over 29 days was made by washing a set of four soiled Nylon swatches with known amounts of soil and by analyzing the wash water. Table II shows the results.

There was no discernible trend. The erratic values for tritium were caused by problems in matching samples to the calibration curve. Wash water may be stored for several days with no adverse effects.

On the basis of the above data, particularly the fact that the water contained the predicted amount of soil, the T-T scintillation solvent seemed to be acceptable for wash-water analyses. Samples were usually taken shortly after the completion of each Tergotometer run.

Laundering Experiments

The laundering experiments were performed in a Tergotometer, using 500 ml of hard water with a built detergent and washing for 10 min at 100 rpm. Each Tergotometer beaker contained four soiled swatches of the same fabric, each 10-cm square. Soiling was done by pipetting a known volume of a benzene solution of the soil as uniformly as possible onto each swatch. Thus the quantity of radioactive soil on each swatch and hence in each beaker was known. The artificial soil used was a seven-component system described earlier (1), which was tagged with tritium and/or carbon-14, depending upon the experiment.

Immediately after a Tergotometer run was completed, the swatches were removed, excess water was squeezed out into the beaker, and the wash water was vigorously stirred and sampled to avoid any maldistribution of the soil components. The fabric swatches were then rinsed in 100 ml of distilled water by vigorous stirring, removed, squeezed out, and set aside for drying and analysis. Analysis of the fabric at the different stages of drying was performed as was analysis of the wash and rinse waters.

The purpose of this study was threefold. First, it was to determine whether or not losses of soil from the fabric were occurring during the various steps in the rinse-dry sequence. Initially, some steps in the drying process had been borrowed from carbon-black studies; thus, such losses were not inconceivable. Second, if any losses were occurring, could they be eliminated so that one could achieve a good mass-balance of the soil, i.e., closure? Third, if closure could be achieved, could the analysis of the wash water then be used to obtain detergency data? This was appealing because the wash water integrates the soil removed over all swatches and provides one with a true average, the precision of which is that of the analysis (i.e., $< \pm 2\%$). Furthermore analysis of the wash water reduces the sample load because fabric analysis requires that each swatch be analyzed. Finally, if analysis of the wash water proved feasible, it would eliminate the drying process.

TABLE II

Effect of Wash-Water Age on Soil Analyses

Fraction	Mg Soil After— Days Wash-Water Age				
	0	4	14	19	26
^{3}H Labeled	14.10	12.53	13.51	13.71	12.85
^{14}C Labeled	24.49	24.31	25.06	24.21	23.79

TABLE III

Effect of Rinsing and Drying Steps on Soil Content of Cotton

Sample and treatment	Soil lost, %	
	^{3}H Fraction	^{14}C Fraction
Unwashed, rinsed	0.4	2
Washed, rinsed	10	8
Unwashed, heat in oven	9	2
Unwashed, hot press	27	30

The conventional drying process of fabric after washing is as follows. The swatches are rinsed under a tap, and the rinse water is normally discarded. Excess water is squeezed out, and the swatches are placed between two cloth pads; the resulting fabric sandwich is sent through a hot press, a photographic print dryer. After hot press the swatches were cut to about 0.5-g sizes, inserted into the empty counting vials, and placed in the oven for 45 min. They were then removed and cooled, then the toluene scintillator was added.

To test the various steps, several cotton swatches were carefully impregnated with known amounts of the doubly labeled, seven-component sebum. Four of these were rinsed and put through the conventional drying process. Four others were laundered in the usual way, and removed from the beaker; excess wash water was squeezed out, then they were rinsed. In both sets the rinse water was collected and counted to determine whether or not the laundered fabric contained soil in a form more easily removed than soiled but unlaundered fabric. The results of this experiment are shown in Table III.

Because freshly washed fabric, after squeezing, contains less than 1% of the original soil in the entrained water, the rinse data clearly demonstrate that washed fabric contains a considerable amount of loosened but not yet dislodged soil. Therefore rinse water must be combined with wash water if the water analysis is to be valid.

Table III also shows major losses owing to the drying steps. As a result, the drying procedure was modified. After the fabric was rinsed in 100 ml of water and the excess water was squeezed out, the swatches were hung in a hood for one hour in which time all (cotton, Nylon, Dacron, Dacron/cotton, Perma-Press Dacron/cotton) reached constant weight. A tracer experiment, using doubly labeled soil on all the above fabrics, established that no soil was lost from any fabric in this drying step. With reliable methods of handling the fabric in hand, the closure studies could now be conducted.

Closure Experiments. A benzene solution of fully formulated but singly labeled soil was spotted onto 10 × 10-cm swatches of four fabrics; cotton, Nylon, Dacron, and Dacron/cotton. The radioactive component was the hydrocarbon fraction labeled with tritium, and the soil concentration in benzene was 55.8 mg/ml. A 1.0-ml gas-tight Hamilton syringe with a repeating dispenser was used to distribute the solution evenly over each swatch. The volume of solution was varied for each fabric to ensure the same soil concentration (approximately 2% wt). From the

TABLE IV

Summary of Closure Tests, Tritiated Hydrocarbon in Full Soil

Fabric	Soil removed, mg[a] In wash water	In rinse water	Total	Soil retained[b] on fabric, mg	Total soil found, mg	Total soil added, mg	Closure, %
Cotton	20.22	0.77	20.99	18.29	39.28	39.06	100.6
Nylon	14.16	1.80	15.96	11.22	27.18	27.90	97.4
Dacron	6.13	0.71	6.84	20.29	27.13	27.90	97.2
Dacron/Cotton	6.47	0.68	7.15	12.70	19.85	20.09	98.8

[a] Per beaker, average of four beakers.
[b] Per four swatches, average of four sets of four.

volumes therefore the quantity of soil per swatch was known, as was the total amount of soil introduced into each beaker (four swatches per beaker).

Each fabric was run in four beakers to provide data about closure within each beaker as well as agreement between beakers. Thus four Tergotometer runs were made in all (16 beakers). Washing was done by use of a nonionic surfactant ($C_{12\text{-}15}$ linear primary alcohol, 9 ethoxylate) in a fully built detergent.[2] Water hardness was 150 ppm, temperature 120F, agitation 10 min. In this experiment the wash and rinse waters were analyzed separately. The fabrics were analyzed after drying. Each swatch was cut into three sections, each section was immersed in the toluene scintillator and counted (2). The results of each set of three sections were summed to give the soil left on each swatch. The results are in Table IV.

Closure was excellent once the extraneous losses had been eliminated. The 97% recoveries for Nylon and Dacron were real, and an attempt to account for this was made by extracting the Tergotometer beakers and stirrers with hot benzene. No significant activity was found. If it were assumed that the water analysis was correct, the only other place for the activity was in the fabric, probably within the fibers where it could not be counted. Therefore the samples of Nylon were Soxhlet-extracted with toluene after counting in the usual way. An additional 1–2.5% of tritiated hydrocarbon was recovered, thus demonstrating that indeed penetration into the Nylon (and presumably Dacron) accounted for the not quite quantitative recoveries of the tritiated hydrocarbon.

Table IV illustrates only closure, i.e., accuracy but not precision. Because each of the values in Table IV was the result of averages of replicates, it was possible to calculate standard deviations.

The most significant were those within a beaker, i.e., of the average of four swatches compared with the average of the wash-water replicates (normally three) from the same beaker and those between beakers. The first two values would provide an idea of the reproducibility of the wash-water analyses and of the reproducibility of washing from swatch to swatch. The latter would indicate whether one could obtain reliable data from one beaker only, a significant advantage, or whether replicate beakers had to be run. The data are expressed as precision of the detergency values, i.e., removed soil.

TABLE V

Detergency Precision[a] of In, and Between Beaker Analyses

	Within beakers									
	1		2		3		4		Between beakers	
Fabric	F[b]	W[b]	F	W	F	W	F	W	F	W
Cotton	3.5	0.6	4.1	0.2	Lost		2.5	0.1	0.40	1.5
Nylon	4.8	0.6	1.5	1.0	2.2	1.7	2.8	0.8	4.0	5.1
Dacron	3.1	1.3	5.3	0.3	6.2	1.1	1.0	1.1	2.0	2.6
Dacron/ Cotton	3.4	1.4	3.4	0.1	1.6	0.3	4.6	0.3	2.1	2.6

[a] Percentage relative standard deviation.
[b] F = values based on fabric analysis, and W = values based on water analysis.

TABLE VI

Closure Data With Perma-Press Fabric mg of Soil in

	Water		Fabric		Total[a]		Recovery, %	
Beaker	^{3}H	^{14}C	^{3}H	^{14}C	^{3}H	^{14}C	^{3}H	^{14}C
1	11.63	23.48	45.72	22.03	57.35	45.51	100.0	97.4
2	12.10	23.17	45.52	21.83	57.62	45.00	100.5	96.3
3	12.73	23.57	44.96	21.31	57.69	44.88	100.6	96.1
4	12.72	24.02	43.60	20.84	56.32	44.86	98.2	96.0
Avg.	12.30	23.56	44.95	21.50	57.25	45.06	99.8	96.5

[a] Soil added per beaker, ^{3}H = 57.36 mg, ^{14}C = 46.72 mg.

The data in Table V require some comment. The F (fabric) values under the "Within Beakers" heading are based on the analysis of a single sample cut from each swatch. This sample was about one-third of the full swatch. The F values under the "Between Beakers" are based on analysis of the complete swatch by cutting it into three sections. Therefore the former F values contain both the deviation within and between swatches; the latter was only between swatches. One would expect the precision of the F values, based on total destruction, to be comparable with those of the water (W) values. However in routine work one would normally analyze single samples from each swatch (because of the great sample load), thus the best comparison between F and W values is that under the "Within Beakers" heading, which clearly demonstrates that water analysis is preferred over fabric analysis.

Since all reported σ values in Table V are those of a single determination, not of the mean, the W values under the "Between Beakers" heading then indicate that one can probably get away with a single beaker run, that is, at the 66% confidence limit one will expect the results to be within about 3% of the true mean, or at the 95% confidence limit one will expect the results to be within about 6% of the mean.

The above data were based on the tritiated hydrocarbon. There was reason to suspect that the carbon-14 fraction was somewhat poorer with respect to closure than the tritium fraction. Evidence of this was obtained from some Perma-Press Dacron/cotton fabric which was used as a test fabric during a normal detergency study. Because this was a new surface, a careful study was made of closure by using a four-beaker test run. Table VI presents the data.

Tritium recovery was excellent, but carbon-14 was 3-4% low. Although this was relatively minor, it was important to determine whether or not this

TABLE VII

Source of Failure to Close

	Fabric	
	Cotton	Nylon
% in Wash water		
^{3}H	53.9	34.6
^{14}C	52.6	64.3
Soxhlet extract of fabric		
^{3}H	45.4	63.0
^{14}C	40.5	34.8
Extracted fabric, direct counting		
^{3}H	0.3	0.23
^{14}C	5.0	0.63
Combusted fabric		
^{3}H	0.3	0.20
^{14}C	6.4	0.28
Closure basis fabric counting		
^{3}H	99.5	97.8
^{14}C	98.1	99.9
Closure basis combustion and counting		
^{3}H	99.6	97.8
^{14}C	99.5	99.6

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[2] 1 g/liter built detergent, 0.15 g/liter active matter plus builders.

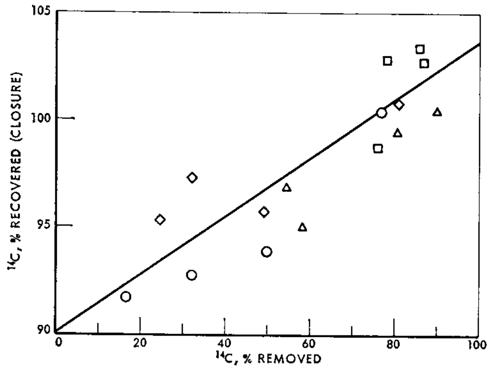

FIG. 1. Effect of fraction of carbon-14 removed on closure.

consistently low recovery was caused by errors in fabric or water analysis. If the former, then one could disregard it because detergency values would, in the future, be based on the water values. A plot was made of the percentage of carbon-14 fraction found in the water vs. the percentage of total carbon-14 recovered (closure). This is shown in Fig. 1 for a number of runs.

Clearly the greater the fraction of carbon-14 removed, the better the closure. This strongly suggests that the error is in the fabric analysis. Since most detergents remove 40–60% of the carbon-14 fraction, the graph shows that the results, at this level, would tend to be 2–4% low, which corresponds to the observed discrepancy for carbon-14 in Table VI.

There are several possibilities for this incomplete recovery of the carbon-14 fraction. First, there is the possibility that this polar fraction is tightly adsorbed and suffers from self-absorption losses. Second, it is possible that some of this fraction is lost by volatility during the padding process since it must hang in the hood. Third, there is always the possibility that the fabric-containing standards, which are used to generate the calibration curves (2) from which the sample efficiency is obtained, may be somewhat different in response to quenching than the samples, i.e., the reflecting ability of the sample swatch is different from the standard.

A simple experiment showed no volatility loss during the padding-drying process. An experiment was then run wherein the fabrics, after laundering, were Soxhlet-extracted with toluene for 24 hr, then part of the extracted fabric was burned to obtain the unremovable tritium and carbon-14, and part of the extracted fabric was counted. The purpose was to determine where the lost soil was. If it could be found in the fabric, as suggested by Fig. 1, then the water analysis was on a sound basis. Table VII presents the results for two fabrics.

It is clear from the data in Table VII that failure to close is attributable to errors in fabric analyses. Cotton fabric, direct counting compared with combustion counting accounts for only 78% (5/6.4) of the residual carbon-14 fraction. Whether this is owing to self-absorption or an inadequacy of the calibration curve is not known. But with combustion, closure for the cotton is excellent, demonstrating that the water analysis is valid. Nylon shows excellent ^{14}C closure and reasonable ^{3}H closure, thus confirming the previous statement.

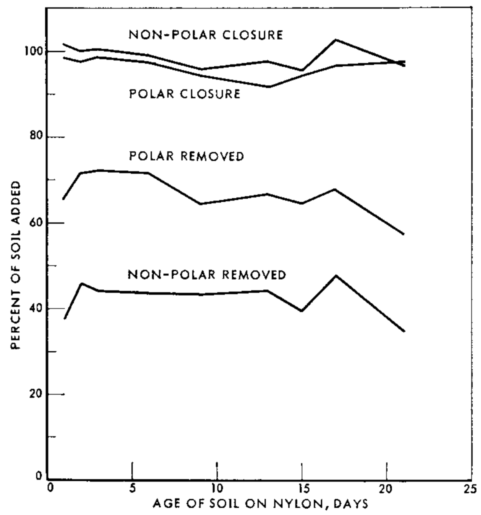

FIG. 2. Effect of soil age on detergency and closure.

Discussion

From the foregoing it is clear that water analysis will give precise and accurate detergency data. The between-beakers precision (Table V) indicates that, on repeat launderings, precision of 1.5–5% is reasonable. This is based on the analysis of the water from a single beaker, which itself has a precision of about 1%. The reduction in sample load is considerable, depending upon the number of replicate waters which are run in comparison with the number of sections from each swatch. Analysis of the water provides a true average detergency value but gives no indication of the variation of soil concentrations within or between swatches.

One limitation in the use of T-T scintillation solvent is that the internal standard method cannot be used as a referee in the case of dubious results. In this case, dioxane scintillator must be used because it forms a homogenous system with wash water. A second limitation lies in the heating-cooling cycle required for the T-T scintillator. This is tedious and somewhat inefficient.

After the demonstration of the feasibility of wash-water analysis, the effect of other parameters, such as padding method and age of soil, on detergency values is being studied. Preliminary results on the effect of age of the padded cloth on detergency are presented in Fig. 2.

These data show that, up to about 15 days, almost all soil removal values are within ±5%. After about 7 days however closure is a few per cent low, reflecting increasing losses to the fabric with time. Because this variation is considerably higher than that of the analysis but is comparable with that found between beakers (Table V), the data show little effect of soil age on detergency at least up to 21 days.

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