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A simple method to avoid sandiness and enhance deodorant efficacy of soaps containing TCC

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Synopsis

The "sandiness" of soap can be caused by TCC. This is shown in that the TCC-content of "sand" grains is very high compared to its microenvironment within the soap and by EDXA-analysis of Cl. The bioavailability of TCC of "sandy" soap (sandiness is caused by agglomerated TCC) is considerably lower than that of regular smooth soap. This was shown by analytical determination by HPLC of the TCC-level at the skin surface. Solubilization of TCC by means of nonylphenolether enhances the transfer of TCC. The amounts of TCC deposited on the skin surface while using soaps containing 1.3% powdered or 0.26% solubilized TCC are comparable. The amount of TCC transferred to the skin surface is approximately linearly proportional to the content of soap of TCC. Addition of wool wax alcohols as refattening agents increases the bioavailability of TCC. An excess of solubilizer decreases the transfer rate of TCC. Sniff tests prove the equivalence of deodorant soaps containing either 0.26% solubilized or 1.3% powdered TCC.

INTRODUCTION

This publication presents a simple method to avoid sandiness and to increase the biological availability of TCC, i.e., the amount of germicide that can be transferred from the soap-water mixture to the skin surface during normal use. The basic method used to avoid a gritty surface structure is to solubilize TCC and to add the mixture to the soap base in amounts necessary for effective deodorant action.

MATERIALS AND METHODS

PREPARATION OF THE SOAP CAKE

0.5 kg of TCC was solubilized in 3.0 kg of nonylphenolpolyglycol ether (Marlophen 814, Chemische Werke, Hüls, FRG) having an average degree of ethoxylation of 14 (1). This mixture was added in portions to 100 kg of soap base in noodle form, together with perfume and 1.65 kg of color paste which may contain 0.6 kg of wool wax alcohols as well as other ingredients. After thorough mixing, the homogenized mixture was processed in the usual manner and finally pressed.

COMPOSITION OF THE SOAP CAKES TO BE TESTED

Soap cakes prepared in the manner described above (with different contents of TCC and wool wax alcohols) were examined:

A. Containing 1.3% regular TCC (standard version, commercially available) with no sandy texture.
B. Containing 1.3% regular TCC (standard version, commercially available), gritty surface when being used.
C. Containing 0.13% solubilized TCC.
D. Containing 0.26% solubilized TCC.
E. Containing 0.5% solubilized TCC.
F. Containing 1.3% solubilized TCC.
G. Containing 0.26% solubilized TCC + 0.06% wool wax alcohols.
H. Containing neither TCC nor wool wax alcohols.
I. Soap G + 0.5% dimethylpolyglycol ether.
K. Soap D + 5.26% nonylphenolpolyglycol ether additionally.

Soaps A and B were prepared on a big scale in the factory; soaps C–K were prepared on a small scale in the laboratory.

EDXA—INVESTIGATION

The surfaces of pieces of soaps (B, C, F) were freshly cut with a knife. The surfaces—covered with carbon—were investigated by a combined SEM (scanning electron microscope, Hitachi S-500) and EDXA (X-ray-fluorescence, Kevex μ X System 7000) technique. The distribution of chlorine was determined to visualize the content and the tendency of TCC to form aggregates. Sodium was determined to show the homogeneity of the distribution of Na-stearate/palmitate.

QUANTITATIVE DETERMINATION OF TCC

TCC, dissolved in ethanol, was determined by HPLC (Hewlett-Packard 1084 B, column Lichrosorb RP8 (10 μ), solvent H_2O:ethanol = 23:77, injection volume 10 μl, wavelength 266 nm).

SAMPLING PROCEDURE FOR DETERMINATION OF THE DENSITY OF TCC AT THE SKIN SURFACE

The quantity of TCC/area unit of skin surface was determined in the following manner: The skin area (the inner side of the lower forearm), previously washed with soap, was covered with a funnel (Ø 60 mm); 5 ml of ethanol were poured into the funnel; the skin site, funnel, and solvent were shaken continuously for two minutes; then the solvent was transferred to a glass bottle, which was sealed afterwards by means of a septum.

DETERMINATION OF TCC BIOAVAILABILITY OF SOAPS A AND B

The comparison of "sandy" soap (B) with soap (A) of good quality was done as follows: ten female volunteers used running tap water of 37°C to wash one lower forearm with one of the two soaps. Analyses of TCC were performed as described above.

SKIN SURFACE CONTENT OF TCC IMMEDIATELY AND 12 HOURS AFTER USE OF SOAPS

To find the equivalence level between powdered and solubilized TCC, the quantitites of

transferred TCC were determined after use of the soaps A, C, D, E, and F. Twenty-four female volunteers always received random pieces of the above-mentioned soaps on Fridays. They were obliged to use these soap bars as they usually use a soap for ~1 week; on Monday and Wednesday morning, samples were taken from the lower forearms to determine the casual level of TCC. Subsequently both arms were washed by rubbing the forearm directly under running tap water of ~30°C with the assigned soap bar for two minutes, and another series of samples was prepared to determine the content of TCC at the skin surface. The following week the soap pieces were substituted by one of the other soaps.

INFLUENCE OF THE DURATION OF WASHING AND OF REFATTENING AGENTS

Soap D was compared with soap G (containing wool wax alcohols) as described above, except that seven volunteers used the soaps for ten seconds, seven volunteers used them for 40 seconds, and nine volunteers for 120 seconds.

INTERRELATION BETWEEN THE LEVEL OF SKIN SURFACE LIPIDS, SKIN SURFACE ROUGHNESS, AND TCC TRANSFER

The skin surface lipids on the inside of one forearm of nine volunteers were determined by solvent extraction (2). The skin surface roughness of contralateral sites was determined by profilometry (3). Afterwards both forearms were washed for two minutes under running tap water of 35°C using soaps I and K respectively. The content of TCC was determined as described above.

INFLUENCE OF THE CONTENT OF SOLUBILIZER ON TCC TRANSFER

Twenty volunteers washed their forearms for two minutes under running tap water of 35°C using soap G and soap K (containing an excess of 5.26% nonylphenolpolyglycol ether). The level of TCC on the skin surface was determined as described above.

SNIFF TEST COMPARING SOAPS A AND D

A panel of 50 volunteers of both sexes was given a control soap to use to wash the axillae in the evening and morning for three days. The axillary odor of the volunteers was then assessed by two independent assessors using a numerical scoring system for odor intensity. On the basis of this assessment, the 30 volunteers with the highest axillary odor were selected and split into two test groups having approximately the same mean and range of odor levels. For the next three days one group used soap A to wash the left axilla and soap B to wash the right axilla, and the other group washed according to the reverse pattern. After three days the odor levels were reassessed and both groups went back to using the control soap for two days before returning for a third assessment. In the final stage there was a product crossover, i.e., each group reversed its washing pattern for three more days, with a fourth assessment at the end of this period. The results were expressed as the ratios of odor intensity between axillae for each volunteer at each assessment. This test was performed by Toxicol Laboratories, Ledbury, England.

SNIFF TEST COMPARING SOAPS C AND H

The investigation was conducted as a double-blind study:
a) On the first day the volunteers, who had refrained from using deodorant products for at least 24 hours and had used a deodorant-free soap, washed both axillae with a deodorant-free placebo soap (=H). After this standardization procedure, the volunteers placed a ball of pure cotton under each axilla, wore a T-shirt made of cotton (washed with perfume-free detergents), and sat quietly for 30 minutes in a room with a temperature of ~30°C. After this period of slight sweating, the cotton balls were removed, sealed in a glass container free of noticeable smell and stored for 1–3 hours in a refrigerator at 2°C. Thirty minutes before evaluation the glass jars were removed from the refrigerator and allowed to warm to room temperature (20°C). Two technicians experienced in this kind of investigation and with sensitive noses evaluated the atmosphere in every container according to quality and quantity of odor.

The following scores were used to describe the odor:

0 = no odor
1 = odor just detectable
2 = odor of slight intensity
3 = odor of moderate intensity
4 = odor of strong intensity

b) On the second day this procedure was repeated, except that soap C (containing 0.13% TCC) and soap H were used (random application sites).
c) The scores (sum of two individual scores) characterizing each sample were compared by the paired t-test.

RESULTS

CONTENT OF TCC "SANDY" GRAINS

The following procedure was used to determine whether the grains on the surface of the "sandy" soap cakes B had a high content of TCC and whether the inhomogeneity therefore consisted mainly of deodorant: grains isolated from the surface of soap B contained aproximately 40 times the amount of TCC found in soap A.

SPATIAL DISTRIBUTION OF Cl AND Na IN SOAP CAKES B, C, AND F

Figure 1 shows the distribution of chlorine—characterized by the little white spots—in soap B, and Figure 2a presents the result of an analogous analysis of Soap F. The uneven distribution of chlorine in soap B is easily recognized when soap B is compared with soap F, i.e., the solubilization of TCC has the expected result. The low intensity of chlorine in Figure 1a compared with Figure 2a—both products contain 1.3% TCC—is probably a consequence of aggregation within soap B that inevitably will cause a decrease in dissolved or finely dissipated powdered compound. The presumably linear relationship between the number of white spots and the content of TCC can be estimated by comparing Figure 2a with Figure 3a, which represents the distribution and quanity of chlorine within soap C; the reduction of solubilized TCC by a factor of 10 is expressed very well by the less intense, but even, distribution of chlorine. In contrast to chlorine, sodium is distributed very evenly in exactly the same area as used for the

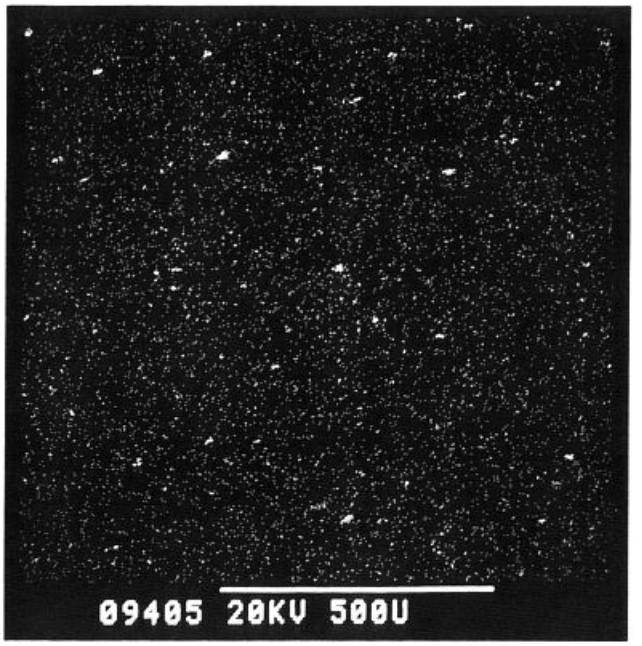

Figure 1a. Distribution of chlorine within an arbitrarily chosen surface district of soap B.

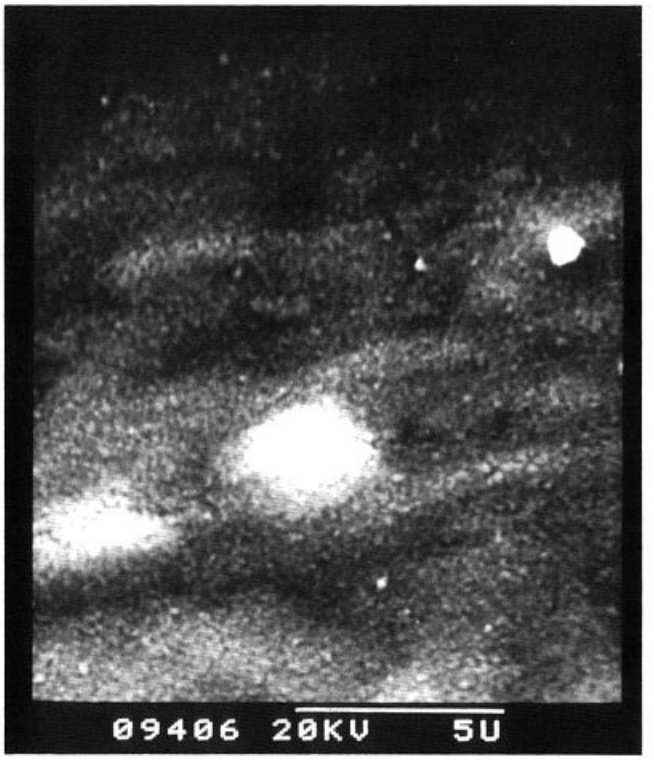

Figure 1b. Surface district of soap B at higher magnification.

Figure 2a. Distribution of chlorine within an arbitrarily chosen surface district of soap F.

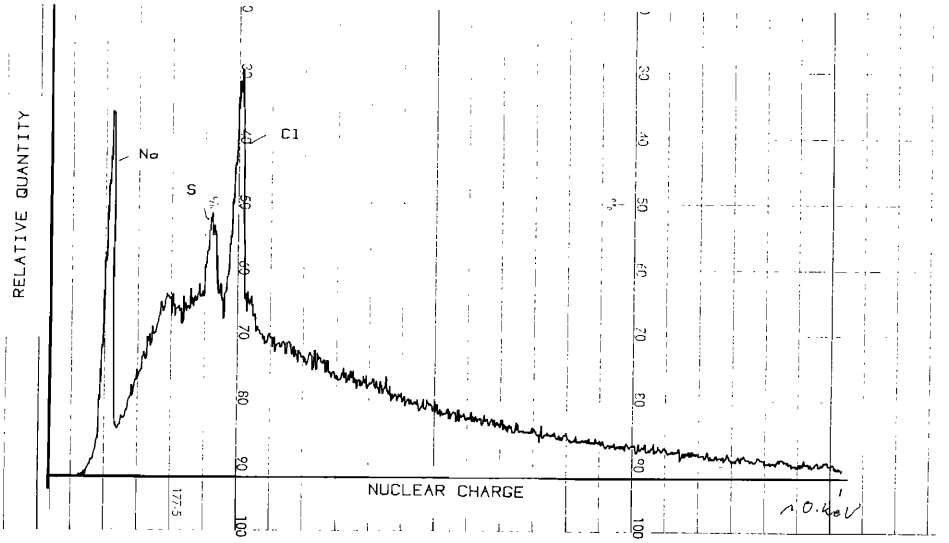

Figure 2b. Relative quantities of elements within the surface of soap F (investigated surface area identical with that of Figure 2a).

Figure 3a. Distribution of chlorine within an arbitrarily chosen surface district of soap C.

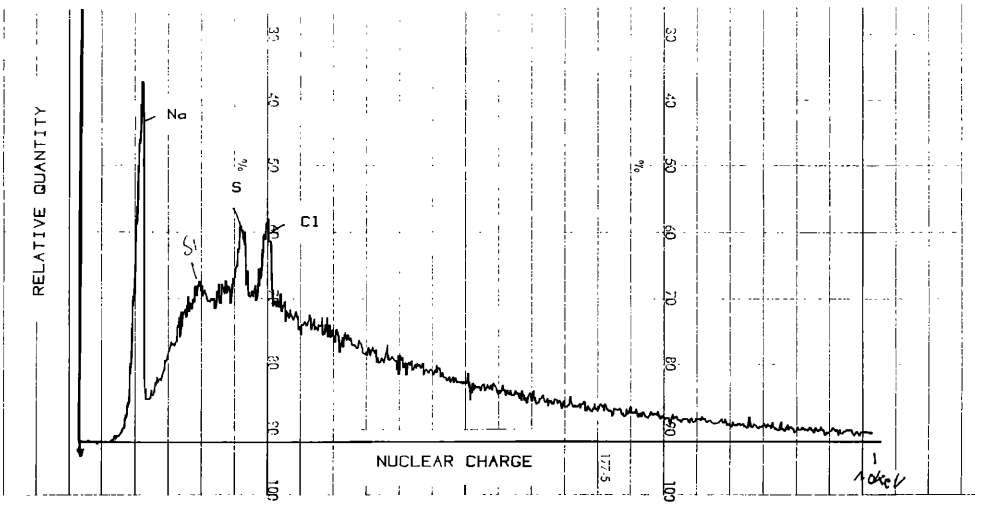

Figure 3b. Relative quantities of elements within the surface of soap C (investigated surface area identical with that of Figure 3a).

analysis of chlorine. Figures 2b and 3b show the same integral intensities of Na and S in the surface districts; the density of chlorine-indicating spots in Figures 2a and 3a are in accordance with the content of chlorine.

BIOAVAILABILITY OF TCC FROM DIFFERENT SOAPS

The velocity of heterogeneous reactions is normally influenced by the distribution of the reaction partners, i.e., the rate of transfer of TCC from the soap to the skin surface will probably depend on such factors as the distribution of the deodorant, the duration of interaction, the reaction temperature, and other ingredients of the soap, which might have a promoting or interfering influence. Presumably the quantity of TCC on the skin surface should strongly influence the deodorant effect.

SOLUBILIZATION ENHANCES TCC TRANSFER

The logical consequence of these results was to look for the effect of TCC dispersed in micelles or evenly dissolved in soap as individual molecules. Some preliminary studies showed that soaps (e.g., soap F) containing solubilized TCC deposited much more TCC on the skin surface than soaps containing powdered TCC (e.g., soap A).

The density of TCC on the skin surface was 0.24 ($\mu g/cm^2$) using soap A and less than 0.1 ($\mu g/cm^2$) using soap B (Figure 4). One might speculate that soaps with a gritty texture due to TCC will probably show a much less pronounced deodorant effect than soaps with the same content of TCC but with fairly evenly distributed powdered TCC. These interesting but preliminary results were confirmed by the following.

DETERMINATION OF TCC BIOAVAILABILITY WITH REGULAR USE OF SOAPS OF DIFFERENT TCC CONTENT

Figure 5 shows the relationship between transferred TCC and TCC content of the soaps:
a) The rate of TCC transfer is an approximately linear function of the TCC content of the soap used.
b) There is a slight tendency to higher values with longer test periods.
c) After solubilization the TCC content of the soap can be reduced to less than ¼ of the TCC content of soap A containing 1.3% powdered TCC to reach the same level of TCC at the skin surface (1).

Statistical differences were found between C and all other tested soaps, between D and E, D and F. No differences were found among A, B, and E.

INFLUENCE OF THE DURATION OF WASHING AND OF REFATTENING AGENTS

The influence of the washing period on the quantity of transferred TCC is summarized in Figure 6. After 10 and 120 seconds, significantly higher values (>95%) were found on the arms treated with soap G. This may be due to a decrease of "free" solubilizer in soaps containing refattening agents.

CORRELATION BETWEEN THE LEVEL OF SKIN SURFACE LIPIDS, SKIN SURFACE ROUGHNESS, AND TCC TRANSFER

There is a weak correlation between the content of skin surface lipids and the quantity

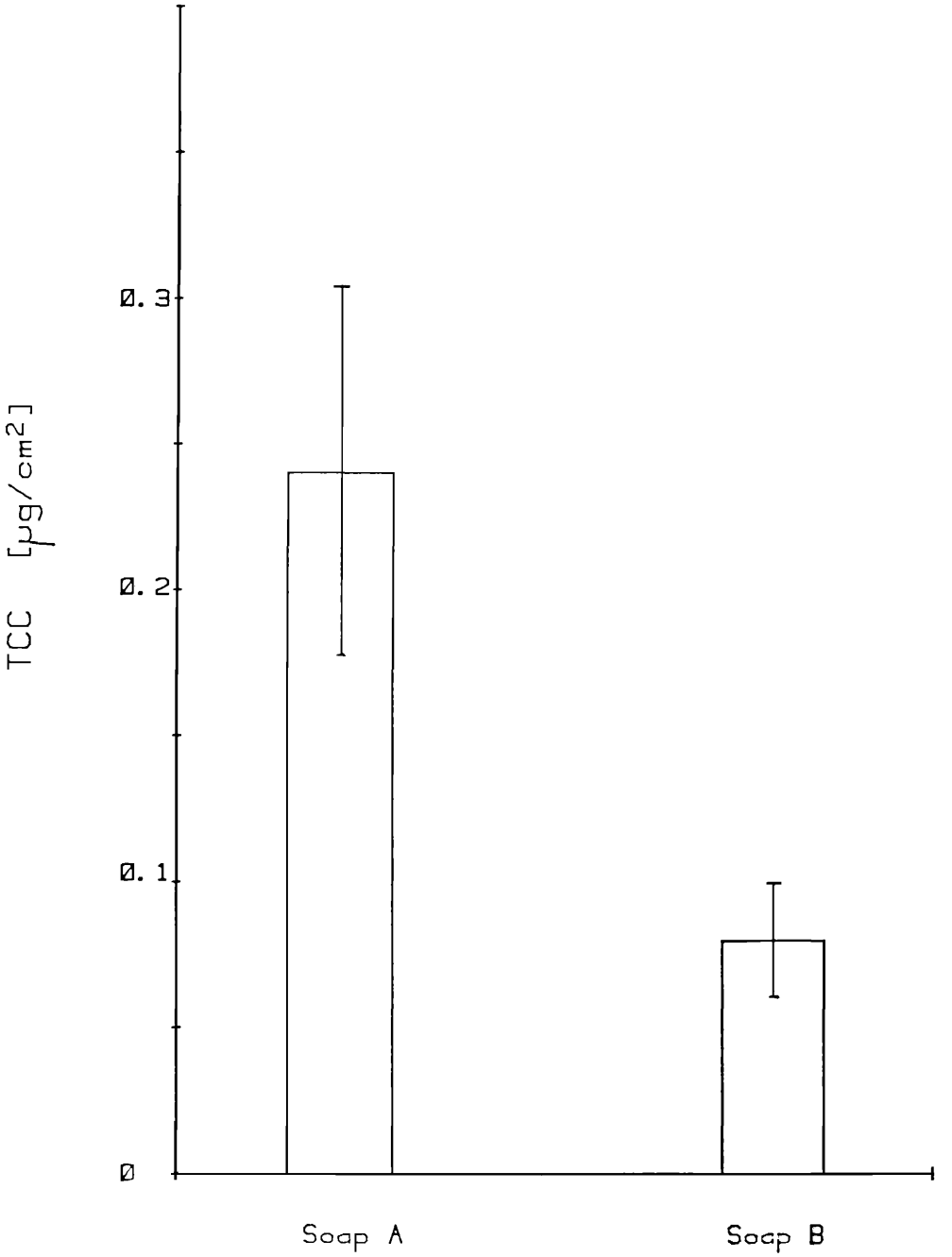

Figure 4. Comparison of TCC transfer rates using normal (A) and "sandy" (B) soap containing 1.3% powdered TCC (single application, 2 minutes, running tap water of 37°C).

of transferred TCC (Figure 7). This could mean that either the skin surface lipids serve as a depot for TCC or that they promote the liberation of TCC from the micelles. This may be in accordance with the promoting action of superfatting agents.

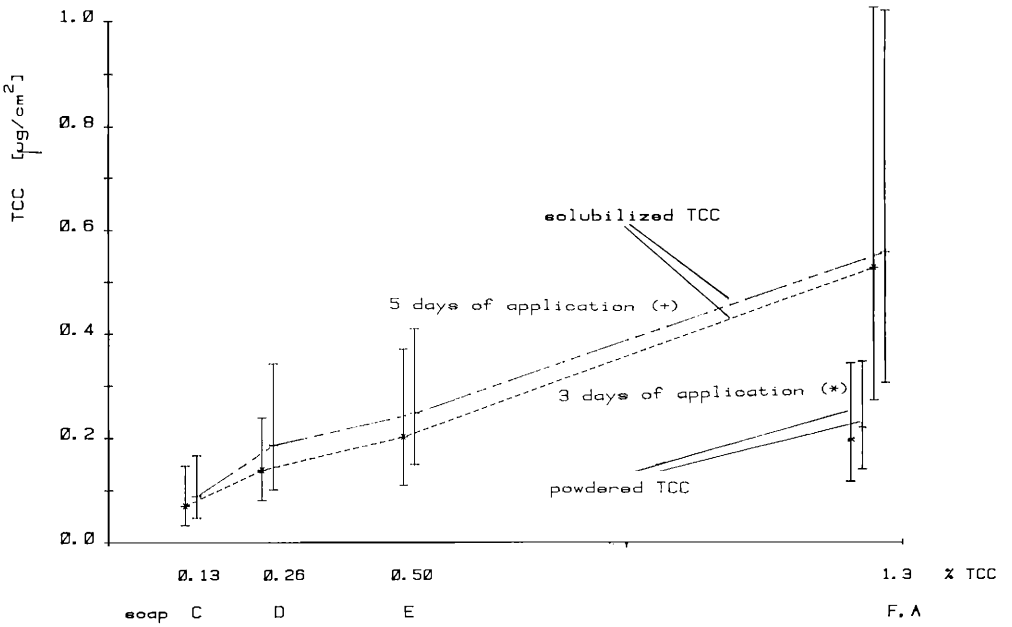

Figure 5a. Comparison of TCC transfer rates using soap A (1.3% powdered TCC) and soaps C–F containing rising amounts of solubilized TCC after 3 and 5 days of regular use. Samples were taken after washing for 2 minutes with running tap water of 30°C.

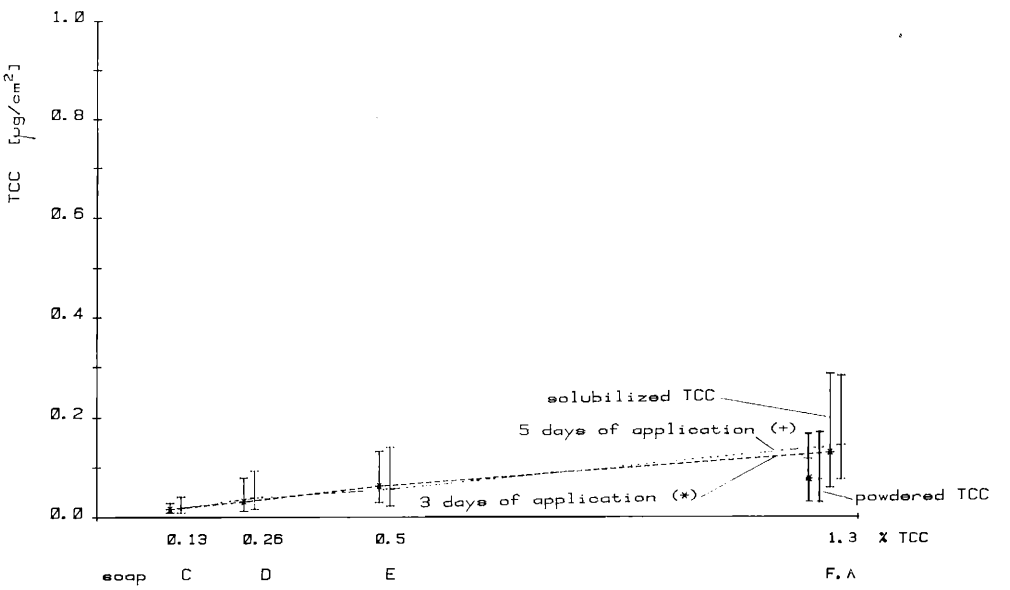

Figure 5b. Comparison of casual levels of TCC using soap A (1.3% powdered TCC) and soaps C–F containing rising amounts of solubilized TCC after 3 and 5 days of regular use. Samples were taken approximately 12 hours after last preceeding use.

Another weak interdependence links skin surface roughness (R_{tm}) with the amount of transferred TCC (Figure 8). A possible explanation could be that increasing R_{tm} values are synonymous with rising surface areas: Larger surfaces may cause greater adsorption.

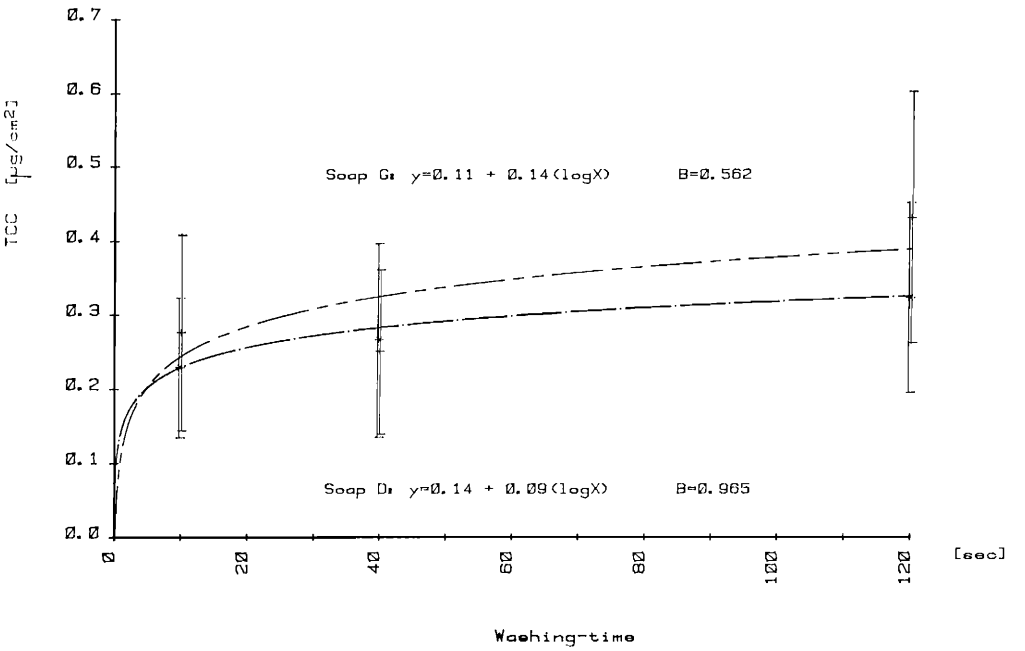

Figure 6. Comparison of TCC transfer rates using soap D (0.26% soluble TCC) and soap G (0.26% soluble TCC + 0.06% wool wax alcohols) after different washing periods (10 sec, 40 sec, 120 sec). Samples were taken after washing with running tap water of 30°C.

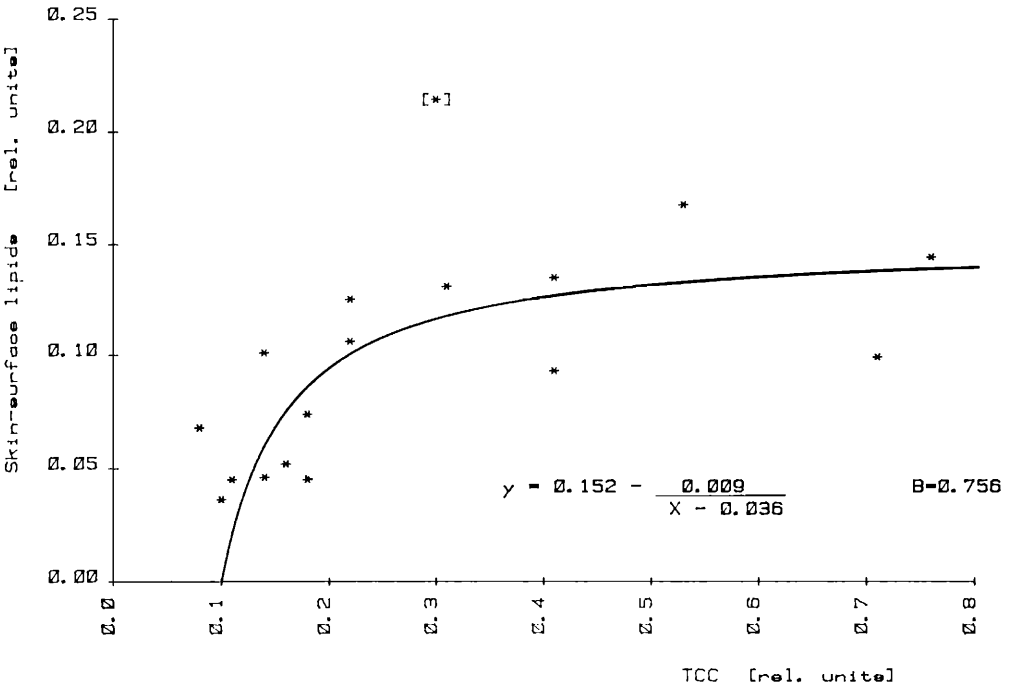

Figure 7. Correlation between skin surface lipids (after treatment) and TCC transfer rate using soap I (0.26% soluble TCC + 0.06% wool wax alcohols + 0.65% dimethylpolyglycolether). Samples were taken after washing with running tap water for 2 minutes.

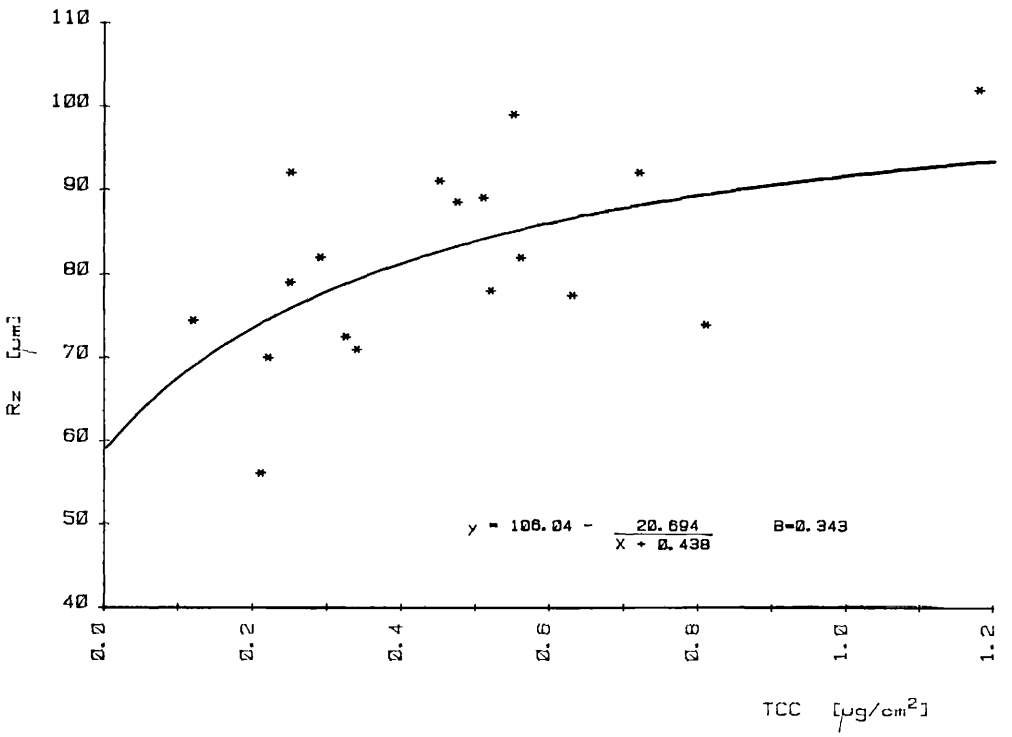

Figure 8. Correlation between skin surface roughness (Rz replica taken before washing) and TCC transfer rate using soap K (0.26% soluble TCC in nonylphenolpolyglycolether). Samples were taken after washing with running tap water of 35°C.

This explanation is supported by the finding that the rougher skin of elderly people absorbs more deodorant than the smoother skin of younger volunteers. These results were also found using soap C and, to a lesser extent, when using soap D.

INFLUENCE OF WATER TEMPERATURE

The transfer rate is influenced by the temperature of the tap water used. In water of 30°C the amount of TCC transferred is higher than when using water of 40°C (Figure 9a). We found here that solubilization of the mixture of the refattening agent and TCC (=variant of soap G) lowers this temperature dependence.

INFLUENCE OF THE CONTENT OF SOLUBILIZER

It can easily be recognized that the content of solubilizer in soap G is at a reasonable level with respect to distribution and bioavailability by comparison of the TCC transfer rate of soap G with that of soap K, which contains an excess of solubilizer (Figure 9b): The amount of transferred TCC drops by about 40% when soap K is used.

ESTIMATION OF THE TIME-DEPENDENT TRANSFER OF TCC

To estimate the percentage of TCC transferred to the skin during the washing procedure, an experiment was performed on one volunteer:

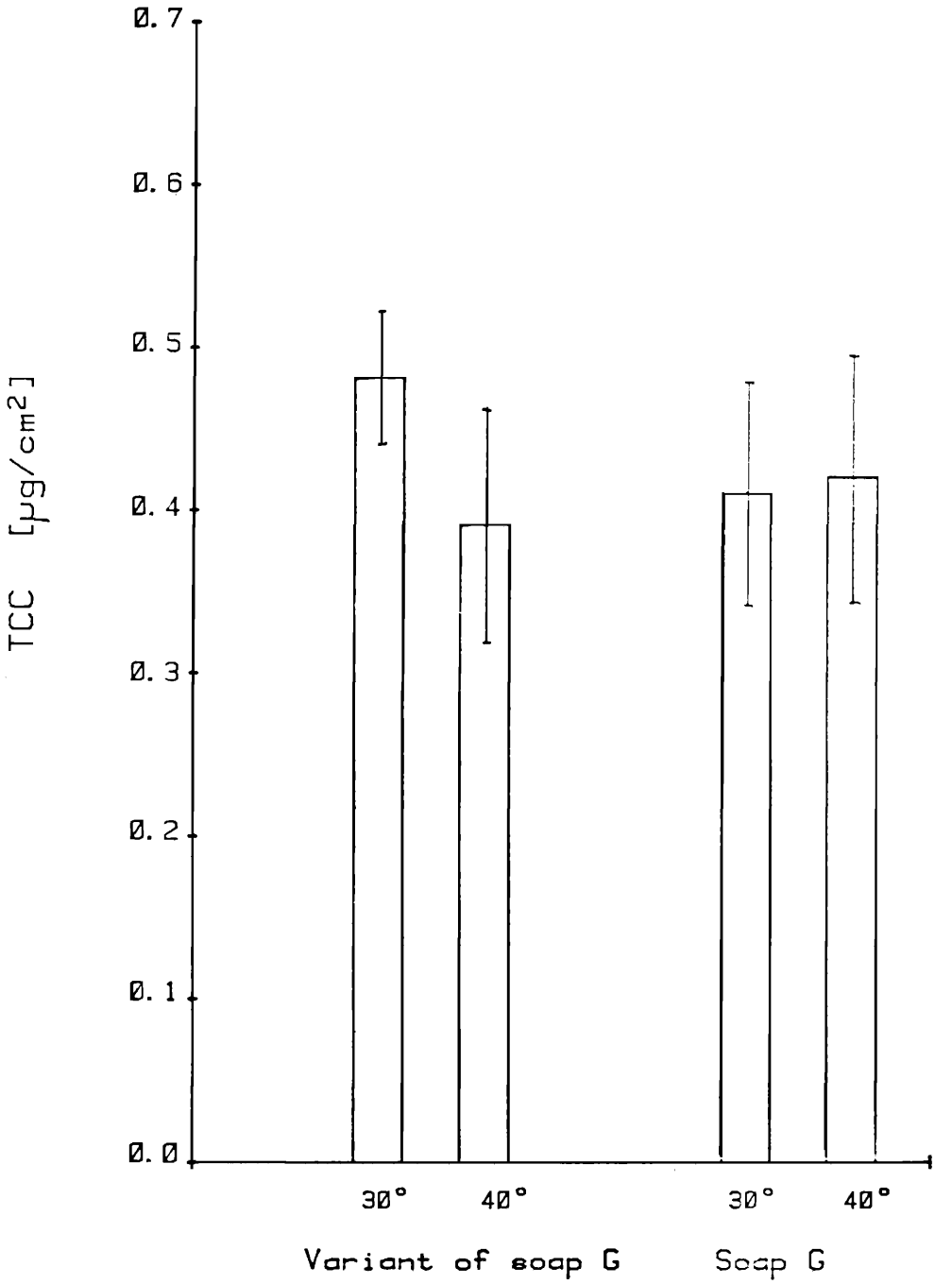

Figure 9a. Influence of temperature (30°C/40°C) on TCC transfer rates. Samples were taken after washing with soap G and a variant of soap G for 2 minutes.

a) The combined surface of lower forearm and hand was estimated to be 1030 cm^2.
b) After 30 seconds of washing (30°C, running tap water), the volunteer had used 1.6 g, and after 120 seconds 6.2 g of soap D.

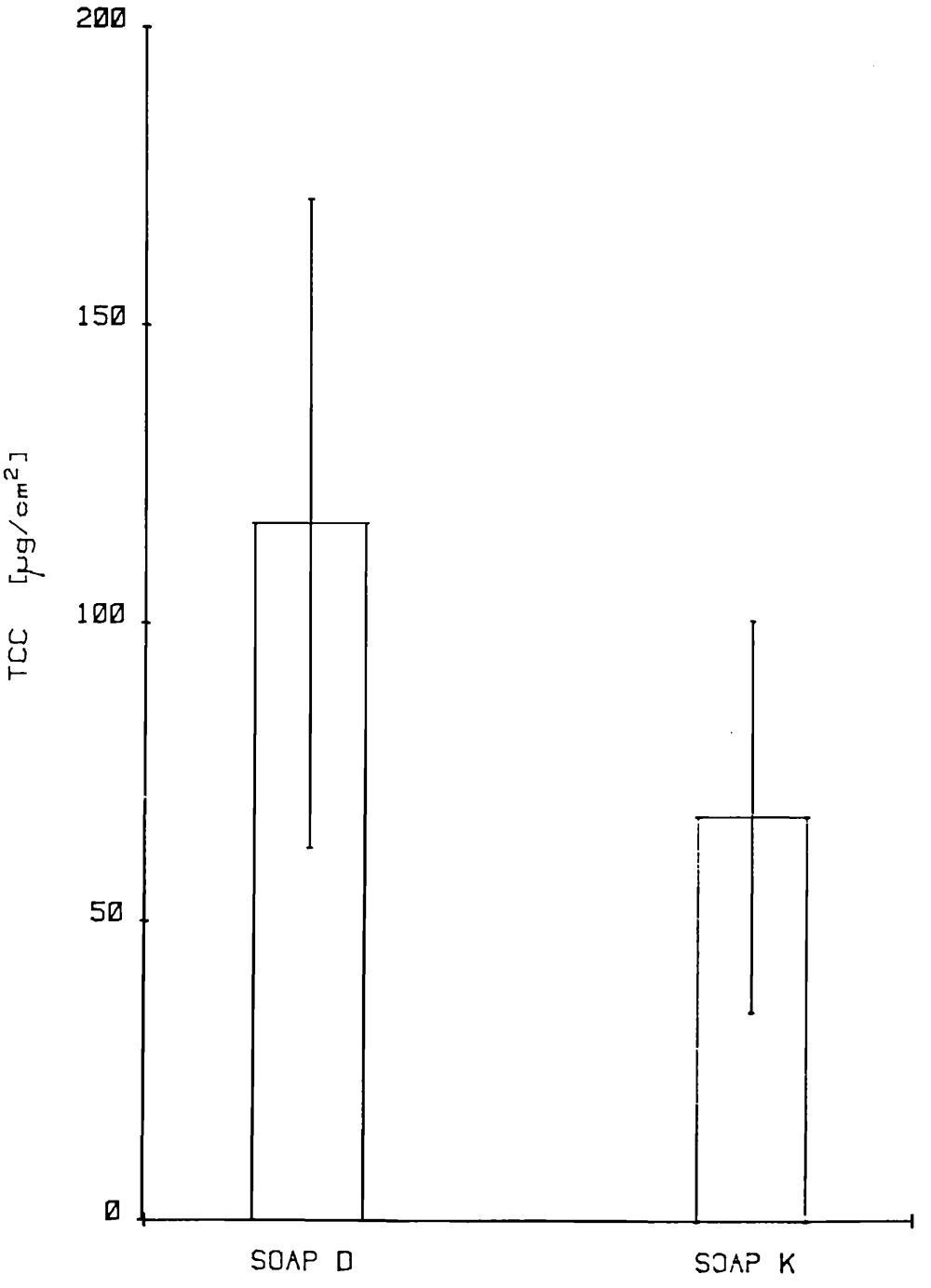

Figure 9b. Comparison of TCC transfer rates using soap D and soap K containing an excess of solubilizer.

c) The level of TCC on the skin surface was ~0.9 μg/cm² after 30 seconds and ~1.0 μg/cm² after 120 seconds.

d) The percentage of TCC transferred to the skin was 23% of the sum of TCC dispersed

after 30 seconds and 6.4% after 120 seconds (approaching saturation level). Similar conclusions can be drawn from Figure 6.

SNIFF TEST COMPARING SOAPS A AND D

Statistical analysis (Student's t-test) of the ratios representing (odor intensity of the left axilla)/(odor intensity of right axilla) showed that there were no significant changes in these ratios in any group on changing from the control soap to the test soaps. This indicated that there was no significant difference between the deodorant efficacies of soaps A and D, which contained 1.3% powdered and 0.26% solubilized TCC respectively.

An analysis of the absolute values of the odor intensity scores showed a significant reduction in score during the first treatment period. The scores increased on returning to use of the control soap. During the second period there was a small but significant increase in absolute scores. The changes in score during the trial may have been influenced by factors other than the deodorant efficacy of the test soaps.

SNIFF TEST COMPARING SOAPS C AND H

This investigation was performed to obtain an estimate of the amount of TCC necessary to provoke a perceptible deodorant effect. No differences could be detected between the axillae of the group after having used soap H on both sides (first day). The application of soap C produced significantly (>95%) lower scores than application of soap H (second day) (Table I). This means that even 0.13% solubilized TCC caused a weak but perceptible difference.

CONCLUSIONS

The experimental data presented for, and the practical experience obtained with, commercial soaps explain and support a number of assumptions:

a) "Sandiness" can be induced by powdered TCC.

b) "Sandy" soap, in which TCC is dispersed in an agglomerate state, reduces the bioavailability of TCC considerably.

c) Solubilization of TCC enhances the transfer of TCC to the skin surface by a factor >4. There is a linear relationship between the transfer of TCC and the content of solubilized TCC of the soap.

d) This transfer is additionally increased by wool wax alcohols.

Table I
Mean Values of Sniff Test Scores, Standard Deviations, and t-Values Comparing Soaps C and H

	Sum of scores (means)		t-Values comparing axillae 1/2
	Axilla 1	Axilla 2	
First day (using soap H)	1.75/0.989	1.625/1.096	0.43 t (95%) = 2.07
Second day (using soaps C and H)	3.1/2.123 (soap C)	3.8/2.102 (soap H)	2.122 t (95%) = 2.046

e) Increasing the content of solubilizer of solvents decreases the amount of TCC transferred. The effects of refattening agents, i.e., wool wax alcohols on the one hand, and solvent, i.e., dimethylpolyglycolether and solubilizer on the other hand, is certainly the consequence of the increased and decreased chemical potential (or "transfer pressure") of TCC respectively.
f) The amounts of TCC transferred (% of the soap used) per second of washing period decrease with the duration of the application period and show a saturation level after about one minute of washing.
g) Sniff tests show that soaps containing either 0.26% solubilized TCC or 1.3% powdered TCC are equivalent deodorants.

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