



Rapid detection of counterfeit and adulterated alcoholic drinks by deployable and direct ESI-MS

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INTRODUCTION

Precedent exists in using direct ESI-MS for the detection of counterfeit and adulterated/non potable alcoholic drinks including the Brazilian cachaça ([de Souza, Augusti, et al., 2007](#), [de Souza, Siebald, et al., 2007](#) and [de Souza et al., 2009](#)), wine ([Catharino et al., 2006](#)), beer ([Araujo et al., 2005](#)) and whisky ([Moller, Catharino, & Eberlin, 2005](#)).

Until the development of the Microsaic 4000 MiD[®] mass detector, this type of analysis was limited to analytical laboratories where highly skilled operators are required to run and maintain the equipment, and also interpret the data generated. In contrast, the 4000MiD[®] is a self-contained deployable single quadrupole mass detector with NO external vacuum pumps, integrated PC and 'plug and play' components that allow non-mass spectrometrists to operate and maintain the equipment with minimal effort and training.

The areas under investigation in this application note are:

- 1) Authentication of branded Scotch Whisky
- 2) Detection of denaturants in counterfeit/non-potable whisky

MiDas[™]



Fig 1. The 4000MiD[®] and MiDas[™] interface module

The MiDas[™] is a compact interface module used to enable mass detection for a multitude of applications. It is a separate unit to the MS, fully controlled by the 4000MiD[®] and associated method files within the on-board Masscape[®] software.

PART 1 - AUTHENTICITY EXPERIMENTAL

A total of 13 Scotch Whisky samples were analysed to test 3 aspects of the method capabilities.

Blended whisky:

- 1) 6 x Different batches (batch variation)
- 2) 6 x Different blends (blend variation)

Single malt whisky:

- 3) 1 x Single malt (Differentiation and reproducibility)

The samples were run using the MiDas[™] to facilitate Flow Injection Analysis (FIA-MS) with a make up flow of 300 μ L/min (50:50 EtOH:water 0.1% NH₄OH) in full scan mode (-ve ESI) and a number of peaks of interest were identified across the mass range. The samples were run again using multiple SIM mode, and the data normalised to the dominant peak in the mass spectrum. Principal Component Analysis (PCA) was performed on the resulting array of data, and 2 principal components were used to explain a total of 83.4% of variability.

PART 1 - AUTHENTICITY RESULTS

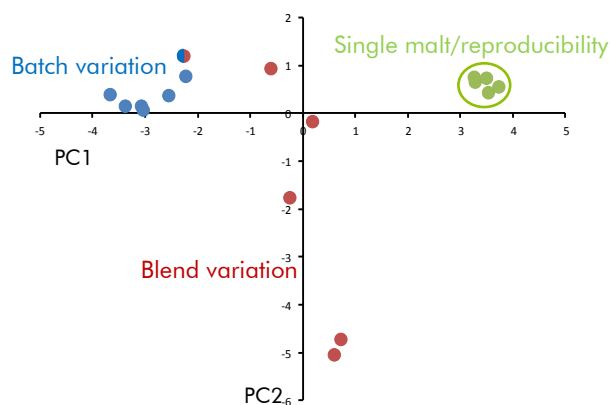


Fig 2. 2D PCA data showing distinctive principle component characteristics

First and foremost, good reproducibility has been demonstrated with repeat injections of the single malt sample, showing **good precision of the method**. There are detectable differences in **different batches of blended whisky**, and in **blend variants**, with all being clearly distinguishable from one another. One of the blend variants was the same as the batch variants, though bottled at a different strength. This has been correctly clustered with the batch variation samples. More targeted analysis would allow for a higher resolution brand model and better discrimination between samples.



Fig 3. Blended Scotch Whisky makes up around 90% of the export market

Bringing mass spectrometry down to size

PART 2 - ADULTERANTS AND DENATURANTS EXPERIMENTAL

In order to identify appropriate m/z values to use for monitoring the compounds of interest (see table 1), a quantity was spiked into 40% aqueous ethanol. The samples were run using the MiDas™ to facilitate Flow Injection Analysis (FIA-MS) with a make up flow of 300 μ L/min (50:50 EtOH:water 0.1% formic acid) in full scan mode (+ve ESI). 9 identical whisky samples were each spiked at a low 'level of interest' with one of the 8 compounds of interest, and one left unspiked as a control. Selected Ion Monitoring (SIM) mode was used to screen the samples, using the m/z values previously identified.

Compound of interest	Purpose
Denatonium Benzoate (bitrex)	Denaturant
Isopropyl alcohol (IPA)	Denaturant
Methyl isopropyl ketone (MIPK)	Denaturant
Ethyl sec amyl ketone (ESAK)	Denaturant
Methyl ethyl ketone (MEK)	Denaturant
Sucrose	Adulterant
Vanillin	Adulterant

Table 1. Potential denaturants and common adulterants in counterfeit whiskies

These results can be further simplified by introducing a threshold relative response of 3, above which it can be considered a positive test for the corresponding compound of interest, and that test will therefore result in a FAIL.

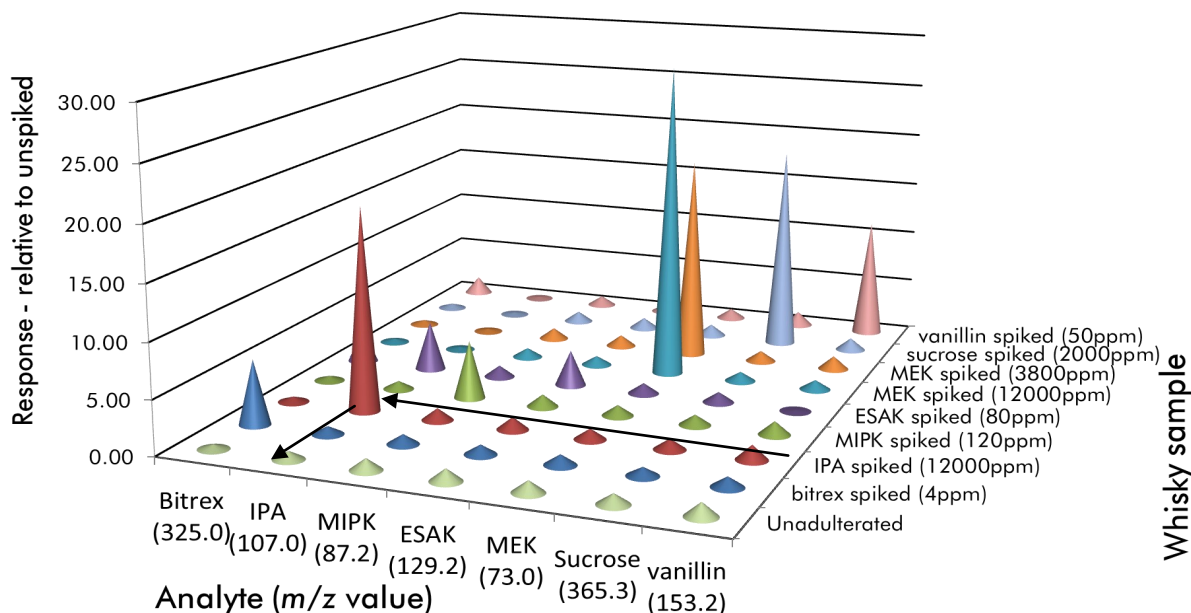


Figure 4. Graph showing positive response for expected analytes in corresponding spiked whisky samples

PART 2 - ADULTERANTS AND DENATURANTS RESULTS

The normalised data is shown as a graph (Figure 4), where whisky samples that have been spiked with compounds of interest show a clear response for that analyte (illustrated in the graph for IPA spiked whisky giving a response for IPA). The 'normal' response was obtained from a separate data set of unadulterated samples, and the y-axis shows the response relative to these (i.e. 1 = normal, 25 = 25 times higher than normal).

This is demonstrated by the genuine sample, which gives a response of around 1 for each analyte.

CONCLUSIONS

Using the 4000MiD® and MiDas™ as a fully stand-alone system, we have demonstrated the ability to distinguish not only a difference in brands of whisky from the same distillery, but a detectable difference in different batches of the same blend. Good method precision has also been demonstrated and most commercially interesting, the ability to separate different brands of Scotch blended whisky. This suggests that each brand has a unique fingerprint and therefore can be easily distinguishable from inferior cheap counterfeit products.

Furthermore, in each case of whisky containing non-potable ethanol (indicated by the presence of denaturants or additives), a test has been devised to indicate abnormal composition using simple PASS/FAIL criteria that can be applied to real life applications, outside of an analytical laboratory. This technique will also apply to white spirits such as vodka and gin where detection of such additives/denaturants is likely to be easier.

Fingerprinting is a useful tool for product characterisation, it is employed by the petroleum industry, and has an important role in the fight against counterfeit goods, including perfumes, essential oils and low cost or high value alcoholic products.

Microsaic Systems strives to create custom solutions for the product characterisation needs of its customers. Use the contact details to find out what we can do for your business.

Whisky sample	Test for Adulterant/Denaturant						
	Bitrex	IPA	MIPK	ESAK	MEK	Sucrose	vanillin
spiked with 4ppm bitrex	FAIL	PASS	PASS	PASS	PASS	PASS	PASS
spiked with 12000ppm IPA	PASS	FAIL	PASS	PASS	PASS	PASS	PASS
spiked with 120ppm MIPK	PASS	PASS	FAIL	PASS	PASS	PASS	PASS
spiked with 80ppm ESAK	PASS	FAIL*	PASS	FAIL	PASS	PASS	PASS
spiked with 12000ppm MEK	PASS	PASS	PASS	PASS	FAIL	PASS	PASS
spiked with 3800ppm MEK	PASS	PASS	PASS	PASS	FAIL	PASS	PASS
spiked with 2000ppm sucrose	PASS	PASS	PASS	PASS	PASS	FAIL	PASS
spiked with 50ppm vanillin	PASS	PASS	PASS	PASS	PASS	PASS	FAIL

Table 2. PASS/FAIL results using a relative response threshold of 3

* Suspected cross contamination during sample preparation

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