The Development of a Particulate Radioactive Soil for Detergency Studies[1]

B. E. GORDON and E. L. BASTIN, Shell Development Company, Emeryville, California 94608

Abstract

A sample of kaolinite clay has been tagged by neutron irradiation. After an extended cooling period (18 months) to allow the short lived nuclides to decay, the clay is still sufficiently radioactive to use it in detergency studies. Extraction tests show that about 25% of the radioactivity is labile, i.e., removed by sodium tripolyphosphate but that the remainder is strongly fixed in the clay matrix, resisting extraction by built detergents. The clay has a number of nuclides emitting both beta and gamma radiation. Analytical methods for both types of radiation have been developed for use with fabrics and wash waters. The clay has been combined with the doubly labeled fatty soil (^{3}H and ^{14}C) to make a triply labeled particulate soil. Tergotometer runs with three test fabrics show good precision for all three labeled components of the soil. Redeposition measurements were also made and showed that a considerable fraction of the residual clay on a washed swatch may in fact be due to redeposition rather than retention. Some problems remain in the application of this synthetic soil: the padding step must be modified so that the clay is more tenaciously bound to the fabric; a more automatic method of padding is required to handle large numbers of samples; the specific activity of the clay should be increased so that liquid scintillation analysis for all three tagged components can be made on a single sample of wash water.

Introduction

DETERGENCY STUDIES are typically carried out using a test soil and a variety of fabrics. In recent years considerable attention has been paid to the composition of the soil (1–4) and there seems to be a consensus that a realistic synthetic soil should contain fatty components and particulate matter (5,6). For the past three years we have been carrying out detergency studies using a radioactive fatty soil labeled with carbon 14 and tritium to distinguish between the high polarity and low polarity components of the soil (7). We wish now to report on some work directed toward the development of a labeled particulate component for the doubly labeled soil.

Radioactive particulate soils have been described by others. Lambert et al. (8) reported adsorption of fission products onto a synthetic soil slurry to make a very high specific activity particulate soil. Adsorption was onto colloidal clay, and the nuclides were mainly cationic in nature. At the pH of detergency Lambert reported little or no desorption. Other particulate matter included labeled iron oxides and carbon black-^{14}C. Lambert also reported that an attempt to prepare a tagged synthetic soil by neutron irradiation was unsuccessful because the induced activity (mainly ^{59}Fe) was loosely bound to the particulate soil. Hensley et al. (9) employed carbon 14 tagged carbon black as did Ashcraft (5) to compare true soil removal with reflectivity change. In 1959 Hensley and Inks (10) prepared a calcium 45 tagged montmorillonite clay by ion exchange followed by calcination at 1,000 C to fix the tracer. The use of clay rather than carbon black has been significantly advanced by the work of Powe (1,2) and Sanders and Lambert (11) which demonstrated its ubiquity in the general environment.

The increasing acceptance of clay as a more realistic particulate component of synthetic soil than carbon black carries with it the problem of adequate analysis. The reflectance of clay is not as great as carbon black, hence a reduction in sensitivity may be expected. Furthermore, the color of some clays is due to adsorbed or otherwise deposited organic matter which can be removed in part or wholly by built detergents without removing any of the particulate matter. Thus a more quantitative measure of the deterged clay would be desirable.

The radiotracer approach is particularly attractive in this regard because it is unequivocal. While it is true that the quantity of residual clay may not be quantitatively related to appearance, it is nevertheless important to know just how much of each component of a test soil is removed to understand better the mechanisms involved and also to arrive at a more realistic evaluation of detergents.

Experimental Procedures

Notwithstanding the earlier results of Lambert et al. (8) we decided to try to take advantage of hot atom chemistry to introduce radionuclides into clay without altering the surface properties by calcination. Hot atom chemistry is the study of chemical reactions of recoiling nuclei created by the capture of nuclear particles. For example, ^{59}Fe is formed by the capture of a neutron by ^{58}Fe and the simultaneous emission of a gamma ray, ^{58}Fe (n,γ) ^{59}Fe. The n,γ reaction is the most common in thermal neutron capture. Harbottle (12) and Wolf (13) have studied hot atom chemistry in inorganic and organic substrates, respectively. In both environments it was found that some fraction of the recoiling atoms ended up in the parent molecule either through recombination or retention. Generally such yields are much higher for inorganic compounds than for organic compounds and are higher in solid (crystal) phase than in solution. This, of course, is true only in those reactions where the product nuclide is an isotope of the parent atom, or

$$_{z}M^{A}\ (n,\gamma)\ _{z}M^{A+1}$$

where $_{z}M^{A}$ is the parent element of mass A and M^{A+1} is the product isotope. For example, iron undergoes nuclear reactions for each of its natural isotopes to yield four isotopes.

^{54}Fe (n,γ) ^{55}Fe radioactive
^{56}Fe (n,γ) ^{57}Fe stable
^{57}Fe (n,γ) ^{58}Fe stable
^{58}Fe (n,γ) ^{59}Fe radioactive

Thus only two radionuclides are produced by neutron bombardment. ^{59}Fe has a 45-day half life and so is unacceptable for long term use. ^{55}Fe has

---

[1] Presented at the AACC-AOCS Joint Meeting, 1968, Washington, D.C.

TABLE I

Composition of Bandy Black Clay and Product Nuclides

Elemental Oxide	Concentration, %w	Product Nuclide	Half Life
P_2O_5	0.07	^{32}P	14 days
SO_3	0.11	^{35}S	88 days
SiO_2	61.00	^{31}Si	2.6 hr
Al_2O_3	24.50	^{28}Al	3.2 min
Fe_2O_3	0.99	^{55}Fe,^{59}Fe	2.7 years, 45 days
TiO_2	1.29	^{51}Ti	8.5 min
MgO	0.12	^{27}Mg	9.5 min
Na_2O	0.36	^{24}Na	15 hr
K_2O	1.60	^{42}K	12 hr

a satisfactory half life (2.7 years) but produces radiation by electron capture to give a weak x-ray which makes detection rather difficult.

The requirements for producing a labeled clay by neutron irradiation are simple. The nuclides must have easily detectable radiation, i.e., gamma or beta radiation of greater E_{max} than carbon 14 if one wishes to use liquid scintillation counting for samples containing soil already tagged with ^3H and ^{14}C. The composite half life of the radionuclides should be reasonably long, i.e., months or even years. The radionuclides should not be removed from the clay by treatment with built detergents.

The clay chosen for this study is a kaolinite known as Bandy Black (H. C. Spinks Co., Paris, Tenn.) recommended by Rutkowski (4). The composition of the clay was supplied by the manufacturer and the expected radionuclides are shown in Table I.

Only iron and sulfur offer any promise of useful nuclides and of these only ^{55}Fe has a reasonable half life. However, ^{55}Fe decays by electron capture to yield a 5.9 Kev gamma ray which places the pulse amplitude in the tritium spectrum thus making analysis by liquid scintillation counting in the presence of the labeled fatty soil very difficult and analysis by gamma ray counting subject to matrix variations.

The above elements are only those detected by macroanalysis. Activation by neutrons may also form useful nuclides from trace elements provided their activation cross sections are large enough. This, in fact, is the basis of neutron activation analysis. Because our long experience with activation analysis of inorganic materials indicated that there would be a high probability of the presence of traces of desirable (but unknown) elements in the clay, two irradiations were made. A small test sample was irradiated for 2 hr in a flux of $1.8 \times 10^{12}n/cm^2$ per second in the Triga reactor at General Atomics, La Jolla, California, and a 100-g sample was irradiated for 24 hr in the Union Carbide reactor at Tuxedo, New York, where the flux was $1 \times 10^{13}n/cm^2$ per second. The latter sample was allowed to cool for several months to allow the short half life nuclides to decay; the former sample was studied after only a few weeks of cooling.

The low activity sample was counted in two ways, liquid scintillation counting (LSC) for beta radiation and crystal scintillation counting (CSC) for gamma radiation. The latter method was applied in three geometrical configurations to determine the sensitivity of each and to compare these with LSC. Gamma ray counting is attractive because there is no quenching and relatively little effect of the sample matrix. The results were expressed as the specific activity/background$^{1/2}$ which is proportional to the limit of detection. A Packard Tri-Carb Model 3375 was used for LSC and a Baird Atomic 530A scaler was used for CSC.

TABLE II

Relative Sensitivities of Various Counting Methods for Clay

Method	Specific activity CMP/mg	Background	SA/B$^{1/2}$
LSC	120	20	27
Solid Crystal (3 × 3 in.)	0.6	45	<0.1
Well Crystal (3 × 3 in.)	65.5	442	3.1
Coincident Counting (Two 5 × 5 in. crystals)	3.1	2	2.2

Liquid scintillation counting is the most sensitive mode of analysis but well crystal counting should not be ruled out because it can accommodate much larger samples than LSC. As will be shown below we can use either mode of analysis because most gamma emitters also emit betas.

For data concerning the decay rate of the clay, a sample of the second irradiation, i.e., the hot clay, has been followed by LSC for more than eighteen months. The sample, 7.44 mg suspended in toluene scintillator gelled with Cab-o-Sil, was counted in the Packard TriCarb counter Model 3003 in an energy channel virtually free of interference from carbon 14 and tritium. It should be noted that this counting arrangement is not the one used in the final method but was set up only to illustrate the effect of time.

After almost two years the specific activity of the clay is still $0.39 \times 10^4/7.44$ or 524 cpm/mg. A simple calculation can be made to determine whether this level of activity is still useful in detergency studies. About 6 g of cloth are placed in a Tergotometer beaker which, on soiling, contains about 120 mg of fatty soil. Assuming a clay level of 15% in the soil, 18 mg will enter the beaker. If the wash water is to be counted (14) and if 10% of the clay is removed, then one expects, in a 5-ml aliquot of 600-ml wash water.

$$18 \times 0.1 \times \frac{5}{600} = 0.015 \text{ mg}$$

At a specific activity of about 500 cpm/mg one would obtain 8 cpm net. This is a very low count rate and virtually precludes quantitative analysis by LSC, unless a long counting time ($\sim$100 min) is allowed for each sample. This is not feasible for detergency screening programs generating hundreds of samples per day. Obviously, a more active clay is required and for this purpose such a clay is under preparation involving a tenfold increase in neutron dose. For this report, therefore, well crystal counting of the clay in the swatches was used because all four swatches could be counted at once. Assuming 90% removal of the clay the four swatches would have left 1.8 mg. The gamma ray specific activity of the hot clay was 850 cpm/mg which gives a count rate of $850 \times 1.8 = 1530$ cpm over a background of 600 cpm. This is quite satisfactory for good quantitative analysis.

TABLE III

Decay of High Energy β- Emitters in Irradiated Clay

Time after irradiation, days	Count rate, cpm $\times 10^{-4}$
35	7.44
76	3.26
131	1.76
311	0.87
631	0.39

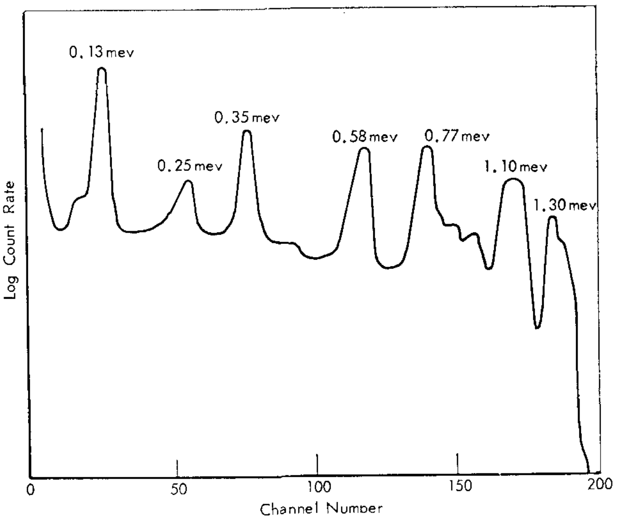

Fig. 1. Gamma Ray Spectrum of Irradiated Clay. After 600 Days.

Extraction Study

Before much effort was invested in developing an analytical method for clay in the doubly labeled fatty sebum (i.e., triplylabeled soil) some tests had to be made to determine whether all or part of the radionuclides would be readily removed during detergency testing. Lambert et al. (8) had suggested this possibility. For this phase of the work gamma counting was employed. There was considerable gamma activity in the clay as shown above and by the spectrum in Fig. 1. It is significant that such an abundance of photopeaks can be obtained from elements present in trace amounts. One concludes that there is a good possibility that most clays will yield useful nuclides from neutron irradiation. The complex spectrum in Fig. 1 would require some effort to identify the nuclides, but because it was unnecessary in this study it was not further pursued. Half life studies showed that the various photoplates decayed with a range of half life peaks from 100 to 1,500 days, entirely satisfactory for use as a tracer in this work. It is sufficient that if one uses an energy channel above about 0.2 mev enough activity will be included to permit a study of extractability by gamma ray counting. This and the subsequent analytical work was with the hot clay. Analysis was with the 3 in. NaI well crystal, the most sensitive of the gamma ray counting configurations.

The first attempt to remove the labeled radionuclides was by column chromatography. The clay was mixed with a filter aid (Johns-Manville Hyflo Supercel) on a 1:1 w/w basis and 1 g of the mixture was packed into a stainless steel tube 3 × ¼ in. A Hoke 316 SS micron filter was attached to the bottom of the tube followed by a glass wool plug. The extraction solution was delivered by a positive displacement pump capable of pressures up to 1,000 psi. The solutions tried were those inorganics normally found in built detergents. These were pumped through the column and aliquots taken for gamma ray counting until the activity fell to zero. The solution was then changed and percolation continued. The results, expressed as percent of activity originally on the clay are in Table IV.

TABLE IV

Elution of Radioactivity from Irradiated Clay

Solution	Per cent activity in eluant
Cold distilled water	0.5
Hot distilled water	0.0
Sodium sulfate, 0.45 g/liter	1.1
Sodium tripolyphosphate (STPP) 0.6 g/liter	4.5 (first 4 hr)
Sodium tripolyphosphate (STPP) 0.6 g/liter	2.4 (next 5 days)
Total	8.5

TABLE V

Extraction Study of Irradiated Clay Radioactive and Mass Loss

Solution	Loss, per cent					
	Basis extract analysis				Basis clay analysis	Weight loss of clay, per cent
	1st	2nd	3rd	Total		
STPP 0.6 g/liter	14.7	3.7	2.0[a]	20.4	24.6	4.4
STPP 3.0 g/liter	20.1[b,c]	1.9	0.9[a]	22.9	23.7	6.7
1.2 N HCl	29.0	4.7[a]	0.6	34.3	37.6	4.6

[a] Extracted with built nonionic detergent, 20 min at 60C.
[b] Highly colored extract.
[c] 60 min at 60C.

The data do not bear out the statement by Lambert et al. (8) that nuclides produced by neutron irradiation are easily removed. Furthermore, it appears that cation exchange is not the only mechanism of removal of nuclides. If it were the sodium sulfate would have removed all the activity. Since sodium tripolyphosphate (STPP) is a detergent it is possible that its effect was to peptize the clay so that a small amount of the fines came through the filter. Furthermore, the STPP removed some of the organic matter which appeared as a dark color in the first fractions of eluant. Because the STPP solution removed more activity than water or sodium sulfate it was used in subsequent extraction experiments. Difficulties in starting and maintaining flow in the column and the necessity for a filter aid to get any flow at all led to the abandonment of the column experiments in favor of slurry extractions.

The problem with slurry techniques is to remove all the clay from the extract before counting. Filtration (10 mμ millipore) followed by ultracentrifugation (200,000 g) showed that 9.9% of the activity was removed by the STPP while filtration through a 10 mμ millipore filter alone showed an extraction of 11%. High speed centrifugation ($\sim$4000 g) gave extract values of about 13% indicating the failure to precipitate about 3% fines. Because of its greater speed and convenience, however, this was used as the separation tool.

A series of extractions was made using STPP at two concentration levels. HCl was included to see if all or most of the radioactivity could be removed at a very low pH. The mass loss was also determined. Extraction was for 20 min at 60 C while stirring vigorously.

It appears from Table V that treatment with the higher concentration of STPP is more effective than with the lower. Two treatments with this concentration of STPP serve to reduce the extractable gamma activity to $\sim$1% using a built nonionic detergent as a test. While HCl removes more activity than STPP, it does not stabilize the clay to extraction by a built detergent. While there is only fair agreement between the total activity lost based on analysis of the extract with that based on the residual clay, it is satisfactory for this test. Because the concentration of radionuclides made in such an

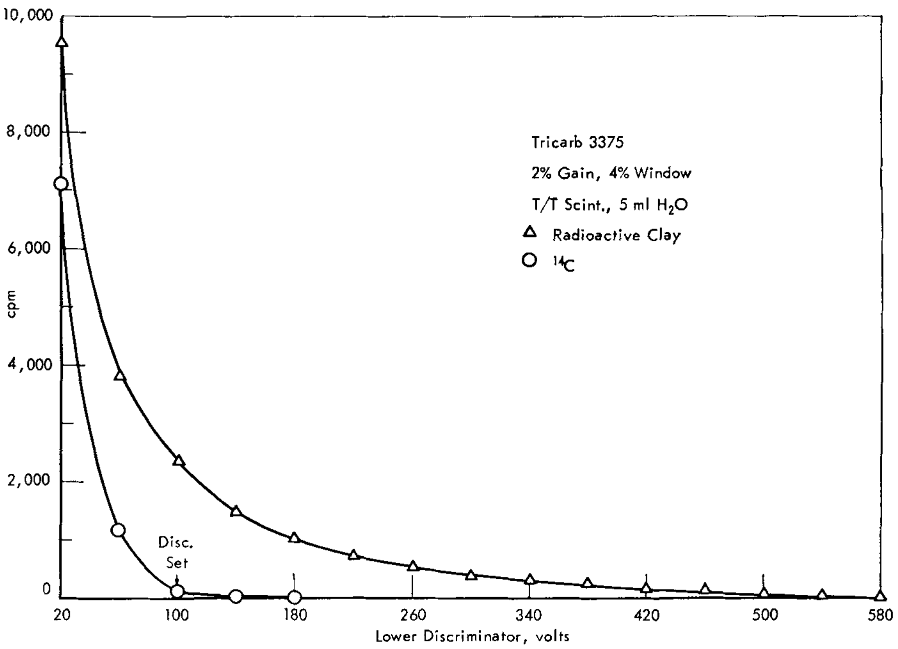

FIG. 2. Beta Ray Spectra of Clay and Carbon-14.

irradiation is at the ppm level, it is not possible to state from the weight loss column whether the activity is removed by ion exchange or solution. Even the small weight loss of the clay may be due to a few percent of fines. However, this test demonstrates that the bulk of activity is not easily removed and shows that one can treat the irradiated clay to remove the labile nuclides.

It was decided, for purposes of detergency studies, that if a built detergent would remove less than 2% of the radioactivity in the clay in a 20 min, 60 C extraction, the clay would be regarded as stabilized. Table V suggests that two extractions for 60 min at 60 C with STPP at 3 g/liter should be adequate to prepare the clay for use as a particulate soil component. Therefore, a 10-g batch of the clay was so treated. After this treatment the clay was washed with distilled water until all the STPP had been removed. The clay was then shaken in a Mix-Mill (Spex Industries, Inc.) to break up aggregates and finally stirred by hand to ensure complete homogeneity.

A final test had to be made before proceeding to the analytical method development. The foregoing data were obtained by gamma ray analyses. Pure beta emitters are, however, not rare and so a test for resistance to extraction of beta emitters was performed. Samples of the prepared clay were subjected to extraction for 20 min at 60 C by three built detergents of the heavy duty powder formulation. The active matter included one nonionic and two anionics. After extraction and centrifugation, 5-ml aliquots of the extracts were emulsified with Triton-X100/toluene scintillator reported previously for wash water analysis (14) of tritium and carbon 14. The activity in the centrifugate was determined by LSC while the total activity of the prepared clay was obtained by suspending several milligrams in the same scintillator using 5 ml of water to make the emulsion. Table VI presents the results.

Thus, from Table VI as well as Table V one concludes that the clay has been stablized with respect to both gamma and beta emitters.

Development of Analytical Method

The determination of beta activity of the clay was mentioned above as taking place in an energy range free of carbon 14 influence. This is better illustrated by Fig. 2 which shows the beta ray spectra of carbon 14 and clay.

This clearly demonstrates that at a lower discriminator setting of 100, carbon 14 interference is quite low. Tritium is of much lower energy than carbon 14 and so does not interfere at all.

Note, however, in Fig. 2 that the clay beta radiation interferes strongly with carbon 14 and of course with tritium. This overlap, known as spillover, must be accurately known so that the observed counts in the tritium and carbon 14 channels can be corrected for the contribution from the clay. The problem is further complicated by the fact that the clay decay rates are different at the various energies. This means that the spillover factor will change with time but, of course, not by the same amount or even in the same direction. Spillover factors were determined from count rates in the three channels over the same time intervals shown in Table III and with the same sample. The results are in Table VII.

Table VII indicates that a complex decay scheme exists in the clay. Decay rates in three energy channels are different causing the spillover factors to change with time, not always in the same direction as shown for carbon 14. These data demonstrate that one must count a clay standard with the sam-

TABLE VI

Stability of Prepared Clay to Extraction by Built Detergents

Active matter[a]	Per cent radioactivity removed
Ethoxylated Alcohol[a]	
C_{12-15} 9.5 EO	1.5
LAS	1.4
Alcohol Sulfate	
C_{12-15} SO_4Na	1.3

[a] Detergent formulation

STPP	0.6 g/liter
Na_2SO_4	0.45 g/liter
Na_2SiO_3	0.075 g/liter
CMC	0.0075 g/liter
Active matter	0.1 g/liter nonionic 0.4 g/liter anionic

TABLE VII
Effect of Clay Age on Spillover Factors

Time from irradiation	Count rate, cpm × 10^{-4}			Spillover factor, cpm ^{3}H or ^{14}C / cpm clay	
	^{3}H channel	^{14}C channel	Clay channel	^{14}C	^{3}H
55 days	3.04	16.7	7.44	2.24	0.41
76	2.80	10.6	3.26	3.25	0.86
131	2.18	6.30	1.76	3.58	1.24
311	1.47	1.99	0.87	2.29	1.69
631	1.30	0.92	0.39	2.36	3.33

Instrument Settings
^{3}H channel, amplifier = 52%, Disc. = 50–500
^{14}C channel, amplifier = 8.2%, Disc. = 100–1000
Clay channel, amplifier = 2%, Disc. = 100–∞

TABLE IX
Detergency Run with Triply Labeled Soil[a]

Fabric	Tergotometer beaker no.	Added clay, mg	Removed, per cent		
			Clay[b]	^{3}H[c]	^{14}C[c]
Cotton	1	20.6	96.6	61.4	57.4
	2	20.9	96.1	59.6	56.1
	3	21.0	96.1	64.4	59.7
	4	20.5	95.7	61.6	57.8
Nylon	1	22.2	75.8	29.5	65.0
	2	22.1	76.4	30.0	65.3
	3	21.5	77.0	30.0	64.3
	4	21.7	74.1	28.5	63.2
Dacron	1	23.2	96.1	20.1	71.8
	2	22.8	96.1	18.7	69.3
	3	22.7	96.3	18.6	70.2
	4	22.4	96.1	18.3	69.5

[a] Wash solution
0.1 g/liter linear primary alcohol $C_{12-15} \cdot 9$ EO
0.4 g/liter STPP
0.3 g/liter Na_2SO_4
0.05 g/liter Na_2SiO_3
0.005 g/liter CMC
150 ppm hardness
120F
10 min wash cycle.

[b] Determined by gamma ray counting of the four washed swatches.

[c] The fatty soil added to each set of four swatches was 64.6 mg nonpolar (^{3}H) fraction and 55.4 mg polar (^{14}C) fraction (7).

ples of wash water to obtain the spillover factors for that day. This is no inconvenience because of the automatic nature of liquid scintillation counting and data workup (14).

To determine whether the presence of the colored clay in the wash water interfered with the determination of the fatty components of the sebum, known amounts of the doubly labeled sebum were mixed with increasing amounts of nonradioactive clay and analyzed by LSC in the emulsion described above. This emulsion effectively suspends the clay particles. Nonradioactive clay was used because it is darker than the treated clay and would be expected to interfere more severely than the treated clay. Quenching by colored materials may cause errors in liquid scintillation counting. Amounts of clay were used far in excess over the maximum possible in a Tergotometer wash water sample (0.18 mg).

There is no doubt that, at the clay concentrations encountered in wash water there will be no interference in the determination of the fatty components of the sebum. There is a definite effect at and above the 2 mg level. Whether this is due to color quenching or to self absorption arising from adsorption of the fatty components on the clay has not been determined. But this deviation should be corrected if higher concentrations of clay in the wash water ever become of interest.

Because the beta specific activity of the irradiated clay was so low it was decided to rely mainly on gamma ray counting for measuring the clay until the higher specific activity clay would be available. The advantages of gamma counting were the high sensitivity achievable by counting all four fabrics at once and the fact that one could also count the fabric before laundering to determine the amount of clay on each set of four swatches. This is a distinct advantage if a precise method of clay padding is not yet at hand. Padding and application of this soil to some Tergotometer runs is discussed below.

As described above, clay interference in the tritium and carbon 14 channels had to be taken into account. (See Table VII.) Thus, clay counts were needed before applying the spillover factors. At the settings of the clay channel there is also a small but significant spillover of carbon 14 into the clay channel. Therefore, in order to obtain the clay contribution to the other two isotopes the following equation was used.

$$G = 0.45\,{}^{14}C + 1.58P \qquad [1]$$
$$B = 0.02\,{}^{14}C + P$$

where G = observed cpm in carbon 14 channel; B = ditto in clay channel; ^{14}C = carbon 14 disintegration rate, dpm; P = clay count rate, cpm in clay channel; 1.58 = spillover factor, clay into carbon 14 channel; 0.02 = efficiency of counting carbon 14 in clay channel; and 0.45 = efficiency of counting carbon-14 in carbon 14 channel.

One solves for P and ^{14}C and subtracts 1.92 P from the tritium channel to get the count rate in the tritium channel free of clay counts. The numerical coefficient were obtained by using a pure clay standard and a pure carbon 14 standard to obtain the interference factors. Even though the carbon-14 dpm is solved, another set of simultaneous equations involving tritium and carbon 14 only are then solved in the usual way (14) to get the tritium dpm.

TABLE VIII
Effect of Clay in Determination of Doubly Labeled Soil

mg clay	Recovered[a]	
	mg ^{3}H fraction	mg ^{14}C fraction
0	0.43	0.35
0.53	0.41	0.34
0.88	0.42	0.35
2.55	0.39	0.34
5.60	0.36	0.34

[a] Added 0.43 mg ^{3}H fraction, 0.35 mg ^{14}C fraction.

Padding and Detergency Runs

The doubly labeled fatty soil is normally applied to fabric swatches by direct pipetting of a 2% benzene solution (14). Ideally one would like to apply the clay in the same manner and from the same solution. Lambert et al. (8) pipetted a 2% aqueous slurry of particulate soil onto cotton swatches but gave no data on the accuracy or precision of this method. Generally particulate soil has been applied to fabrics by agitating the fabrics in a slurry followed by drying and sometimes a working step for better impregnation into the fabric interstices (4).

As a first step, however, 500 mg of labeled clay was added to 100 ml of a benzene solution of the doubly labeled sebum. One milliliter aliquots of this were manually applied to 4 × 4 in. swatches of the fabrics using a pipette while continuously stirring the solution vigorously with a magnetic stirrer. After evaporation of the benzene four swatches of each fabric were inserted into a plastic vial, 30-ml volume, and counted in a 3 × 3-in. Na I well crystal (30 × 56 mm) at an energy range >0.3 mev. The scaler-printer assembly was a Baird Atomic Model 530 A

TABLE X
Comparison of Clay Detergency Values by Beta and Gamma Ray Counting

Fabric	mg Clay Removed		
	Fabric analysis, gamma ray	Water analysis, gamma ray	Water analysis, beta ray
Cotton	20.0	21.5	18.2
Nylon	16.6	16.4	14.6
Dacron	21.9	22.6	21.1

spectrometer. The purpose was to determine the amount of clay on each set of four swatches as well as the reproducibility of clay padding. Because of the possibility of irregular positioning of the swatches in the vial, each vial was counted once with the cap end up and once inverted. The count rate was taken as the average. Comparison of the count rates of each of the fabric sets with a standard prepared by dispersing a weighed amount of clay among four cotton swatches gave the weight of clay per set of four. The swatches were then laundered, and recounted in the well counter. In addition, 30-ml aliquots of each wash solution was also counted to obtain a clay balance based on gamma ray counting. (The difference between fabric and solution densities had a negligible effect on counting efficiency.) Finally 5-ml aliquots of the wash water were also taken for the fatty component analysis (i.e., ^{3}H and ^{14}C). As a test of the possibility of using only liquid scintillation counting as the method for all three components, an additional set of calculations for clay removal were made using the value of P obtained from equation [1] above. The first set of results are shown in Table IX.

Table IX shows that padding by direct pipetting is quite precise. The increase in quantity of clay added going from cotton to nylon to dacron is due in part to evaporation of the benzene and in part to the not quite homogenous suspension of the clay by this method of stirring. It is encouraging to note the precision in clay detergency between beakers. The poorest set of values, nylon, shows a one σ value of 2%, entirely acceptable for detergency studies. The only matter for concern are the high removal values, evidence that the clay is too loosely attached to the fabric and probably should be worked in.

The values for the ^{3}H and ^{14}C fractions came, as mentioned above, from liquid scintillation analysis of the wash water which required the determination of the clay beta activity in the clay channel so that corrections could be made to the tritium and carbon 14 counts before computing the fatty sebum detergency. One can also use this clay activity, P in equation [1], to determine the deterged clay, bearing in mind the low count rate because of the low specific activity of the clay. To do this the calculated value of P (in cpm) is divided by the specific activity of the clay, in cpm/mg, obtained from a carefully weighed sample of clay suspended in the Triton/Toluene scintillator. This specific activity of course changes with time and should be determined daily. For this experiment the value was 842 cpm/mg. These clay detergency values were compared with those obtained by gamma counting the fabric and also by gamma counting 30-ml aliquots of the wash water. The purpose of the latter measurement was to see if the clay removed from the fabric could be found suspended in the wash water, i.e., if closure was achieved.

TABLE XI
Redeposition of Tagged Clay

Fabric	Beaker no.	Milligram clay deposited	Per cent redeposited[a]
Cotton	1	0.10	0.55
	2	0.12	
	3	0.10	
	4	0.11	
		avg 0.11	
Nylon	1	0.89	5.4
	2	0.85	
	3	0.92	
	4	0.91	
		avg 0.89	
Dacron	1	0.14	0.73
	2	0.13	
	3	0.15	
	4	0.20	
		avg 0.16	

[a] Basis clay in wash water.

The values in Table X are the average of four beakers each. Agreement between gamma ray analysis of fabric and wash water is satisfactory indicating that the deterged clay can be found in the wash water and does not deposit on the beaker surfaces. Agreement between liquid scintillation counting of the clay and gamma ray analysis while not entirely satisfactory is encouraging considering that the clay count rate was about 100 cpm and the spillover of carbon 14 into the clay count was also about 100 cpm. The data strongly suggest that using a clay of higher specific activity or reducing the specific activity of the carbon 14 labeled fraction, or both, by a factor of about two LSC of the clay will be both precise and accurate.

The ease of analysis, by gamma ray counting of the fabric, suggested that redeposition of the clay could be readily determined so one unpadded swatch was inserted into each beaker and counted after the wash-rinse sequence. Table XI presents the results.

Redeposition is also repeatable. Nylon, which showed the greatest retention of clay (25%) also showed the greatest redeposition, by almost a factor of 10 greater than the other fabrics. Bearing in mind that redeposition was measured with one swatch while detergency with four, it turns out that the amount redeposited per swatch for cotton is about half the residual clay per swatch. For dacron and nylon this value is about 70%. This suggests that a significant if not major amount of the residual clay on the washed fabrics arose from redeposition rather than nonremoval.

ACKNOWLEDGMENT

Miss L. B. Skinner and W. T. Shebs assisted in performing many of the analyses and preparation of the padded fabric.

REFERENCES

1. Powe, W. C., Textile Res. J. *29*, 879 (1959).
2. Powe, W. C., W. L. Marple, JAOCS *37*, 136 (1960).
3. Spangler, W. G., H. D. Cross and B. R. Shaafsma, JAOCS *42*, 723 (1965).
4. Rutkowski, B. J., JAOCS *44*, 103 (1967).
5. Ashcraft, E. B., ASTM Special Techn. Publ. No. 215, 30 (1956).
6. Boyd, T. F., Industrial Test Laboratory, Philadelphia Naval Shipyard, Reports Nos. 6200 A-1 through A-6 (1952–1955).
7. Gordon, B. E., J. Roddewig and W. T. Shebs, JAOCS *44*, 289 (1967).
8. Lambert, J. M., J. H. Roecker, J. J. Pescatore, G. Segura and S. Stegman, Nucleonics *12*, No. 2, 40 (Feb. 1954).
9. Hensley, J. W., M. G. Kramer, R. O. Ring and H. R. Suter, JAOCS *32*, 138 (1955).
10. Hensley, J. W., and C. G. Inks, ASTM Special Tech. Bulletin 268, 27 (1959).
11. Sanders, H. L., and J. M. Lambert, JAOCS *27*, 153 (1950).
12. Harbottle, G. Ann., Rev. Nucl. Sci. *15*, 89 (1965).
13. Wolf, A. P., Ibid. *10*, 259 (1960).
14. Shebs, W. T., and B. E. Gordon, 1967 Meeting of the AOCS, Paper No. 17.
15. Gordon, B. E., W. T. Shebs and R. U. Bonnar, JAOCS *44*, 711 (1967).

[Received May 23, 1968]