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Whisky analysis by electrospray ionization-Fourier transform mass spectrometry

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ABSTRACT

Electrospray ionization (ESI) coupled to ultra-high resolution and accuracy Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was employed for the direct analysis of whisky samples. No pre-separation or extraction steps were employed and, owing to the gentleness of ESI, characteristic profiles of polar constituents of authentic whiskies from five different brands were obtained, which greatly contrast to those of counterfeit samples. Owing to the accuracy of FT-ICR MS mass measurements, elemental composition of the main ions detected were also securely determined, and related to a series of carboxylic acids, phenols, saccharides, fat acids and sulfur or nitrogen constituents of whisky. The accurate mass measurements and the number of detected ions, together with the direct, no sample preparation procedure employed, make FT-ICR MS a highly reliable approach to fingerprint whisky and to control its quality, and to screen for aging, counterfeiting and adulteration at the molecular level.

1. Introduction

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is a powerful technique for complex mixture analysis due to its unsurpassed ability to determine chemical formulas with ultra high resolution and accuracy (better than 1 ppm) (Marshall et al., 2007). Due to its unique characteristics, FT-ICR MS is a powerful tool for resolving the elemental composition of large molecules and can be used in distinct applications.

The use of the gentle ESI technique or ambient ionization techniques (Corilo et al., 2010) also permit the detection of constituents in intact molecular forms, and when FT-ICR MS analysis is employed, direct characterization of very complex mixtures such as of crude oils can be directly performed without pre-separation methods. For crude oils, ESI FT-ICR MS have allowed unambiguous assignments of polar heteroatom-containing organic components of crude oils with 20,000 or more distinct elemental compositions (Rodgers, Schaub, & Marshall, 2005) and for wine around 30 compounds were identified employing negative-ion ESI FT-ICR analysis (Cooper & Marshall, 2001). Herein, we describe an investigation aimed at testing the use of ESI FT-ICR MS in the analysis of whisky samples.

Scotch whisky is a prime spirit drink and a leading category of choice between spirit consumers (Gordon, 2003). The Scotch whisky in UK is on the range of several billions of dollars (Rhodes, Heaton, Goodall, & Brereton, 2009) and whisky is one of the top export products of Scotland. Due to its large commercialization and relatively high prices, Scotch whisky counterfeiting and/or adulteration is quite common worldwide. Whisky contains a great variety of constituents from different chemical classes such as alcohols, ethyl and isoamyl esters, acetates, ketones, fatty acids, monoterpenes, and phenols. This variable chemical composition is mainly influenced by the cereals used in fermentation and by distillation, maturation and blending regimes. Some of these compounds originate from raw materials and during the production steps (mashing, fermentation and distillation), while others are related to the spirit maturation in oak casks. Whisky constituents can be present in a wide range of concentrations, with contrasting volatilities and polarities, being common in distinct whisky brands but differing considerably in relative quantities (Câmara et al., 2007).

Due to this complex chemical composition, whisky authenticity analysis normally requires sample extraction and pre-separation procedures. The most common strategy for establishing whisky brand authenticity is to determine the profile of volatile organic compounds (VOC congeners) such as acetaldehyde, methanol, ethyl acetate, propanol, isobutanol, diethyl acetal and the amyl alcohols: 2- and 3-methyl butanol (Aylott, Clyne, Fox, & Walker, 1994). Usually, VOC profiles of whisky are obtained via gas chromatography (GC) analysis (MacKenzie & Aylott, 2004; Nascimento, Cardoso, & Franco, 2008;

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Rhodes et al., 2009). However, spirit adulteration is becoming more sophisticated and sometimes counterfeit samples may display similar VOC profiles. GC coupled to isotope ratio mass spectrometry (GC/IRMS) has also been used to characterize whisky and to screen for adulteration (Parker, Kelly, Sharman, & Howie, 1998).

Direct mass spectrometry (MS) analysis has also been employed to characterize spirits and screen for adulteration and counterfeiting. We, for instance, have employed direct "unit-resolution" MS analysis with electrospray ionization (ESI-MS) for quality control of spirits, including the Brazilian cachaça (de Souza, Augusti, et al., 2007; de Souza, Siebald, et al., 2007; de Souza et al., 2009), wine (Catharino et al., 2006), beer (Araujo et al., 2005) and whisky (Moller, Catharino, & Eberlin, 2005).

2. Experimental details

2.1. Whisky samples

A total of 80 samples, divided into two groups (50 authentic and 30 counterfeit) were used. The authentic whiskies include Scotch whiskies from different brands: Johnnie Walker Red Label (n = 10), Johnnie Walker Black Label (n = 12), White Horse (n = 12), Buchanan's (n = 6) and J&B (n = 10). Counterfeit samples (n = 30) from different whisky "brands" were also analyzed. The counterfeit street samples were provided by the Brazilian Federal Police.

2.2. ESI FT-ICR MS analysis

Samples were analyzed using a hybrid 9-T Fourier transform ion cyclotron resonance mass spectrometer (LTQ FT; Thermo Scientific, Bremen, Germany) equipped with a chip-based direct infusion nanoelectrospray ionization source (Triversa; Advion Biosciences, Ithaca, NY, USA). Nanoelectrospray conditions comprised a flow rate of 200 nL/min, backing pressure of ca. 0.3 psi, and electrospray voltages of 1.5 to 2.0 kV during 120 s, controlled by ChipSoft software (version 8.1.0, Advion Biosciences, Ithaca, NY, USA). Mass resolution was fixed at 200,000 at *m/z* 400. Data were obtained as transient files (scans recorded in the time domain).

All the samples were evaluated in negative ESI(−) and positive ESI(+) ion modes and spectra were acquired in the *m/z* 100–800 range. For ESI(+), the samples were analyzed directly (without any sample treatment or dilution); for ESI(−), samples were diluted 1:1 (v/v) using a solution containing methanol (Mallinckrodt Baker, Phillipsburg, NJ, USA) and 0.1% (v/v) NH_4OH (Mallinckrodt Baker, Phillipsburg, NJ, USA).

The spectra were processed by the Xcalibur Analysis software package (version 2.0, Service Release 2, Thermo Electron Corporation).

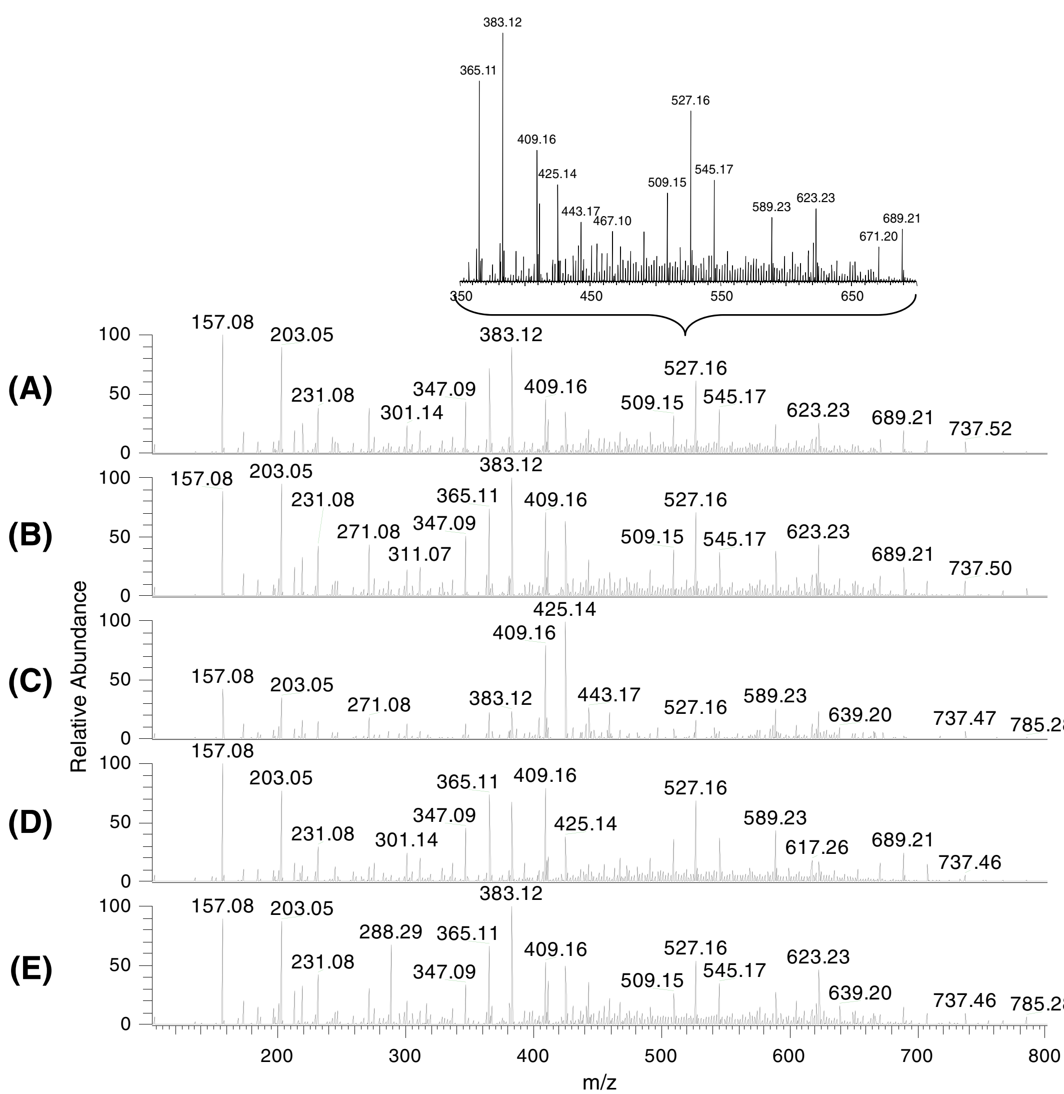

Fig. 1. Representative ESI(+) FT-ICR MS of five distinct Scotch whisky brands: (A) Johnnie Walker Red Label, (B) Johnnie Walker Black Label, (C) J&B, (D) White Horse and (E) Buchanan's.