METHOD FOR ANALYSIS OF VOLATILE CONSTITUENTS OF *WHISKEYS* USING GAS CHROMATOGRAPHY WITH FLAME IONISATION DETECTION

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Volatile compounds play an important role in the organoleptic characteristics of whiskeys. Several compounds from different chemical families, such as higher alcohols, ethyl esters, fatty acids and carbonyl compounds, contribute to whiskey flavour. Some of these volatile compounds are formed from the fermentation and distillation processes, while some others arising during the conservation and ageing period and quite a few are oak derived.

The analysis of volatile compounds is normally carried out by GC/MS after previous extraction and concentration steps. Several analytical methods such as liquid-liquid extraction (LLE), ultrasound extraction, supercritical fluid extraction, purge and cold trapping extraction, simultaneous distillation-solvent extraction and more recently solid-phase microextraction, have been applied to analyse volatile compounds. In spite of this great variety of analytical methods, LLE continues to be the reference technique for the extraction of volatile compounds from several samples including whiskeys samples.

Due to the importance and impact of volatile components on whiskey flavour, the present work proposes the development, validation and characterisation of a sensitive method for rapid and routine determination of these components. The method allows the recovery and quantification of the aroma constituents by dichloromethane extraction and concentration under a nitrogen

flow, followed by GC analysis with flame ionisation detection. Applications of this quantitative method to several commercial Famous Grouse whiskeys, are reported and enables to acquire the chemical profile and to quantitatively determine the concentration of the flavour volatiles in the selected whiskeys. The volatiles were identified by their retention time in a solution of a pure compound; by comparing mass spectra (Scan Mode) and retention times with those of standard references; and by comparing the Kováts indices and the mass spectra in the NIST library database. Multivariate analysis (PCA and SLDA) was used in order to study the main sources of variability present in the data sets and to establish relations between samples (objects) and volatile compounds (variables).

The method used allows a good recovery of volatile compounds and a rapid and easy quantification, with high sensitivity and repeatability, and good linearity with *r* values ranging from 0.9863 (phenoxyethanol) to 0.9996 (ethyl butirate). The LODs, based on three-times the base line noise, ranged from 0.7 mg l-1 for ethyl butirate to 12.5 mg l-1 for ethyl laurate. Characteristic profiles were determined for each whiskey and the flavour compounds were quantified using octan-3-ol and 4-methylpentan-2-ol as internal standards.

From the relative composition of the flavour volatiles of the whiskey it can be concluded that ***higher alcohols***, ***ethyl esters*** and ***fatty acids***, formed enzymatically during the fermentation process, are main chemical groups. From the higher alcohols, the *fusel oils* (propan-1-ol, 2-methylpropan-1-ol and 3-methylbutan-1-ol) are the most important ones. The isoamyl alcohols are the congener that was found in the highest concentration in all of the whiskey samples studied. The ethyl esters form an essential group of aroma components in whiskey, to which they confer a pleasant aroma, with “fruity” odours. Qualitatively the isoamyl acetate, with “banana” aroma, was the most interesting. Quantitatively significant components are ethyl esters of caprylic, capric and lauric acids. The highest concentrations of fatty acids were observed for caprylic and capric acids.

The authors gratefully acknowledge the Famous Grouse Company and the PrimeDrinks, S.A. for the supply of whiskey samples.