

SPME Analysis of Scotch Whisky

from the Bruichladich Distillery, Isaly, Scotland

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SUMMARY

This paper details the several possible methods for conducting SPME (solid phase microextraction) GC (gas chromatography) analysis of Scotch whisky samples collected at the Bruichladdich Distillery in Islay, Scotland. It may serve as a starting point for those conducting SPME whisky research in the future.

INTRODUCTION

Scotch whisky is produced at the the Bruichladdich Distillery in Islay, Scotland using traditional methods that have existed for hundreds of years. Much of the process equipment still used at Bruichladdich was built in the second half of the 19th century. Production methods have been perfected at the distillery and other distilleries over time, but many of the chemical processes involved in the mashing, fermentation, distillation, and aging steps of production have not been documented.

Insight into these processes will be beneficial in the operation of existing distilleries and in the design of new facilities. It may also prove useful in understanding the manufacture of other ethanol-based products.

Additionally, analysis of whisky production at the Bruichladdich Distillery can serve as a powerful teaching tool to help chemical engineering students and students in other disciplines understand these types of processes and get a better feel for some of the historical aspects of their fields.

To facilitate this, Bruichladdich has set up a hands-on whiskymaking course called “The Academy.” In the course, students get the opportunity to experience each part of the production process by working alongside experienced distillery employees to produce whisky.

The Bruichladdich Distillery has also allowed students at the University of Tennessee (UT) the unique opportunity to study the process in more detail. Samples of spirits have been collected during several distillation runs and at different stages of aging and transported to the university. Several studies have already been performed with these samples and many more are planned.

The Chemical Engineering department at Lafayette College is collaborating with UT Chemical Engineering on this research. To ensure that it is easy to compare results obtained by the two research groups, it is important to establish a standard procedure for analysis of whisky samples. This report details initial attempts to establish a method for characterization of samples from Bruichladdich using solid-phase microextraction.

BACKGROUND

Distillation at Bruichladdich is performed in two stages in pot stills. The first stage is performed in a 17,275 L “wash still,” and the second stage is performed in a 12,274 L “spirit still.” Distillation samples collected during the 2003 Bruichladdich class were analyzed by UT Chemical Engineering graduate students using an Agilent Gas Chromatograph-Mass Spectrometer (GC-MS) provided by Bush Brothers, Incorporated. A model for ethanol concentration during distillation was developed using Hysys software.

During ethanol production a number of congeners arise that give different whiskies their characteristic flavors. The congeners commonly found in different types of Scotch whisky include fusel alcohols, fatty acids, and esters. Some of these are detectable through liquid GC injection, but many are present in such small concentrations that they are not. Detection of these low-concentration compounds is possible using solid-phase microextraction GC injection (Fitzgerald et al., 351).

EXPERIMENTAL METHOD

Several SPME runs were performed at Lafayette College using a Perkin-Elmer Autosystem XL GC with a 15m - .25 micron - .5 mm ID Restex Stabilwax-DA column on a vat sample from Bruichladdich collected during the Summer 2003 whiskymaking. An MS detector was not available at the time the runs were conducted, so flame-ion detection (FID) was used. The SPME device was a manual injector supplied by Supelco. Liquid immersion was used instead of headspace analysis because of its better response.

Sample Preparation

To compare different SPME GC runs, samples must be diluted to the same concentration. Samples acquired during distillation are between 30% and 70% ethanol by volume, and samples acquired during aging fall within that range. Standards of ethanol in water were prepared in concentrations of 30%, 40%, 50%, 60%, 70%, and 80% ethanol by volume. Using these standards along with a pure water sample, a calibration curve can be generated using GC analysis. Ethanol concentration of samples can then be calculated and the samples can be diluted accordingly. Because only one sample (the vat sample) was used for the initial study, no dilution was necessary and a calibration curve was not generated. The sample was sealed in an injection vial with a stir bar.

Fiber Selection/Sorption

The poly(dimethylsiloxane) (PDMS) SPME fiber was selected for the extraction due to its good response to the compounds present in scotch whisky and the availability of this type of fiber at the two schools. The fiber was conditioned for 2 hours at 230°C in the GC injection port before the first run. It was conditioned for 1 hour at 250°C before each subsequent run.

The sample was adsorbed onto the SPME fiber for 30 minutes immediately before each GC run. During adsorption, the sample was stirred.

GC Method

During each run the SPME fiber was left to desorb throughout the duration of the run. Helium was used as the carrier gas.

Four different GC methods were tested. The following table summarizes the methods. Note that method 4 is essentially the same as method 1.

Table 1: GC Methods

Method	Run Time	Injector Temperature	Detector Temp	Oven Program
1	60 min	250°C	230°C	Initial Temp: 60°C Initial Hold: 2 minutes Ramp 1: 5°C/min to 100°C (hold 0 min) Ramp 2: 5°C/min to 240°C (hold 22 min)
2	90 min	Initial: 60°C Hold: 2 min Ramp: 10°C / min to 250°C	230°C	Initial Temp: 60°C Initial Hold: 5 minutes Ramp 1: 5°C/min to 100°C (hold 0 min) Ramp 2: 5°C/min to 240°C (hold 49 min)
3	60 min	Initial: 100°C Hold: 3 min Ramp: 50°C / min to 250°C	230°C	Initial Temp: 60°C Initial Hold: 5 minutes Ramp 1: 5°C/min to 100°C (hold 0 min) Ramp 2: 5°C/min to 240°C (hold 19 min)
4	48 min	250°C	230°C	Initial Temp: 60°C Initial Hold: 2 minutes Ramp 1: 5°C/min to 100°C (hold 0 min) Ramp 2: 5°C/min to 240°C (hold 22 min)

RESULTS

Method 1

Method 1 shows good peak separation and intensity. There is some baseline drift.

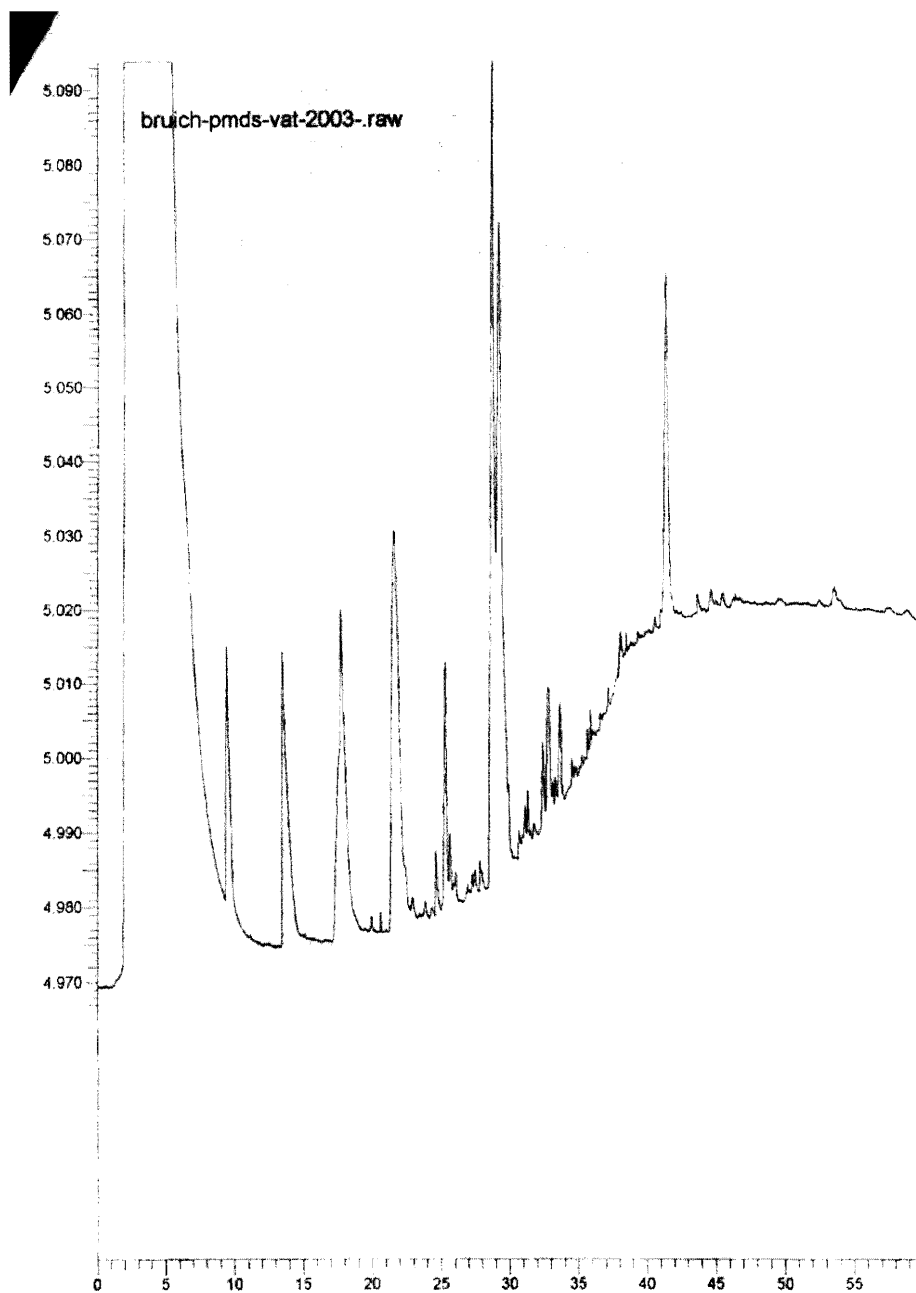


Figure 1: Method 1

Method 2

Method 2 gives wider peaks and poorer separation than method 1. Many peaks are lost in the background noise.

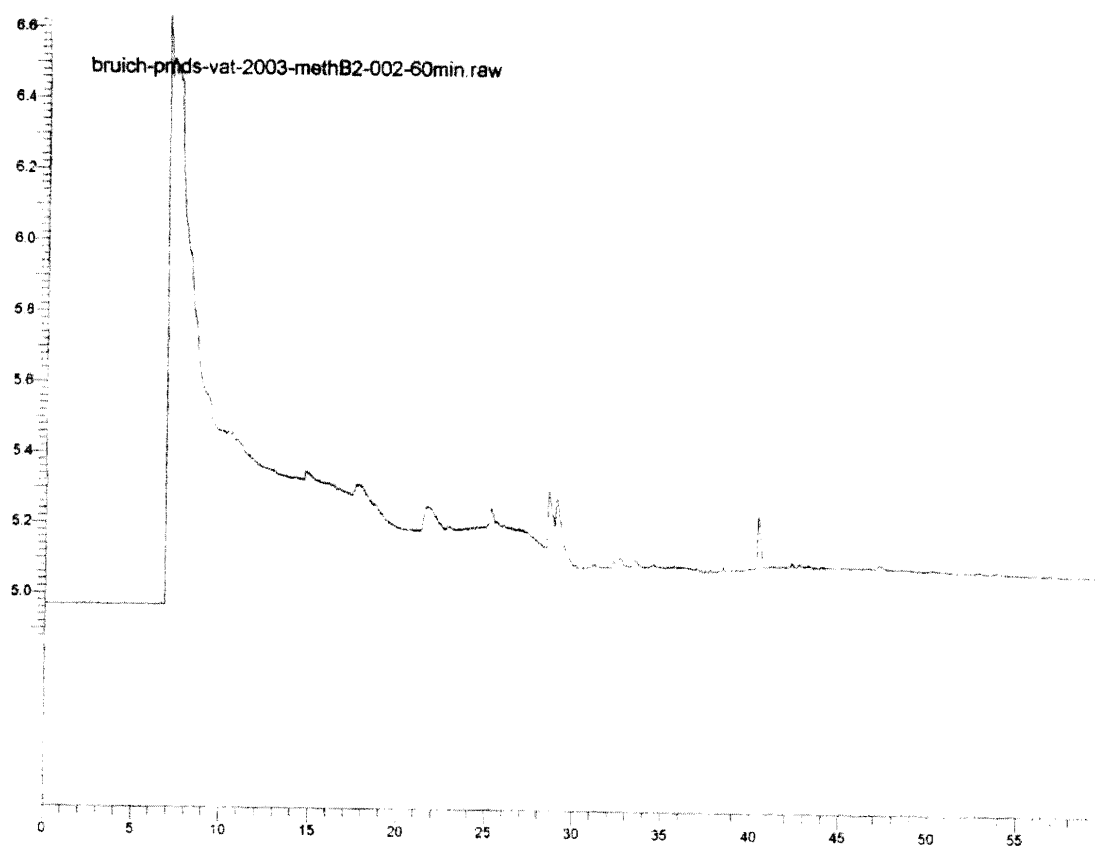


Figure 2: Method 2

Method 3

Method 3 has better separation and shows more peaks than method 2, but peaks are slightly wider than in method 1. It should be noted that it was suspected that the column was degrading during the experiment, which might account for greater peak widening on later runs.

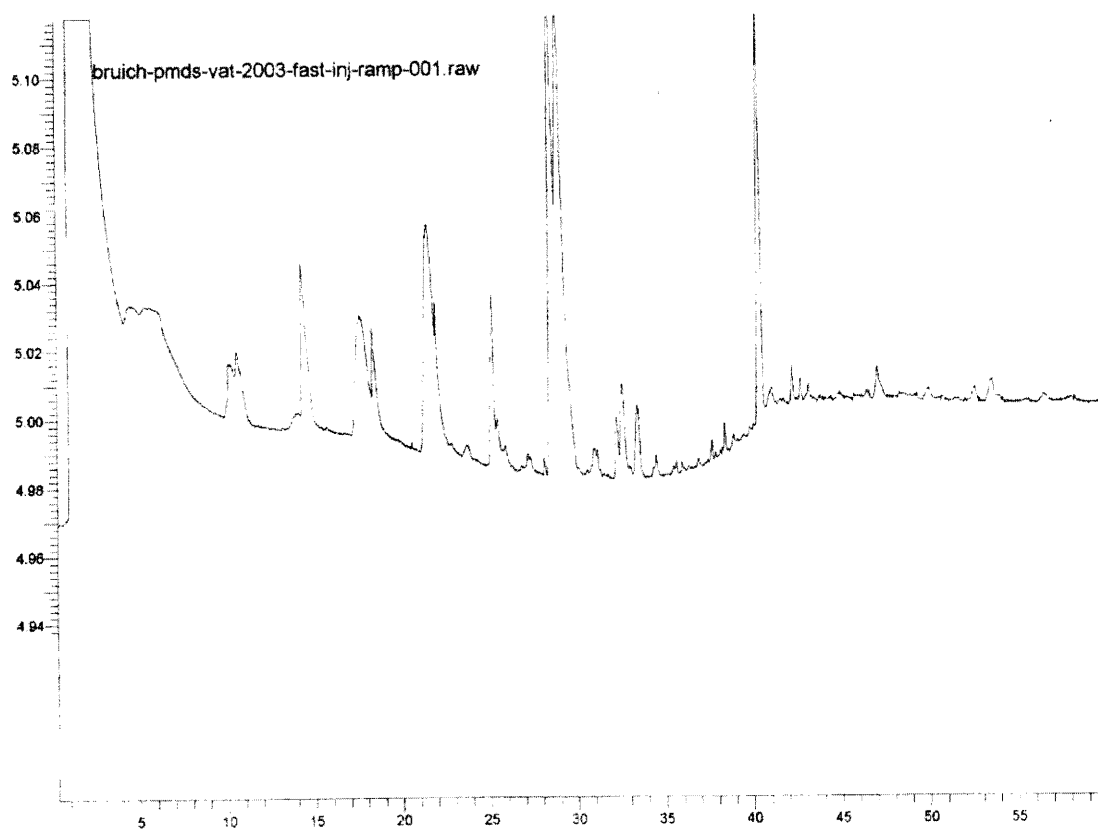


Figure 3: Method 3

Method 4

Method 4 is essentially the same as method 1. It was cut short to save time because there were no peaks after about 45 minutes using method 1. Even though the column had degraded, method 4 still had better separation and narrower peaks than methods 2 or 3. Figure 5 shows a closer view of method 4.

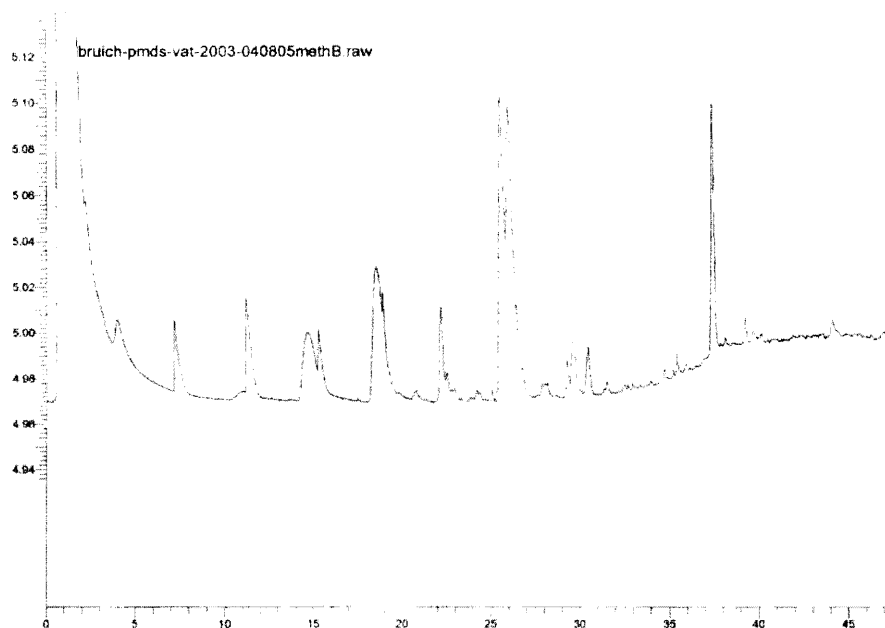


Figure 4: Method 4

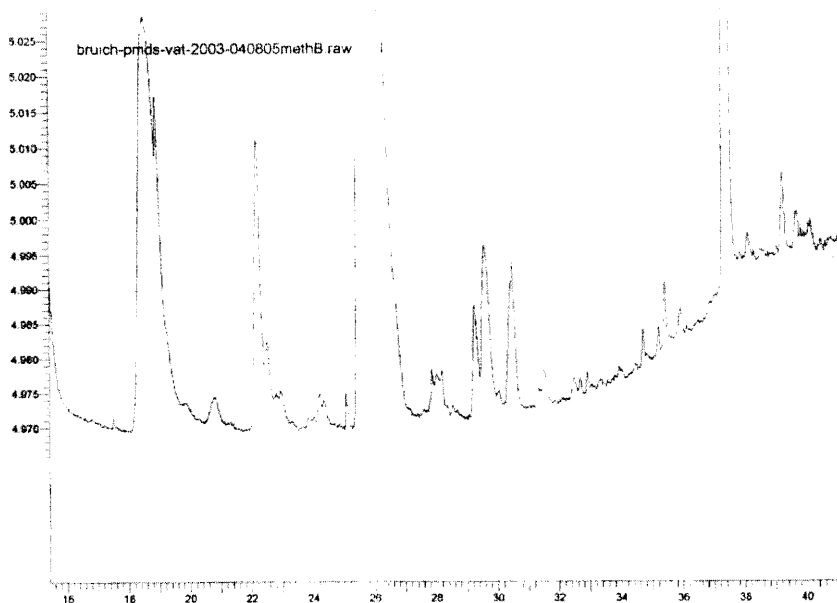


Figure 5: Method 4 Close-up

CONCLUSIONS

The GC method used in methods 1 and 4 appear to give the most meaningful results for SPME analysis of Scotch whisky using a PDMS fiber of all the methods tested. These methods require a constant injector temperature of 250°C with an oven temperature that holds at 60°C for 2 minutes, then ramps up by 5°C/min to 100°C, then ramps up again by 5°C/min to 240°C and holds until the end of the run.

Initial attempts were made to identify some of the peaks in the chromatograms from methods 1 and 4. Using an MS detector instead of FID would make identifying spectra more reliable. Also, the column used in the study was a 30 meter column. Using a 60 meter column would reduce the width of peaks and give better peak separation.

This information will prove useful to researchers at the University of Tennessee and at Lafayette College as a starting point. It will give them an example of a working method for SPME analysis of distillation and aging samples from Bruichladdich. If results from different experiments are to be compared, a standard procedure including sample preparation, adsorption, and GC method should be used. The four methods used in this experiment show how drastically different results can be when only a few parameters are changed.

SOURCES

Fitzgerald, Gillian and Kevin J. James and Kevin MacNamara and Mary A. Stack.

“Characterisation of whiskeys using solid-phase microextraction with gas chromatography-mass spectrometry.” Journal of Chromatography A. 896 (2000): 351-59.

Rogers, Thomas Benton. “Analysis and simulation of a batchwise Scotch whisky production process.” (2004).