Determination of Volatile Compounds in Cider Spirits by Gas Chromatography with Direct Injection

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Abstract

Two analytical methods based on gas chromatography with direct injection are described for the quantitative analysis of volatile compounds (acetals, aldehydes, esters, alcohols, and volatile phenols) in cider brandies. Analytes were divided into major, 15, and minor volatile, 24, compounds depending on their usual concentration in samples. Parameters usually tested for method validation are evaluated. Correlation coefficients are calculated to estimate linearity, obtaining values higher than 0.999. Detection limits range between 0.325 mg/L (1-propanol) and 1.663 mg/L (methanol) among the major volatile compounds and between 0.086 mg/L (ethyl 2-methylbutyrate) and 0.332 mg/L (ethyl tetradecanoate) among the minor volatiles. Mean recoveries ranged between 109% (ethyl lactate) and 95% (1-butanol) for major volatiles and between 109% (1-octen-3-ol) and 94% (ethyl 2-methylbutyrate) for minor volatiles, thus confirming the accuracy of both methods. Reproducibility for major volatiles is < 5.4% (furfural) in all cases and < 9.6% (hexyl acetate) for minor volatiles. Moreover, the accuracy of the methods is evaluated by analyzing a certified whisky and five samples from interlaboratory assays, generally obtaining results in accordance with previous values.

Introduction

Alcoholic beverages are complex mixtures mainly comprised of ethanol and water and a large number of minor compounds that may be present in the raw materials or formed during the distinct stages of the manufacturing process such as: alcohols, acids, esters, aldehydes, polyphenols, metals, aminoacids, etc. The different concentrations of these substances confer the particular characteristics to each product, affecting sensorial properties appreciated by consumers such as odor, taste, and color.

One of the most relevant steps in the elaboration of spirits is the distillation process. During this stage, heat facilitates the incorporation of volatile compounds into the resulting ethanol–water mixture. Accordingly, the most appropriate technique for analyzing these compounds is gas chromatography (GC).

The analysis of volatile compounds in spirits is important for several reasons. On the one hand, it is necessary to control the levels of certain toxic substances, such as methanol, or to guarantee the origin of the alcoholic beverage according to minimum levels of higher alcohols (1). On the other hand, the study of volatile compounds can provide significant information about the raw materials and technological processes employed. For instance, the use of raw materials in deficient sanitary conditions can lead to the presence of undesirable flavors in fresh distillates (2,3). Moreover, the composition of fresh distillates can be considered as the basis for the aromatic perception of matured distillates, as described for cider and wine distillates (4,5). Finally, the study of the volatile composition in spirits may be used for characterization purposes (6–10).

The analysis of volatiles is usually divided into major and minor volatiles, depending on their levels in samples and the strategies followed to analyze them are different. Major volatiles are analyzed by direct injection in micropacked (7,8,11) or capillary columns (4,9,10), sometimes in the split mode in order to avoid overloading of capillary columns. These methods allow the quantitation of aromas from a few mg/L to several g/L. However, the study of minor compounds has certain drawbacks resulting from their low concentrations and the large number of compounds present, thus leading to poor resolution. For this reason, the quantitation of minor compounds sometimes requires a classical liquid–liquid extraction, as recommended by the Office International de la Vigne et du vin (OIV) for ethyl esters (13). The extracts are often concentrated by prior drying (14), though on other occasions this step is avoided by microextractions (15), with the corresponding time consumption and the use of pollutant solvents. Sometimes, these methods require a prior dilution, which could cause the insolubilization of some components that are soluble in high alcohol proportions or modify the equilibrium between ethanol

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and reactive compounds, thus altering the original composition of the spirit. Other techniques such as solid-phase microextraction are obvious alternatives, although several factors such as sampling mode, fiber coating, and fiber exposure time can influence the extraction procedure (16,17), thus affecting the kind of compounds extracted in each case. Direct injection, in contrast, exactly reflects the sample composition, thus avoiding the formation of artifacts, and requires low sample volume.

Columns typically used with good results in these analyses are of the polar kind, belonging, in many cases, to the polyethylene glycol family (PEG) or derivatives. However, the use of distinct columns to analyze major and minor volatiles in the same sample is widespread (6,7,18), with the corresponding cost in material and maintenance.

In this paper, two GC methods with flame ionization detection (FID) and direct injection on the same capillary column are described and validated for the analysis of major and minor compounds in cider spirits. These methods were applied to a set of commercial and interlaboratory assay samples.

Experimental

Reagents and standards

Standards used were of analytical quality, of at least 97% purity, and were purchased from Sigma-Fluka-Aldrich (Madrid, Spain), Merck (Darmstadt, Germany), and Panreac (Barcelona, Spain).

The standard working solutions were prepared by dilution of individual compounds in an ethanol–water mixture (40:60). Ethanol (high-performance liquid chromatography quality) was purchased from Panreac (Barcelona, Spain), and ultra pure water was obtained from a Milli-Q system from Millipore (Milford, MA). All standards were injected in triplicate.

Samples

Ten cider spirits were purchased from local markets in Asturias (Spain). Prior to GC analysis, samples were filtered through a 0.22-µm polyvinylidene difluoride membrane filter from Teknokroma (Barcelona, Spain). Furthermore, five samples (two cider spirits, two fruit spirits, and a brandy) from interlaboratory assays [Bureau InterProfessionnel d'Etudes Analytiques (BIPEA), Gennevilliers, France] and a certified reference whisky (LGC, Middlesex, UK) were used to test the optimized methods. All samples were injected in duplicate.

GC analysis

Analyses were carried out on the same equipment: an Agilent 6890 N GC (Agilent Technologies, Palo Alto, CA) equipped with an FID system, a 7673 autosampler, a split/splitless injector, and GC Chemstation software (version A.09.03). Separations were carried out on a Meta.WAX capillary column (100% polyethylenglycol, 30 m × 0.25 mm; phase thickness 0.5-µm) supplied by Teknokroma (Barcelona, Spain). All compounds were assigned by comparing their retention times with those of the standards and spiked samples. Quantitation was performed according to an external standard method.

Chromatographic conditions for major volatiles

The oven temperature was: initial isotherm at 60°C (10 min), raised to 70°C at a rate of 8°C/min, and finally raised to 220°C at a rate of 15°C/min, with a final isotherm of 220°C (15 min). Flow conditions were: initial flow, 0.6 mL/min (5.2 min), raised to 1.5 mL/min at a rate of 3 mL/min each min; this flow was maintained for 10 min; and finally raised up to 2.5 mL/min at a rate of 1 mL/min each min. Other conditions were: injector temperature, 260°C; detector temperature, 275°C; injection volume, 1 µL; and split ratio, 1:20.

Chromatographic conditions for minor volatiles

The oven temperature was: initial isotherm at 35°C (5 min), raised to 60°C at a rate of 5°C/min, raised to 90°C at a rate of 10°C/min, and finally raised to 220°C at a rate of 8°C/min, and final isotherm of 220°C (10 min). Flow conditions were: 0.8 mL/min (constant flow). Other conditions wrere: injector temperature, 260°C; detector temperature, 275°C; injection volume, 1 µL; split ratio, 1/3.

Results and Discussion

Separation

The large number of analytes and the great variability in their contents counseled, dividing the analysis in two ways: major volatiles, those compounds present in levels usually higher than 10 mg/L; and minor volatiles, in the lower ranges (Table I).

Major volatile compounds

Several split ratios were initially tested in real samples to achieve both the best resolution of all pairs of peaks, such as acetal and ethyl acetate, amylic alcohols (2-methyl-1-butanol, 3-methyl-1-butanol), and ethyl lactate and 1-hexanol, as well as a suitable signal-to-noise relation. A ratio of 1:20 was selected, as a lower ratio could overload the column and would distort the peak symmetry, whereas higher ratios could impede the analysis in the less concentrated samples. This split ratio enabled the simultaneous resolution of the analytes of interest, as it reduced the interference of minor peaks and avoided the need to dilute samples. This point is of great importance because dilution of the spirit could modify several equilibria established in the original distillate, such as acetals (19), or affect the solubility of compounds, such as ethyl esters, which are less soluble in water than in ethanol (20).

Furthermore, it should be noted that when the liners used in the injector are filled with fused silica wool, vaporization is promoted and the symmetry of the peaks eluting before ethanol (mainly methanol, sometimes at levels of above 1 g/L) increases. Moreover, the life of the column is lengthened by retaining non-volatiles that could damage it. In routine analysis, a daily change of silica wool should be enough to assure an adequate work of the injection port. A typical chro-

matogram and final conditions for the analysis of major volatile compounds is displayed in Figure 1.

Minor volatile compounds

In this case, the first step was to increase the amount of sample entering the column in order to obtain a measurable signal. The best compromise between peak symmetry and signal-to-noise ratio were obtained at a 1/3 split ratio. All minor peaks showed adequate symmetry except the acids detected, which showed a pronounced tail, as a consequence of

Table I. Analytical Characteristics of the Calibration Graphs of Volatile Compounds in Cider Spirits

	Calibration curve (n = 18)					
Compound	Linear range (mg/L)	Slope	Intercept	Correlation coefficient	LOD* (mg/L)	Recovery range (min-max in %)
Aldehydes						
Acetaldehyde†	3.96–396	0.173	-0.006	0.9999	1.268	91–102
Furfural†	1.26–63	0.271	-0.039	1.0000	0.419	100–106
Benzaldehyde‡	0.11–4.36	1.684	0.021	0.9994	0.250	101–106
Acetals						
Acetal†	2.67–267	0.243	-0.213	0.9997	1.626	103–109
1,1,3-Triethoxypropane‡	0.29–5.8	1.007	0.033	0.9992	0.133	95–103
Alcohols						
Methanol†	20.54–2054	0.191	-0.644	0.9998	1.663	99–100
2-Butanol†	2.94–294	0.336	-0.275	0.9998	0.525	98–99
1-Propanol†	3.87–387	0.335	-0.299	0.9999	0.325	98–100
2-Methyl-1-propanol†	3.60–360	0.396	-0.345	0.9998	0.651	97–98
2-Propenol†	1.42–142	0.400	-0.313	0.9999	1.066	99–100
1-Butanol†	2.16–216	0.381	-0.253	0.9999	1.029	93–96
2-Methyl-1-butanol†	10.41–1041	0.411	-1.316	0.9997	0.839	94–98
3-Methyl-1-butanol†	20.63–2063	0.403	-1.726	0.9999	1.618	94–99
1-Hexanol†	1.19–119	0.367	0.236	0.9995	0.506	100–108
2-Phenylethanol†	5.41–541	0.560	-0.132	1.0000	0.429	95–99
3-Methyl-3-buten-1-ol‡	0.33–6.56	1.646	0.057	0.9993	0.134	104–108
3-Methyl-2-buten-1-ol‡	0.32–6.48	1.797	0.165	0.9995	0.116	99–104
Z-3-Hexen-1-ol‡	0.33–6.52	1.703	0.041	0.9992	0.156	99–103
1-Octen-3-ol‡	0.31–6.24	1.522	-0.007	0.9991	0.161	107–112
1-Octanol‡	0.32–6.4	1.693	0.054	0.9991	0.222	102–107
1-Decanol‡	0.33–6.6	1.812	0.019	0.9995	0.265	104–110
Benzyl alcohol‡	0.42–8.5	3.106	0.112	0.9991	0.116	95–99
Esters						
Ethyl acetate†	20.45–2045	0.203	-1.102	0.9998	1.072	102–103
Ethyl lactate†	2.60–260	0.182	0.030	1.0000	1.519	102–114
Ethyl butyrate‡	0.14–7.0	0.983	-0.007	0.9991	0.168	91–98
Ethyl 2-ethylbutyrate‡	0.13–6.5	1.073	0.024	0.9997	0.086	92–96
Ethyl hexanoate‡	0.30–14.7	1.212	0.010	0.9999	0.163	90–102
Ethyl octanoate‡	0.30–15.6	1.390	0.024	0.9999	0.240	92–108
Ethyl decanoate‡	0.30–15.9	1.519	-0.044	0.9999	0.158	95–108
Ethyl dodecanoate‡	0.30–16.2	1.726	-0.068	0.9999	0.307	91–106
Ethyl tetradecanoate‡	0.40–18.5	1.879	-0.184	0.9999	0.332	91–109
ethyl hexadecanoate‡	0.30–16.4	2.278	-0.319	0.9998	0.227	90–107
Diethyl succinate‡	0.10–10.0	1.229	0.120	0.9992	0.163	99–109
3-Methyl-1-butyl acetate‡	0.31–15.3	1.038	-0.047	0.9995	0.108	91–110
Hexyl acetate‡	0.16–7.9	1.172	0.042	0.9991	0.098	92–101
2-Phenylethyl acetate‡	0.11–4.2	1.762	0.270	0.9992	0.188	99–108
Micellaneous						
4-Ethylguaiacol‡	0.22–10.8	1.906	0.157	0.9996	0.206	93–105
4-Ethylphenol‡	0.12–11.9	2.763	0.242	0.9998	0.131	101–109
3-Ethoxy-1-propanol‡	0.18–8.90	1.276	0.027	0.9999	0.164	91–108

* limit of detection (LOD).
† major volatiles.
‡ minor volatiles.

their interaction with the stationary phase and the silica wool. The interaction with the stationary phase was evidenced when the samples were injected without silica wool; when silica wool was used, the peak tails were even more noticeable. Figure 2 shows a typical chromatogram of a cider spirit.

Validation procedure

Once the separation had been optimized, the first parameter evaluated in the validation procedure was the repeatability of the system. To do so, two standard solutions were injected five times, one for each group of flavors, with analyte contents within the expected ranges. In the worst case, repeatability was 1.6% (ethyl hexadecanoate). Quantitation by means of the external standard method was thus considered appropriate. This option avoids the introduction of another source of error, such as the addition of an internal standard.

A linear regression analysis of absolute areas versus concentration of analytes was used to check the linearity of the detector response. Linearity was determined by the square correlation coefficients of the calibration curves generated by three repeated injections of standard solutions at six concentration levels (Table I), covering the ranges expected in real samples. Detection limits were determined by analysis of low level standards.

As can be seen in Table I, all the compounds showed good linearity, with regression coefficients higher than 0.9990. The detection limits ranged between 0.325 mg/L (1-propanol) and 1.663 mg/L (methanol) among the major volatile compounds and between 0.086 mg/L (ethyl 2-methylbutyrate) and 0.332 mg/L (ethyl tetradecanoate) among the minor volatiles. The results obtained suggest that both of the proposed methods are sufficiently sensitive for determining each group of compounds if their respective levels in cider spirits (4,6,11,21) are taken into account.

In order to study the accuracy of the methods and to detect matrix effects, standard additions were performed by adding known amounts of pure standards to a cider distillate at three different concentration levels, covering the calibration range (Table I). Mean recoveries ranged between 109% (ethyl lactate) and 95% (1-butanol) for major volatile compounds and between 109% (1-octen-3-ol) and 94% (ethyl 2-methyl-butyrate) for minor volatiles, thus confirming the accuracy of both methods.

Furthermore, the reproducibility of the methods was evaluated during recovery experiments, the relative standard deviation being < 9.6% (hexyl acetate) for minor volatile compounds and < 5.4% (furfural) for major volatiles.

Although the aim of this study was the use of these methods for the analysis of cider spirits, it is well known that the volatile components in different distillates are quantitatively

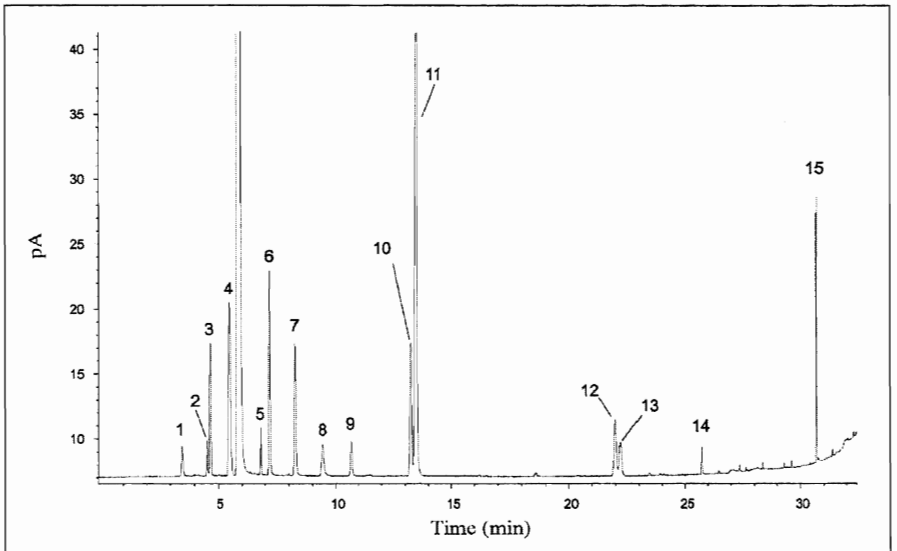

Figure 1. Typical chromatogram of major volatile compounds in a cider spirit. Peak numbers are: acetaldehyde, 1; acetal, 2; ethyl acetate, 3; methanol, 4; 2-butanol, 5; 1-propanol, 6; 2-methyl-1-propanol, 7; 2-propen-1-ol, 8; 1-butanol, 9; 2-methyl-1-butanol, 10; 3-methyl-1-butanol, 11; ethyl lactate, 12; 1-hexanol, 13; furfural, 14; 2-phenylethanol, 15.

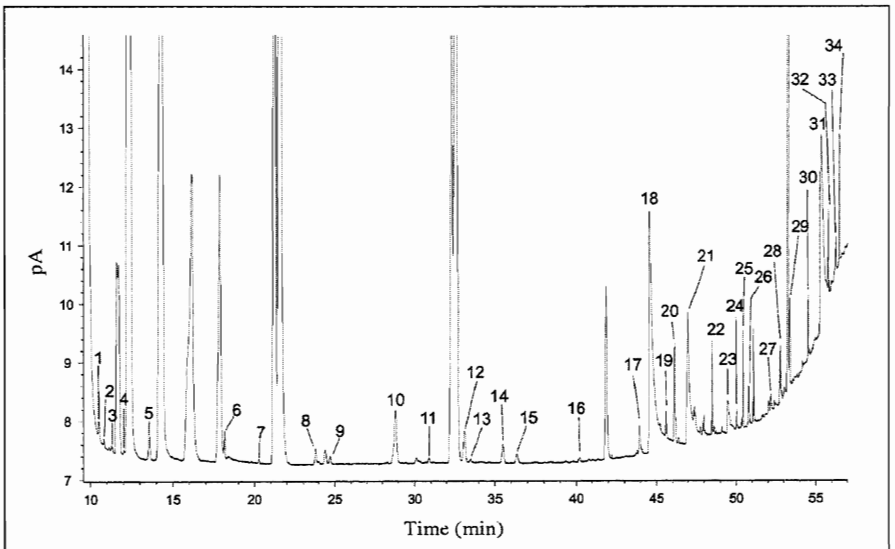

Figure 2. Typical chromatogram of minor volatile compounds in cider spirit. Ethyl butyrate, 1; ethyl-2-methylbutyrate, 2; ethyl-3-methylbutyrate, 3; butyl acetate, 4; 3-methyl-1-butyl acetate, 5; ethyl hexanoate, 6; hexl acetate, 7; 1,1,3-triethoxipropane, 8; 3-methyl-3-buten-1-ol, 9; acetoin, 10; 3-methyl-2-buten-1-ol, 11; ethyl octanoate 12; E-3-hexen-1-ol, 13; Z-3-hexen-1-ol, 14; 3-etoxi-1-propanol, 15; 1-octen-3-ol, 16; benzaldehyde, 17; acetic acide, 18; 1-octanol, 19; ethyl decanoate, 20; propanoic acid, 21; diethyl succinate, 22; 3-methylbutiric acid, 23; 1-decanol, 24; ethyl dodecanoate, 25; 2-phenylethyl acetate, 26; hexanoic acid, 27; benzyl alcohol, 28; ethyl tetradecanoate, 29; 4-ethylguaiacol, 30; octanoic acid, 31; ethyl hexadecnoate, 32; eugenol, 33; and 4-ethylphenol, 34.

similar, with certain particularities depending on the raw material. Thus, the analysis of different matrices could contribute valuable information on the suitability of these methods. Six spirits (five from interlaboratory comparisons and one certified reference whisky) were, therefore, analyzed to evaluate the accuracy of the method. In general, the results were in agreement with those obtained in the recovery study for all samples. Although a slight deviation could be the result of the uncertainty associated with real values (Table II), the high deviations detected for acetaldehyde and acetal may be due to different reasons. According to OIV methods (13) for determining acetaldehyde and acetal in samples containing sugars, a prior distillation should thus be performed, avoiding any loss of alcoholic strength so as to avoid altering the equilibrium acetaldehyde–acetal. However, it was observed that even though the samples were properly distilled (i.e. without any loss of ethanol) equilibrium was also altered, a certain amount of time being needed to restore said equilibrium (data not shown). This period could depend on factors such as pH (which is higher in distilled samples) or composition (19), and would explain the high tolerance values (sometimes around 50%) reported by the interlaboratory assay organizers for these compounds. In this respect, it should be pointed out that, irrespective of the method applied (direct injection or distillation and injection), the results are equally valid for evaluating total acetaldehyde (calculated as acetaldehyde + 0.373 x acetal) as a part of the volatile substances according to European legislation (22), although the information obtained might be uncertain from the technological point of view. Another factor that must be taken into consideration is the ratio acetal–total acetaldehyde. The values calculated for the samples from interlaboratory assays (data not shown) gave a mean value of (14.1 ± 1.1%), which is in agreement with the experimental values of 14.9% reported by Misselhorn (19) for synthetic mixtures at 40% alcoholic strength. The ratio acetal–total acetaldehyde could thus be employed as an indicator for equilibrated samples. A ratio of 13.9 for acetal/total acetaldehyde was estimated in the certified whisky, obtaining 109% recovery, which may be interpreted as an indicator of sample stability and accuracy.

The five samples from interlaboratory assays were also analyzed to evaluate the proposed method for minor aromas (Table II). The information reported by these samples could be extrapolated to the remaining analytes because discrimination due to sample treatment need not be taken into account. The ethyl esters analyzed showed recovery values in the ranges obtained by the addition method or slightly lower, but in all cases it was greater than 88% (except diethyl succinate), which could be considered satisfactory. As mentioned earlier, the differences obtained in the comparative results for ethyl esters could be related to the analytical method (dilution, extraction, concentration, etc), which affects the solubility and equilibria involving volatile compounds in distilled beverages.

Table II. Recovery Results in Spirits from Interlaboratory Assays and Certified Material (Expressed in % of Recovery)

Compound	Sample					
	CB1*	CB2*	FB1†	FB2†	B‡	CW§
Acetaldehyde	101	108	102	114	109	109
Acetal	110	103	115	113	140	–
Ethyl acetate	93	98	97	100	92	99
Methanol	103	105	93	96	102	106
2-Butanol	95	96	100	101	111	–
1-Propanol	98	99	96	98	106	109
2-Methyl-1-propanol	94	94	93	96	102	105
2-Propenol	95	95	–	–	–	–
1-Butanol	98	93	96	100	106	96
2-Methyl-1-butanol	95	96	94	95	103	106
3-Methyl-1-butanol	96	96	95	96	104	106
Ethyl lactate	88	91	97	96	98	–
Ethyl butyrate	–	–	89	91	–	–
Ethyl octanoate	95	96	92	–	90	–
Ethyl decanoate	88	94	96	95	92	–
Diethyl succinate	–	–	–	–	86	–
Ethyl dodecanoate	–	94	90	–	–	–

* CB = Cider brandy.
† FB = Fruit brandy.
‡ B = Brandy.
§ CW = Certified whisky

Commercial samples

Analyses carried out on commercial samples (Table III), with alcoholic strengths ranging from 37.1% to 45.9% (v/v), showed values in keeping with the literature (3,5,18). All the cider spirits analyzed satisfied the legal requirements in regards to methanol and contents in volatile substances (1). With respect to ester contents, ethyl esters were usually more abundant than acetic acid esters (except ethyl acetate). However, samples 7, 9, and 10 showed higher concentrations of 2-phenetyl acetate, 3-methyl-1-butyl acetate, and hexyl acetate (respectively imparting floral, fruity, and green notes). Note should be taken, on the other hand, of the low levels of 1-butanol and 1-hexanol in Sample 4, which could be related to the raw material. In this respect, 1-butanol and 1-hexanol contents are higher in spirits made from cider elaborated with fresh fruit (5). However, when the distilled cider is made from apple concentrate, the spirit is richer in furfural (11), as detected in the mentioned sample. Other organoleptically relevant compounds are 1,1,3-triethoxypropane and 3-methyl-2-buten-1-ol, associated with an "acrolein" defect by Ledauphin et at. (23). Furthermore, several minor compounds such as 4-ethylphenol, 4-ethylguaiacol, and Z-3-hexen-1-ol, relevant to the sensorial profile of cider spirits (23), were successfully determined. Thus, the proposed methodology could be an appropriate tool for the study of these distillates.

Conclusion

The analytical methods proposed to study the volatile compounds of cider spirits enabled the determination of several compounds with distinct functional groups, such as esters, acetals, aldehydes, and alcohols, with a good degree of reproducibility and accuracy. The analytical methods described are suitable for routine analysis in the determination of congeners established by law, and for the study of minor compounds that are important in technological or sensorial studies, avoiding sample treatments that could modify the equilibria in the matrix or generate artifacts.

Acknowledgements

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Table III. Content of Volatile Compounds in Cider Spirits (Expressed in mg/L)

	Cider spirit									
Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Major volatile										
Acetaldehyde	78.79	113.31	103.72	107.20	86.71	87.44	11.60	103.40	21.36	84.10
Acetal	34.80	48.86	46.88	44.95	43.72	60.82	4.69	43.97	11.24	56.53
Ethyl acetate	292.58	411.17	395.54	198.23	207.22	462.28	272.37	302.07	744.18	384.43
Methanol	389.36	559.23	557.06	679.44	501.12	471.99	203.31	435.91	213.38	343.89
2-Butanol	33.46	19.70	19.99	4.03	35.05	59.22	22.53	16.51	38.69	80.30
1-propanol	221.59	244.57	246.03	92.25	185.33	400.53	128.30	219.01	149.48	192.16
2-Methyl-1-propanol	116.12	139.63	140.01	132.05	132.53	133.23	158.10	120.19	180.73	110.55
2-Propenol	43.50	115.18	115.43	5.83	55.71	68.82	53.31	102.04	68.57	47.94
1-Butanol	46.44	61.34	61.70	12.16	38.58	72.28	46.14	45.58	50.66	55.02
2-Methyl-1-butanol	182.41	215.96	216.85	119.29	176.35	243.50	288.58	180.01	326.74	234.57
3-Methyl-1-butanol	895.34	1003.70	1009.24	594.17	920.96	1177.87	1126.99	848.10	1259.22	974.86
Ethyl lactate	135.54	257.06	267.56	18.32	172.20	183.76	126.00	212.99	117.53	137.63
1-Hexanol	35.47	41.11	41.35	8.38	48.06	46.59	54.74	37.11	61.29	44.21
Furfural	5.53	13.36	14.09	80.79	20.26	7.70	1.00	7.55	1.20	5.11
2-Phenylethanol	117.50	105.65	107.33	13.70	56.09	61.80	151.42	87.14	146.05	102.19
Minor volatile										
Ethyl butyrate	0.72	0.87	0.92	0.61	0.65	1.52	1.25	0.68	2.08	1.42
Ethyl 2-ethylbutyrate	0.41	0.44	0.48	0.54	0.23	0.77	0.32	0.35	0.58	0.63
3-Methyl-1-butyl acetate	1.95	3.28	3.39	1.23	2.63	3.72	7.50	2.33	9.06	6.61
Ethyl hexanoate	1.76	2.02	2.07	3.19	1.32	3.06	2.00	1.87	2.05	1.99
Hexyl acetate	n.d	n.d	n.d	n.d	n.d	n.d	0.96	n.d	0.63	0.63
1,1,3-triethoxypropane	2.77	1.66	1.89	1.20	1.86	9.58	6.15	1.33	0.09	4.83
3-Methyl-3-buten-1-ol	0.31	0.31	0.39	0.21	0.34	0.33	n.d	0.28	0.11	0.34
3-Methyl-2-buten-1-ol	n.d	0.33	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Ethyl octanoate	5.22	4.56	4.52	15.36	3.03	6.98	3.11	4.79	4.40	4.98
Z-3-Hexen-1-ol	1.10	0.93	1.01	0.22	1.22	1.09	1.92	1.42	2.01	1.56
3-Ethoy-1-propanol	0.83	1.36	1.38	2.36	0.97	1.03	1.05	1.50	1.49	0.80
1-Octen-3-ol	n.d	n.d	n.d	0.36	n.d	n.d	n.d	n.d	n.d	n.d
Benzaldehyde	0.95	2.43	2.45	1.76	1.54	0.76	n.d	2.06	n.d	1.10
1-Octanol	0.73	0.67	0.73	n.d.	0.41	1.78	0.26	0.40	0.31	0.91
Ethyl decanoate	3.66	3.66	3.79	12.82	3.80	5.43	1.92	4.39	2.70	4.76
Diethyl succinate	4.97	6.31	6.82	1.50	3.44	5.04	0.59	6.14	0.64	3.33
1-Decanol	0.29	0.31	0.37	0.46	n.d	0.74	n.d	0.11	0.04	0.51
Ethyl dodecanoate	1.04	1.29	1.60	4.16	1.85	1.64	1.55	1.83	0.97	2.21
2-Phenylethyl acetate	0.90	1.53	1.63	1.59	2.11	1.24	4.14	1.25	2.93	2.69
Benzyl alcohol	0.44	0.44	0.42	0.50	0.22	n.d	0.36	0.38	0.42	0.36
Ethyl tetradecanoate	0.42	0.47	0.67	1.25	0.90	0.94	1.69	0.70	0.92	1.46
4-Ethylguaiacol	2.07	2.38	2.52	1.76	0.99	2.19	2.57	2.26	2.45	2.67
Ethyl hexadecanoate	0.39	0.50	0.71	0.79	0.82	1.12	1.48	0.75	1.18	1.45
4-Ethylphenol	2.53	3.19	3.44	49.08	1.65	2.21	3.48	3.23	3.29	2.83
Alcoholic streght (% v/v)	39.1	40.2	40.0	38.8	42.6	45.6	37.1	40.0	41.1	45.0

* n.d. = not detected.

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