

Analysis of Whisky by Electrospray FT-ICR Mass Spectrometry: Proof of Origin by Statistical Methods

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Introduction

Whisky is a high-class consumed alcoholic beverage with a several billion dollar market. Due to the high value of this liquor counterfeiting and manipulation have been observed. Therefore, the proof of the origin of this luxury alcoholic drink is of major interest of distillers and beverage importers. Whisky consists beside water and alcohol of a variety of volatile and non-volatile chemical components, e.g. organic acids and esters, aldehydes, phenols, polyphenols and lactones. [1] Several mass spectrometry techniques have been applied to analyze volatile compounds in whisky [2,3]. Recently the proof of origin and authenticity of whisky has been studied by electrospray mass spectrometry [4].

- [1] Fujieda, M., Tanaka, T., Suwa, Y., Koshimizu, S., Kuono, I., *J. Agric. Food Chem.* **2008**, *56*, 7305.
- [2] Kinton, V. R., Adam, L., *Abstr. Pap. Am. Chem. Soc.* **2002**, *224*, U90.
- [3] Fitzgerald, G., James, K. J., MayNamara, K., Stack, M. A., *J. Chromatogr. A* **2000**, *896*, 351.
- [4] Møller, J. K. S., Catharino, R. R., Eberlin, M. N., *Analyst* **2005**, *130*, 890.

Methods

In our study we used ultra-high resolved mass spectrometry to study whiskies from different origins using statistical methods and fingerprinting. The whiskies have been diluted 1:20 in 50% MeOH for direct infusion measurements using electrospray FT-ICR in negative ion mode. The spectra have been acquired with the new Bruker solariX FTMS platform equipped with a 12T magnet using a resolving power of 300.000 at m/z 400. Three repetitive measurements have been performed of each whisky to proof the concept of the principal component analysis (PCA) for this kind of samples.

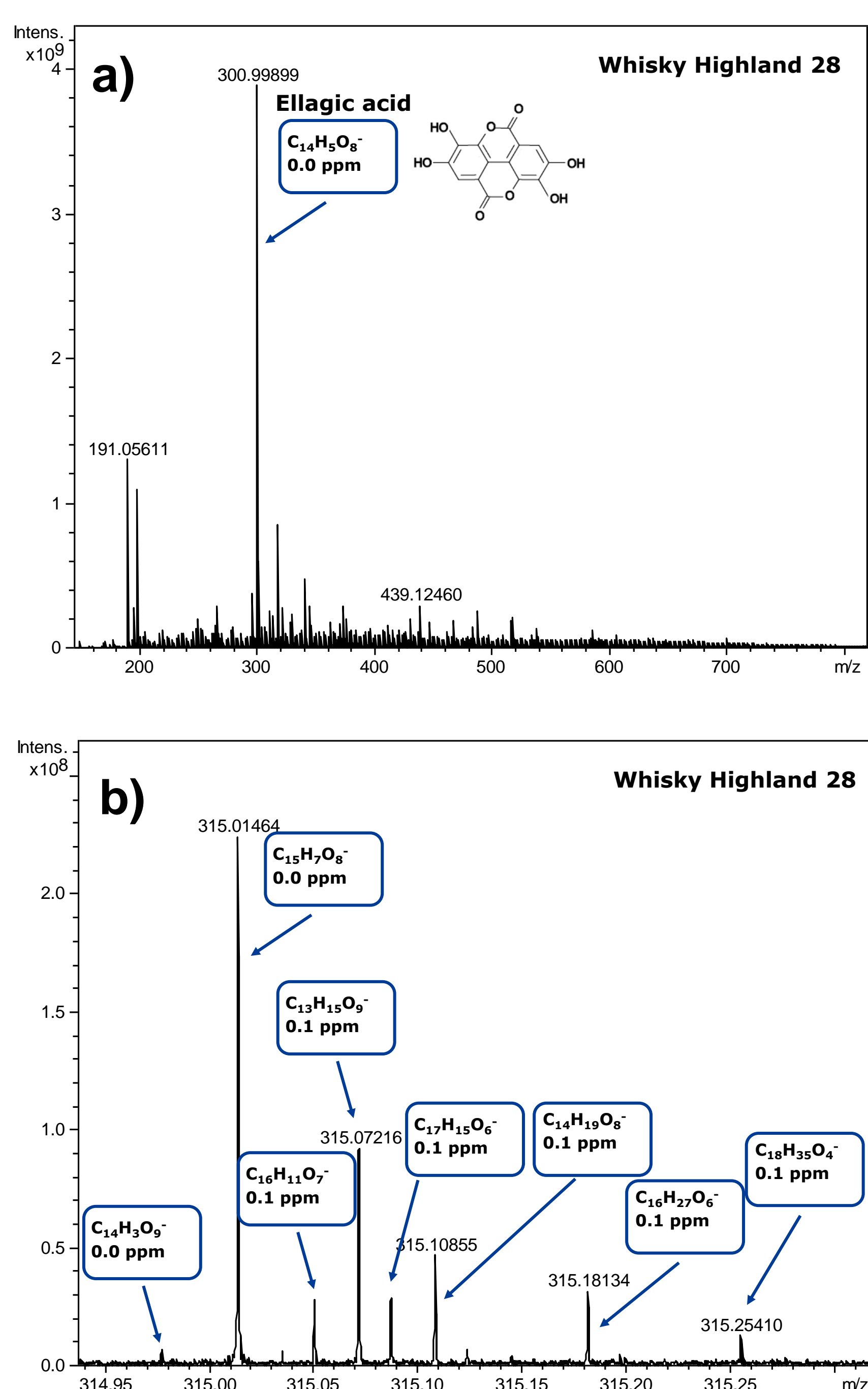


Figure 1. Electrospray mass spectrum of a Highland whisky in negative ion mode: a) full mass spectrum, b) part of spectrum to show the fine structure, mass resolution and peak annotation including molecular formula and mass errors.

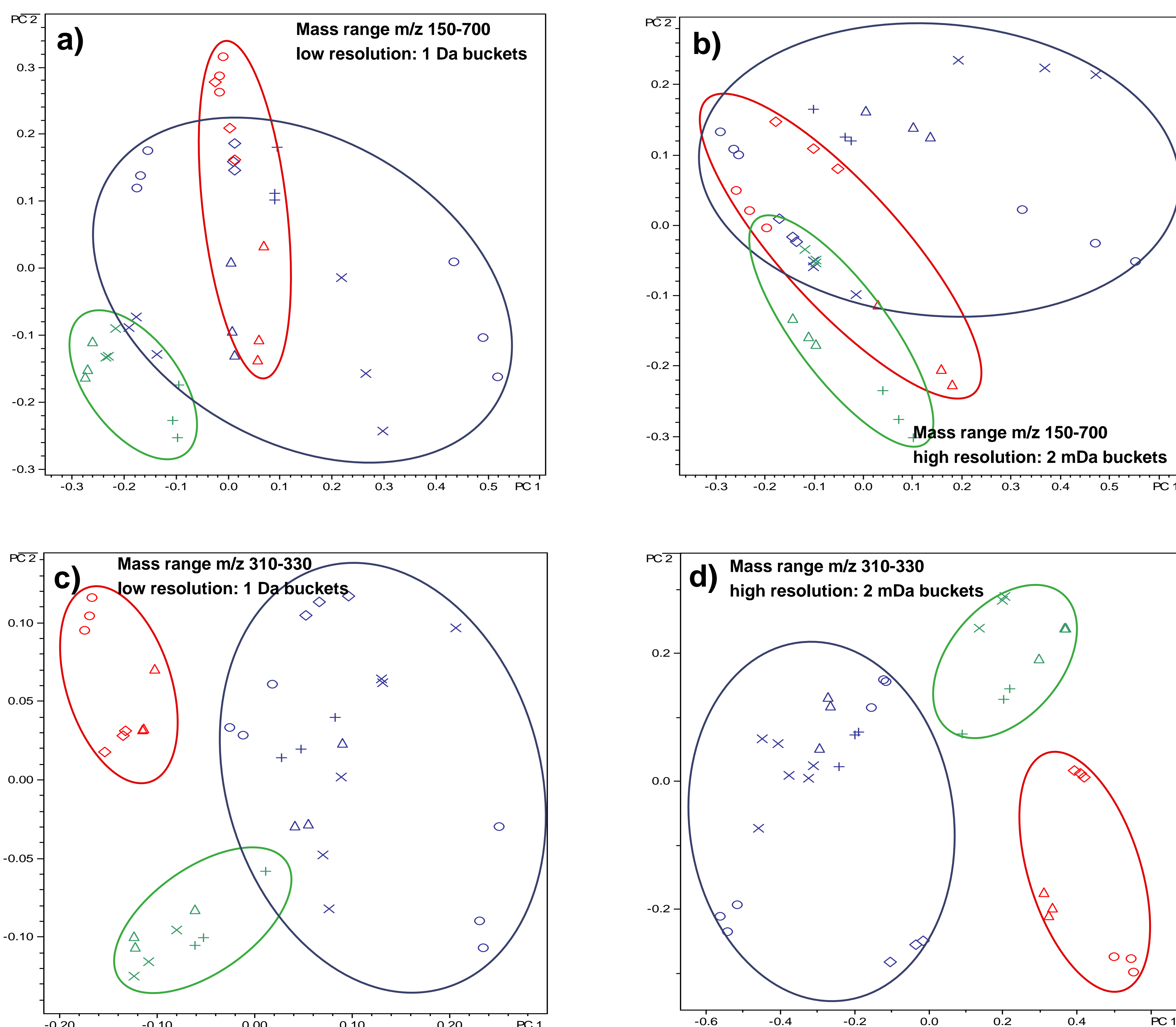


Figure 2. PCA score plots of whisky mass spectra: Analysis of a) full mass spectrum with 1 Da buckets, b) full mass spectrum with 2 mDa buckets using fine structure, c) mass range m/z 310-330 with 1 Da buckets and d) mass range m/z 310-330 with 2 mDa buckets using fine structure (origin market with different colours; red: Whisky from Spey, green: Japanese Whisky, blue: Whisky from Highland; repetitive measurements have the same symbol)

Results

Several Scottish whiskies from two different origins (Highland and Spey) as well as several whiskies from the Japanese distillery Suntory have been analyzed. Using electrospray ionization the most polar components of whisky are detected. Ellagic acid, a polyphenol present in fruits and vegetables with antiproliferative and antioxidant properties, and gluconic acid have been found as the most dominant species (Figure 1a). Beside major components, the mass spectra of whisky show a complex pattern with several peaks at one nominal mass resulting in several thousand peaks in a mass spectrum (Figure 1b). The molecular formulae of more than thousand compounds have been identified.

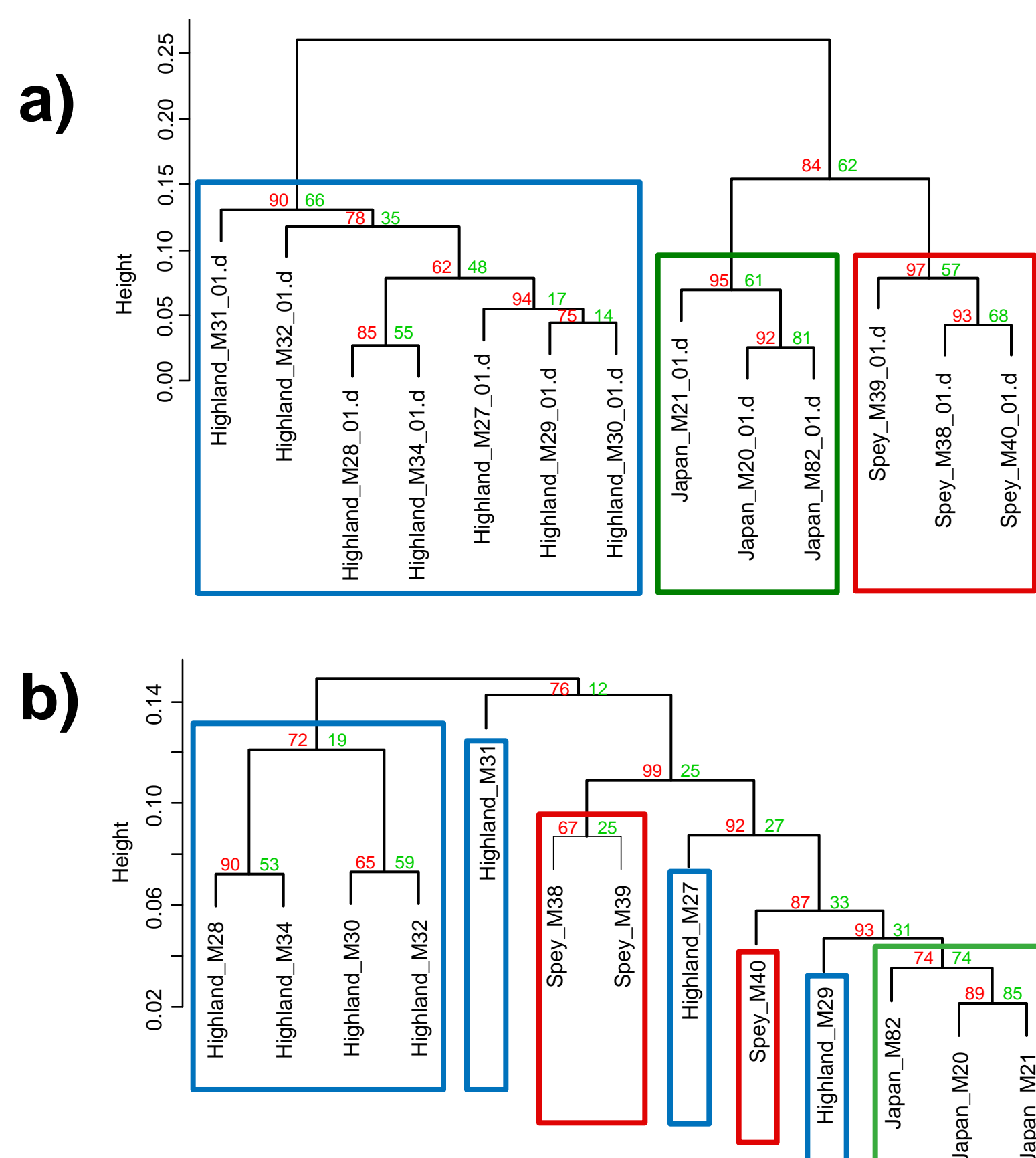


Figure 3. Cluster analysis: a) whiskies of the same origin have been correctly clustered using 2 mDa buckets in the mass range m/z 310-330. b) the three different origins of whiskies have been clustered using cluster analysis with the full mass spectrum and fine structure (2 mDa buckets)

PCA (Figure 2) as well as cluster analysis (Figure 3) have been carried out of the full and of a part of the mass spectra (m/z 310-330) with and without using the fine structure to validate the origin of the studied whiskies and to probe the relevance of the highly resolved mass spectra for the characterization of whisky. Whiskies of the same origin are in the same area of the PCA score plot and grouped in the cluster analysis using a mass spectrum area mainly of humic compounds. The fine structure improves the correct clustering based on the origin of the samples. Repetitive measurements in the PCA plot (identical colour and symbol) show the reproducibility of the measurements.

Summary

- The mass spectra of whisky are very complex even if only polar compounds are detected in electrospray negative ion mode.
- Using negative ion mode mainly $C_xH_yO_z$ compounds have been detected.
- Specific compounds can be allocated in whisky like ellagic acid or gluconic acid with accurate mass measurement.
- Using the fine structure of a mass spectrum area mainly consisting of humic compounds, the origin of unknown whiskies can be allocated using both statistical methods, PCA or cluster analysis.

Conclusions

ESI-FT-ICR-mass spectrometry has been proven as a powerful tool for the characterization of complex mixtures such as whisky.