Application Note: 10087

GC Analysis of Surfactants through On-column Injector with H.O.T. Device

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Key Words

- Cold On-column injector
- Shortened analysis time
- Surfactants
- Total absence of discrimination
- Triglycerides, Sterol Esters, Bees Wax

Introduction

The aliphatic ethoxylated alcohols are a group of compounds used as surfactants in many application fields, usually preferred to the polyethoxylated alkylphenols due to the lower toxicity of their degradation products. Ethoxylated alcohols are produced from aliphatic alcohols of petrochemical and oleochemical origin reacting with ethylene oxide. Industrial processes used to prepare detergents require knowledge of free alcohols content, mole average degree of ethoxylation and presence of alcohols with a higher ethoxylation number. These parameters are important to ensure the quality of the final product.

Generally, the GC analysis of such heavy compounds requires oven temperatures up to 400 °C, with non-polar capillary columns providing separation of the components according to their different molecular weights. Due to the high molecular weight nature of these components, the ideal method will necessarily call for the use of a totally non-discriminating inlet [1].

The present note teaches how the Thermo Scientific TRACE GC Ultra™ equipped with the true Cold On-column injector and H.O.T. device (High Oven Temperature) permits to achieve quicker and discrimination-free characterization of these surfactants. Besides, shorter residence times will minimize the risk of degradation of components affected by column activity. This feature positions the H.O.T. OC injector as the most suitable injection system also for the analysis of other classes of heavy components, such as triglycerides, sterol esters and waxes.

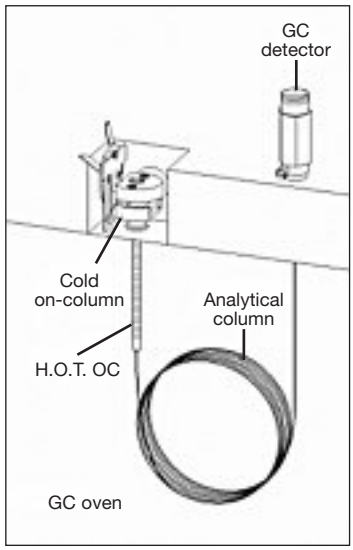

Figure 1. High Oven Temperature Cold On-column injector.

H.O.T. On-column Injector

The application is performed using a TRACE GC Ultra equipped with the H.O.T. Cold On-column injector and a FID detector kept at high temperature (400 °C).

The High Oven Temperature device, shown in Figures 1 and 2, is basically a metal cooling sheath placed around the upper 15 cm of the column. It replaces the classical secondary cooling jacket and is used to maintain that portion of the capillary column at a low temperature, while the oven temperature can be far higher (Figure 3). This allows for the injection of the sample at a high oven temperature, preventing any sample back-ejection and loss under these critical conditions.

In case of analysis of mixtures containing compounds with relatively low volatility and a low boiling solvent, this injection system offers all the advantages of the On-column injection plus a dramatic reduction of the analysis time. In fact, the oven can operate almost isothermally, or with relatively high initial temperatures, thanks to the capability of the H.O.T. device to keep a significantly lower temperature in the injection zone. As a further consequence, the residence time is strongly reduced as well, thus preserving compounds that might undergo partial degradation from column activity.

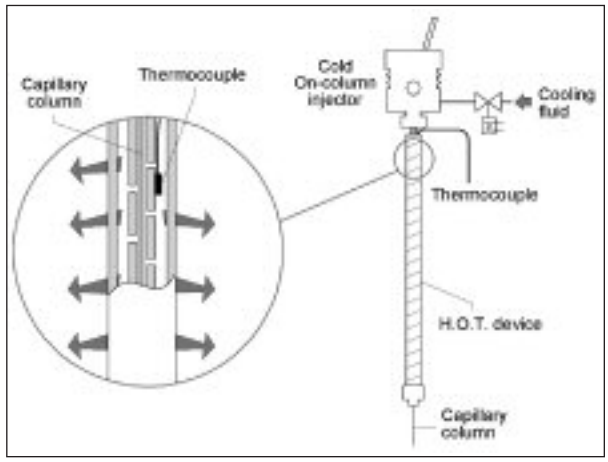

Figure 2. Detailed schematic drawing of the H.O.T. device.

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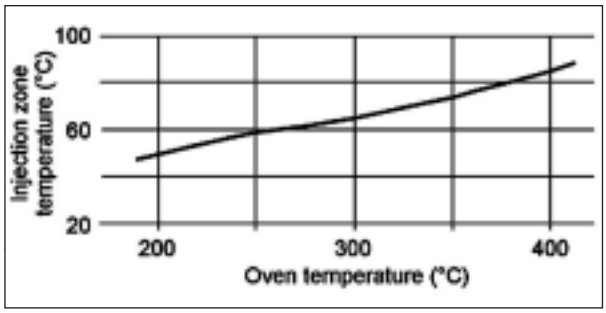
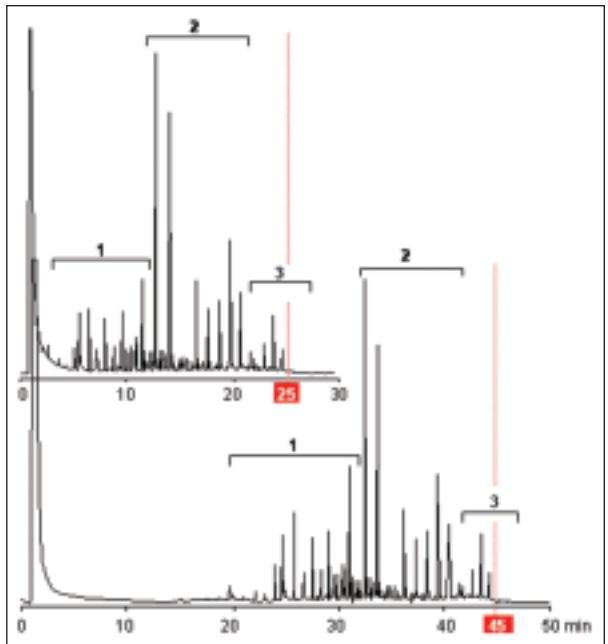


The system uses compressed air coolant for the extended cooling device (H.O.T.); the injection is performed through a semiautomatic actuator or using an electrically driven actuator automated in synchronization with the Thermo Scientific TriPlus™ Autosampler (Figure 4).

Figure 4. On-column injector with electrically driven actuator, and TriPlus AS.

In Figure 5, a comparison between performances of the On-column injector with and without the H.O.T. device is reported: a bees wax sample diluted in methylene chloride has been injected at the temperature of 43 °C (no H.O.T.), and at 200 °C through the H.O.T. device. The analysis time is reduced to about half (25 minutes instead of 45).

Combining the advantage of this injection system and the ability of the TRACE GC Ultra oven to be heated and cooled very fast, high temperature capillary GC can be applied with high efficiency and speed of analysis.



1 Hydrocarbons and fatty alcohols
2 Fatty acids and fatty alcohols esters
3 Triglycerides

Figure 5. Bees wax analysis through On-column injector with and without H.O.T. device.

Ethoxylated Alcohols

The general formula is the following:

$R—[-O-CH_2-CH_2-]_m-OH$ m=0-22
R= C_nH_{2n+1}, C_nH_{2n-1}, C_nH_{2n-3}
n= 8…18

The compounds originated can be constituted by both linear and branched aliphatic chains with a consequent difficult separation of the various isomers that call for columns featuring high efficiency and high temperature stability.

A linear aliphatic chain sample, and a linear plus branched chain sample are analyzed with the OC injector (Figures 6 and 7). For both the analyses a SE54 column, 20m long, 0.32 mm i.d., 0.15 µm film thickness is used. The FID detector is kept at 400 °C, and the helium (carrier) flow is 2mL/min, in constant flow mode. For the first sample, the H.O.T. device is used with an oven ramp from 180 °C (2 min) up to 390 °C (11 min) at 20 °C/min, to get an analysis time of 25 minutes. The second sample, containing more volatile components and requiring a higher system resolution, is analyzed with the OC injector without H.O.T. device with an oven ramp from 100 °C (2 min) up to 390 °C (11 min) at 6 °C/min: the analysis time is over 60 minutes.

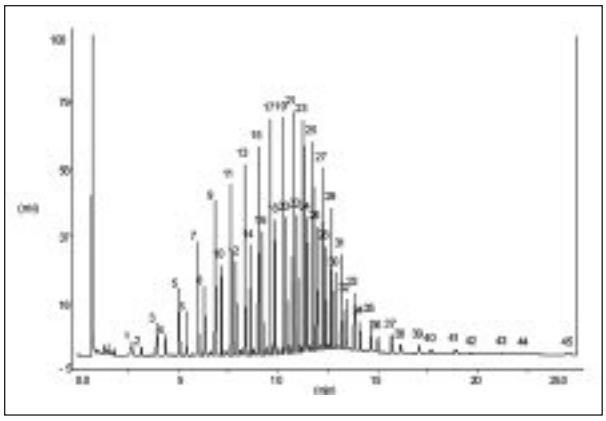


Figure 6. Polyethoxylated alcohols C14-15 Lin 9EO derivatized with BSTFA.

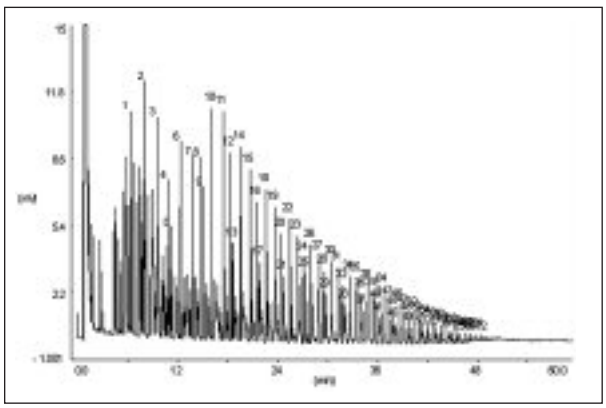


Figure 7. Polyethoxylated alcohols C12-13-14-15 Lin + Iso 3EO derivatized with BSTFA

The system, providing the separation of compounds according to the alkyl chain length and to the number of ethylene oxide units, is proved to be the analytical technique capable of delivering the highest degree of separation throughout a wide range of molecular weight distribution in the shortest time.

The analysis can be performed with or without derivatization with sylilating agents (e.g. BSTFA). When sylilation is applied, a better resolution is obtained and the range of compounds that can be analyzed is hence wider.

A comparison with the PTV injector has also been performed. The discrimination effect, becoming important at 16 moles of ethoxylation, together with the more critical set of parameters to be controlled (e.g. injector temperature, splitless time, liner design and carrier gas flow) makes the PTV injector unsuitable for this application. H.O.T. OC is still preferred whenever the sample contains non-volatile components.

Conclusions

The On-column has demonstrated to be the most suitable injection system for the characterization of ethoxylated alcohols used as surfactants in many application fields. The H.O.T. device further enhances the high performance of the TRACE GC Ultra's On-column injector, already recognized as the reference for the recoveries of high boiling components. It dramatically shortens the analysis time by starting the ramp at a higher initial temperature, hence avoiding additional oven cooling for the injection.

Furthermore, the residence time is strongly reduced, so minimizing the breakdown of components normally affected by column activity.

Due to all of these advantages, this injector is also suitable for the analysis of other heavy molecules like triglycerides, sterol esters and bees wax, generally considered as highly demanding compounds for a conventional GC injection system.

References

[1] The Influence of the Syringe Needle on the Precision and Accuracy of Vaporizing GC Injections, K. Grob, H.P. Neukom, The Journal of High Resolution Chromatography, January 1979.

Acknowledgement

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