Optimizing GC Injections when Analyzing 2H of Vanillin for Traceability Studies

Hansen, Anne-Mette Sølvbjerg; Fromberg, Arvid; Frandsen, Henrik Lauritz

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

DTU Food
National Food Institute

Optimizing GC Injections when Analyzing δ^2H of Vanillin for Traceability Studies

Anne-Mette Sølvbjerg Hansen, Arvid Fromberg, Henrik Lauritz Frandsen
National Food Institute. Technical University of Denmark. Mørkhøj Bygade 19. DK-2860 Søborg. Denmark
Corresponding author: asoha@food.dtu.dk

Column overloading is a problem when analyzing δ^2H, due to the low natural abundance of deuterium and poor ionization efficiency of H_2. This problem can be overcome by using split injections instead of splitless. In this study we have compared the influence upon the measured isotopic ratios when using the two injection methods.

Introduction

In traceability studies of vanilla, the main aroma constituent 4-hydroxy-3-methoxybenzaldehyde (vanillin) was analyzed for its δ^2H values by Gas Chromatography Pyrolysis Isotope Ratio Mass Spectrometry (GC-P-IRMS). To obtain good precision, it is normally required to have at least 30ng of hydrogen on column depending on the instrument. However, the amount of vanillin in extracts of vanilla pods will overload a DB-5ms column with a film thickness of 0.25µm when injecting 1µL using splitless injection – as seen in figure 1. Chromatography can be improved by using split injections with a split ratio of 1:20. δ^2H should in theory not be affected by sample amount and therefore be the same independently of injection method.

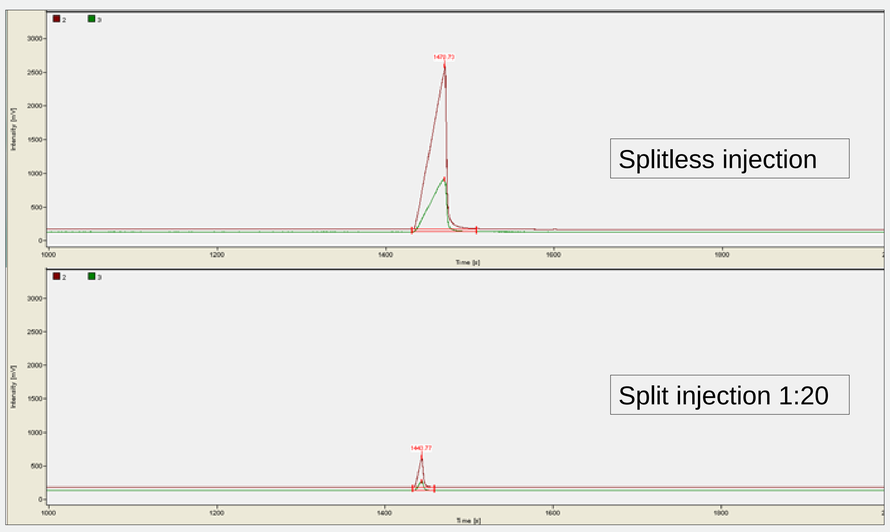

Figure 1: Standards of vanillin containing 1578ng/µL analyzed using GC-P-IRMS with splitless injection (top) and split injection of 20:1 (bottom).

Results

In this study we compared values of δ^2H for vanillin using split and splitless injection. Splitless injections maintains a constant level of δ^2H (see figure 2) with standard deviation around 3‰ corresponding to the expected precision of the instrument. At low concentrations of vanillin the δ^2H values decreases when using split at 1:20.

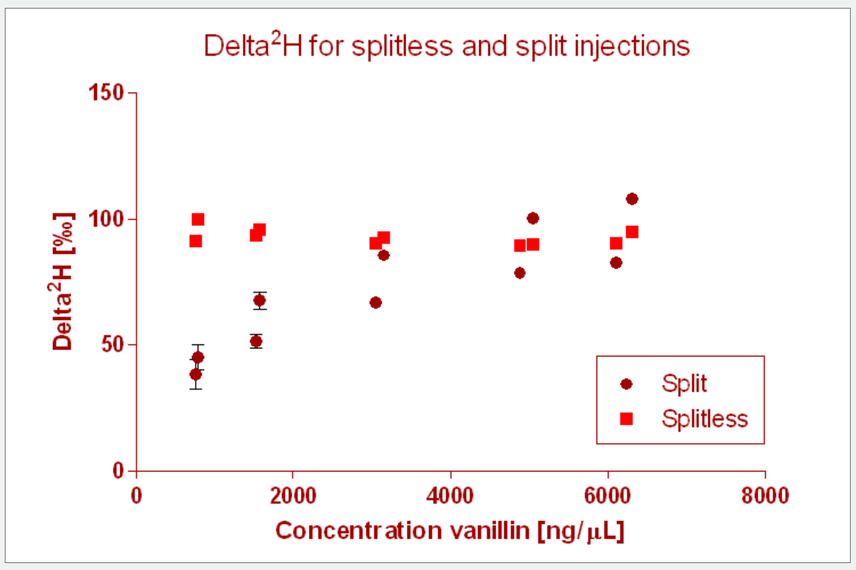

Figure 2: δ^2H for different concentrations of vanillin analyzed with GC-P-IRMS with splitless injection and split injection of 20:1. All other parameter was kept the same for the two experiments. Results are not standardized against V-SMOW because this would require that standards was run at the exact same conditions as the samples.

Accordingly, using split injections at low concentration will lead to discrimination against ^2H compared to splitless injections. It is therefore recommended to use splitless injections for analysis of δ^2H when analyzing extracts of vanilla pods for traceability studies.

When injecting 40ng vanillin on column for both methods, a deviation above 10‰ was found (data not shown). This indicates differences in the obtained values is not solely due to amount-dependent isotopic fractionation, but partly also due to fractionation during split injection.

Materials and methods

GC-IRMS: Trace GC Ultra fitted with a DB-5 capillary column (Agilent Technologies, Böblingen, Germany) (30m x 0.250mm i.d., d_f 0.25 µm) coupled to Delta V Advantage Isotope Ratio Mass Spectrometer (Thermo Scientific, Bremen, Germany). High Temperature Conversion Reactor consisting of a ceramic tube with no catalyst was operated at 1420 C. Helium was used as carrier gas at 1.2mL/min. Injector temp. 230 C.

DTU Food
National Food Institute