Chapter 16

Fluorescence Spectroscopy for the Analysis of Spirit Drinks

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Additional information is available at the end of the chapter

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Abstract

There are many prescribed methods for the analysis of important components and parameters of spirit drinks. Nevertheless, there is a continuous search for new rapid and simple alternative methods that can be used together with recommended methods. The aim of the chapter is to make a review about themes such as quantification of individual components in the spirit drinks, classification of spirit drinks, and determination of adulterants. The chapter shows that fluorescence spectroscopy has a significant potential for being used in spirit drink research because many alcoholic beverage products contain intrinsic fluorophores. Fluorescence spectroscopy allows the determination of some compounds at concentration as low as 0.1–1 μg/L often without sample preparation, there is no use of chemicals and the time of analysis can be very short. The combination of fluorescence data with chemometric tools is a promising approach for the classification of spirit drinks and for the detection of spirit drink adulteration.

Keywords: fluorescence spectroscopy, chemometrics, beverage, spirit drink, classification

1. Introduction

Fluorescence, like the other molecular spectroscopies, represents an attractive option for food and beverage analysis because it is rapid, sensitive and non-destructive. The reviews on this matter have been reported [1–3]. According to Regulation (EC) No 110/2008 [4], 'spirit drink' means an alcoholic beverage possessing particular organoleptic qualities, having a minimum

alcoholic strength of 15% vol., having been produced: (i) either directly (by the distillation, with or without added flavorings, and/or by the maceration of plant materials in ethyl alcohol of agricultural origin, and/or by the addition of flavorings to ethyl alcohol of agricultural origin), (ii) or by the mixture of a spirit drink with one or more other spirit drinks. The Regulation (EC) No 110/2008 defines 46 different categories of spirit drinks. For the purposes of this review, spirit drinks are divided into two general classes: (1) unaged (vodka, gin, juniper-flavoured spirit drink and fruit spirit) and (2) aged in wooden casks (brandy, whisky, mezcal, tequila, cachaça and calvados). The term age refers to the actual duration of storage, while maturity expresses the degree to which chemical changes occur during storage. Most governments specify storage time for various products.

The major constituents of each spirit drink consist of ethanol and water. The minor or trace constituents are higher alcohols, carbonyl compounds, esters, aldehydes, lactones, organic acids, etc. [5]. However, there are almost the same fluorophores in the different spirits, among others, volatile phenols and anisols in unaged spirits, and phenolic compounds and coumarins in spirits aged in wooden casks.

Fluorescence spectra of distilled spirits are typically composed of broad overlapping fluorescence bands containing chemical, physical and structural information of all sample components. Therefore, conventional fluorescence technique based on recording of single emission or excitation spectra is often insufficient for analysing spirit drinks. In some cases, total luminescence or synchronous scanning fluorescence techniques may improve the analytic potential of fluorescence measurements. The analytical information should be extracted from fluorescence spectra using multivariate and multiway methods, which allow to group samples with similar characteristics, to establish classification methods for unknown samples (qualitative analysis) or to perform methods determining some property of unknown samples (quantitative analysis) [6].

There are many prescribed methods for the analysis of important components and parameters of spirit drinks. The most widely used methods are sensory evaluation, gas chromatography, liquid chromatography, mass spectrometry, ultraviolet–visible (UV/VIS) spectrophotometry and infrared spectrometry [5]. Nevertheless, there is a continuous search for new alternative methods that can be used together with recommended methods.

The aim of the chapter is to make a review about themes such as quantification of individual components in the spirit drinks, classification of spirit drinks and adulteration detection in order to highlight the potential of fluorescence spectroscopy in the beverage analysis.

2. Fluorescence spectra of spirit drinks

Conventional fluorescence spectroscopy uses either a fixed excitation wavelength (λex) to record an emission spectrum or a fixed emission wavelength (λem) to record an excitation spectrum. The broad shape of both the excitation and emission fluorescence bands limits the possibility of finding a unique λex and λem for each potential analyte [7]. Selectivity is often

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improved through fluorimetric strategies such as total luminescence, synchronous scanning fluorescence or total synchronous scanning fluorescence.

Total luminescence spectrum (TLS) presents simultaneously all the excitation and emission spectra over the range of wavelengths scanned [8] and can be shown as a contour map with λem and λex as x- and y-axes, respectively, and contours linking points of equal fluorescence intensity (**Figure 1a**). In TLS, two types of scattering peaks can be found: Rayleigh scattering at the λex = λem, and Raman scattering at a distance from the Rayleigh peak that is characteristic for the solvent. Because TLS spectra represent the total fluorescence profiles of the samples, they are particularly useful in pattern recognition of samples characterised by small differences in their composition [9].

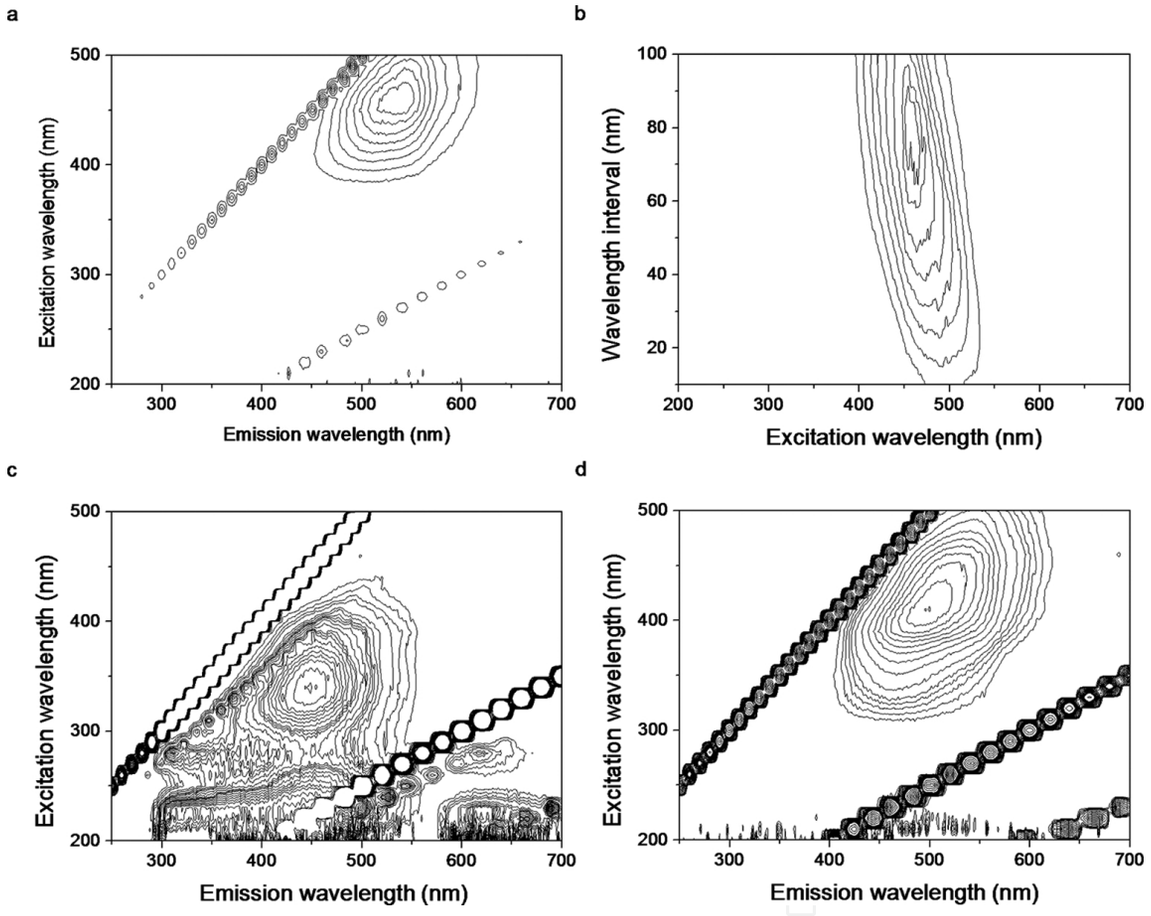

Figure 1. Total luminescence spectra (a,c,d) and TSFS (b) of undiluted (a,b,d) and diluted (c) brandy obtained using right-angled (a,b,c) and front-face geometry (d). **TLS and TSFS were recorded using the Perkin–Elmer LS 50 Luminescence Spectrometer equipped with the Xenon lamp. Samples were placed in 10 × 10 × 45 mm quartz cell. Excitation and emission slits were both set at 5.0 nm. Scan speed was 200 nm.min^{-1}.

In synchronous fluorescence spectroscopy [10], the λex and λem are scanned simultaneously in such a way that a constant wavelength interval $\Delta\lambda = \lambda\text{em} - \lambda\text{ex}$ is kept between them. When a value of $\Delta\lambda$ is chosen properly, the resulting synchronous fluorescence spectrum (SFS) shows one or a few features that are much more resolvable than those in the conventional fluorescence

spectrum because synchronous fluorescence reduces spectral overlaps by narrowing spectral bands and simplifies spectra by amplifying strong fluorescence bands. A choice of $\Delta\lambda$ could be either the difference between the wavelength of emission maximum (λem, max) and the corresponding wavelength of excitation maximum (λex, max) to provide the highest sensitivity, or the particular difference to give a compromise between sensitivity and selectivity [11, 12].

Total synchronous fluorescence spectrum (TSFS) is obtained by plotting fluorescence intensity as a function of the wavelength and $\Delta\lambda$ value (**Figure 1b**) and combine the advantages of TLS and SFS. Because λem is always higher than λex, Rayleigh scattering is not found in TSFS.

Independent of the type of spectrum, the apparent fluorescence intensity and spectral distribution is affected by both the optical density of the sample (**Figure 1a** and **c**) and the geometry of sample illumination (**Figure 1a** and **d**). The most common geometry is right-angle observation of the center of a centrally illuminated cuvette. It is typically used to analyse dilute solutions and other transparent samples (absorbance < 0.1). At high optical densities, signal reaching detector will be significantly disturbed due to the inner filtering effects. In the front-face geometry, the excitation light is focused to the front surface of the samples and then fluorescence emission is collected from the same region at an angle that minimizes reflected and scattered light. Front-face illumination is generally used to decrease the inner filtering effects [7].

2.1. Spirit drinks unaged in wooden casks

The major constituents of each spirit drink, ethanol and water molecules do not exhibit fluorescence. However, when ethanol mixes with water, ethanol and water molecules form molecular clusters by hydrogen bonding and emit different fluorescence photons [13]. When excited by λex = 236 nm, there were eight kinds of luminescence structures in the ethanol–water mixtures, giving the emission bands at 292, 304, 314, 330, 345, 355, 365 and 377 nm, respectively. The fluorescence bands at 355 and 377 nm have maximum intensity when the percent of ethanol is 20%. The other six kinds have maximum intensity for 60% ethanol content [14].

Different flavour exhibits different effect on the fluorescence of 60% ethanol–water mixture characterised by the main band centred at λex/λem = 225/335 nm. The simultaneous addition of eight major flavours (acetaldehyde, ethyl acetate, methanol, propyl alcohol, isobutyl alcohol, isoamyl alcohol, ethyl lactate and acetic acid) make the band at 225/335 nm in excitation/emission disappear and cause the appearance of bands at λex/λem of 285/325 nm as well as at 375/425 nm. The 225/335 nm fluorescence band initially increases and then decreases with increased ethyl acetate or acetate concentration in the 60% ethanol–water mixture. For the Fenjiu samples aged in ceramic containers, the effect of total ester concentration is consistent with the result of ethyl acetate in the 60% ethanol–water mixture, however, the effect of acetic acid differs [15].

Vodka is the simplest distilled spirit, the character of which comes from the ethanol, normally distilled from grain fermentation. Vodka Finlandia (40%) is amongst the purest in the world, its typical TLS and TSFS are shown in **Figure 2**. The short-wavelength band in TLS, which has

maximum at λex/λem = 230/335 nm, corresponds to the band at 220–230 nm (Δλ = 90 – 100 nm) in TSFS and can be assigned to luminescence structures in the ethanol–water mixture. It should be noticed that there is no available information or data on the origin of fluorescence of vodka. However, some of the volatile compounds (1,3,5-trimethylbenzene and p-cymene) identified by GC-MS in vodka [16, 17] are known fluorophores. The micro array based on fluorescence dye solutions and their binary mixtures shows vodka pattern with a certain similarity but slightly different from the aqueous ethanol pattern [18].

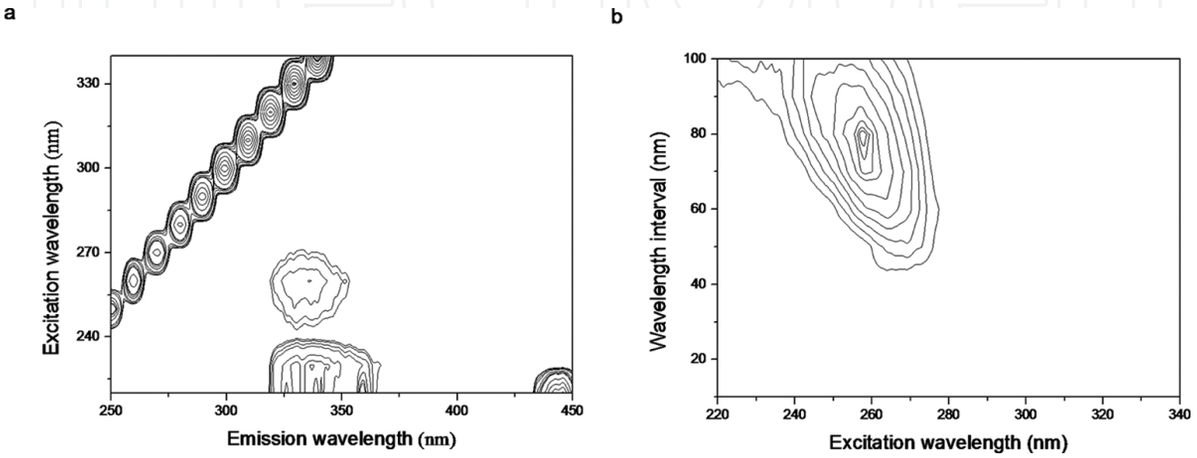

Figure 2. Total luminescence spectrum (TLS) (a) and total synchronous fluorescence spectrum (TSFS) (b) of vodka Finlandia **TLS and TSFS were recorded using the Perkin–Elmer LS 50 Luminescence Spectrometer equipped with the Xenon lamp. Samples were placed in 10 × 10 × 45 mm quartz cell. Excitation and emission slits were both set at 5.0 nm. Scan speed was 200 nm.min^{-1}.

Juniper-flavoured spirit drinks (JFSDs) are produced by flavoring ethyl alcohol of agricultural origin and/or grain spirit with juniper (*Juniperus communis L.* and/or *Juniperus oxicedrus L.*) berries. Eugenol, totarol, *o*-cymene, *p*-cymene, *p*-cymene-8-ol, calamenene, calacorene, phenolic acids, flavonoids, biflavonoids, coumarins, tyrosol and chlorophyll are the best known fluorescent molecules in juniper berries (see references in [19]). Volatile compounds that survived distillation (*o*-cymene, *p*-cymene, calamenene, calacorene [20, 21] and totarol [22], were found in gin, and more than 30 possible fluorophores were detected in JFSDs (mainly substituted benzenes, phenols and anisols) [19, 20]. Many substituted phenols or anisols and diterpenoids show similar fluorescence properties, e.g., λex/λem = 288/315 nm for eugenol [23], λex/λem = 275/315 nm for totarol [24].

The most popular JFSD is gin, which TLS is characterised by the main fluorophores centred at λex = 220 and 304 nm and λem = 337 nm. The first pair of wavelengths (λex/λem = 220/337 nm) is similar to that observed for vodka, the second one (λex/λem = 304/337 nm) is characteristic for London gin. Other JFSDs show band with excitation at about 250–290 nm and emission at about 330–340 nm. Moreover, Belgian and Czech JFSDs show additional band at longer wavelength (**Table 1**). Modelling of TLS allowed relating the fluorescence bands of drinks to 2-phenylethanol, eugenol, carvacrol, 4-allylanisole, *p*-cymene and coumarin derivatives [19]. JFSDs are sometimes marketed in the glass bottles containing dried berries or twig inside. Such

JFSDs had abnormally high fluorescence intensity at about 260/335 nm in excitation/emission, which could be attributed to compounds extracted from berries or twig [25].

Spirit drink	$\lambda_{ex,max}$ (nm)	$\lambda_{em,max}$ (nm)	Reference
Unaged in wooden casks			
Vodka Finlandia	230, 260	335	This work
London Gin	220, 302–306	335–340	[19]
Juniper-flavoured (Slovak)	277–290	330–343	[19]
Juniper-flavoured (Belgian)	280–290	330–340	[19]
	317–350	426–447	
Juniper-flavoured (German)	250–260	331–333	[19]
Juniper-flavoured (Czech)	260–265	335–337	[19]
	300–304	400–402	
Apple	250	327	[26]
	300	419	
Apricot	290	317	[26]
Pear	235	349	[26]
	302	420	
Plum	266	330	[26]
	304	417	
Apricot spirit with fruit	270	360	[26]
	350	443	
Pear spirit with fruit	260	366	[26]
	330	423	
Mixed wine	390–400	480–500	[27]
Aged in wooden casks			
Brandy	450–460	520–540	[27]
Mezcal	514	580	[35]
Tequila	337	430	[38]
Tequila	255	470	[39]
	330	460	[39]
	365	460	[39]
	405	510	[39]
Cachaça (amendoim)	330	400	[44]
Cachaça (balsam)	340	480	[44]
Cachaça (oak)	280	320	[44]
Cachaça (jequitibá)	260	370	[44]
Cachaça (umburana)	380	450	[44]
Calvados	410	506	[26]

$\lambda_{ex,max}$ wavelength of excitation maximum, $\lambda_{em,max}$ wavelength of emission maximum.

Table 1. Fluorescent properties of bulk spirit drinks obtained using right-angled geometry.

Spirit drink	Dilution	$\lambda_{ex,max}$ (nm)	$\lambda_{em,max}$ (nm)	Reference
Apple	40-fold	-	-	[26]
Apricot	40-fold	278	337	[26]
Apricot with fruit	40-fold	280	334	[26]
Pear	40-fold	278	318	[26]
Pear with fruit	40-fold	280	322	[26]
Plum	40-fold	259	329	[26]
Mixed wine	100-fold	280	350	[28]
		330	430	
Brandy	100-fold	280	360–370, 450–460	[28]
		340	450	
Calvados	40-fold	340	450	[26]

$\lambda_{ex,max}$ wavelength of excitation maximum, $\lambda_{em,max}$ wavelength of emission maximum

Table 2. Fluorescent properties of diluted spirit drinks.

Fruit spirits are made of different varieties of fruits by the alcoholic fermentation and distillation. They are usually aged in glass containers, marketed as 'pure' beverages or in the bottles containing a whole dried fruit. **Table 1** shows the characteristic λex,max and λem,max corresponding to the four types of fruit spirits. Bulk apple, pear and plum spirits exhibit two fluorescent bands, one with fluorescent maximum between 250 and 290 nm in the λex and between 330 and 350 nm in the λem range, whose exact position depended on the fruit type, and the second with excitation maximum at about 300 nm and emission at about 420 nm. In contrast, bulk apricot spirit exhibits only the short-wavelength band. Bulk spirits containing fruit show two fluorescent maxima at longer wavelengths (**Table 1**). The UV absorption of bulk fruit spirits is from 2 up to 4 absorbance units when scanning from 225 to 300 nm, and therefore the inner filter phenomena affect the right-angle spectra considerably. One way to reduce the inner filter effects is to dilute the sample with an appropriate solvent. On the other hand, dilution can reduce concentration of some components bellow limit of detection. As an example, **Table 2** shows the λex,max and λem,max of fruit sprits upon dilution. Apple spirits exhibited no reasonable fluorescence upon 40-fold dilution. Both diluted apricot and pear spirits exhibit a band with a maximum fluorescence at λex = 280 nm. The different position of emission band for apricot and pear spirits enables us to distinguish between them. In addition, λex,max and λem,max of diluted plum spirits are different from the other fruit spirits. The compounds such as 1-phenylethanol, 2-phenylethanol, eugenol, 4-allylanisole, 4-vinylanisole,

4-ethylphenol, 4-ethylguaiacol and p-cymene can be detected using λex /λem of 280/320 nm after separation by HPLC. In the case of spirits containing fruit, there is a wider variety of fluorescent compounds, including not only those found in pure spirits but also benzoic and cinnamic acids and their aldehydes [26].

Mixed wine spirits are wine distillates diluted with ethanol from other sources, frequently blended with sugar, brandy aroma and caramel. Some mixed wine spirits contain honey or colourants. TLS contours of bulk mixed wine spirits are concentrated in the λem region from 460 to 530 nm and the λex between 380 and 420 nm [27]. The spectra recorded in right-angled geometry are distorted due to inner-filter effect. Diluted wine distillates exhibit two fluorescence bands centered at the λex /λem pairs of 280/350 nm and 330/430 nm, respectively (**Table 2**). The short-wavelength band is similar to the one observed in the fluorescence spectra of other distilled spirits and it may partly originate from compounds of the grape distillate. The long-wavelength band originates mainly from caramel [28].

2.2. Spirit drinks aged in wooden casks

Freshly distilled spirits are colourless and possess only the flavour and aroma of the grain and the alcohol. Many producers use "ageing wooden barrels" to mature distilled spirits like brandy, Calvados, whisky, mezcal, cachaça and tequila. Barrels are typically made of French or American oak, but chestnut and redwood are also used. The ageing involves several processes: lignins decompose with formation of phenolic compounds (vanillin, syringaldehyde, coniferaldehyde, sinapaldehyde, cinnamic and benzoic acids), hydrolysable tannins and their products (gallic and ellagic acids) and coumarins (particularly scopoletin) are extracted from wood, and reactions may occur between components of wood and spirit. These processes and their products are very important for the quality of the matured spirits (taste, flavour and colour) [29]. In addition, phenolic compounds and coumarins are well-known fluorophores.

Brandy is a spirit drink produced from wine spirit, whether or not blended with a wine distillate. Types of brandies, originally at least, tended to be location-specific. Brandy has to be aged for a certain period in oak casks. Using right-angled geometry, the TLS contours for bulk brandy are concentrated in the λem region from 510 to 570 nm and λex region from 430 to 480 nm [27]. Using front-face geometry, the total luminescence contours for bulk brandy are concentrated in the λem region from 470 to 520 nm and λex region from 390 to 430 nm [30]. Undiluted brandy exhibits a high UV/VIS absorption, thus the fluorescence recorded on the bulk brandy is severely distorted due to the inner filter effects. The short-wavelength fluorescence, with λex,max = 280 nm and λem,max =370 and 450 nm, is clearly observed for diluted brandy samples, along with the longer-wavelength fluorescence, with excitation at 340 nm and emission at 450 nm (**Table 2**). The former band is preliminary attributed to the tryptophol, tyrosol and phenolic acids, the latter band to cinnamic acids, coumarins, tannins and other unknown fluorescent compounds [28].

Whisky (whiskey) is spirit-based drink made from malted or saccharified grains, which should mature for at least 3 years in wooden barrels. Plain spirited caramel of a specific grade is added simply in order to adjust the consistency of the colour [31]. Regarding bulk whisky, front-face fluorescence spectrum recorded at λex = 404 nm exhibit a wide emission band in the 450–700

nm range with maximum at 520 nm. The fluorescent band arises from the caramel, coumarins, tannins and other fluorescent compounds originating from wooden casks [32]. Tequila and mezcal are two traditional Mexican distilled beverages with similar production phases. Tequila must be made exclusively from Agave tequilana Weber blue variety, whereas mezcal is made from different agave species, among them A. salmiana, A. angustifolia and A. potatorum [33]. Maturation of mezcal and tequila is optional, contributing flavour in a similar way to all the other wood-matured spirits. Using liquid chromatography with ion trap mass spectrometry detection, ten phenolic acids were quantified in tequilas [34]. Fluorescence spectra of bulk mezcal obtained using right-angled geometry have emission maximum at about 580 nm (λex = 517 nm). White/young mezcal exhibit spectra similar to ethanol. On the other hand, aged mezcal, and the other types of mezcal differ in the intensity of the emission spectra due to the higher concentration of organic molecules extracted from the wood cask [35, 36]. Using the fluorescent background of Raman spectra, it has been possible to distinguish tequila blanco (unaged) from aged tequila [37]. Later fluorescence between 370 and 510 nm of bulk tequila excited at 337 nm has been observed [38]. Recently reference [39] reported the right-angled fluorescence spectra recorded at four λex (255, 330, 365 and 405 nm) by original tequilas and counterfeit tequilas.

Cachaça, the most popular distilled alcoholic beverage in Brazil, is a distilled spirit made from sugarcane juice. It can be aged in barrels of amendoim (*Pterogyne nitens*), balsam (*Myroxylon peruiferum*), jequitibá (*Cariniana estrellensis*), umburana (*Amburana cearensis*) and oak (*Quercus sp*.). Using HPLC-ESI-MS(n), 14 phenolic compounds and two coumarins were detected in sugarcane spirit extracts of six different Brazilian woods and oak, commonly used by cooperage industries for ageing cachaça [40]. TLSs of bulk cachaça exhibit excitation and emission maxima in the range 260–380 nm and 320–480 nm (**Table 1**), respectively, corresponding to phenolic acids (gallic, syringic, vanillic and ellagic), phenolic aldehydes (sinapaldehyde, coniferaldehyde, syringaldehyde and vanillin) and coumarin [41].

Calvados is an apple-brandy of France. Fluorescent compounds such as 4-vinylanisole, 4-methylguaiacol, methyleugenol, 4-ethylguaiacol, eugenol, 4-ethylphenol and 4-vinylguaiacol are found in freshly distilled Calvados [42], while 2-phenylethanol, 4-methylguaiacol, methyleugenol, 4-ethylguaiacol, eugenol and 4-ethylphenol [43] in matured Calvados. Bulk Calvados is easily distinguishable from the other fruit drinks because its λex,max and λem,max are considerably higher. Diluted Calvados revealed the same fluorescence band as that observed for diluted grape brandies—wine spirits aged in oak barrels. The band could be due to the presence of phenolic compounds extracted from wood [26].

The absorption of undiluted aged spirit samples is from 1 up to 5 absorbance units, thus, brandies, cachaças and mezcals have by far the highest absorbances, regardless of wavelength [33, 44, 45]. Therefore, the analysis of spectra recorded using right-angled geometry, which are affected by inner filter effects, may lead to spectral misinterpretation and invalid assignments of origin of some fluorescent bands. So far, fluorescence spectra unaffected by inner filter effects are available only for diluted brandy, mixed wine spirit and Calvados.

3. Applications of fluorescence spectroscopy

3.1. Quantification of individual components

3.1.1. Naturally occurring components

To determine alcohol, several fluorescence biosensors have been produced by integrating alcohol oxidase or alcohol dehydrogenase enzymes with optical fibers. The utility of enzyme biosensors is restricted due to their low stability and short lifetime determined mainly by enzyme kinetics, the necessity to add the coenzyme to the solution and the temperature [46–48].

Chemosensors are another big group of devices for the determination of alcohol. The application of a fluorescent reagent, fluorescein octadecyl ester, in a fiber optic sensor for the determination of aliphatic alcohols in a range of 10–60 v/v % has been reported [49]. Fluorescence intensity was enhanced due to the formation of hydrogen bonds between alcohol and the hydroxyl group of fluorescein octadecyl ester [49]. The fluorescence quenching of the 5,10,15,20-tetraphenyl porphyrin doped on polyvinyl chloride film by ethanol showed a linear response over the ethanol concentration in the range of 1–75 v/v % with a detection limit of 0.05 v/v % [47]. Using admixture of terphenyl-ol and sodium carbonate, which exhibited bright sky-blue fluorescence in the solid state upon addition of small quantities of ethanol, detection limit at about 5 v/v % of ethanol was demonstrated [50]. A simple visual test has been developed to check the ethanol content of drinks and to detect counterfeit beverages containing methanol. When imidazolium-based dication C10(mim)2 and dianionic 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) are mixed together, they self-assemble into a supramolecular ionic material (SIM). The product is capable of encapsulating the fluorescent dye Rhodamine 6G (R6G) to form SIM-R6G. The addition of ethanol destructs the R6G-SIM structure, resulting in the release of R6G. Alcohol content can be determined by measuring the fluorescence line of R6G on a thin-layer chromatography (TLC) plate within a concentration range from 15 to 40%. The addition of a trace amount of methanol leads to a large increase of the length of R6G on TLC plates [51]. Another supramolecular material has been prepared with 1,4-bis(imidazol-1-ylmethyl)benzene (bix) as the ligand, Zn^{2+} as the central metal ion and encapsulated fluorescent dye Rhodamine B (RhB). The formed RhB/Zn(bix) is stable in ethanol, however, the addition of water results in the release of RhB, allowing the determination of alcohol content within a linear range from 20 to 100 v/v % [52].

The appropriateness of both spectrofluorimetry and HPLC to determine the level of individual coumarins (umbelliferone, scopoletin and 4-methylumbelliferone) in commercial white rum samples has been demonstrated [53]. Recently a simple multivariate calibration spectrofluorimetric method has been developed for the simultaneous determination of gallic, vanillic, syringic and ferulic acids and scopoletin in brandy samples, providing comparable results with those obtained by HPLC method [12].

Ellagic acid is the most explored phenolic acid compound, probably due to direct extraction of free ellagic acid and hydrolysis of wood ellagitannins [54]. Two spectrofluorimetric methods have been developed for the rapid determination of ellagic acid in brandy samples. The first

method was based on the complex formation between ellagic acid and borax in methanol solution (λex/λem = 383/456 nm). In the second method, the complex was formed between ellagic acid and boric acid in ethanol solution (λex/λem = 387/447 nm). The limit of determination was at about 0.3 μg/L. The results were found to be in good agreement with those obtained by HPLC method [55]. The potential of SFS ($\Delta\lambda$ = 40 nm) has been demonstrated to differentiate caramel from oak wood extract. The method was selective for the determination of caramel in the presence of common components of brandies (gallic acid, syringic acid, vanillic acid, caffeic acid, ferulic acid, p-coumaric acid, vanillin, syringaldehyde, coniferaldehyde, sinapaldehyde, furfural, 5-hydroxymethylfurfural and scopoletine). The limit of determination was 5 mg/L for caramel [56].

3.1.2. Contaminants

AMPHORA project, which assessed the quality of illegally and informally produced alcohol in the European Region, reports that compared to the health effects of ethanol, the contamination problems may be of minor importance as exposure will only in worst-case scenarios reach tolerable daily intakes of the substances as ethyl carbamate, copper manganese, acetaldehyde, methanol, higher alcohols and phthalates [57]. The incidence of the aldehydes, especially of formaldehyde, in the Asian samples was considerably higher than that found in European alcoholic beverages [58].

Fluorimetry with Hantzsch reaction is commonly used for the determination of formaldehyde. Cyclohexane-1,3-dione (CHD) [59] and 4-amino-3-penten-2-one (Fluoral-P) [60, 61] have been used as Hantzsch reaction reagents. The Fluoral-P method is based on the reaction of 4-amino-3-penten-2-one with formaldehyde, producing 3,5-diacetyl-1,4-dihydrolutidine, which fluoresces at 510 nm when excited at 410 nm. The method is specific for formaldehyde, allowing for the determination of this analyte even in the presence of acetaldehyde concentrations 1000 times higher than formaldehyde [60]. Limit of detection was 3 μg/L for formaldehyde in cachaça, rum and vodka [61]. Aldehydes, such as formaldehyde, acetaldehyde, propionaldehyde and *n*-butyraldehyde, can completely react with CHD to form fluorescence derivatives (9-substituted decahydroacridine-l,8-diones) in the presence of ammonium acetate in 1 h at 60°C. The application of microwave irradiation accelerates considerably the derivatisation reaction of formaldehyde with CHD and allows attaining a limit of detection 0.02 μg/L for formaldehyde in a shorter derivatisation reaction time. Tolerated ratio of acetaldehyde was 100 in the determination of 0.500 mg/L formaldehyde [59].

Based on the fluorescence properties of 2,4-(1H,3H)-quinazolinedione (λex/λem = 310/410 nm), a product of the reaction between cyanate and 2-aminobenzoic acid, a method for the determination of cyanate was developed with a limit of detection 4 μg/L. A correlation between the cyanate and ethyl carbamate concentrations in the sugar cane spirit was observed [62].

Fluorescent molecularly imprinted polymer (fluorescein 5(6)-isothiocyanate-3-aminopropyltriethoxysilane /SiO_2 particles) has been used for the selective recognition and the determination of λ-cyhalothrin (pesticide) in Chinese spirits. Based on fluorescence quenching, the limit of detection 4 μg/L was obtained [63].

Recently, a rapid methodology has been proposed for simultaneous quantification of five PAHs (acenaphten, anthracene, benzo[*a*]pyrene, fluoranthene and pyrene) in three types of spirits (rum, cachaça and vodka) [64].

3.1.3. Drugs

Three most commonly used drugs in drink spiking are ketamine, benzodiazepines, including diazepam and flunitrazepam, and gamma-hydroxybutyric acid (GHB).

The determination of diazepam in commercial beverages, previously spiked with drug, has been implemented through photo degradation of diazepam and detection of degradation products at λem= 463 nm (λem = 262 nm). The limit of detection was 2 mg/L [65]. A screening method for flunitrazepam in colourless alcoholic beverages is based on emission at 472 nm of protonated drug given the limit of detection 1 mg/L [66].

Zhai group has recently reported the first fluorescent sensor for gamma-butyrolactone (GBL), the pro-drug of GHB. GBL sensor was named Green Date and required an extraction to eliminate alcohol effects for GBL detection in real drinks [67]. The team also found that an orange fluorescent compound named GHB Orange is capable of detecting GHB in different beverages with explicit intensity change under the irradiation of a hand-held 365 nm lamp [68].

3.2. Classification of spirit drinks

Visual inspection of fluorescence spectra seldom shows that they fall naturally into a number of groups [25, 39]. Thus, pattern recognition methods are usually required to gain significant meaningful information from the spectrometric data (**Table 3**). Non-supervised pattern recognition methods as hierarchical cluster analysis (HCA) or principal component analysis (PCA) discover, previously unknown, the group structure in the data. With supervised pattern recognition methods, the number of groups is known in advance and representative samples of each group are available. This information is used to develop a suitable discriminating rule or discriminate function with which new, unknown samples can be assigned to one of the groups. Supervised pattern recognition methods as linear discriminant analysis (LDA), general discriminant analysis (GDA), k-nearest neighbour (kNN), support vector machine (SVM) and partial least squares discriminant analysis (PLS-DA) can be used. The choice of the chemometric method often depends on preference of the analyst and the complexity of the data. LDA requires the number of variables (wavelengths) smaller than the number of samples in each group. Consequently, large spectral datasets with few samples cannot be analysed using LDA. As PCA is a dimensionality reduction method, combining LDA with a PCA overcomes this problem. On the other hand, PLS-DA is well suited to deal with a much larger number of variables than samples [6]. Parallel factor analysis (PARAFAC) is commonly used for modeling fluorescence excitation-emission data. PARAFAC decomposition gives the loading and the score profiles of the components. The comparison of loading profiles of component with the fluorescence spectra for a standard of the analyte often leads to the identification of the fluorophore. Calibration model can be obtained by PLS regression between the scores related

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to the fluorophore and the reference concentrations of the fluorophore in the calibration samples [69].

Sample	Spectral region[a]	Multivariate analysis[b]	Purpose of analysis and quality of method (the percentage of correct classification in the prediction step)[a, b, c]	Reference
Quality				
Brandy	EX (225–425 nm), λem = 440 nm; EM (360–650 nm), λex = 350 nm; SFS (200–700 nm), Δλ=90 nm	PCA, HCA	Classification of bulk brandies and mixed wine spirits using front-face geometry	[30]
	EX (225–460 nm), λem=470 nm; EM (400–650 nm), λex=390 nm; SFS (200–700 nm), Δλ=80 nm	PCA-LDA, HCA	Classification of bulk brandies and mixed wine spirits using right-angled geometry; SFS (PCA-LDA): 99.6% classification	[27]
	EX (240–380 nm), λem= 450 nm; EM (400–470 nm), λex=340 nm	PCA, HCA	Classification of diluted brandies and mixed wine spirits	[28]
	SFS 220-700 nm, Δλ = 40 nm	PCA-LDA, HCA	Classification of diluted brandies and mixed wine spirits; SFS (PCA-LDA): 99.2% classification	[70]
Mezcas	EM (540-800 nm), λex=514 nm	PCA	Classification of the group including white mezcals (non-maturated) and ethanol from the group including rested (matured 2 months in wood casks), abocado (white or young mezcal artificially coloured and flavoured) and distilled mezcals (coloured white mezcal)	[35]
Fruit	SFS (200-500 nm), Δλ=10, 90 and 100 nm	PCA-LDA, GDA	Classification of apple, apricot, pear, and plum spirits ; PCA-LDA: 100, 90 and 90% classification for Δλ = 10, 90 and 100 nm, resp.; GDA: 100% classification regardless Δλ used	[26]
Tequila	EM (250-800 nm), λex = 255, 330, 365 and 405 nm		Discrimination adulterated and counterfeit tequilas from the genuine ones (λex = 255 nm), and aged, rested, and mixed tequilas from fake ones (λex = 330, 365, and 405 nm).	[39]
Cachaça	UV/VIS (190-500 nm); EM (260-600 nm), λex=250, 280, 330, 360, and 450 nm; fusion of the UV/VIS and EM	PLS-DA, NPLS-DA	Prediction of the wood used in the ageing of commercial cachaças; UV/VIS (PLS-DA): 56–89% classification; EM (NPLS-DA): 37–91% classification; Low-level fused UV/VIS and EM data (PLS-DA): 60–94% classification	[44]
Whisky	UV-Vis (290-600 nm); NIR (1200-1880 nm); EM (450-700 nm), λex= 404 nm	PCA-LDA	Distinguishing between the single-malt whiskies and the commercial-grade blended whiskies; 100% classification	[32]

Sample	Spectral region[a]	Multivariate analysis[b]	Purpose of analysis and quality of method (the percentage of correct classification in the prediction step)[a, b, c]	Reference
Region				
Whisky	UV-Vis (290-600 nm); NIR (1200-1880 nm); EM (450-700 nm), λex= 404 nm	PCA-LDA	Classification of single-malt whiskies come from two main production areas, the islands and the highlands, respectively: 89% classification	[32]
JFSD	UV (250–325 nm); SFS (250–450 nm), $\Delta\lambda$ = 10 nm; TLS (λem = cx275–490 nm, λex = 250–400 nm)	PCA-LDA, PARAFAC-LDA	Distinguishing between Slovak, Belgian, German, Czech and British JFSDs; UV (PCA-LDA) 88 %, SFS (PCA-LDA) 97 %, TLS (PARAFAC-LDA) 88 %	[19]
Plum	SFS (230–550 nm), $\Delta\lambda$ = 60 nm	PCA-LDA	Differentiation of Czech, Hungarian and Slovak plum spirits; 100 % classification	[72]
Producer				
JFSD	SFS (250–350 nm), $\Delta\lambda$ = 10 nm	PCA-LDA, GDA, *k*NN, SVM	Distinguishing between (1) drinks from different producers and (2) distillates of different geographical indications and others; GDA: 100 % classification	[25]
Adulteration				
Brandy	TLS (λem = 485–580 nm, λex = 363–475 nm)	PARAFAC-PLS	Determination of the mixed wine spirit in adulterated brandy; RMSEP: 1.9%, R^2Pred: 0.995.	[73]
Brandy	TLS (λem = 510–600 nm, λex = 393–497 nm)	PARAFAC-PLS	Determination of the adulterants (water, ethanol, methanol) in adulterant-brandy blends; RMSEP: 0.24%, 0.20% and 0.22%, R^2 Pred 0.993, 0.997 and 0.995 for water, ethanol and methanol, respectively.	[74]
Fruit	TLS (λem = 315–450 nm, λex = 240–305 nm)	PARAFAC-PLS	Determination of water or ethanol in adulterant-fruit spirit blends; apple spirit: RMSEP: 1,8% and 1.9%, R^2 Pred 0.92 and 0.90, for ethanol and water, respectively; plum spirit: RMSEP: 3.5% and 0.7%, R^2 Pred 0.66 and 0.99, for ethanol and water, respectively.	[75]

[a] EX excitation wavelength, EM emission wavelength, SFS synchronous fluorescence spectrum, $\Delta\lambda$ wavelength interval, UV/VIS ultraviolet/visible, NIR near infrared, TLS total luminescence spectrum.
[b] PCA principal component analysis, HCA hierarchical cluster analysis, LDA linear discriminant analysis, GDA general discriminant analysis, PLS-DA partial least squares regression discriminant analysis, NPLS-DA multi-way partial least squares discriminant analysis, PARAFAC-LDA parallel factor analysis-linear discriminant analysis, *k*NN k-nearest neighbour, SVM support vector machine.
[c] RMSEP root mean square error of prediction, R^2Pred coefficient of determination of prediction.

Table 3. Application of fluorescence spectroscopy and pattern recognition methods.

3.2.1. Classification of spirit drinks according to the quality

Spirit drinks can be sometimes adulterated in the flavour and colour to imitate the sensorial and visual characteristics of the authentic matured beverages. Thus, one way of classifying spirit drinks is as aged or unaged—for example, brandy or less expensive mixed wine spirit. The λex/λem values of the major peaks of the bulk brandies are generally longer than those

recorded for bulk mixed wine spirits. Thus, both PCA and HCA carried out on the front-face emission spectra recorded at λex = 350 nm and SFSs collected at $\Delta\lambda$ = 90 nm provided very good differentiation between brandies and mixed wine spirits. Less good classification was obtained using excitation spectra recorded at λem = 440 nm [30]. Right-angle fluorescence spectroscopy can be used as an alternative method to front-face fluorescence technique, exigent of special front surface accessory, as both the techniques provide similar classification [27]. Regardless of fluorescence technique used, scattering is much more intense and/or heterogeneous for mixed wine spirits than for brandies and can result from the presence of the colloids in mixed wine spirits. Although the phenomenon was not studied in detail, the differences between brandy and mixed wine spirit are also due to scatter bands [27, 30]. Regarding classification of diluted samples, again better results were obtained from excitation and synchronous fluorescence spectra [28, 70].

UV-absorption and fluorescence spectroscopy have been compared for the evaluation of the authenticity of matured mezcal. The results showed that PCA conducted over a set of UV absorption spectra allows a reliable discrimination between artificially and naturally maturated mezcals. On the other hand, PCA conducted over fluorescence spectra allowed the identification of two main groups, not necessarily correlated with maturation in the wood casks (**Table 3**) [35].

Raman spectroscopy has been able to distinguish unaged (silver) tequila from aged tequilas by the application of a PCA to the fluorescence background of the Raman spectra [37]. The same authors observed that the lower and highest fluorescence background of the Raman spectra corresponds to the Herradura tequila and Rancho Escondido distillated of the given samples, respectively. It is supposed that this fluorescence background behaviour is related with the production processes of the samples [37]. PCA performed on the combination of Raman spectra and the fluorescent background information has been used to classify various brands of whiskies based on flavour, age and type of cask. The fluorescence decay constant can be also used as another parameter to distinguish whisky types which are otherwise non-distinguishable [71].

The character and potential nutritional value of spirits is reliant, among others, on the type of wood used for the barrel in which spirits may be aged. UV-Vis spectrophotometry and fluorescence spectrometry have been compared for the discrimination of the cachaças according to the wood used in their ageing. It was observed that the PLS-DA based on UV-Vis spectrophotometry provided better results for two classes of aged cachaça, amendoim and jequitibá, whereas NPLS-DA of emission spectra recorded at λex = 250, 280, 330, 360, and 450 nm provided better results for the other two classes of aged cachaças, balsam and oak. For the class of cachaça aged in umburana, both models provided similar and good results. Consequently, a fused PLS-DA model based on the UV-Vis and emission spectra was developed, providing highest classification for four out of the five analysed classes. The only exception was the class of samples aged in oak, better classified using emission spectra and NPLS-DA [44].

Using the combination of absorption (UV/VIS, NIR) and fluorescence spectroscopic data, it has been possible to distinguish the single-malt whiskies from the commercial-grade blended

whiskies. First, PCA was applied to each data-block. Next a joint-data matrix containing PC1 and PC2 scores from UV/VIS data, PC1, PC2 and PC3 scores from NIR data and PC1 scores from fluorescence data was created. Then, LDA was applied to this matrix, and 100% classification was obtained [32].

3.2.2. Classification of spirit drinks according to the region of production

A few papers have been published on the use of fluorescence to classify spirit drinks according to the region of production. UV absorption spectra, TLS and SFS combined with PCA, PARAFAC and LDA were applied to distinguish between Slovak, Belgian, German, Czech and British JFSDs. PCA-LDA performed on the UV spectral data showed a good discrimination of Slovak, British, German and Czech drinks; however, the UV spectra failed to discriminate Belgian samples. LDA applied to the PARAFAC components calculated on TLS showed correct classification for German, Czech and Belgian drinks, whereas British samples were classified as belonging to Slovak group. PCA-LDA performed on the SFS data lead to the best discrimination as only one Slovak sample was classified as Belgian in the prediction step [19].

SFS combined with PCA-LDA have been used for the differentiation of plum spirits according to their geographical origin. The samples were divided in two categories: colourless and coloured. All colourless and Czech and Hungarian coloured samples were properly classified in both calibration and prediction sets. A group of Slovak coloured was classified as belonging to the Hungarian group in the calibration set; however, it was correctly classified in the prediction step [72].

SFS and pattern-recognition methods have been used for searching the natural grouping among Slovak JFSDs. LDA was applied to the first PCs; however, GDA, *k*NN and SVM were performed on the whole SFS. Regarding different producers, both GDA and SVM resulted in 100% correct classification. Regarding geographical indication, 100% correct classification was obtained using GDA [25].

3.3. Determination of adulterants

TLS and PARAFAC-PLS have been used for the determination of the adulterants (mixed wine spirits, water, ethanol and methanol) in adulterant-brandy blends [73, 74]; the best results were obtained for ethanol (RMSEP = 0.20% and R^2 Pred = 0.997). A comparison with UV/VIS absorption and NIR spectroscopy showed that the fluorescence method is slightly less sensitive than UV/VIS absorption, but more sensitive than the NIR technique in the process of determining the percentage of adulterant (water, ethanol and methanol) in the adulterant–brandy blend. NIR technique showed the best discrimination of the adulterant type [74]. Regarding determination of water or ethanol in adulterant-fruit spirit blends, PARAFAC-PLS provided a model with very limited predictive ability for ethanol-plum spirit blends (RMSEP = 3.5% and R^2 Pred = 0.66) [75].

4. Conclusions

Our literature survey revealed that the intrinsic fluorescence from spirit drinks contains valuable information on the quality and origin of such products. Many of the reported studies examining the potential of fluorescence spectroscopy to classify spirit drinks and/or quantify adulterants in spirit drinks until now have been preliminary or feasibility studies, performed on a limited number of samples. This was mainly due to the price and complexity of collecting an adequate number of samples with sufficient variation within the sample set. Therefore, appropriate verification should always be performed before implementation of any such method. The results presented were usually achieved using a conventional spectrophotometer, which can be replaced by diode lasers or bright light-emitting diodes as good alternative light sources. This reduces hardware complexity and can lead to a compact portable device to be used for authentication or fraud detection. The increasing research work is needed to better explore the connection between chemical composition and fluorescence spectra, which in most cases is not fully described. Instead, the tentative assignments of fluorophores are suggested in the application studies. Thus, fluorescence spectroscopy presents several opportunities for future research with potential application in spirit drink analysis.

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