

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

Fausto Munari, Andrea Cadoppi - Thermo Electron Corporation, Milan, Italy

## 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].

This application note discusses how the TRACE™ GC Ultra equipped with the true Cold On-column injector and H.O.T. device (High Oven Temperature) enables quicker and discrimination-free characterization of these surfactants. 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 for the analysis of other classes of heavy components, such as triglycerides, sterol esters and waxes [2].

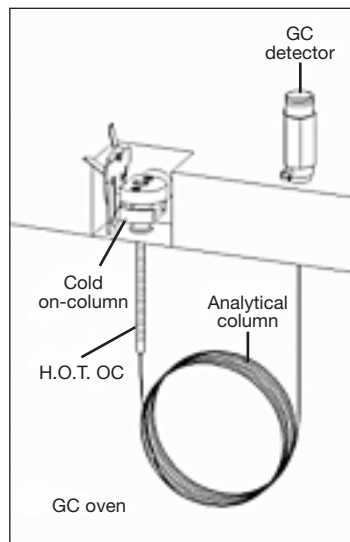


Figure 1. High Oven Temperature Cold On-column injector.

## 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 selectable 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.

For the analysis of mixtures containing compounds with relatively low volatility in 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.

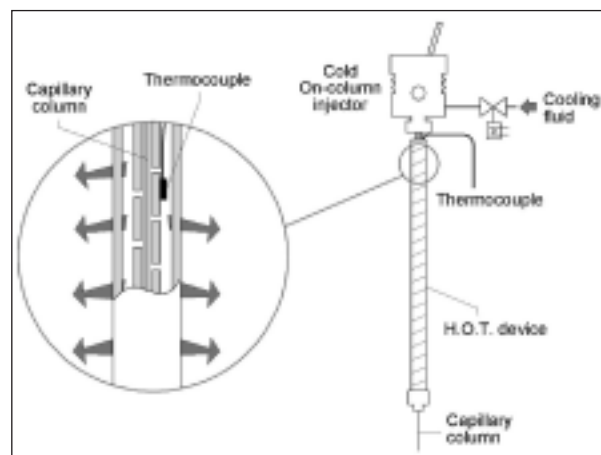


Figure 2. Detailed schematic drawing of the H.O.T. device.

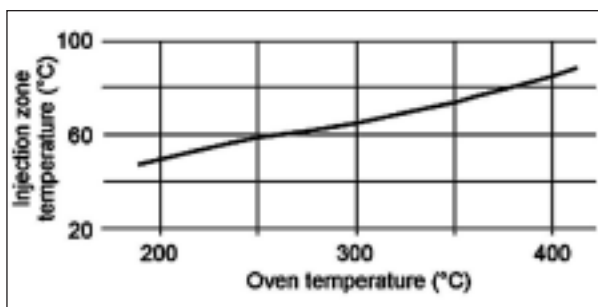


Figure 3. Allowable H.O.T. On-column injection temperatures versus oven temperatures using compressed air (500-600 kPa) as cooling fluid.

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 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.

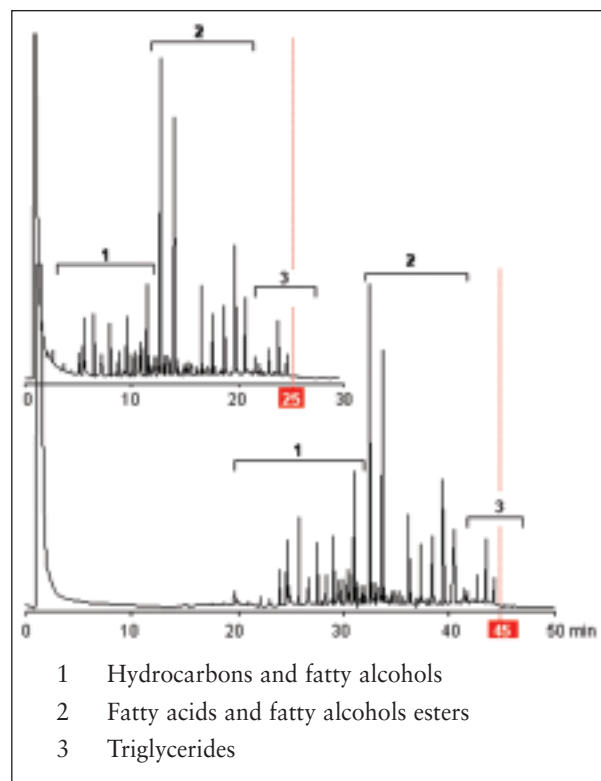
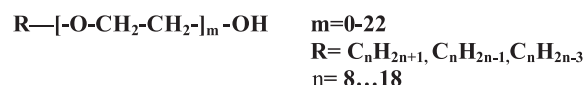


Figure 5. Bees wax analysis through On-column injector with and without H.O.T. device.

### Ethoxylated Alcohols

The general formula is the following:



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, 20 m 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 2 mL/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.

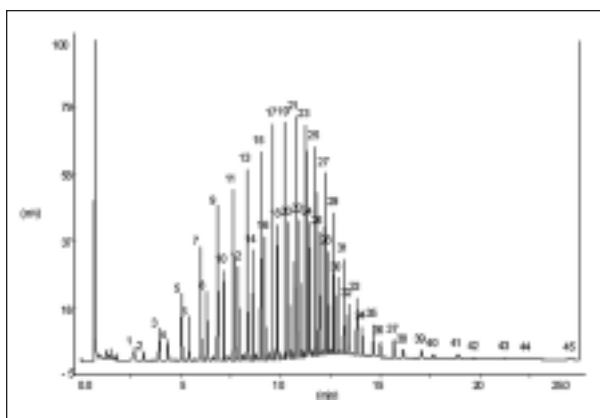


Figure 6. Polyethoxylated alcohols C14-15 Lin 9EO derivatized with BSTFA.

1. C 14	13. C 14-6EO	24. C 15-11EO	35. C 14-17EO
2. C 15	14. C 15-6EO	25. C 14-12EO	36. C 15-17EO
3. C 14-1EO	15. C 14-7EO	26. C 15-12EO	37. C 14-18EO
4. C 15-1EO	16. C 15-7EO	27. C 14-13EO	38. C 15-18EO
5. C 14-2EO	17. C 14-8EO	28. C 15-13EO	39. C 14-19EO
6. C 15-2EO	18. C 15-8EO	29. C 14-14EO	40. C 15-19EO
7. C 14-3EO	19. C 14-9EO	30. C 15-14EO	41. C 14-20EO
8. C 15-3EO	20. C 15-9EO	31. C 14-15EO	42. C 15-20EO
9. C 14-4EO	21. C 14-10EO	32. C 15-15EO	43. C 14-21EO
10. C 15-4EO	22. C 15-10EO	33. C 14-16EO	44. C 15-21EO
11. C 14-5EO	23. C 14-11EO	34. C 15-16EO	45. C 14-22EO
12. C 15-5EO			

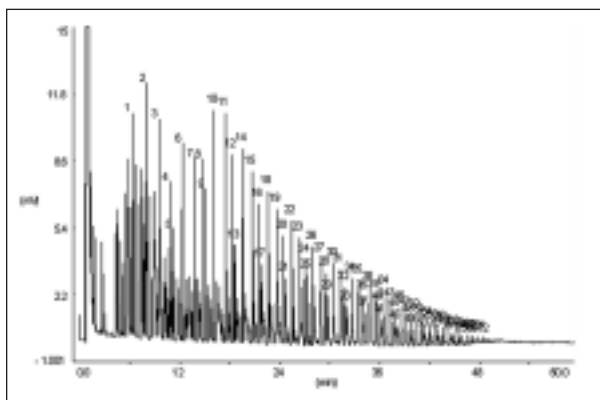


Figure 7. Polyethoxylated alcohols C12-13-14-15 Lin + Iso 3EO derivatized with BSTFA

1. C 12 Lin	19. C 14 Lin 4EO	37. C 15 Lin 8EO	55. C 14 Lin 13EO
2. C 13 Lin	20. C 12 Lin 5EO	38. C 13 Lin 9EO	56. C 12 Lin 14EO
3. C 14 Lin	21. C 15 Lin 4EO	39. C 14 Lin 9EO	57. C 15 Lin 13EO
4. C 12 Lin 1EO	22. C 13 Lin 5EO	40. C 12 Lin 10EO	58. C 13 Lin 14EO
5. C 15 Lin	23. C 14 Lin 5EO	41. C 15 Lin 9EO	59. C 14 Lin 14EO
6. C 13 Lin 1EO	24. C 12 Lin 6EO	42. C 13 Lin 10EO	60. C 12 Lin 15EO
7. C 14 Lin 1EO	25. C 15 Lin 5EO	43. C 14 Lin 10EO	61. C 15 Lin 14EO
8. C 12 Lin 2EO	26. C 13 Lin 6EO	44. C 12 Lin 11EO	62. C 13 Lin 15EO
9. C 15 Lin 1EO	27. C 14 Lin 6EO	45. C 15 Lin 10EO	63. C 14 Lin 15EO
10. C 13 Lin 2EO	28. C 12 Lin 7EO	46. C 13 Lin 11EO	64. C 12 Lin 16EO
11. C 14 Lin 2EO	29. C 15 Lin 6EO	47. C 14 Lin 11EO	65. C 15 Lin 15EO
12. C 12 Lin 3EO	30. C 13 Lin 7EO	48. C 12 Lin 12EO	66. C 13 Lin 16EO
13. C 15 Lin 2EO	31. C 14 Lin 7EO	49. C 15 Lin 11EO	67. C 14 Lin 16EO
14. C 13 Lin 3EO	32. C 12 Lin 8EO	50. C 13 Lin 12EO	68. C 12 Lin 17EO
15. C 14 Lin 3EO	33. C 15 Lin 7EO	51. C 14 Lin 12EO	69. C 15 Lin 16EO
16. C 12 Lin 4EO	34. C 13 Lin 8EO	52. C 12 Lin 13EO	70. C 13 Lin 17EO
17. C 15 Lin 3EO	35. C 14 Lin 8EO	53. C 15 Lin 12EO	71. C 14 Lin 17EO
18. C 13 Lin 4EO	36. C 12 Lin 9EO	54. C 13 Lin 13EO	72. C 15 Lin 17EO

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 silylating agents (e.g. BSTFA). When silylation 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, 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.
- [2] AN630: GC Analyses of Fats and Oils, Waxes and Surfactants: A Demanding Task for the Injection System. Thermo Electron Corporation.

*In addition to these offices, Thermo Electron Corporation maintains a network of representative organizations throughout the world.*

**Australia**  
+61 2 8844 9500

**Austria**  
+43 1 333 50340

**Belgium**  
+32 2 482 30 30

**Canada**  
+1 800 532 4752

**China**  
+86 10 5850 3588

**France**  
+33 1 60 92 48 00

**Germany**  
+49 6103 4080

**India**  
+91 22 2778 1101

**Italy**  
+39 02 950 591

**Japan**  
+81 45 453 9100

**Netherlands**  
+31 76 587 98 88

**Nordic**  
+46 8 556 468 00

**South Africa**  
+27 11 570 1840

**Spain**  
+34 91 657 4930

**Switzerland**  
+41 61 48784 00

**UK**  
+44 1442 233555

**USA**  
+1 800 532 4752

**[www.thermo.com](http://www.thermo.com)**

**ISO 9001**  
DNV-CERT-00203-94-AQ

*Thermo Electron S.p.A. Milan, Italy  
is ISO Certified.*

*©2005 Thermo Electron Corporation. All rights reserved. All trademarks are the property of Thermo Electron Corporation and its subsidiaries.*

*Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.*

AN10087\_E 03/05C

**Thermo**  
ELECTRON CORPORATION