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Non-polar hydrocarbon analysis in powder detergent compositions

ABSTRACT
Since 1989 the BATTELLE–Geneva Research Centre has carried out a World Detergent Program aimed at supplying subscribers with analytical data on compositions of major brands of detergents on a multi-client basis. Due to the continual technical evolution of detergent compositions, the development of new analytical methods is a crucial element for this program. Recently, some European detergent producers have introduced very small percentages (0.01-0.5%) of non-polar hydrocarbons to powder detergent formulations in order to work as antifoaming agents.
This study aimed at developing an analytical method allowing the extraction of linear, non-polar hydrocarbons in detergents by using supercritical fluid extraction as well as their quantification and characterization using gas chromatography.

INTRODUCTION

Laundry detergent compositions used in closed drum washing machines require foam control to prevent oversudsing. Usually, antifoam granules containing silicone oil in admixture with an antifoam promoter (*i.e.* hydrophobic silica) sorbed into or onto a solid carrier material, are incorporated in detergent powder formulations. In foam control granules where the carrier material has a primary particle size of 100-300 μm with an intraparticle pore system of 10 μm, the silicone oil is entrapped within the granules and then released during the wash process[1]. However, some modern, highly efficient surfactant systems have such a high foaming tendency that larger amounts of silicone oil are required to give adequate foam control during a wash. Silicone oils with higher viscosities are generally used in order to increase the foam control efficiency, but in this case difficulties are encountered for their incorporation into porous granular carrier material. For this reason, some viscosity-modifying agents including hydrocarbons (*e.g.*, petroleum jelly) premixed with an antifoam promoter (*e.g.*, alkylphosphoric acid or salt) are introduced in admixture with the silicon oil[1, 2]. Advantageously, the hydrocarbons themselves have foam control properties.

MATERIAL AND METHODS

Antifoam granules. Dehydran 760 (Cognis), a combination of silicone and paraffin on carrier material, was found to be used as granular defoamer in detergent powder compositions[3]. The quantity of hydrocarbons was calculated from the difference of the total active matter and silicon oil fraction.
Quantification of active matter in Dehydran 760 was performed according to an internal method (BWDP 1.6) used for the quantification of alcohol soluble fraction in detergents [4] where ethanol was replaced by hexane (FLUKA). The silicon oil fraction was determined by a routine method (BWDP 3.1) used in the laboratories of Battelle Geneva for silicon oil determination[4].
In a first step, Dehydran 760 was used to evaluate the supercritical fluid extraction (SFE) variables[5].
The aim of this was to minimize or eliminate the risk of surfactant interferences present in real detergent samples. The optimised conditions achieved with Dehydran 760 were then applied to a certified reference detergent of known composition, containing 5% of Dehydran 760. The quality control standard detergent (QCS) was produced and certified by HELD AG (Switzerland) (Table 1).

Table 1: Ingredient composition of the reference detergent (QCS)

LAS	12.5 %
Alcohol ethoxylated (Coco 3 EO)	4.0 %
Alcohol ethoxylated (Coco 7 EO)	3.0 %
Sodium perborate tetrahydrate	14.0 %
TAED 4049 (Clariant)	6.0 %
Sodium carbonate	17.3 %
Sodium sulphate	1.2 %
Sodium disilicate	10.0 %
Sokalan CP 45 (90-94%) (BASF)	2.0 %
Dehydran 760 (Cognis)	5.0 %
Zeolite A	25.0 %
Total	100.0 %

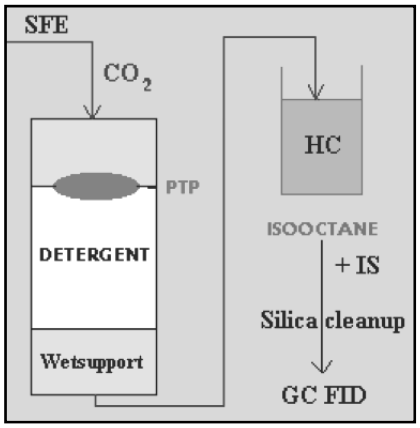

Figure 1: Schematic representation of the SFE-extraction

SFE extraction. The SFE-procedure used in this work had been developed through an internal method (SOP NO. 5-202-01), used by Battelle Geneva for the extraction of petroleum hydrocarbon compounds in soil and sediment samples. Dehydran 760 (0.3 g), QCS (2 g), or commercial detergent samples (4 g) were placed in 10 mL extraction cells containing SFE wet-support (ISCO). 100 μL p-terphenyl (PTP; SIGMA) at a concentration of $4x10^{-3}$ g mL^{-1} in dichloromethane (FLUKA) was added prior to the extraction. Pure CO_2 was chosen as the extraction fluid. Extracted analytes were collected in 15 mL of isooctane (FLUKA) (Figure 1).

Extraction parameters were optimised by :

(i) Varying the extraction pressure from 250 to 550 bars while keeping the cell temperature at 80°C, the flow rate at 1.5 mL min^{-1} and [co-solvent] = 0.

(ii) Varying the cell temperature from 60 to 80°C while keeping the pressure at 300 bars, the flow rate at 1.5 mL min^{-1} and [co-solvent] = 0.

(iii) Varying the flow rate from 1.5 to 3 mL min^{-1} while keeping the extraction pressure at 300 bars, cell temperature at 70°C and [co-solvent] = 0.

(iv) Varying the [toluene] used as a co-solvent from 0 to 6% while keeping the pressure at 200 bars, cell temperature at 70°C and the flow rate at 1.5 mL min^{-1}.

In all cases the restrictor temperature was maintained at 70°C and the extraction time was set to 30 min. Furthermore, in order to optimise the extraction time, the pressure, the temperature and the flow rate were fixed at 300 bars, 80°C and 1.5 mL min^{-1}, respectively, while replacing the trapping solvent every 5 minutes for the first 20 minutes and every 10 minutes for the last 40 minutes.

GC analysis. The quantification of linear non-polar hydrocarbons (HC) was performed by gas chromatography (GC). After adjusting the final volume to approximately 10 mL of isooctane, 100 μL of an internal standard solution of 5-α-androstane (SIGMA) at a concentration of $3.7x10^{-3}$ g mL^{-1} in dichloromethane was added. Then the solution was passed through a fritted glass chromatographic column (φ: 2cm) filled with 20 cm silica gel (type 60 silanyzed 70-230 mesh Merek) and rinsed with 30mL isooctane, in order to eliminate the surfactants. The collected fraction was evaporated to approximately 10 mL and analysed by GC with flame ionisation detector (280°C; hydrogen flow: 30.0 mL min^{-1}; air flow: 400 mL min^{-1}) and a capillary column, model J&W DB5-MS (15 m x 250 μm internal diameter, 1.0 μm film thickness). Injector (split-less mode) temperature was 290°C and the injection volume was 1μL.

The hydrocarbon calibration was performed using Dehydran 760 active matter as reference material at concentration range: 10 to 500 ppm. The HC total surface for each concentration was plotted as a function of HC concentrations. In order to determine the retention times of C_8-C_{42} hydrocarbons an isooctane solution containing C_8-C_{42} alkanes (40 ppm) was injected onto the GC.

The extraction recovery percentages during the optimisation phase were calculated on the basis of (i) the known HC quantity in Dehydran 760 - (ii) the recovered surrogate quantity.

RESULTS AND DISCUSSION

Optimisation of the extraction parameters

The active matter content in the antifoam granules (Dehydran 760) was determined to be (9.5 ± 1.1)%. Furthermore, concentrations of silicon oil and hydrocarbons in the active matter of Dehydran 760 were determined to be 16.5% and 83.3% respectively. Therefore the quantity of hydrocarbons used to calculate the recoveries of SFE-extractions in Dehydran 760 and QCS were 7.9% and 0.4%, respectively.

As shown in Figure 2, the majority of hydrocarbons were extracted in the first 10 minutes and 90% of them were extracted after 30 minutes.

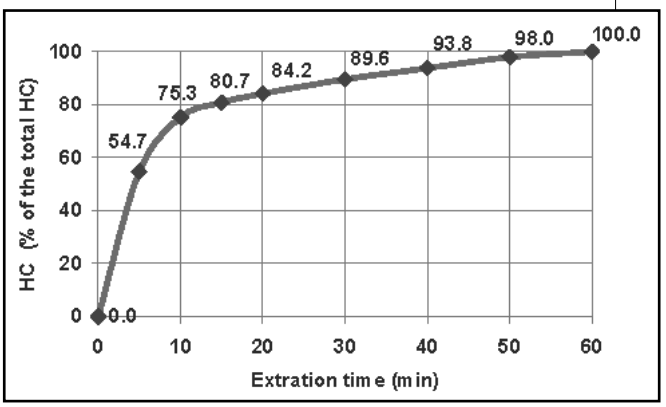

Figure 2: Extraction time as a function of HC extracted

An extraction time of 30 minutes was chosen in order to get a rapid analysis. The calculated recoveries based upon both methods were similar up to 400 bars; above this value an increase up to 105% was observed for recoveries based on the HC quantity (Figure 3a). An increase of the flow rate from 1.5 to 3 mL min^{-1} elevated slightly the quantity of extracted hydrocarbons (Figure 3b).

The recoveries calculated based upon PTP recoveries decrease to 80% at high flow rate due to the evaporation of surrogate. Therefore, it was established that a flow rate of 1.5 mL min^{-1} was more convenient since both types of recovery calculations were similar.

When the extraction temperature was varied, the HC recoveries calculated using the HC value in Dehydran 760 or the surrogate PTP were between 95 and 100% (data not shown) with a slight maximum at 70°C.

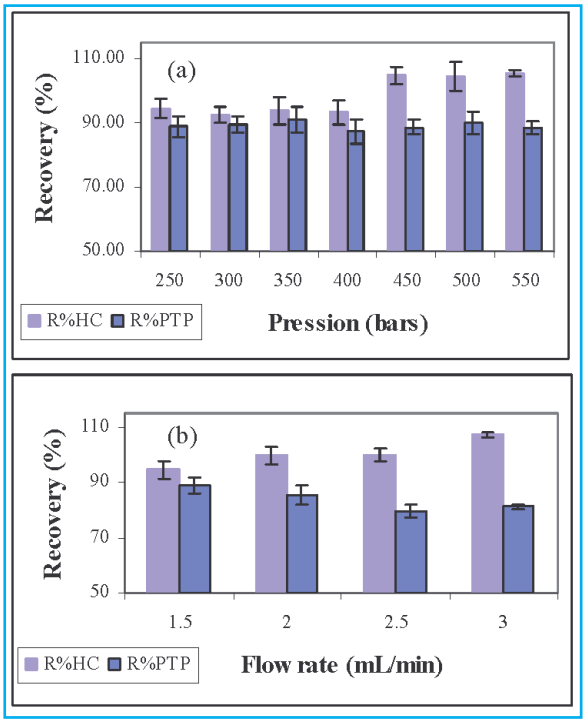

Figure 3: HC and PTP recoveries as a function of the extraction parameters: a) pressure (CO_2 flow rate = 1.5 mL min^{-1}, T = 80°C); (b) CO_2 flow rate (p = 300 bars, T = 70°C). Error bars represent standard deviations (n = 3)

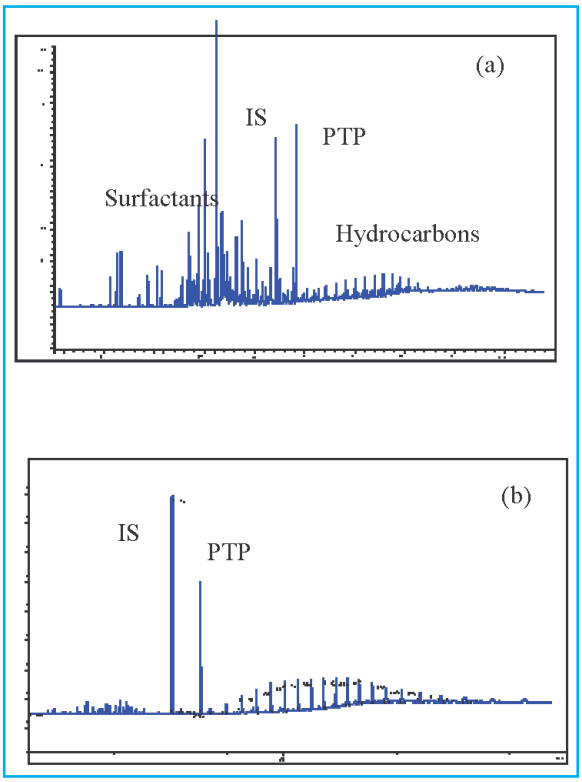

Figure 4: GC-Chromatogram of QCS before (a) and after (b) cleanup process

No special improvement in extraction was noticed when the co-solvent was used (data not shown).
As a result, the SFE parameters chosen for the extraction of non-polar hydrocarbons in real detergent samples were determined to be: see table 2.

Table 2: SFE optimized extraction parameters

Operational conditions	
Pressure	300 bars
Temperature	70 °C
Flow	1.5 mL min^{-1}
Extraction time	30 min

Quantification of HC in commercial detergent samples
Commercial powder detergents can cause problems during extraction because they contain different surfactants, which can be partially co-extracted from the sample with the hydrocarbons. Therefore matrix interferences were observed during the GC-analysis (Figure 4a). For this reason, a clean-up process was developed to eliminate the matrix interferences prior to GC-FID analysis (Figure 4b).
The recoveries for the surrogate were about 82% and the recoveries of hydrocarbons were 75%. The lower values of the recoveries calculated on the basis of the known quantity of HC in QCS when compared with those calculated on the basis of the surrogate could be explained by the compact and complex detergent matrix. A batch of 9 commercial detergents was analysed and the HC recoveries were found to be between 65 and 80% (Table 3). The low recoveries in some cases may be due to the type of carrier used in the antifoam granules. Moreover, the builder system can also influence the HC recoveries.

Characterization of hydrocarbons
For the determination of the hydrocarbon chain length distribution, the surfaces representing each hydrocarbon were taken into consideration and each one was calculated as a percent of total hydrocarbons (Figure 5).
Among the analysed commercial samples only sample Nr. 5 had similar HC distribution (Figure 5) to HC in QCS. Moreover, the ratio HC/silicon oil in this sample was equal to 4, the same as in QCS. Conversely, in the other detergent samples the HC/silicon oil ratio was different from 4 (data not shown). It appears that the foam control agent contained in these detergent samples was different from Dehydran 760.

Table 3: Hydrocarbon content in commercial detergents after correction using the PTP recovery ($R_{\%PTP}$ (%))

	Nr.1	Nr.2	Nr.3	Nr.4	Nr.5	Nr.6	Nr.7	Nr.8	Nr.9	QCS
HC (wt. %)	0.05	0.09	0.12	0.03	0.15	0.09	0.08	0.10	0.13	0.04
$R_{\%PTP}$ (%)	80	77	69	65	77	68	76	74	79	82

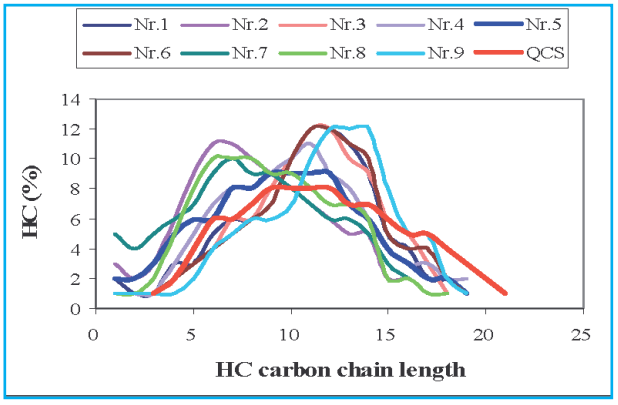

Figure 5: Hydrocarbon chain length distribution in 9 commercial detergent samples and QCS

CONCLUSION

This method allows the quantification and the characterization of non-polar hydrocarbons in powder detergent samples, even if they are present in very low percentages. In some of the studied commercial powders, the hydrocarbon chain length distributions were different from the model antifoam system used, demonstrating that antifoam material other than Dehydran 760 are incorporated in these products.

Since the calculations of the hydrocarbon fraction in detergent samples were performed using the Dehydran 760 as reference, a little discrepancy may be expected in the results.

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