



B99 Shampoo Investigations in Relation to a Rape Investigation

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After attending this presentation, attendees will the participant will appreciate the possibilities of surfactant compositions for forensic investigations of toilet products such as shampoo.

This presentation will impact the forensic community and/or humanity by demonstrating surfactants which are used in many industrial products can be encountered as forensic evidence and needs to be characterized and compared to other evidence material. Presently surfactant component information is hardly used at all for forensic investigations. The results of this presentation demonstrate the possibilities in using this information. It is expected more forensic applications will follow. By making forensic practitioners aware of these possibilities it is expected they will access this source of information.

Introduction. Results are presented of shampoo investigations in relation to a suspected anal rape of a young boy by an older teenage boy. The victim stated that the suspect used shampoo as a lubricant during the rape. Victim's anal swabs, the victim's clothes and underwear, the suspect's underpants as well as all surfactant containing products from the suspect's bathroom were submitted by the police. In this investigation we used visual methods, LC-MS, GC-MS and MALDI MS techniques to detect and identify surfactants as well as other relevant chemical components.

The victim and suspect's samples were first investigated for the presence of potential shampoo components. Afterwards component compositions on the various items were compared. We focused at first on involatile surfactant components. Investigations were performed using a Crimescope system for visual characterization at a number of wavelength regions, GC-MS for component analysis, LC-MS and MALDI MS for surfactant analysis. Sodium lauryl ether sulphate is a surfactant that is widely used in shampoos. All shampoos in the submitted products contain this ingredient according to the product label. The chemical formula $C_nH_{2n+1}-(OC_2H_4)_xOSO_3Na$ where x denotes the number of ethylene oxy-segments and $n=12$ for the pure chemical form. This is a synthetic chemical component not produced naturally by plant or animal and not secreted by humans. Even one industrial single surfactant consists already of a large number of similar components differing, e.g., in the exact alkyl group (in the above example n) and the number of ethylene oxy segments (x in the example) in a poly ethylene oxy segment. This variation offers possibilities in a forensic investigation to determine the presence of these component mixtures and make comparisons. Apart from the product label information further confidential product information was obtained from a number of shampoo producers.

Visual investigation. The victim and suspect's clothes were investigated visually for potential shampoo residues. Samples of the products from the bathroom of the suspect were dried and investigated similarly. Both the tops of the anal swabs and the white cotton front inside of the suspect's underpants displayed fluorescent stains.

Using a Crimescope (irr. 515 nm, det. > 550 nm) a light yellow pattern was observed at the same position on the front inside of the suspect's underpants. On the victim's clothes no clear stains could be observed in daylight. For the victim's clothing stains were especially expected on the (rear inside of the) underpants. Further investigations of the victim's clothing were therefore directed on the underpants.

Only two shampoos from the relevant toilet products (including all shampoos) from the suspect's bathroom displayed similar fluorescence behavior as described above. Only one shampoo (named A below) displayed a light yellow color upon drying. Application of the two fluorescent shampoos on the green material of the victim's underpants after drying resulted in stains that were not visible in day light and did not fluoresce using the Crimescope.

LC-MS. Instrumental conditions were selected to detect and identify anionic surfactants such as lauryl ether sulphate. Using these conditions mostly groups of compounds with different alkyl terminal groups will be separated. Compounds with identical alkyl terminal group but with different numbers of ethylene oxy segments in the poly ethylene oxy segments can be discriminated by mass spectrometry. In a preliminary separate Flow Injection Analysis (FIA) MS experiment, bypassing the LC separation part, it was determined that the bathroom products not investigated in the above fluorescence experiments did not contain sodium lauryl ether sulphate.

Methanol extracts of different fluorescent parts of the white cotton inside on the front of the suspect's underpants as well as the cotton swabs with material from the victim's anus (anus swabs) and some selected parts of the victim's underpants were investigated using the LCMS method. In all these different samples lauryl ether sulphate was identified with the alkyl part varying in the range decyl to hexadecyl ($n=10, 12, 14, 16$) and the number of ethylene oxy units, dependant on the alkyl group, varying in the range $x=0$ to $x=12$. The results for the clothing samples and the victim's anus swabs corresponded well in lauryl ether sulphate composition. Methanol diluted samples of the two fluorescent shampoos were investigated using this LC-MS method. Results for shampoo A corresponded well with the results for both underpants and the anal swabs. The alkyl distribution for the other shampoo (named B below) was somewhat narrower.



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MALDI MS. This technique was applied to water extracts of the suspect's underpants and an anal swab from the victim. Also samples of the two shampoos A and B were investigated using this technique. Experiments were performed for us using facilities at Unilever Research. Best results were obtained detecting positive ions and using a Tetrakis matrix. Four different ion series were detected. Two ion series are interpreted as $C_{12}H_{25}-(OC_2H_4)_xOSO_3Na_2^+$ and $C_{12}H_{25}-(OC_2H_4)_xOSO_3NaK^+$ ion-series. These were identified in the water extracts of the suspect's underpants, the anal swab and both shampoos. A third, as yet unidentified ion series ($m/z = 413, 475, 519, 563, 607, 651, 695, 739$ and 783) was detected in all the above samples except shampoo B. The fourth non-specific ion series has not been interpreted.

GC-MS was applied to methanol extracts of suspect and victim's underpants and an anal swab of the victim. Samples of the two shampoos A and B were diluted in dichloromethane and investigated with a standard GC-MS method. Mainly non-specific background components

are detected in the clothes and anal swab samples. These are identified as compounds introduced during sample preparation and compounds already present in blank clothing and swab samples. Among this background extra compounds were detected in the methanol extracts of the suspect's and victim's underpants and the anal swab. These extra compounds are not observed in blank samples or the sample of shampoo B but are again observed in the sample of shampoo A. For now these compounds have not been identified.

Conclusions:

1. Lauryl ether sulphate components were detected on the suspect's and victim's underpants as well as the anal swabs. Lauryl ether sulphate is an anionic surfactant that is widely used for shampoos and shower/bath products. The human body does not secrete it.
2. The lauryl ether sulphate components were detected locally on the inside front of the suspect's underpants. The distribution of the lauryl ether sulphate components on the victim's underpants was less clear, partly as a consequence of different fluorescence product behavior on this underpant.
3. Shampoos A and B are the only products of the 13 products from the suspect's bathroom that correspond in some characteristics with the residues on both suspect's and victim's underpants and the anal swabs.
4. Results from visual, LC-MS, MALDI MS and GC-MS investigations on the samples of victim and suspect correspond better with shampoo A than with shampoo B.

In our opinion the residues on the suspect's underpants and the victim's anal swabs are from the same category of products, probably a shampoo, shower or bath product. Out of all the products in the suspect's bathroom shampoo A is the most likely candidate for this.

Shampoo, Surfactants, LC-MS