

# APPLICATION NOTE

## Cosmetics – STA-GC-MS

### Heat Protection Sprays for Hair and their Gas Emissions at Maximum Application Temperature

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#### Introduction

Heat protection sprays are widely used to safeguard hair from the damaging effects of high temperatures generated by styling tools such as flat irons and curling irons, which can reach up to 220°C or 230°C. While these sprays create a protective barrier to reduce heat-induced degradation of keratin and moisture loss, studies suggest that under such extreme heat, the evaporation or thermal degradation of certain ingredients in these sprays may result in the release of potentially harmful gases like VOCs (volatile organic compounds). Certain polymer-based and silicone-containing sprays may undergo structural breakdown, emitting small amounts of thermal decomposition products that may pose health risks to both individual users and hairdressers.

Irrespective of the styling result, a number of different commercial products were tested for their gas emissions at maximum application temperatures of 220°C. The temperature-dependent mass loss was determined with an instrument of the STA *Jupiter*® series. The released gases were analyzed by a GC-MS system coupled to the STA.

In this study, two silicon-containing and two polymer-based sprays were used as examples.



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### Sample Preparation and Measurement Conditions

The sprays were shaken by hand and the emulsions were pipetted into the crucible. The evolved compounds were

collected in the GC cryo trap at -50°C and separated and identified after the TGA run. The TGA measurement parameters are detailed in table 1 and the GC-MS parameters in table 2.

**Table 1** TGA measurement parameters

Sample	1 (polymer-based)	2 (polymer-based)	3 (silicon-containing)	4 (silicon-containing)
Sample mass	22.9 mg	27.0 mg	34.5 mg	19.7 mg
Crucible	Al <sub>2</sub> O <sub>3</sub> crucible (200 µl), open			
Sample carrier	TGA pin, type S + slip-on plate			
Furnace	SiC			
Temperature program	RT-220°C, 30 min isotherm			
Heating rate	10 K/min			
Gas atmosphere	Nitrogen			
Gas flow (total)	70 ml/min			

**Table 2** GC-MS Parameter

Cryo Trap Mode	
Column	Agilent HP-5ms
Column length	30 m
Column diameter	0.25 µm
Cryo trap temperature	-50°C, 50 min
Column temperature	45°C, 52 min isotherm, 45°C - 300°C, 10 K/min
Gas	He
Gas flow (split)	20 ml/min (10:1)
Valve	Every 30 seconds

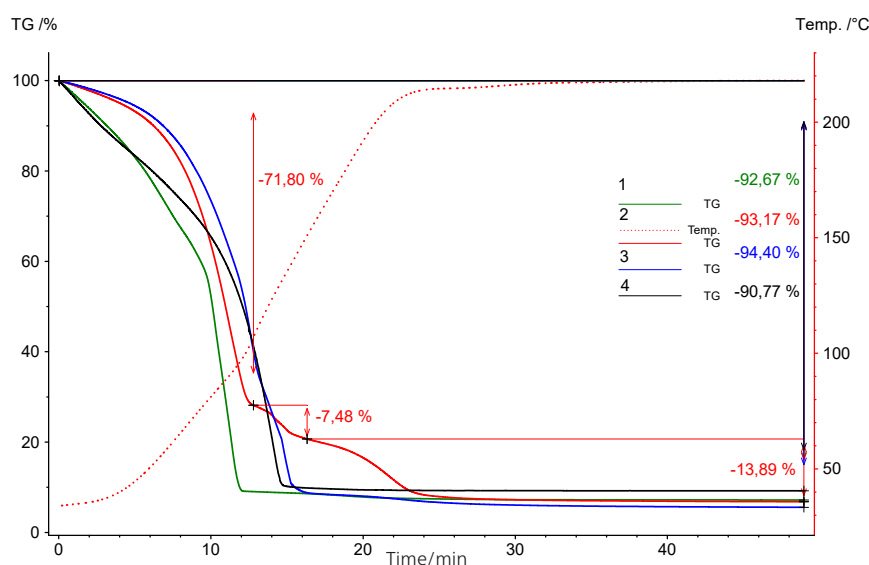
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### Results and Discussion

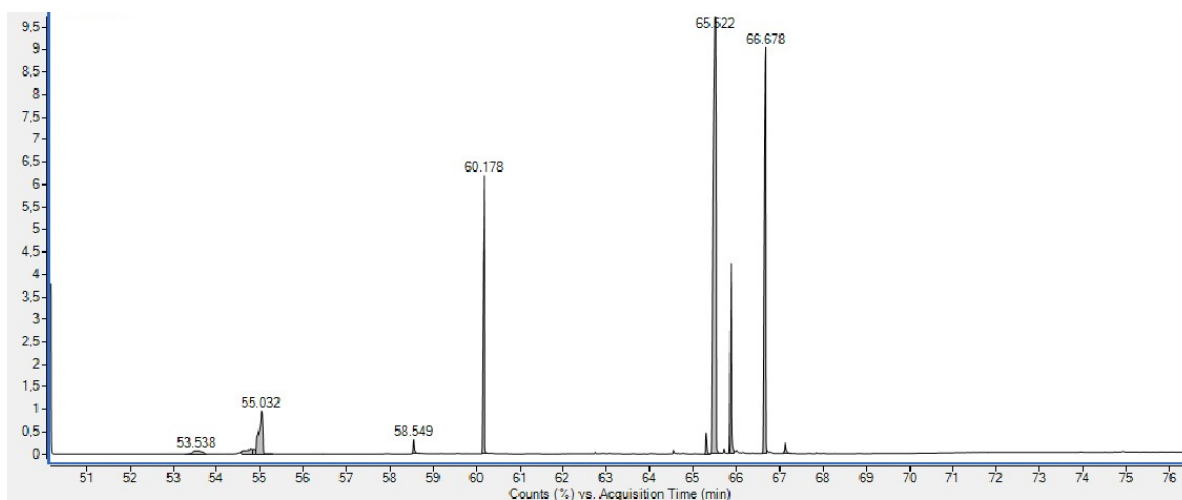
Each of the four samples shows a very different thermogram (figure 1). Samples 1 and 4 show an immediate mass loss already starting at room temperature, suggesting the release of highly volatile solvents such as alcohols in addition to the evaporation of the water base. For samples 1, 3 and 4, the mass loss was complete at approximately 140°C. Only sample 2 showed three separate mass-loss steps up to the isotherm temperature of 220°C. It can be assumed that a larger quantity of high-boiling substances was used in this case. In total, all four

samples released more than 90% of their initial masses during heat treatment.

The evaluation of the obtained GC-MS data is illustrated by samples 2 and 4, which represent a polymer-based and a silicone-containing heat protection spray, respectively. Figure 2 displays the resulting total ion current (TIC) of sample 2 after heating the cryo trap at the end of the TGA run. Separation of multiple peaks was achieved, and identification of the resulting compounds was carried out by comparison with the NIST MS library.



1 Time-dependent mass change (TGA) and temperature profile (red, dotted) of four different commercial heat protection hair sprays



2 Total ion current of sample 2 after heating the cryo trap

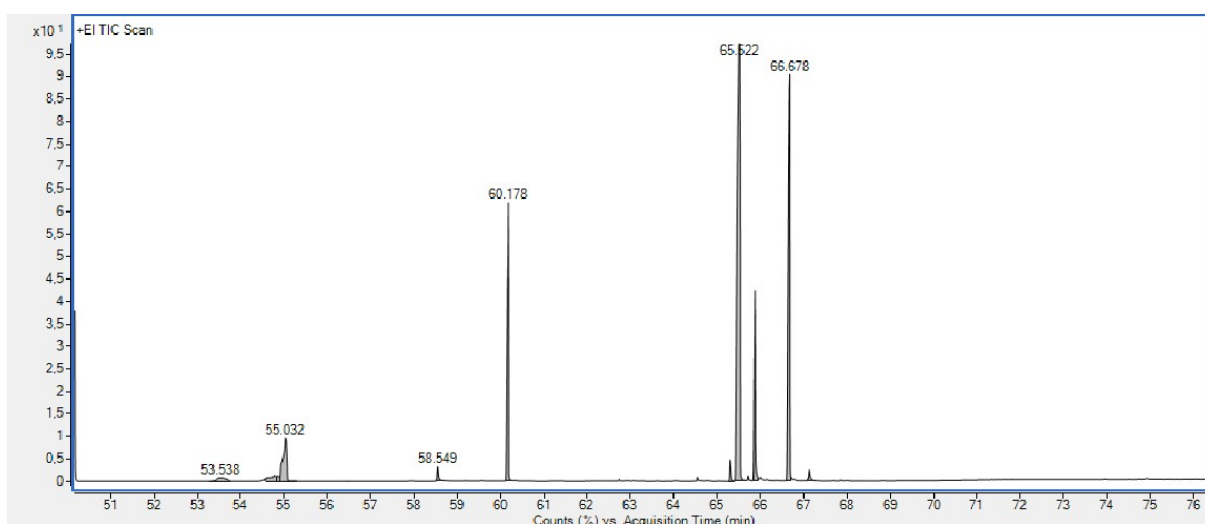
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The compounds with the highest hit quality are shown in table 3. As specified on the ingredients list, no silicone compound was identified. Mainly some carboxylic ester compounds were released up to 220°C.

In comparison, sample 4 released completely different compounds within the same temperature treatment. Figure 3 depicts the resulting total ion current.

**Table 3** Library search report for sample 2

RT	Score	Name
55.03	85.72	Water
58.55	97.07	Pantolactone
60.18	97.87	Dodecane
65.30	95.57	Isopropyl myristate
65.52	90.17	Isoamyl laurate
65.86	90.40	Dimethyl palmitamine
66.01	95.00	Hexadecanoic acid, methyl ester
66.68	93.48	Isopropyl palmitate
67.13	88.95	9-Octadecenoic acid (Z)-, methyl ester



**3** Total ion current of sample 4 after heating the cryo trap

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**Table 4** Library search report for sample 4

RT	Score	Name
54.37	95.03	Disiloxane, hexamethyl-
55.80	95.80	Cyclotrisiloxane, hexamethyl-
58.14	96.25	Heptane, 2,2,4,6,6-pentamethyl-
58.51	92.45	2,2,4,4-Tetramethyloctane
58.65	91.98	Decane, 2,5,9-trimethyl-
58.79	94.70	2- Propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester
58.82	87.45	Heptane, 5-ethyl-2,2,3-trimethyl-
62.06	94.12	Heptasiloxane, hexadecamethyl-
63.42	87.80	Heptasiloxane, hexadecamethyl-
64.64	79.22	Heptasiloxane, hexadecamethyl-
65.75	75.79	Heptasiloxane, hexadecamethyl-
66.75	76.94	Heptasiloxane, hexadecamethyl-
67.68	76.14	Heptasiloxane, hexadecamethyl-
66.46	93.86	2-Propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester
69.52	75.70	Heptasiloxane, hexadecamethyl-
69.23	78.01	Heptasiloxane, hexadecamethyl-

Table 4 shows a list of the identified compounds. Here, mainly alkanes and siloxane compounds were released, which also fit with the list of ingredients. As the mass spectra of the different siloxanes are very similar, there is a possibility that the release of slightly different derivatives is occurring as well.

### Conclusion

The coupling of STA and GC-MS enables simulation of the application of heat protection hair sprays to their maximum application temperature. The gas chromatography-mass spectrometry (GC-MS) technique has been proven to facilitate the identification of the composition of the primary gases evolved. Furthermore, it can be utilized to determine the presence of silicon compounds within a given product. This information may assist in the optimization of cosmetic products with regard to their environmental compatibility, biodegradability, and health risks for hairdressers and individual customers.