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A Brief History of Whiskey Adulteration and the Role of Spectroscopy Combined With Chemometrics in the Detection of Modern Whiskey Fraud

Mary Deasy

Technological University Dublin, mary.deasy@tudublin.ie

Aoife C. Power

Technological University Dublin, aoife.power@tudublin.ie

Sinead Currivan

Technological University Dublin, sinead.currivan@tudublin.ie

See next page for additional authors

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Authors

Mary Deasy, Aoife C. Power, Sinead Currivan, Sive Geoghegan, and Daniel Cozzolino

1 Review

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3 *A brief history of whiskey adulteration and the role of*
4 *spectroscopy combined with chemometrics in the detection of*
5 *modern whiskey fraud*

6 **A.C. Power 1; C. Ní Néill 2; S. Geoghegan 3; S. Currvivan 1 M. Deasy 3,4; D. Cozzolino 5**

7 1 CREST, Technology Gateway of TU Dublin, Dublin, Ireland

8 2 School of Chemical and Pharmaceutical Sciences, TU Dublin, Dublin, Ireland

9 3 MiCRA – Biodiagnostics, Technology Gateway of TU Dublin, Dublin, Ireland

10 4 Centre of Applied Science for Health, TU Dublin, Dublin, Ireland

11 5 Centre for Nutrition and Food Sciences, Queensland Alliance for Agriculture and Food Innovation
12 (QAAFI), The University of Queensland, Brisbane, Queensland 4072, Australia

13

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15 **Abstract:** Food fraud and adulteration is a major concern in terms of economic and public health.
16 Multivariate methods combined with spectroscopic techniques have shown promise as a novel
17 analytical strategy for addressing issues related to food fraud that cannot be solved by the analysis
18 of one variable, particularly in complex matrices such distilled beverages. This review describes
19 and discusses different aspects of whisky production, and recent developments of laboratory, in
20 field and high throughput analysis. In particular, recent applications detailing the use of
21 vibrational spectroscopy techniques combined with data analytical methods used to not only
22 distinguish between brand and origin of whisky but to also detect adulteration are presented.

23 **Keywords:** whisky; fraud; chemometrics; spectroscopy

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25

26 **Introduction**

27 Whisky is a distilled alcoholic beverage produced from fermented grain mash where various
28 grains are used for different varieties (e.g. barley, corn, rye, and wheat). This alcoholic beverage is
29 generally classified by their country of origin, the nature of the grain, storage conditions and the type
30 of blends. The production of this type of alcoholic beverages was first reported in Ireland in the
31 *Annals of Clonmacnoise* from 1405 whereas in Scotland the early records dates from 1494 [1, 2]. Irish
32 and Scotch remain the two main European whiskies to this day. Other major producers include the
33 United States, Canada and Japan.

34 This review describes and discusses different aspects of whisky production, and the recent
35 development of laboratory, in field and high throughput analysis. In particular, recent applications
36 detailing the use of vibrational spectroscopy techniques combined with data analytical methods used
37 to distinguish between brand and origin of whisky as well as to detect adulteration are presented.

38 **History, origin and economic impact**

39 Whisky is legally defined under European Community Council (ECC) regulation no. 1576/89 [3]. The
40 regulation first defines a spirit drink (Article 2) as an alcoholic beverage that is (a) *intended for human*
41 *consumption; (b) possessing particular organoleptic qualities; and (c) having a minimum alcoholic strength of*
42 *15% vol and contains a distillate of a naturally fermented agricultural product. None of the alcohol contained*

43 *in a spirit drink shall be of synthetic or non-agricultural origin [Article 3(4)]. The nature of the raw material*
44 *that may be considered agricultural in origin is contained in the Treaty on the Functioning of the European*
45 *Union (TFEU) in Annex I [4].*

46 Within this definition Scotch and Irish whiskeys are further circumscribed, as they are both internationally
47 recognised by Geographic Indication [2, 3]. According to the European Union (EU) definition [Article
48 4, Annex II] [4] (a) Whisky or whiskey is a *spirit drink produced exclusively by (i) distillation of a mash*
49 *made from malted cereals with or without whole grains of other cereals, which has been: – saccharified by the*
50 *diastase of the malt contained therein, with or without other natural enzymes, – fermented by the action of*
51 *yeast; (ii) one or more distillations at less than 94.8% vol., so that the distillate has an aroma and taste derived*
52 *from the raw materials used, (iii) maturation of the final distillate for at least three years in wooden casks not*
53 *exceeding 700 L capacity. The final distillate, to which only water and plain caramel (for colouring) may be*
54 *added, retains its colour, aroma and taste derived from the production process referred to in points (i), (ii) and*
55 *(iii). (b) The minimum alcoholic strength by volume of whisky or whiskey shall be 40%. (c) No addition of*
56 *alcohol as defined in Annex I(5)4, diluted or not, shall take place.—(d) Whisky or whiskey shall not be*
57 *sweetened or flavoured, nor contain any additives other than plain caramel used for colouring.*

58 Thus ‘Scotch whisky’ must be produced and matured in oak casks for a minimum of three years
59 in Scottish distilleries from one of five designated regions Speyside, Highlands, Lowlands, Islay &
60 Campbeltown [5-7]. Since 2005, the Scotch whisky definition was refined to include five distinct
61 categories, determined by its production process in the whiskey industry; (I) Single Malt (SM) Scotch
62 Whisky - distilled at a single distillery (i) from water and malted barley without the addition of any
63 other cereals, and (ii) by batch distillation in pot stills; (II) Single Grain (SG) Scotch Whisky - distilled
64 at a single distillery (i) from water and malted barley with or without whole grains of other malted
65 or unmalted cereals, and (ii) which does not comply with the definition of SM.; (III) Blended, a blend
66 of one or more SMs with one or more SGs; (IV) Blended Malt (BM) Scotch Whisky, a blend of SMs
67 distilled at more than one distillery; and (V) Blended Grain (BG) Scotch Whisky a blend of SGs
68 distilled at more than one distillery [6-8]. The bulk of the Scotch whisky is blended from 60% to 70%
69 grain whisky and 30 to 40% malt whiskies. This blended whisky usually contains up to 40
70 individual malts which are blended to produce a consistent brand flavour. Every component of the
71 blend must be matured for the minimum period or the specified date indicated on the bottle [5-8].

72 Irish whisky on the other hand is produced from either malted barley or a mixture of malted
73 and un-malted other cereals and barley of which a minimum of 25% must consist of malted barley.
74 The combination of the use of partially malted barley and a specialised processing approach. This
75 involves the drying of the malt in closed kilns rather than over open peat fires and the application of
76 a triple distillation process, the first of which produces ‘low wines’ a pot still distillate, which is re-
77 distilled in another pot still to produce ‘feints’, before being placed in a Coffey still for the final
78 distillation. It is this production process that gives Irish whiskeys their smooth and natural flavour.
79 It is unique [2, 6, 9, 10] particularly in comparison to whiskies from other regions.

80 American whisky developed under an alternative legislative framework [9, 11, 12], US whisky
81 is broadly defined as the distillate of a fermented grain mash at less than 95% alcohol. Consequently,
82 US whisky consist of a broader range of distinct products in comparison to the Irish and Scotch spirits.
83 There are six major types, rye, rye malt, pure malt, wheat, Bourbon and corn, all of which are
84 produced from a different type of cereal grain. The exact type of grain and its required percentage
85 (not less than 51%) in the mash used to produce the whiskey product are governed by Title 27 of the
86 U.S. Code of Federal Regulations [11, 12]. All US whisky must also conform to additional standards
87 outlined by title 27 of the U.S. Code of Federal Regulations, and so they must be distilled to not
88 more than 80% alcohol by volume, to ensure the proper flavour profile; producers are prohibited
89 from adding any colourings, caramel or flavour additives and finally, all of these whiskies (with the
90 exception of corn whisky) must be aged in charred new oak container. There is no minimum period
91 of aging specified, which creates opportunities for distilleries to differentiate their product based on
92 the aging process. One such distinction is a ‘straight whisky’. For a given whisky to be designated
93 thus, it should not be blended with any other spirit, be no more than 80% alcohol by volume and
94 aged for a minimum of two years [2, 11, 12]. There are several other types of American whisky,

95 which do not specify a dominant grain. These include Blended Whisky, a Blend of Straight Whisky,
 96 Light Whisky (one which has been distilled at greater than 80% alcohol by volume) and Spirit Whisky
 97 (where a 'neutral spirit', a non-flavoured *alcohol* of 95% is mixed with at least 5 percent of a
 98 particular type of whisky).

99 Commercial distilleries began producing scotch in the late 18th century, despite its first being
 100 recorded in the 1492 Exchequer Rolls of Scotland. As of 2018, the Scottish Parliament recognised 245
 101 distilling related businesses. The Distillers Company (DCL) is a dominant player in the industry
 102 since the "Big Amalgamation" the merger of the 'Big Five' brewing houses Buchanan, Dewar, Walker,
 103 Haig, and Mackie in 1925 [6-8, 12, 13].

104 American Whisky was first produced in the states of Virginia, Maryland and Pennsylvania in
 105 eastern United States around late 18th century and was originally a predominately rye-based spirit.
 106 Early distillers were often farmers who produced and distributed whiskey as a supplementary
 107 income. In 1791, Alexander Hamilton, the U.S. Secretary of the Treasury, in an effort to generate
 108 revenue, established a 25% tax on whiskey distillers. The majority of distillers operated small
 109 production facilities and the federal tax was greatly opposed. This opposition became known as "The
 110 Whisky Rebellion" when it was necessary for the federal government to send troops to enforce the
 111 tax [14]. This resulted in a larger number of producers relocating West, most notably to Kentucky.
 112 Over time, the number of states producing whiskey increased, including Tennessee which produced
 113 the famous Jack Daniel's brand. America's whisky industry suffered repeated setbacks, including a
 114 13-year Prohibition on alcohol between 1922 and 1933, which barred production of all alcohol; the
 115 supporters of prohibition saw alcohol as a major catalyst for the ills experienced in the society. By the
 116 1933, however, it became apparent that prohibition was going to remain a noble experiment. The
 117 popularity of whiskey grew reaching its heyday in the 1950s in the U.S. before falling out of favour.
 118 Today, whisky popularity is resurging as established brands such as Jack Daniel's and Jim Beam offer
 119 single-barrel whisky aimed at connoisseurs and new distilleries are appearing annually [11, 14, 15].

120 Conversely, the number of Irish distilleries remains limited compared to the number producing
 121 scotch and American whiskies. Prior to the 1900s Irish whisky led the world's spirits trade until a
 122 perfect storm of the newly formed Irish Republic's national politics, the American prohibition, and
 123 technology decimated the industries producers. At the turn of the last century the Irish whiskey
 124 industry was at its pinnacle, with 88 licensed distilleries producing an estimated 12 million cases
 125 primarily for export. This coupled with the impact of the Irish War of Independence and Civil War
 126 and the fledgling Irish State's economic policies debilitated the industry. Arguably however, far
 127 more devastating was the reluctance of Irish whisky producers to adopt and capitalise on the
 128 invention of the column still, which allowed for the easier production of palatable spirits which
 129 Scottish distillers producing whisky blends incorporated readily. This ultimately handed an
 130 overwhelming advantage to Scottish whisky producers [16, 17]. By the 1930s there were only five
 131 active Irish distilleries, Old Bushmills, Jameson, John Powers, Cork (Paddy) and Tullamore Dew. In
 132 1966, all bar Old Bushmills combined to constitute the Middleton centre in Cork. In 2007 there were
 133 only four distilleries – Old Bushmills, Middleton, Cooley and Kilbeggan in operation [1, 9, 10]. By
 134 the end of 2019 there were 56 revenue registered Irish Whiskey Producers in Ireland (Table 1).

Table 1: List of Revenue registered Irish Whiskey producers in Ireland (2019)

1. Admiralford Ltd., 113-119 IDA Industrial Estate, Waterford

2. All Technology Ireland Ltd., Pearse Lyons Distillery, James Street, Dublin 8.

3. Ballykeefe Distillery, Kyle, Cuffsgrange, Co. Kilkenny.

4. Blackwater Distillery, Church Road, Ballyduff, Co. Waterford.

5. Clonakilty Distillery Ltd., Dunowen Farm, Ardfield, Clonakilty, Co. Cork.

6. Clonakilty Distillery Ltd., The Waterfront, Clonakilty, Co. Cork.

7. Cooley Distillery, Riverstown, Dundalk, Co. Louth.

8. Copeland Distillery, 43 Manor Street, Donaghadee, Co Down, BT210HG.

9. Dingle Distillery, Ballinaboula, Dingle, Co. Kerry.

10. Dingle Distillery, The Old Mill, Dingle, Co. Kerry.

11. Drioglann Shliabh Liag, Line Road, Carrick, Co. Donegal.

12. Dublin Liberties Distillery, 33 Millstreet, Dublin 8.

13. Great Northern Distillery, BAK Bulk Services, RED Barnes, Drumcar Road, Dunleer, Co. Louth.

14. Great Northern Distillery, Carrick Road, Dundalk, Co. Louth.

15. Great northern Distillery, Christianstown, Readypenny, Co. Louth.

16. Great Northern Distillery, Cliven, Rathescar, Co. Louth.

17. Great Northern Distillery, Oberstown, Ardee, Co. Louth.

18. Great Northern Distillery, Rathlust, Ardee, Co. Louth.

19. Great Northern Distillery, Snie Hill, Ardee, Co. Louth.

20. Great Northern Distillery, Tullamore, Co. Offaly.

21. Hanlon Transport Ltd., Greenore Ind. Est., Dundalk, Co. Louth.

22. Hazlewood Demesne Ltd., Hazlewood House, Hazlewood Avenue, Sligo.

23. Irish Distillers, Midleton Distillery, Midleton, Co. Cork.

24. Irish Distillers, Robinhood Road, Clondalkin, Dublin 22.

25. Kilbeggan Distillery, Main Street, Kilbeggan, Co. Westmeath.

26. Killowen Distillery Ltd., 29 Kilfeagan Road, Rostrevor, Co. Down, BT3434W.

27. Lambay Irish Whiskey, Lambay Island, Malahide, Co. Dublin.

28. Liam Connaughton & Sons, Grand Canal Quay, Dublin 2.

29. Niche Drinks Company Ltd., 10 Rosstown Road, Londonderry, BT476NS.

30. O'Connell Heritage Ltd., Lakeview House, Fossa, Killarney, Co. Kerry.

31. P.J. Rigney Distillery, The Food Hub, Drumshambo, Co. Leitrim.

32. Piranha Beverages Ltd., 3 Turvey Business Park, Turvey, Donabate, Co. Dublin.

33. Powerscourt Distillery Ltd., Powerscourt Estate, Enniskerry, co. Wicklow.

34. PRL Group Logistics, Chancellors Mills, Talbots Inch, Freshford Road, Kilkenny.

35. PRL Group Logistics, Talbots Inch, Freshford Road, Kilkenny.

36. R & A Bailey, Western Estate, Nangor Road, Dublin 12.

37. Rademon Estate Distillery Ltd., The Distillery, Rademon Estate, Ballynahinch Road, Co. Clare.

38. Renegades Waterford Distillery, 9 Mary Street, Waterford.

39. Rober A Merry & Co. Ltd., Cashel Road, Clonmel, Co. Tipperary.

40. Roe & Coe Distillery, St. James Gate, Dublin 8.

41. Roe & Coe, Visitor Experience Centre, St. James Gate, Dublin 8.

42. Royal Oak Distillery Ltd., Royal Oak, Co. Carlow.

43. Slane Castle Whiskey Ltd., Slane Castle Distillery, Slane, Co. Meath.

44. Stafford Bonded Warehousing Ltd., Killasem, Ballygarran, Co. Waterford.

45. Stafford Wholesale Ltd., Sinnottstown Lane, Drenagh, Co. Wexford.

46. Stafford Wholesale Ltd., Waterford Airport Business Pk, Ballygarran, Co. Waterford.

47. Teeling Whiskey, 13-17 Newmarket, Dublin 8.

48. Terra Spirits & Liqueurs, Baileboro, Co. Cavan.

49. The Chapel Gate Irish Whiskey Co., Gowerhass, Cooraclare, Co. Clare.

50. The Connacht Whiskey Co. Ltd., Beeleek, Ballina, Co. Mayo.

51. The Echlinville Distillery, 62 Cransha Road, Kircubbin, Newtownards, BT221AJ.

52. The Old Bushmills Distillery, Jameson Distillery, Bow Street, Dublin 7.

53. Watercourse Distillery, The Jameson Experience, Middleton, Co. Cork.

54. West Cork Distillers Ltd., Market Street, Skibbereen, Co. Cork.

55. West Cork Distillers Ltd., Marsh Road, Skibbereen, Co. Cork.

56. William Grant & Sons, Tullamore Distillery, Clonminch, Tullamore

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The global whisky market size was valued at USD \$57.96 billion in 2018 and it is projected to reach USD \$89.60 billion by 2025. This growth is driven by multiple factors, including, increasing disposable income, consumer preferences and changing lifestyles [15, 18-20]. Scotland's brewing and distilling sectors play a vital role in the Scottish economy, and in 2019 the spirits industry

140 contributed approximately 3% to total Scottish GDP. Moreover, since 2000 the spirits/distilling
141 sector has contributed an average of 2.8% with a high of 3.3% in 2013 to total GDP [19].

142 In 2018, the US spirits industry gained market share over beer and wine, with sales rising seven-
143 tenths of a point to 37.4% of the total beverage alcohol market. This was the ninth straight year of
144 record spirits sales and volumes, reflecting continued market share gains. Supplier sales were up
145 over 5.1%, rising from USD \$1.3 billion to a total of USD \$27.5 billion [20].

146 In 2019, Ireland's total agri-food sector exports amounted to €14.5 billion, with the food and
147 beverages sector accounting for 21% of all industrial turnover and 23% of all manufacturing industry
148 turnover. This represents a 67% increase in export values compared to 2010. International exports
149 account for 31% and makes Ireland's Food and Drink industry the most global indigenous industry
150 exporting to 180 markets worldwide [18]. Growth in Irish alcohol exports grew 8% in 2019 (€1.45bn)
151 with Irish Whisky accounting for 50% of the €137m in beverage export growth. In 2019, Irish whisky
152 exports increased 11% from the previous year contributing to an overall value of €727m, accounting
153 for an overall climb of 370% between 2010 and 2019. Domestically, this growth is underpinned by
154 new distillery openings and increased development of whisky heritage tourism [18].

155 Brand recognition is central to whisky global market growth, following a trend of 'drink less but
156 better'. As imitations are often a response to increased demand, the growing global market for whisky
157 has sparked concerns within the Industry that counterfeit and adulterated products may infringe on
158 laws governing labelling and sales [12, 21-24]. The International Chamber of Commerce's 2017
159 report titled 'The Economic Impacts of Counterfeiting and Piracy' estimates that the global economic
160 value of counterfeiting and piracy costs could hit USD \$1.9 trillion by 2022. This, combined with the
161 additional negative impacts of counterfeiting and piracy such as displaced economic activity,
162 investment and public fiscal losses, the overall impact on the economy would be an estimated loss of
163 USD \$4.2 trillion from the global economy, while also endangering 5.4 million legitimate jobs in the
164 sector [25].

165 **Adulteration, fraud and public safety**

166 The rebranding of lower quality commercial whiskeys as top-shelf products can significantly
167 damage a producer's reputation and bottom line. In 2018 the BBC [26] and other media outlets [27,
168 28] reported that a third of commercial Scotch whiskies tested were fraudulent. Of greater concern
169 is the potential risk to consumers and their health [29-35]. Such incidences as the 'Czech Republic
170 methanol poisonings' of September 2012, where 38 people in the Czech Republic and 4 people in
171 Poland died as a result of methanol tainted bootleg spirits [34]. Several poisoning incidents were
172 reported in Iran with the poisoning of 768 people (including 96 deaths) by illicit and non-standard
173 alcoholic beverages; 62 people (11 fatalities) were poisoned with methanol laced counterfeit spirits in
174 Shiraz in 2004 and 694 (6 deaths) and poisonings recorded in Rafsanjan, Iran in 2013 [31]. More
175 recently toxic moonshine was reported to have killed 154 people in India in two separate incidents in
176 2019 [36]. In March 2020, Iranian media reported that nearly 300 people have been killed and more
177 than 1,000 sickened by drinking methanol laced bootlegged spirits, in the mistaken belief that it was
178 effective against Covid-19 [37].

179 Other dangers to public health from the illicit production of spirits include the addition of
180 industrial alcohol, the presence of chemicals used to denature industrial alcohol and the resultant
181 contamination (e.g. ethyl acetate, which can cause irritation of the digestive tract) [38]. Ingestion of
182 toxic concentrations of some of these chemicals can result in pronounced acidosis accompanied by
183 cardiovascular shock and cause central nervous depression. Lower volumes of such adulterants can
184 cause headache, nausea, fatigue, and dizziness.

185 High levels of chloroform are also often detected in illegally produced alcoholic products [39],
186 most likely as a result of counterfeiters adding hypochlorite to the fake spirits in an attempt to remove
187 denatonium benzoate, a widely used denaturant with a characteristic bitter taste, from denatured
188 alcohol, via the addition of hypochlorite [40]. Ingestion of chloroform can result in damage to the
189 central nervous system (brain), liver, and kidneys of unwitting consumers [41].

190 An additional danger to the public is the leaching of toxins from the improvised illegal
 191 distillation tools utilised by counterfeiters, particularly as the illicit stills and other production
 192 materials are often unfit to come into contact with food products. Genuine producers carry out testing
 193 to ensure that there is no unwanted contamination from beverage contact materials. Illegal
 194 producers are either unaware or indifferent to the potential of harmful toxins may be present in their
 195 illegal product. This was highlighted in a new report by Lachenmeier [42], which showed that a
 196 large number of fruit spirits in the Slovak Republic and Hungary were contaminated with the heavy
 197 metal elements lead and cadmium.

198 Consequently, fraud, particularly in the distilling sector is causing increasing levels of concern.
 199 It is an incredibly lucrative business, with perpetrators profiteering at comparatively lower risk as
 200 the legal repercussions are much more lenient than those for other illegal activities, such as drug
 201 trafficking [21-23, 30, 35, 43, 44]. It is apparent that without a proper verification technique that
 202 derives from the beverage itself rather than some externally affixed marker or associated paperwork
 203 (e.g. blockchain), the system will always be vulnerable to the inclusion of illegal or otherwise non-
 204 compliant material [45-48].

205 In order to assess the composition and identity of the beverage directly, the development of
 206 rapid and non-destructive analysis methods are critical for the future of the whisky industry. In
 207 addition, methods to verify the compliance of producer declarations regarding origin and source, as
 208 defined and requested by quality assurance standards in the production value chain will be of benefit.
 209 The current trend in analysis (as well as in all fields of research in food fraud) is towards fast, simple
 210 and reliable analytical techniques with the potential to partly or fully replace the complex and
 211 expensive reference methods that dominate the landscape [49-55]. The traditional chromatographic
 212 based techniques are expensive, time consuming and require highly trained operators.

213 In order to preserve and protect the premium status of its merchandise the global whisky
 214 industry must assure product safety and quality. This requires not only continuous monitoring, ~~and~~
 215 but also the development of analytical systems aimed at safeguarding consumer confidence in
 216 whisky and related spirit drinks. Therefore, significant research on flavour and quality, consumer
 217 safety and anti-counterfeiting/authenticity is now being carried out. Moreover, in recent years there
 218 has been an observable effort by researchers and stakeholders within the industry to develop new
 219 technologies and processes aimed at anti-counterfeiting and authenticity checking, supported by
 220 initiatives like the pan-European food integrity project [56]. Key to this effort is the development of
 221 sensors and rapid methods for the analysis of suspect products, particularly those that are field-
 222 portable and can be used at point-of-sale or distribution [44, 53, 57].

223 Standard methods of analysis

224 The authentication of spirit and alcoholic beverages, and the detection of counterfeits is an
 225 arduous task. Their chemical profiles are dominated by two major constituents, ethanol and water,
 226 which can often mask adulterants or other constituents present in the liquid product. This has
 227 required exhaustive method developments in the area of beverage analysis to date, to ensure that
 228 trace levels of adulterant constituents can be well separated from the dominant ethanol and water to
 229 allow for their characterisation and quantitation. Analysts rely on other flavour providing
 230 compounds, generally at trace concentrations (ppm and ppb) to definitively identify and differentiate
 231 between samples. However, the cost of such analysis is high, as state of the art, highly selective and
 232 sensitive instrumentation is required. Moreover, exceptionally skilled staff are required to maintain
 233 the instrumentation, conduct the analysis; and develop and optimise testing protocols.

234 A variety of these analytical methods that are currently employed to ensure the safety, quality
 235 and authenticity of spirits are summarised in **Table 21**. These methods are utilised to ensure that a
 236 given sample is consistent with the production requirements legislated by either the EU, Commission
 237 Regulation (EC) No 2870/2000 [58, 59], or the AOAC International Official Methods of Analysis [60]
 238 mandated by the United States Alcohol and Tobacco Tax and Trade Bureau.

Table 21: Standard analytical methods utilised and their application [58-60]

Analytical technique	Indicative data or analyte	Authenticity issue / information
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Densitometry	Alcohol Strength (not suitable for spirits with significant levels of dissolved solids e.g. sugars)	Dilution
Distillation and Densitometry	Alcohol Strength	Dilution
Gas Chromatography with flame ionisation detector (GC-FID)	Major -Volatile <u>Compounds</u> congeners	Category and brand discrimination
GC-FID	Denaturants (Methanol, isopropanol, methyl ethyl ketone etc.)	Detection of non-potable alcohol
UV-Vis Spectroscopy (UV-Vis)	Spectroscopic profile	Brand discrimination
Ultra-High-Performance Liquid Chromatography - UV-Vis (UHPLC-UV)	Maturation Congeners	Category discrimination, lack of maturation, addition of flavouring
pH	pH	Lack of maturation
Atomic Absorption Spectroscopy (AAS)	Trace Metals	Brand Discrimination
Ion Chromatography (IC)	Trace Metals	Brand Discrimination
Inductively coupled plasma - optical emission spectrometry (ICP-OES)	Trace Metals	Brand Discrimination
Inductively coupled plasma - Mass Spectrometry (ICP-MS)	Trace Metals	Brand Discrimination
Ion Chromatography-Pulsed Amperometry Detection (IC-PAD)	Sugars	Addition of sweetening
Ultra-High-Performance Liquid Chromatography – Reflective Index Detection (UHPLC-RI)	Sugars	Addition of sweetening, brand discrimination
Gas Chromatography - Mass Spectrometry (GC-MS)	Flavourings, Denaturants, Fingerprinting	Brand discrimination, addition of flavourings, detection of non-potable alcohol
Liquid Chromatography - Mass Spectrometry (LC-MS)	Flavourings, Denaturants, Fingerprinting	Brand discrimination, addition of flavourings, detection of non-potable alcohol
Nuclear Magnetic Resonance spectroscopy (NMR)	Ethanol	Botanical origin of ethanol, detection of synthetic alcohol
¹⁴ C dating by Liquid Scintillation Counting or Accelerator Mass Spectrometry	Ethanol	Date of production

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The alcohol content of a whisky is measured to ensure that quality standards are met and to ensure product integrity. Its measurement is also necessary since there is a minimum alcohol strength requirement in the legislation which genuine products must meet consequently a strong indication of counterfeit products. If the alcohol content of the sample falls below the minimum

244 alcohol strength limit and/or a definitive difference between the measured alcoholic strength and the
245 stated label value is often an indication of some manipulation of the original product. The accepted
246 reference methods associated with alcoholic strength exploit the liquids density. Gas
247 chromatographic (GC) methods coupled with a variety of detectors are utilised to monitor most of
248 the major volatile congeners and denaturants present in alcoholic beverages. These include but not
249 only limited to acetaldehyde and ethanal, 1-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-
250 methyl-1-butanol and 3-methyl-1-butanol, ethyl acetate and methanol. Similarly, GC-MS and LC-MS
251 are useful for the detection and quantification of both volatile and non-volatile flavouring additive
252 compounds.

253 Counterfeiters commonly add sugars fraudulent products in an attempt to improve their taste
254 and mimic the natural sweetness of a genuine product. However, the sugar profile of a suspect
255 material will differ significantly to that of a genuine product. For example, genuine Scotch whisky
256 products contain considerably less sucrose than glucose and fructose. Chromatographic methods
257 such as UHPLC-RI, IC and IC-PAD are utilised to measure trace levels of individual sugars present
258 naturally in certain spirits in order to define appropriate sugar profiles which can be later utilised to
259 detect adulteration.

260 Current trends within the industry are focused on the potential of testing not only during the
261 production process but at multiple key points in the supply chain. This has prompted research in
262 the application of alternative analysis approaches with an emphasis on field based rapid, portable,
263 user – friendly (i.e. for the non- specialist) options.

264 **Spectroscopic methods and the use of chemometrics**

265 Spectroscopy techniques have shown considerable promise in the fight against counterfeit and
266 fraud, as they are non-destructive, non-invasive and possess unique analytical capabilities, the
267 development of a materials chemical 'fingerprint'. Their usefulness is further enhanced by the
268 development of chemometric or multivariate analysis methodologies which allow the rapid
269 identification and classification of similar samples using their molecular properties (e.g. fingerprint)
270 [61-64].

271 Spectroscopy methods and techniques are often the preferred analytical approach for the
272 qualitative and quantitative characterisation of chemical mixtures, as a large amount of data can be
273 generated in a rapid and non-invasive manner. However, interpreting the data to form a clear and
274 concise conclusion from such analysis is not always straightforward. The use of certain techniques,
275 like UV-VIS spectroscopy can lead to spectral response overlaps with overlaps with other
276 components in the whisky, which has very many trace components that can carry over from the
277 malts/grains in the distillation process. These can inhibit the determination of an individual
278 component (or adulterant) concentrations in the sample being tested. Therefore, the precision and
279 accuracy of identification can be challenging because of the similarity of many spectral responses
280 [65]. Consequently, analysts will often apply a work around, which might include the addition of a
281 component to interact with the adulterant you wish to identify so that its response can be well
282 separated out and measured. However, the majority of spectroscopic 'fixes' or sample pre-treatments,
283 to aid in the extraction of results from the spectral data work less well than is ideal. That being said,
284 there is a considerable wealth of "information" gathered in a spectral scan that is not used for
285 identification or measurement. Scientists have begun to look at this unused data to determine if
286 some data points can be used to elicit different patterns that could be used to verify the measurements
287 of similar species better and without the need for a second type of confirmation test to be conducted.
288 This type of forensic investigation of all of the spectral data is commonly referred to as a chemometric
289 study. It relies heavily on the use of mathematics and statistics in interpreting the data to provide
290 definitive results. While chemometrics was first mooted back in 1995, it took almost twenty years for
291 spectroscopic instrumentation to be fitted with effective and reproducible software tools to allow
292 researchers to incorporate chemometrics into the processing of their spectral data to give absolute
293 verifiable identification and quantitation of chemical components that would otherwise have been
294 missed [66-68].

295 The combination of scientific analysis with software tools underpinned by mathematical systems
 296 is of enormous use to those companies trying to track fraudulent products. It is timely now that as
 297 the number of whisky producers is on the increase that adulterant measurement and analysis has
 298 become more robust. The integration of chemometrics with spectroscopy allows the analyst to better
 299 mine the data and extract relevant information for the generation of more confidence in a specific
 300 result. While chemometric software can certainly add more certainty to analysis results it is still
 301 challenging where one is trying to measure whether a single or small amount of an adulterant is
 302 present or not in a sample that already has many components present natural. Food and beverages
 303 are examples of such complex samples, and the data may have to be analysed at different spectral
 304 wavelengths or channels to be of use. The data generated often has a high number of correlations
 305 from one measurement channel to the next and from one chemical species to the next over those same
 306 channels. This high serial correlation decreases the use of much the data and this can be a limiting
 307 factor. However, all is not lost, as the data results can be refined using chemometric software to allow
 308 for such redundancy of data. Nowadays, spectroscopic instruments have inbuilt chemometric
 309 methods which are extremely efficient at extracting unique and redundant information from
 310 multichannel data such as spectra [61-64].

311 The field of chemometrics is still evolving and consequently its definition requires continued
 312 modification to allow for its development, the international chemometrics society defines
 313 chemometrics as the chemical discipline that exploits mathematical and statistical methods to design
 314 or select optimal measurement procedures and experiments to provide maximum chemical
 315 information by analysing chemical data [62].

316 ~~For example, it is very hard to find a wavelength channel in a standard UV–Vis spectrum to~~
 317 ~~distinguish between alanine and glycine, both essential amino acids in foodstuffs, as chemically they~~
 318 ~~are very similar, and both tend to absorb over the same sets of wavelengths. However, because~~
 319 ~~chemometrics expects this correlation, it allows the analyst to take advantage of the correlations~~
 320 ~~similarity or redundancy to increase the methods precision, similar to the manner that a mean takes~~
 321 ~~advantage of the redundancy of a set of numbers. This is referred to as multivariate analysis.~~

322 Recent innovations in adulterant analysis

323 The recent literature presents a number of spectroscopic techniques for the rapid and more
 324 reliable identification of adulterants in whisky (Table 32). ~~In all cases the studies~~ A variety of
 325 spectroscopic techniques, ~~not just the traditional UV–VIS spectroscopy,~~ have been combined with
 326 multivariate analysis software tools to (I) characterise whisky from different geographical origin; (II)
 327 provide key information to indicate differing maturation process (e.g. maturation time); and (III) to
 328 detect fraud or the presence of an adulterant. Some highlights from the literature are described in
 329 more detail below.

Table 32: Application of Spectroscopy and Chemometrics

Technique	Application	Number of samples	Validation Method	Reported Classification	Ref
UV-Vis (PCA)	Authentication of Scotch Whiskies	Ref set 50 Test set 35	Complimentary gas chromatographic authentication	100 %	69
UV-Vis (PLS-DA)	Discrimination & identification of Scotch whiskies	Ref set 164 Test set 73	Two independent data sets not part of the reference set	Ref 98.6 % Test 93.1 %	70

UV-Vis (PLS-DA)	Discrimination of whiskies	27	N/A	N/A	71
NIR (PCA/SIMC A)	Authentication & provenance of whiskies	Ref set 40 Test set 69	Cross Validation	100 %	72
FT-IR (PLS-DA)	Discrimination & authentication of whiskies	200	Validation set containing 25 % of samples	96.3 %	73
NIR (Machine Learning)	Determination of ethanol & methanol concentration	44	Leave one out Cross Validation	100 %	74
Raman (Machine Learning)	Discrimination & identification of Scotch whiskies	6 classes (400 samples)	5-fold cross validation	70 – 90 %	75
ATR-IR (PLS-DA)	Discrimination & identification of whiskies and other spirits	Ref set 85 Test set 23	Validation set 43	≥ 96 %	76
FT-IR (PCA)	Authentication of whiskies and detection of methanol	150	Cross Validation	≥ 97 %	77
FT-IR/UV- Vis (PLS-DA)	Authentication & provenance of whiskies	11	Cross Validation	100 %	78
Raman/NIR (PLS-DA)	Discrimination & authentication of whiskies	114	N/A	100 %	79
Raman (PC-DFA)	Discrimination & authentication of whiskies	144	N/A	100 %	80

330

331 MacKenzie and Aylot [69], reported the development of a novel spectroscopic method for Scotch
332 whisky brand authentication. The UV-Vis based technique clearly distinguished between genuine
333 Scotch samples and counterfeits, the majority of which were a combination of cheap local alcohol

334 flavoured with a smaller proportion of the genuine whisky and colour. The authors also reported
335 the method's ability to classify various Scotch whisky brands. It was illustrated that the UV-Vis
336 technique combined with chemometric analysis could be used as complimentary method to the
337 traditional GC authentication methodology. This study highlighted some distinct advantages of the
338 spectroscopy approach, including, the portability of the handheld spectrophotometer which enabled
339 field-testing. The spectroscopic method was also quicker (i.e., sample could be analysed in less than
340 a minute compared to a GC analysis time of approximately 20 minutes), was more cost and resource
341 effective when in compared to the standard methods [69].

342 Martins and co-workers [70], determined that UV – Vis spectroscopy combined with partial least
343 squares discriminant analysis (PLS – DA) modelling was an efficient method for discriminating
344 between seven brands of whisky. The method proposed by the authors was also very useful for the
345 detection of adulterants in other spirits. The method was able to differentiate between all genuine
346 samples and detected the counterfeit samples with correct identification rates of between 93 – 100%
347 (depending on the brand).

348 Similarly, Joshi et al [71], also reported the successful application of UV-Vis combined with
349 chemometrics to classify whisky samples from several geographical regions. The authors reported
350 that PLS – DA models correctly classified 100% of the whisky samples belonging to the USA and
351 Canada and 98% of those belonging to Scotland and Ireland respectively. Moreover, Joshi and co-
352 workers also determined that the scanning temperature of the whiskey samples did not impact the
353 UV – Vis spectra of the sample and therefore the classification rates. However, they do recommend
354 that if an analytical protocol to analyse this type of alcoholic beverages will be developed to target
355 authenticity, integrity, or country of origin in a consistent manner it would be appropriate to define
356 an appropriate scanning temperature for quality assurance and certification purposes [71].

357 Infrared spectroscopy both near (NIR) and mid (MIR) combined with chemometrics has proven
358 to be a popular technique for determining whisky quality either solely or in unison with other
359 spectroscopy methods. Pontes et al [72], developed a classification method for distilled alcoholic
360 beverages and verification of adulteration, with water, methanol and industrial ethanol, using NIR
361 spectroscopy and chemometric methods such as principal component analysis (PCA) and soft
362 independent modelling of class analogy (SIMCA). The authors reported that their strategy was an
363 effective tool in the classification and verification of adulteration in whisky, brandies, rums and
364 vodkas. Pure and adulterated samples were successfully classified (100% at the level of 95% of
365 confidence). Other benefits of the approach include, direct sample analysis, and pre-treatment
366 required; use of small volumes allowing for high sample analysis throughput; and no additional
367 use of reagents thereby reducing costs; can be carried out by untrained personnel to name a few,
368 thereby, making this strategy suitable for screening analysis to verify adulteration of alcoholic
369 beverages [72].

370 Sujka and Koczon [73] have reported the development of a rapid, simple, and non-destructive
371 analytical procedure for the discrimination and authentication of whisky samples originating from
372 Scotland, Ireland and USA using MIR spectroscopy combined with multivariate analysis models. The
373 procedure was also found to be useful for identifying the whiskies time of maturation (two, three, six
374 and twelve years). The authors describe the construction of eight discriminant models which
375 allowed analysts to distinguish Scottish, Irish, and American whisky samples. As well as completely
376 differentiating between beverages matured for 2 – and 3 – years from those aged for between 6 – and
377 12 – years. The authors also reported 100 % accuracy when discriminating between American and
378 Scottish whiskies.

379 Large and co – workers [74] demonstrated the ability to determine the alcohol concentration non
380 – invasively in arbitrary bottles using NIR spectroscopy in combination with machine learning.
381 While the authors reported that the determination of ethanol concentration was possible with high
382 accuracy the determination of methanol concentrations within a consistent overall alcohol level was
383 more difficult. Backhaus et al [75] combined chemometrics with NIR spectroscopy to classify the
384 age, maturing cask, distillery and product variety of Scotch with very high accuracy. The authors
385 also highlight that the technique reduced overall cost and processing time of analysis.

386 Mid-infrared spectroscopy was also reported by Picque et al [76], to analyse and discriminate
387 between Cognacs and other distilled drinks including whisky, bourbons, and counterfeit products.
388 Chemometrics was applied by the authors to the spectral data with good levels of accuracy, and 96%
389 of samples in the test set were correctly assigned to Cognacs and non-Cognacs by PLS – DA. The
390 authors also have come up with a means of applying a sequence of combined analytical techniques
391 to provide enhanced accuracy for the discrimination between Cognacs. They propose that a single
392 chemometric process could be used to the combined data outputs of IR, UV-vis, NMR and GC
393 analysis, coupled with neural network information could further enhance the determinations of
394 counterfeit products from Cognac and other products [76].

395 Chen et al [77] have employed chemometrics and IR spectroscopy integrated with information
396 from digital labelling to develop a means of rapidly detecting fraudulent liquors, for the presence of
397 methanol, which is the most important and difficult adulterant to detect with accuracy. The spectral
398 bands of methanol were labelled using iterative discrete wavelet transform for classification, and
399 PCA and PLS analysis were then applied to discriminate problematic samples using the iterative
400 discrete wavelet transform filtered signals. By using digital pre-processing methods, the authors
401 could extract spectral features of methanol from the alcoholic drinks in the presence of a diverse array
402 of uncontrolled matrix effects. The technique boasted a recognition accuracy of higher than 97.0%,
403 with each measurement taking 3 min, illustrating the promise of the tool. The authors also indicated
404 that the method could be extended to detect of other targeted volatile substance in complex matrixes.
405 In a 2017 study Wiśniewska and colleagues [78] utilised headspace mass-spectrometry (HS-MS), MIR
406 an UV – Vis to authenticate whisky samples from multiple origins and ways of production (Irish,
407 Spanish, Bourbon, Tennessee whisky and Scotch). The authors used PLS-DA to build classification
408 models which fully classified the five groups of whisky samples. The authors also reported that it
409 was also possible to differentiate samples within this product class, demonstrating that production
410 processes were impactful on the quality of the spirits [78].

411 Recently work by Ellis et al [79, 80], has investigated the use of Raman spectroscopy combined
412 with chemometrics as a means for rapid *in situ* through-container analysis of whisky samples; the
413 authors report detection of multiple chemical markers known for their use in the adulteration and
414 counterfeiting of Scotch whisky, and other spirit drinks without any physical contact with the sample;
415 with the ability to discriminate between and within multiple well-known Scotch whisky brands, and
416 the detection of methanol concentrations well below the maximum human tolerable level of 2% v/v.

417 **Conclusion**

418 The implementation and adoption of spectroscopy techniques combined with chemometrics
419 allows for the rapid and non-destructive analysis, characterisation and detection of fraud in whiskies.
420 The most promising and significant developments point to the use of NIR, MIR and Raman
421 spectroscopies combined with data mining tools as the means for analysis of fraudulent whisky and
422 related beverages, giving greater confidence in quality evaluation and adulterant analysis. It has
423 been also demonstrated by several authors that both the accuracy and robustness of the methods
424 described are comparable to those obtained by traditional analytical tools such as GC-MS techniques.
425 The field of study however is still in its early stages and it should be noted that the application of
426 calibration models requires continuous validation and as it is the critical step to ensure the robustness
427 of the method.

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