GC-IRMS: Differentiating natural and synthetic sources of menthol by carbon and hydrogen isotope fingerprints

Authors: Mario Tuthorn<sup>1</sup>, Dieter Juchelka<sup>1</sup> and Philippe Merle<sup>2</sup>, <sup>1</sup>Thermo Fisher Scientific, Bremen, Germany <sup>2</sup>Firmenich, Corporate R&D, Innovation in Analytical Chemistry, Geneva, Switzerland

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## Goal

Trace the origin of menthol using carbon and hydrogen isotopes.

## Introduction

Menthol is a basic ingredient of mouth fresheners, food, chewing gums, fragrances, cosmetics, tobacco, pharmaceuticals, and many more products which are widely used in everyday life. Menthol can be obtained from natural sources, e.g. from mint oil produced by steam distillation of *Mentha arvensis*<sup>1</sup>, or it can be made synthetically through different synthetic pathways.



Natural products are often targets of adulteration such as mixing with cheaper synthetic products, and the diversity of menthol source creates an opportunity for economically motivated fraud. The mint market is a growing business, representing a total market value of approximately 1.2 Billion Dollars<sup>2</sup>. However, menthol price and availability fluctuate depending on the climate conditions which influences the economy of the major producers of mint oil in the world, India (80%), China (9%), Brazil (7%), and the US (4%)<sup>1</sup>. A reliable solution to prevent false labeling of products containing menthol is required to protect both consumers and producers.



Authenticating if menthol originates from natural or synthetic source can be done by investigating carbon and hydrogen isotope fingerprints.

This application brief reports carbon and hydrogen analysis from 10 menthol samples using Gas Chromatography Isotope Ratio Mass Spectrometry.

#### Carbon and hydrogen isotope fingerprints of menthol

Menthol has a fingerprint, a unique chemical signature that allows it to be identified. The carbon isotope fingerprints ( $\delta^{13}$ C) of different plant groups vary because of photosynthetic processes and environmental conditions<sup>3</sup>. Hydrogen fingerprint is associated with local-regional rainfall, and can also be influenced by cultivation practices, soil processes and geological characteristics of the local area<sup>4</sup>. By combining the carbon and hydrogen isotope fingerprints, menthol source can be assessed.

### **Analytical configuration**

All measurements are performed using a Thermo Scientific<sup>™</sup> GC IsoLink II<sup>™</sup> IRMS System, consisting of the Thermo Scientific<sup>™</sup> TRACE<sup>™</sup> 1310 GC, the Thermo Scientific<sup>™</sup> GC IsoLink II<sup>™</sup> Interface, the Thermo Scientific<sup>™</sup> ConFlo IV<sup>™</sup> Universal Interface and the Thermo Scientific<sup>™</sup> DELTA V<sup>™</sup> Isotope Ratio Mass Spectrometer. For carbon measurement 32 ng of menthol and for hydrogen 350 ng of menthol were injected via liquid injection using Thermo Scientific<sup>™</sup> TriPlus<sup>™</sup> RSH<sup>™</sup> Autosampler. All measurements were controlled by Thermo Scientific<sup>™</sup> Isodat Software Suite allowing for unattended switch between hydrogen and carbon analysis within a measurement sequence.

#### **Results**

In this study, 10 menthol samples were analyzed in triplicates. Carbon isotope fingerprints ranged from -26.8‰ to -31.2‰ with STDEV of individual measurements <0.09‰ (n=3), and hydrogen isotope fingerprints ranged from -70.1‰ to - 377.9‰ with STDEV of individual measurements <1.6‰ (n=3).

By combining carbon and hydrogen isotope data in twodimensional XY plot (Figure 1), naturally and synthetically obtained menthol were clearly differentiated. This provides a platform for source identification of different sample types containing flavors, which are widely used in foods, pharmaceutical and cosmetics industry.

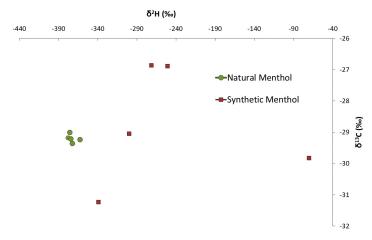


Figure 1. Combined C and H isotope fingerprints of menthol samples.

### Conclusions

Isotope fingerprints analyzed by GC-IRMS are a powerful tool to determine source of flavors, e.g. menthol, enabling correct labeling of products. This is critical for consumer confidence, brand reputation and producer revenue alongside reducing fraudulent activities. With the GC IsoLink II IRMS System, laboratories gain an effective analytical solution based on the compound specific identification of the isotope fingerprint within challenging matrices. This reliable solution is underpinned by optimal GC resolution, followed by fully automated and unique combustion/pyrolysis system to meet complex analytical challenges.

#### References

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