Detection of Counterfeit Scotch Whisky using ^{2}H and ^{18}O Stable Isotope Analysis to Determine Provenance

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"Food authenticity is a term that refers to whether the food purchased by the consumer matches its description. Mis-description can occur in many forms, from the undeclared addition of water or other cheaper materials, or the wrong declaration of the amount of a particular ingredient in the product, to making false statements about the source of a food product or its ingredients i.e. their geographic, plant or animal origin" (FSA, UK).

Introduction

Stable isotope techniques have become one of the key methods in food authenticity control. Thus far, stable isotope techniques employed to combat food mis-declaration have focused on the detection of addition of minor quality oils to high quality, high premium single seed vegetable oil or the potential differentiation between wild and farmed salmon. In addition they have looked at variations on isotope abundance of ^{13}C, a stable isotope marker particularly suited to detect adulteration of e.g. corn (maize) oil with oils from other sources or evidence of non-marine feed influence in fish flesh as indicator of fish farming. However, while ^{13}C signatures on their own can denote plant source of e.g. particular oils, they cannot provide any information on geographic provenance and are thus ineffective in combating fraudulent mis-description of regional speciality products such as Scottish whisky.

Here, we present a study of ^{2}H and ^{18}O stable isotope signatures of neat spirits as well as source water used in whisky production to develop a proxy for geographic provenance of whisky and thus as an exclusion criterion for its authenticity.

Materials & Methods

List of samples collected from 12 different distilleries (Fig. 1) for stable isotope analysis.

1. **Source water:** water added the ground barley (grist) to produce the mash.
2. **Wash:** fermented mash. Sampled either at the end of the exponential phase or in the stationary phase (~ 50 to 70 hours old). Usually has an alcoholic strength of between 7-10%.
3. **Draff:** the spent grains left after mashing has taken place.
4. **"New make spirit":** distillate (alcohol content usually between ~68% and 72% but can be as much as 95%).
5. **Reduced "new make spirit":** that goes into cask (collected from a vat after reduction water added – casks mostly filled at 63.5%).
6. **Cask reduction water:** water added to the "new make spirit" before cask filling.
7. **Cask sample**.
8. **Bottle strength reduction water**: after whisky has matured in casks water is added at the bottling hall to bring it down to bottle strength, ~ 40%, (43% is also common).
9. **Pre chill filtration**: sample of bottle strength whisky before filtration takes place (usually collected from a vat after cask disgorgement, reduction water added and vat roused).
10. **After chill filtration** (below 46%; some fatty acid esters come out of solution making the resultant whisky appear hazy – whisky is chill filtered usually between -4 and 4 °C to produce a final bottled product that is bright and clear).
11. **Tap water:** collected from every site (distillery or bottling hall).
12. **Surface water:** in addition to the samples listed above a sample (where possible) was collected from an open fresh water source nearby to each distillery or bottling hall.

Figure 1 Location of the 12 distilleries studied

^{2}H / ^{18}O isotope analysis by TC/EA-IRMS

The working reference gas, H_2 (BOC, Guildford, Surrey, UK) was calibrated against VSMOW using the international calibration material VSMOW ($\delta^{2}H_{VSMOW}$ = 0 ‰) (IAEA, Vienna, Austria) and checked against the international reference materials (RMs) SLAP and GISP. A batch analysis typically comprised 10 samples, with each sample being injected 5 times to account for carry over (needle memory), preceded and followed by a set of RMs (VSMOW, GISP and SLAP; IAEA, Vienna, Austria). Sample volume injected was 0.15 µL. Measured $\delta^{2}H$ and $\delta^{18}O$ values were two-end-point normalised to the VSMOW scale using VSMOW ($\delta^{2}H$= 0 ‰; $\delta^{18}O$ = 0 ‰) and SLAP ($\delta^{2}H$ = -428 ‰; $\delta^{18}O$ = -55.5 ‰).

Results

- Stable isotope analyses of water used by Scottish distilleries during mash production, which converts barley starch into fermentable sugars, and water used for bottle strength reduction of matured whisky showed that their isotopic composition was in very good agreement with the Global Meteoric Water Line (GMWL); see Figure 2.
- A bi-variate plot of the results from bulk ^{2}H and ^{18}O isotope analysis of bottled whiskies showed a clear separation of counterfeit whiskies from China and Northern Cyprus from genuine Scottish whiskies (Figure 3).
- A principal component analysis (PCA) supported the conclusions drawn from the bi-variate plot of the observed $\delta^{2}H$ and $\delta^{18}O$ values (Figure 4).

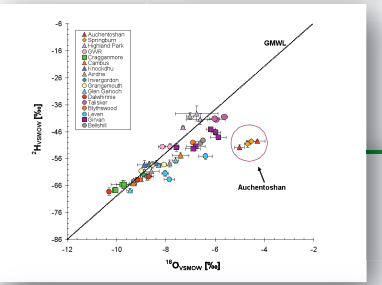

Figure 2 Isotopic Composition of Mashing and Bottling Water

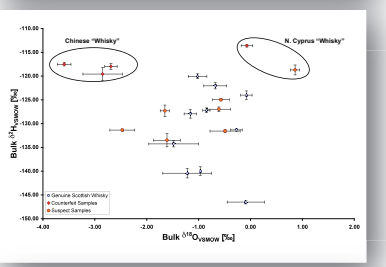

Figure 3 Bivariate Isotope Plot of Genuine and Counterfeit Whiskies

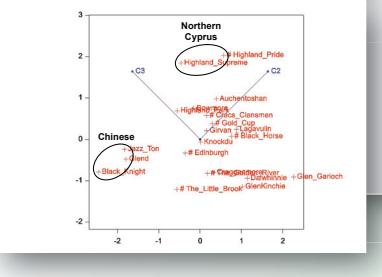

Figure 4 Principal Component Analysis Biplot

Conclusions

- While the results of a blinded analysis of counterfeit, suspect and genuine whiskies were quite promising, we do not know as yet if the lack of separation between the majority of suspect and genuine whiskies means that the suspect sample did indeed originate from Scotland or if the lack of discrimination by PCA is the result of the limited data set.
- Clearly, more work has to be carried out with the aim to increase the data set and to identify additional variables or qualifiers, both of which should improve our ability to distinguish between genuine and counterfeit whiskies

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