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Determination of the substantivity of emollients to human hair

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Synopsis

The determination of silicones and hydrogenated didecenes deposited on human hair from shampoo applications is described. For silicones, induced coupled plasma optical emission spectroscopy (ICP-OES) of extracts and X-ray fluorescence analysis (XRF) of hair strands without any further sample preparation have been applied. Three shampoos from the European and Asian markets have been investigated at repeated shampoo applications followed by the determination of the removability with sodium laureth sulfate. Hydrogenated didecenes have been quantified by GC-MS of extracts. A transparent shampoo containing 1.8% of hydrogenated didecenes delivered via a nanoemulsion was examined in the same way as the commercial shampoos. Finally, the substantivity data were compared with performance data from combability determination and hair volume measurements. Good correlations of analytical data and performance profiles have been obtained.

INTRODUCTION

In addition to basic ingredients like surfactants, preservatives and fragrances, modern shampoos contain several "care" products such as polymers, emollients and waxes to improve sensorial and conditioning properties and the appearance of both the shampoo and the treated hair. These ingredients must be carefully selected and formulated to ensure that sufficient quantities of the substances adsorb to the hair to provide the desired effect, yet avoiding overloads or build-up effects. Therefore, the determination of the adsorbed amounts of each "care" ingredient can help select the type and concentration of a specific ingredient used and all other ingredients of a formulation. This can be achieved either directly—if an appropriate analytical method for the detection at surfaces is available—or by extraction and analytical determination of the specific substance, whereby both steps must be specifically adapted to the specific ingredient. In this paper, we describe our approaches for the determination of silicones and hydrocarbons applied as conditioning agents via shampoos.

For silicones detection methods specifically determining Si can be applied. In the

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literature, several methods for the direct detection of silicones on human hair have been described including atomic absorption spectroscopy (AAS; 1), electron spectroscopy for chemical analysis (ESCA; 2), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS; 3), and X-ray fluorescence spectroscopy (XRF; 4). We have selected X-ray fluorescence due to the ease of use without sample preparation. Organic extracts of human hair can be evaluated by a wide range of analytical methods, for silicones we have applied induced coupled plasma optical emission spectroscopy (ICP-OES; 5) due to a very low limit of detection.

Hydrogenated didecene was selected as example for the use of hydrocarbons in hair rinse products. Since there is no specific method available for hydrocarbons, a GC-MS method was developed to quantify the amount of hydrogenated didecene in extracts of hair. The results of build-up effects and removability of substances by pure surfactant solutions are presented. In addition, two examples of how these analytical data can be linked to consumer relevant performance properties, like conditioning and hair volume effects, are presented.

EXPERIMENTAL

Strands of human hair were purchased from International Hair Importers (New York). Shampoos containing dimethicone and dimethiconol were taken from the current markets in Germany and Thailand. The shampoos from the German market were tested with dark brown Caucasian hair and the shampoo purchased in Thailand was tested with Japanese hair.

The shampoo with hydrogenated didecene was formulated according to Table I. Tests with this shampoo were performed using the dark brown Caucasian hair. Hair strands were washed with the shampoos at 1 g shampoo/1 g hair, incubated for 5 min and rinsed off using a special device to ensure reproducibility for all experiments. With this device each hair strand is rinsed with water at 38°C, 1 L/min and combed during rinsing. After rinsing the hair strands were dried for 60 min with warm air (65°C). The removability of the emollients from the hair was tested by repeating the procedure described above 5 or 9 (for the hydrogenated didecene) times followed by 1, 2 and 3 times shampooing with a solution of 12% Sodium laureth sulfate (SLES) (pH 6.5) respectively. All strands were treated together and samples were taken out of the process after 1, 3, 5 (7 and 9 for the shampoo with hydrogenated didecene) and also after 1, 2 and 3 times treatment with SLES. Hair strands which were just cleansed by SLES were extracted to determine

Table I
Test Shampoo with Hydrogenated Didecene

Ingredient (INCI)	Concentration [%]
Sodium laurethsulfate	9
Cocoamidopropylbetain	3
Polyquaternium 10	0.2
Methyldibromo glutaronitrile and phenoxyethanol	0.1
PEG-150 distearate	1.25
Hydrogenated didecene (via a nanoemulsion)	1.8
Water	ad 100

the baseline values of all analytical methods. In the case of X-ray fluorescence spectroscopy the values result from silicon on the surface of the hair which is influenced by inorganic silicon from the hair itself.

The amount of silicones adsorbed on the hair was determined by ICP-OES analytics preparing extracts from the strands. For this purpose the hair was cut into pieces and the adsorbed silicone was extracted with a mixture of o-xylene and isopropanol. The extracts were analyzed on a Vista MPX Radial (Varian Inc.) ICP device using a certified polydimethylsiloxane calibration standard (Conostan®). The concentration of silicon was calculated by taking the mean of the signals at 5 silicon specific wavelengths. The concentrations of silicones were derived from the amounts of silicon by multiplying with a factor (2.64) derived from pure PDMS. Since for dimethiconol only the terminal methyl groups are substituted by hydroxyl groups, this factor is also valid for this type of silicone.

Hair strands were examined without further treatment via X-ray fluorescence spectroscopy by mounting them into a sample holder and analyzing in an Axios-Advanced (Panalytical) spectrometer. A 4kw Rh anode was used for the excitation and a PE002-C crystal for analyzing the wavelength of the fluorescent radiation. The amount of hydrogenated didecene of treated hair strands was determined by extracting the hair with isopropanol. The extracts were derivatized with a mixture of N, O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) and N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTAFA) to reduce the boiling temperature of the matrix components and increase selectivity. The GC-MS analysis was performed applying hexadecane as internal standard. Due to the structural complexity of didecene, only selected ion traces in a part of the didecene signals were used comparing chromatograms of the pure hydrocarbon and extracts of hair treated with a placebo shampoo without hydrogenated didecene.

Wet combing performances were determined using a robotic system combing 10 treated strands per formulation and number of applications. The combing work was determined by integrating the force versus distance curve. The residual combing work was calculated as ratio of (work after shampoo application) / (work before shampoo application) for each strand.

The influence of the shampoos to the volume of hair strands was determined applying an imaging system. Images of the hair strand were taken under 5 angles from 0° to 180° calculating the volume from the 5 derived projections. Relative volumes were calculated as ratio of volume after versus before shampoo application for each strand.

RESULTS AND DISCUSSION

DETERMINATION OF THE AMOUNTS OF SILICONE ADSORBED TO THE HAIR FROM SHAMPOO APPLICATION

Figure 1 shows the amounts of silicone found on hair strands after repeated application of a commercial 2-in-1 shampoo from the European market determined from ICP-OES analysis.

It can be seen that already after a single treatment with the shampoo a huge amount of dimethiconol was found adsorbed to the hair. There is no variation within the margin

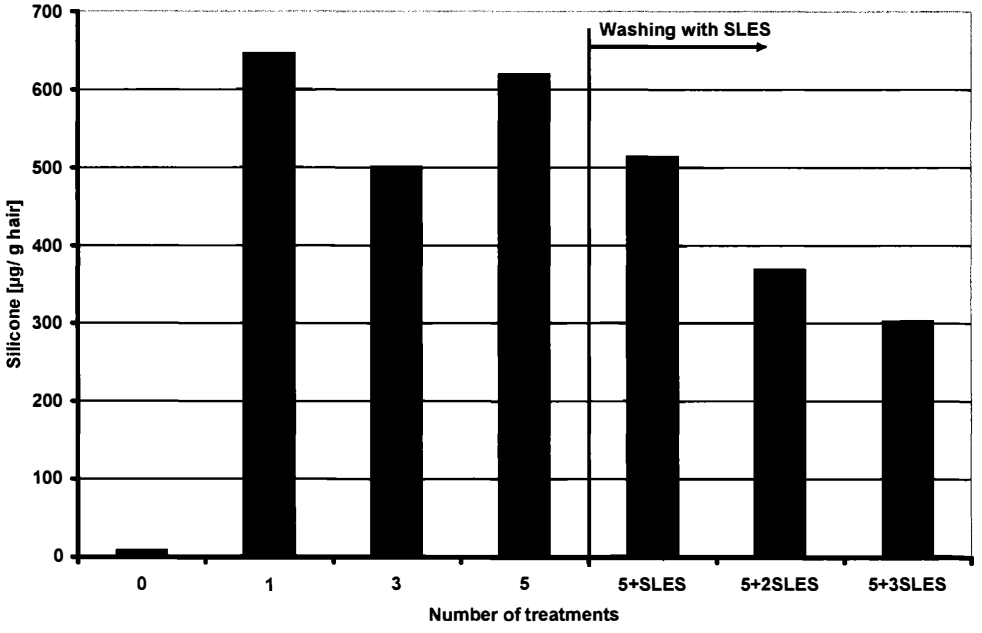

Figure 1. Amount of silicone deposited at hair strands repeatedly washed with a 2-in-1 shampoo and determined by ICP-OES.

of error of the method after 3 and 5 times treatment. By checking the removability with SLES it can be seen that even after 3 times washing with the surfactant about 50% of the silicone remains on the hair.

In Figure 2 the amounts of silicone detected on hair strands treated with 2 shampoos of the same brand and type, from the European and the Asian markets are given, respectively. These data were also derived by ICP-OES.

As the Asian shampoo contains more than 3.5 times more dimethicone than the European version, the different amounts of silicone found adsorbed to the hair can be easily understood. For both shampoos there seems to be a build-up effect after repeated treatment. In contrast to the example given in Figure 1, the silicone was removed to a higher extent.

Hair strands treated in the same way but analyzed with X-ray fluorescence spectroscopy gave the XRF signals depicted in Figure 3. Since there is a background signal resulting from (inorganic) silicon in the hair, and the effect of the hair matrix to the XRF signal is unknown, this method currently delivers relative data only. For the Asian shampoo, the results from ICP-OES analytics were confirmed. On the other hand, the signals resulting from the small amounts of dimethicone adsorbed on the hair from the European shampoo are in the range of the background signal for untreated hair and thus below the limit of detection.

DETERMINATION OF THE AMOUNTS OF HYDROGENATED DIDECENE ADSORBED ON THE HAIR FROM SHAMPOO APPLICATION

In contrast to silicones, for emollients without chemical elements allowing the application of specific detection methods, chromatographic methods have to be developed.

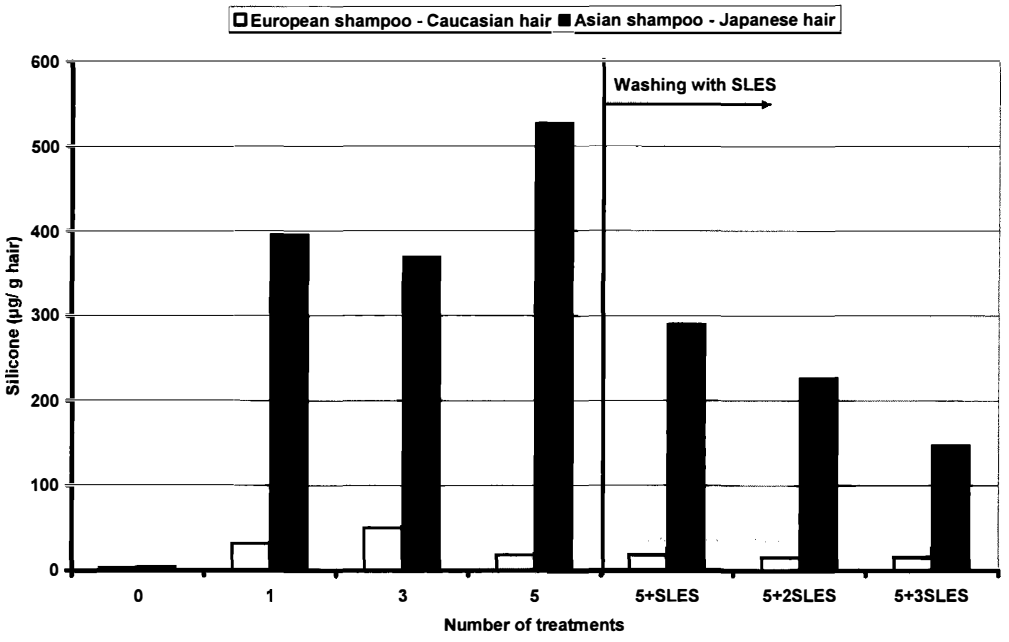

Figure 2. Amount of silicone deposited at hair strands repeatedly washed with an European shampoo and an Asian shampoo, determined by ICP-OES.

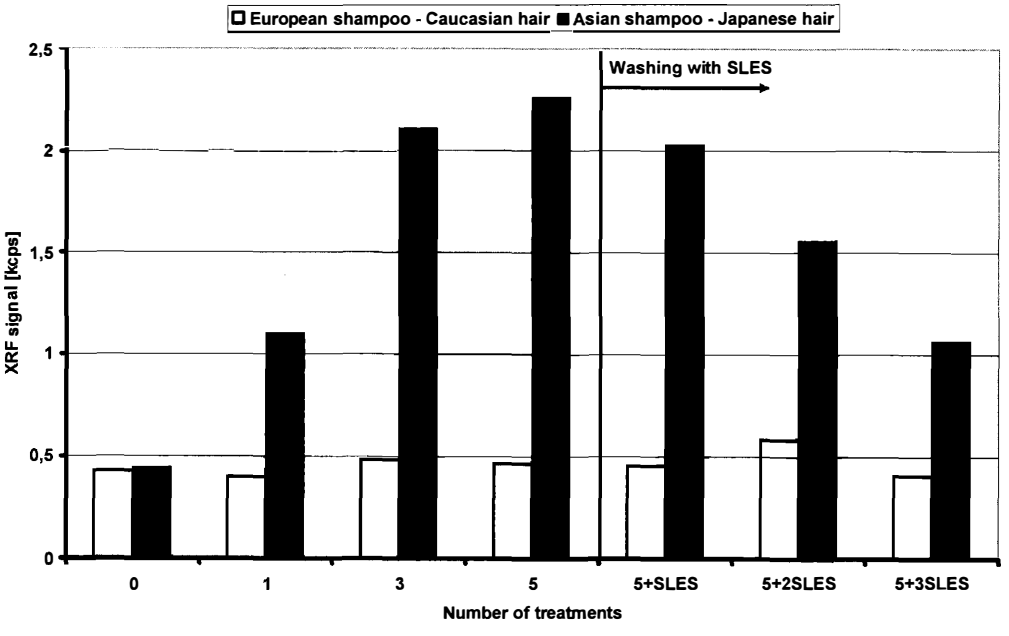

Figure 3. X-Ray fluorescence of hair strands treated as in Figure 2.

For the hydrogenated didecenes, GC-MS was selected. The quantification was done using hexadecane as internal standard.

In Figure 4 the amounts of hydrogenated didecene are displayed versus the number of shampoo applications. A clear build-up effect can be seen, but the level of the emollients

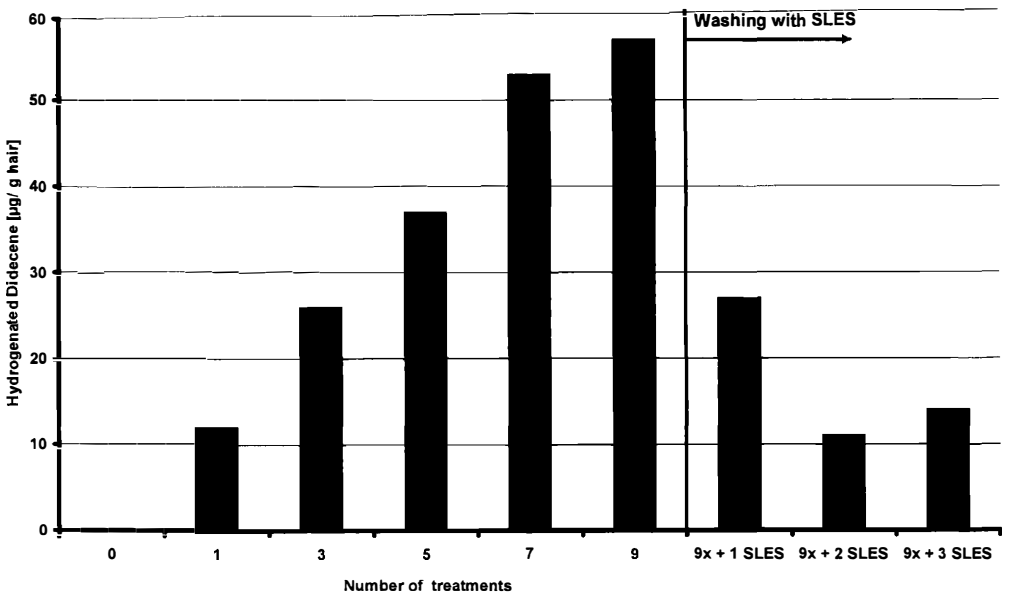

Figure 4. Amount of hydrogenated didecene deposited at Caucasian hair repeatedly washed.

adsorbed on the hair is about 10 times lower compared to the amounts of silicones found in the examples shown before. Also, in contrast to the silicones, the hydrocarbons can be removed easily by washing the hair with surfactant.

COMPARISON OF THE SUSTANTIVITY DATA WITH PROPERTIES OF TREATED HAIR

It is interesting for a formulator to know how much of a specific ingredient is adsorbed to the hair and if there are build-up effects, but these experiments cannot answer the question as to what are the effects to the treated hair. As an example how to correlate analytical and performance data, studies were done on wet combability and hair volume in addition. With the first method, conditioning effects on wet hair can be determined. Hair volume is especially interesting for all people with fine, straight Caucasian hair.

In Figure 5 the residual wet combing work is given for all shampoos mentioned before. It can be seen that the 2-in-1 shampoo exhibits the highest reduction of combing work even after 1 application. This finding correlates with the analytical results for this shampoo, compared to the level of silicones found for the other shampoos. The differences in dimethicone levels for the European and the Asian shampoo are in line with the differences in wet combing performance. The build-up effect found for the Asian shampoo is manifested as a further decrease of wet combing work. The same correlation between build-up and wet combing work can be seen for the shampoo with the hydrogenated didecene.

The effects of the 2-in-1 shampoo and the shampoo with the hydrocarbon on the volume of the treated hair strands are given in Figure 6 for 1, 3 and 5 times treatment. The volumes of the hair strands shampooed with the 2-in-1 product are only at about 60% of the initial volume. There is no significant change in the volume after repeated

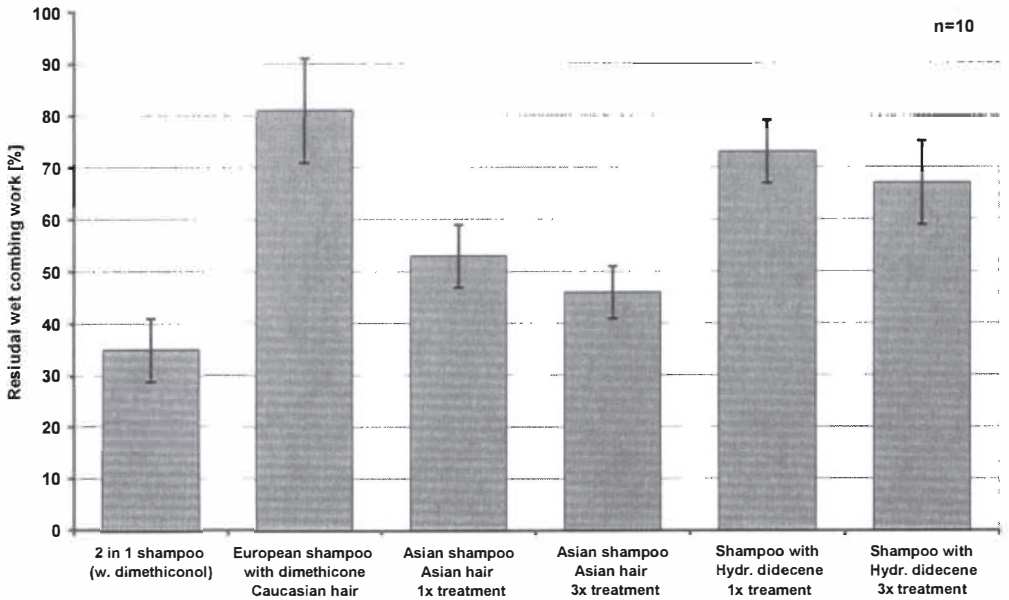

Figure 5. Residual wet combing work of different shampoos.

treatments. Again, these performance properties are in good accordance with the high amount of dimethiconol adsorbed to the hair, without changing the level at repeated shampooing. In contrast, hair strands washed with the shampoo containing the hydrogenated didecene retain their volume even after repeated application. This can be explained by the low levels of emollient found on the hair.

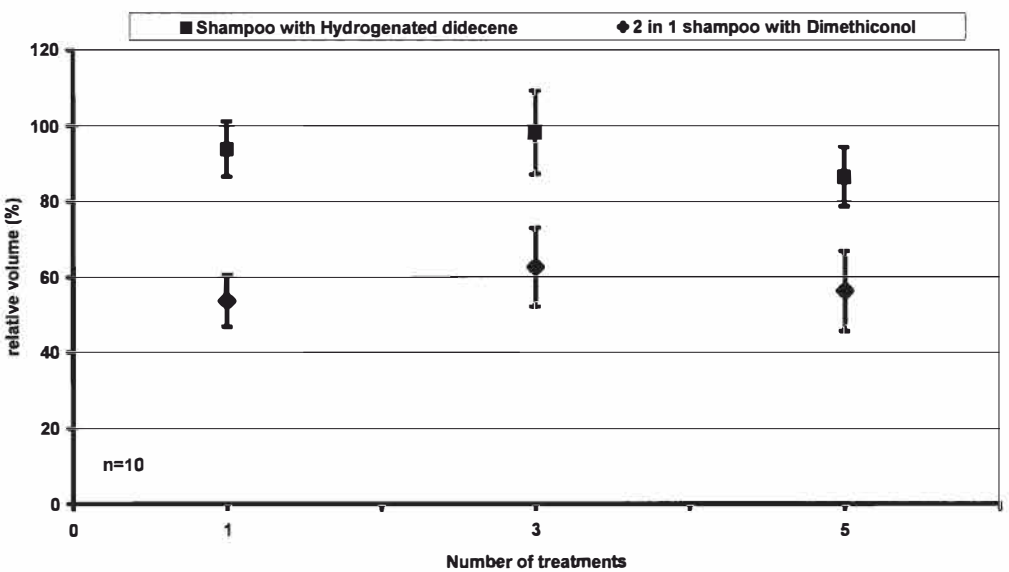

Figure 6. Relative volume of hair strands after repeated treatment with a 2-in-1 shampoo and with the shampoo containing hydrogenated didecene.

CONCLUSIONS

Both investigated methods for the determination of silicones adsorbed on human hair from shampoos can be usefully applied for substantivity studies. While the main advantage of the X-ray fluorescence method is the applicability to hair strands without extraction and the possibility to repeat treatments and measurements at the same hair strands, the benefit of ICP-OES of extracts is a smaller limit of detection and the fact that quantitative data can be obtained. In contrast, the faster XRF method delivers just semi-quantitative data which allow detecting build-up effects and removability of silicones.

The analytical method developed for the quantification of the hydrogenated didecenes allows the quantification of low hydrocarbons levels in extracts of treated hair strands. It was demonstrated that a comparison of analytical data with results from performance measurements can be used to understand the effects of emollients on hair properties like conditioning and hair volume. The shampoo with hydrogenated didecene shows a good conditioning performance while retaining the volume of the shampooed hair strands.

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