Determination of Sulfur-Containing Species in Scotch Whiskies Using Gas Chromatography with Pulsed-Flame Photometric Detection

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Introduction

Scotch whisky is widely regarded as one of the most complexly-flavored and cherished spirits in the world, with annual exports in 2013 of £5.6 bn1 (approx. USD 8.8 bn). There are six distilling regions in Scotland: Campbeltown, Highlands, Islands, Islay, Lowlands, and Speyside (Figure 1). Scotch whisky, as defined by the Scotch Whisky Regulations 20092, is whisky that is 1) produced at a distillery in Scotland from water and malted barley (to which only whole grain cereals may be added), all of which must be 2) processed at that distillery into a mash; 3) converted by enzyme action into a fermentable substrate that is then 4) fermented by adding only yeast; 5) distilled at an alcoholic strength of less than 94.8%; 6) aged in a warehouse in Scotland in oak casks for no less than 3 years; and 7) must retain the natural color, aroma, and taste acquired in its production and maturation; 8) contain no additives save water or plain caramel color (E150A); and, 9) comprise a minimum alcoholic strength of 40% ABV. There are numerous variables in the process of production, including the quality of barley, the malting process, the shape of the still head, the kind of fuel that is burned during distillation, the kind of oak used in the maturation barrels, etc.

The character of the distillery regions imparts a particular set of flavors to the finished whisky, as do the distillation and aging processes. Efforts are underway, chiefly at The Scotch Whisky Research Institute (SWRI), to better characterize the flavor components of aged Scotch whiskies in order to determine the fingerprint of each to ensure quality and authenticity. SWRI was established in 1912 to maintain the good global reputation of Scotch whisky by providing analytical services and technical information on whisky production to its member companies.

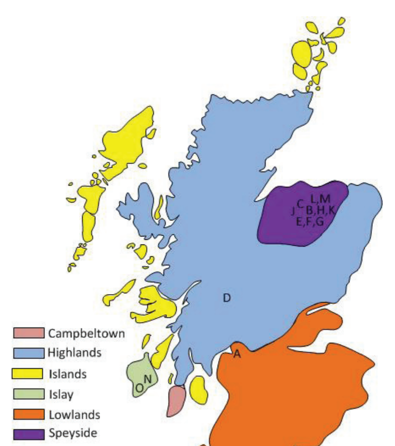

Figure 1. Stylized map of Scotland with distillery regions and sample sources indicated.

OI Analytical offers a pulsed-flame photometric detector (PFPD), which operates by first detonating a plume of analyte as it exits the end of the GC column and then detecting the photons emitted by the detonation event. It is a sensitive detector that can be configured with optical filters and time gates to simultaneously detect the presence of a number of elements; and for this work, it was configured to detect sulfur and carbon, the principle components of the flavor compounds found in Scotch Whisky. For the purposes of this poster, we will focus on the sulfur-containing flavor compounds found in Scotch whiskies as relates to the peat content and maturation age of the whiskies, as well as the geographic area of the distilleries in which they are produced. To that end, we have sampled a selection of single-malt Scotch whiskies, separated their sulfur-containing species using gas chromatography, and detected them using two channels of PFPD (carbon and sulfur), with some complementary analysis on a quadrupole mass spectrometer. The samples are as follows in Table 1, and their distillery of origin is marked on the map in Figure 1.

Table 1. Scotch Whisky Samples Examined

	Distillery, variety	Region	Years Aged	% ABV
A	Auchentoshan	Lowland	12	40
B	Balvenie, Doublewood	Speyside	12	43
C	Cragganmore	Speyside	12	40
D	Deanston	Highland	12	46.3
E	Glenlivet	Speyside	12	40
F	Glenlivet, Madura	Speyside	16	54.3
G	Glenlivet, Sherry Oak	Speyside	18	43
H	Balvenie, Doublewood	Speyside	17	43
I	Macallan	Speyside	12	43
J	Macallan	Speyside	18	43
K	Balvenie, Portwood	Speyside	21	43
L	Aberlour, A'Bunadh	Highland	-	60.3
M	Aberlour, Sherry Cask	Speyside	17	58.5
N	Ardbeg	Islay	10	46
O	Lagavulin	Islay	16	43

Experimental

Table 2. Gas Chromatograph and Detector Parameters

Gas Chromatograph			
Column	Restek Rxi-1ms 30 meter, 0.32 mm ID, 4 µm df		
Carrier Gas	Zero grade helium		
Inlet Temperature	250 °C		
Column Flow Rate	1.0 mL/min		
Split Ratio	5:1		
Oven Program	Hold at 60 °C 0 minute; 16 °C/min to 260 °C; 20 °C/min to 300 °C		
Detector	OI Analytical PFPD	**Channel 1**	S (sulfur)
Model	5380	Interpolation	spline
Temperature	250 °C	Attenuation	32
Hydrogen Flow	13 mL/min	Zero Output	10
Air Flow	14 mL/min	**Channel 2**	C (carbon)
Makeup Flow	12.0 mL/min	Interpolation	spline
PMT Voltage	575	Attenuation	128
Ignitor Current	2.8	Zero Output	3000
Trigger Level	500	Sulfur Gate	6-24 msec
Range	10	Carbon Gate	1-3 msec

Scotch whisky samples were purchased commercially and small aliquots were taken for analysis by GC with detection by PFPD. Details of the experiment including GC details and PFPD settings are listing in Table 2.

Standards were combined at a few low-level concentrations, and two of the labeled chromatograms are shown in Figure 2a and Figure 2b. Flavor compounds were identified through two principle methods: RT matching using standard reference materials or GC-MS fragmentation patterns. All Scotch whisky analyses were checked against these lists of compound retention times, for identification of components in the unconcentrated whisky aliquots.

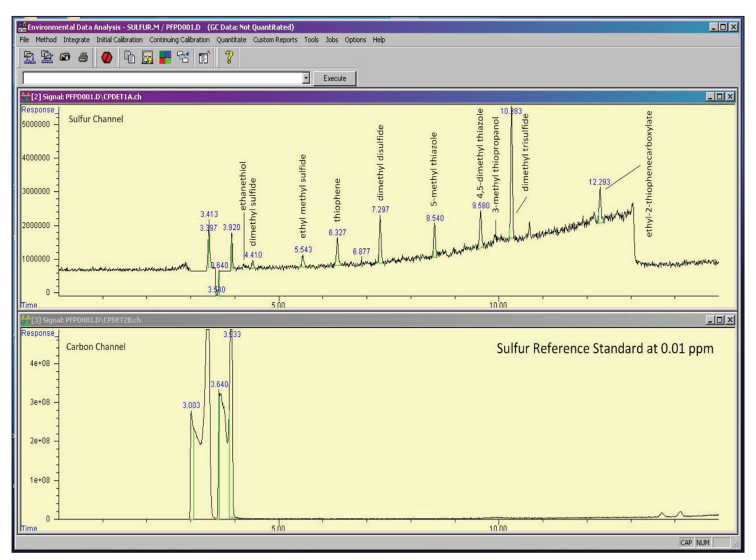

Figure 2a. Sulfur Reference Materials Chromatogram at 0.01ppm

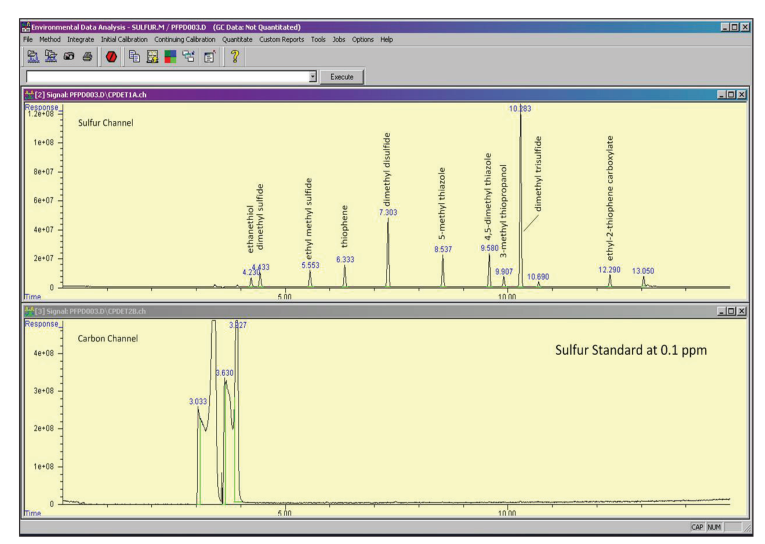

Figure 2b. Sulfur Reference Materials Chromatogram at 0.1

Interestingly, the standard reference materials available to establish the identification map were far from a complete collection of the sulfur-species present in the Scotch whiskies examined. In fact, none of the species from the map were found at all in the commercial samples, see Figure 3 as an example. What we show in Figure 4 is a composite of the results for 4 single-malt Scotch whiskies referenced in the distillery map, and the blended Scotch whisky that we used to establish sampling parameters.

Figure 3. PFPD Chromatogram of Ardbeg 10-year old Whisky

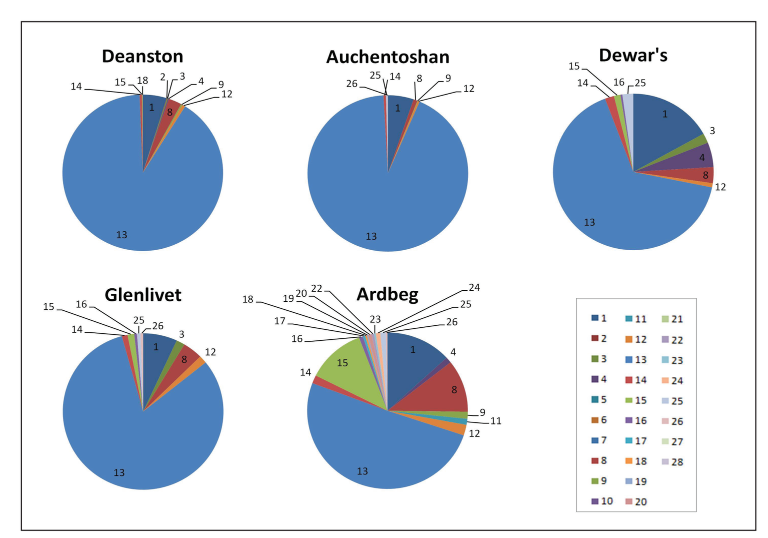

Figure 4. Proportions of Sulfur Specied in Selected Scotch Whiskies

Results and Discussion

The number of sulfur-containing (and non-sulfur containing) compounds comprising a Scotch whisky is large, as evidenced by the 28 sulfur species found in some proportion in the whiskies selected for this work. Analysis of industry publications and the limited commercial availability of known sulfur-containing Scotch components led us to purchase the compounds that were analyzed in Figure 2. These were thought to be likely candidates for the Scotch flavor compounds with which to establish our reference data. However, all of our Scotch samples, including those not shown here, did not exhibit any detectable concentration of the species in our reference standards.

Our reference standards did contain dimethyl trisulfide, which is a degradation product and has an unpleasant taste and odor that is detectable at very low levels, so its absence in the tested scotches indicates that none of them had degraded. Our ability to quantitate sulfur species in the whiskies follows from the data, but as element-specific detectors do not provide conclusive identification, a more effective sampling method, such as solid-phase microextraction (SPME) or headspace sampling coupled to a GC-MS for identification by fragment pattern could be used to identify more of the species in the sulfur fraction of the whiskies. Once the species retention times are established through identification with pre-concentration, more routine assays could be carried out using the PFPD, as it is significantly more sensitive to sulfur species than the mass spectrometer used in the study.

Summary & Conclusions

PFPD can be successfully used to detect sulfur-containing flavor compounds found in Scotch whiskies, with or without pre-concentration via SPME, whereas GC-MS is not a very sensitive tool for the detection of many sulfur species. While some sulfur-containing species present in Scotch whiskies are commercially available as reference materials, many more are not. The lack of reference standards, combined with the relative insensitivity of mass spectrometry for sulfur species makes identification difficult, but detection and quantitation of the sulfur species with an element-specific detector is still possible.

References

1. The Economic Impact of Scotch Whisky Production in the UK, January 28, 2015, The Scotch Whisky Association.
2. The Scotch Whisky Regulations 2009. United Kingdom Statutory Instrument 2009 No. 2890, 2009.

Acknowledgments

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