Vitis 16, 295—299 (1977)

Oenological and Viticultural Research Institute, Stellenbosch, South Africa

Quantitative simultaneous gas chromatographic determination of specific higher alcohols and esters in wine

by

J. P. Snyman

Gleichzeitige quantitative gaschromatographische Bestimmung spezifischer höherer Alkohole und Ester in Wein

Zusammenfassung. — Die Methode von Gruss *et al.* (1975) zur gaschromatographischen Bestimmung höherer Alkohole und Ester in Bier wurde für die Anwendung bei Wein abgewandelt. Die Methode ist schnell; Reproduzierbarkeit und Wiederfindung sind hoch.

Higher alcohols and esters contribute significantly to wine flavour. Quantitative analyses of these compounds are therefore a prerequisite for studies on wine quality. Koch *et al.* (1971) proposed a method for the determination of esters in wine and brandy. This method was modified by Gruss *et al.* (1975) to determine esters and higher alcohols in beer. This latter method was used to measure the concentrations of higher alcohols and esters in wine, but because of the different composition of wine compared to beer, the method did not give completely satisfactory results.

Very slight modifications of the method were necessary to obtain satisfactory results on wine. Firstly, the internal standards had to be changed because the hexyl acetate and hexanol used by Gruss *et al.* (1975) occur naturally in wines. Ethyl nonanoate and iso-octyl alcohol were found to be good internal standards and do not normally occur in wine in measurable concentrations. Secondly, it was found that by using 6 μl of the CS_2 extrakt, the peaks on the gas chromatogram were too small for accurate work. By increasing the injection volume to 15 μl, statisfactory peaks were obtained. Thirdly, the temperature programming of the gas chromatograph was changed to allow better separation of the peaks under our conditions. The program found to be most useful was:

5 min at 40 °C
40—56 °C at 2 °C min^{-1}
56—170 °C at 9,5 °C min^{-1}
35 min isothermal at 170 °C

Total program time is approximately 60 min, which is important for a laboratory where many samples have to be analysed. It was necessary to lower the peak temperature to 170 °C, because bleeding of the Carbowax 4000 monostearate began above this temperature.

Using the noted modifications, the reproducibility of the method was tested on both a synthetic medium containing all the components noted in Table 1 in concentrations occurring in wine. Each solution (a, b, and c) of the synthetic medium, was made up separately, and extracted and analysed in duplicate. The results are summarized in Tables 1 and 2 for the synthetic medium and wine, respectively. It is clear that a high degree of reproducibility and recovery was obtained in both media and that the method can be used with confidence in studies on wine quality. An example of an analysis of a wine is shown in the figure.

Table 1

Gas chromatographic determination of esters and higher alcohols in a CS_2 extract of a synthetic wine medium
Gaschromatographische Bestimmung von Estern und höheren Alkoholen in einem CS_2-Extrakt eines synthetischen Weinmediums

Components	Calibration factor	Solution a		Solution b		Solution c		Average recovery %	C %	S mg/l
		Added mg/l	Recovered mg/l	Added mg/l	Recovered mg/l	Added mg/l	Recovered mg/l			
Ethyl acetate	16,5670	5,23	5,28	10,46	10,73	23,54	23,49	100,78	0,62	0,0844
			5,34		10,43		23,61			
Ethyl butyrate	0,7694	0,53	0,47	1,06	1,12	2,67	2,61	101,30	3,04	0,0412
			0,56		1,14		2,72			
i-Butanol	70,2336	10,13	10,08	13,52	13,61	16,89	16,95	100,21	0,35	0,0467
			10,16		13,60		16,82			
i-Amyl acetate	1,1909	2,71	2,83	4,06	3,95	4,06	4,12	99,38	1,87	0,0645
			2,65		3,98		3,96			
Amyl alcohol	21,1973	15,71	15,59	20,94	20,79	20,94	21,13	99,75	1,18	0,2101
			15,82		21,21		20,33			
Ethyl caproate	1,1015	0,69	0,71	1,39	1,52	1,39	1,54	101,58	7,56	0,0802
			0,72		1,25		1,31			
Hexyl acetate	1,0602	0,57	0,59	1,14	1,21	0,57	0,54	98,66	2,89	0,2426
			0,55		1,08		0,55			
Hexanol	4,9586	0,70	0,68	1,40	1,64	2,80	2,57	100,83	8,11	0,1213
			0,73		1,23		2,99			
Ethyl caprylate	1,0728	1,46	1,59	2,20	2,41	2,93	3,21	104,78	3,49	0,2116
			1,42		2,49		3,34			
Ethyl caprate	1,1423	0,51	0,50	1,03	1,06	1,03	1,05	102,08	1,56	0,0177
			0,53		1,05		1,07			
Diethyl succinate	4,7411	0,32	0,30	0,64	0,62	0,96	0,98	98,58	2,06	0,0122
			0,31		0,66		0,95			
β-Phenyl ethyl	0,7704	1,18	1,26	1,78	1,89	1,18	1,15	98,67	5,99	0,0770
acetate			1,15		1,56		1,14			
Ethyl laurate	0,9091	0,53	0,51	0,53	0,55	1,07	1,12	101,72	6,38	0,0441
			0,50		0,52		1,21			
β-Phenyl ethanol	27,6747	11,29	10,86	22,59	22,13	22,59	22,23	99,64	1,48	0,2584
			11,52		22,97		22,87			
Octanoic acid	4,0098	11,31	11,89	16,97	17,47	11,31	10,76	99,00	2,73	0,3370
			10,89		16,45		11,05			

C: Coefficient of variation. S: Standard deviation.

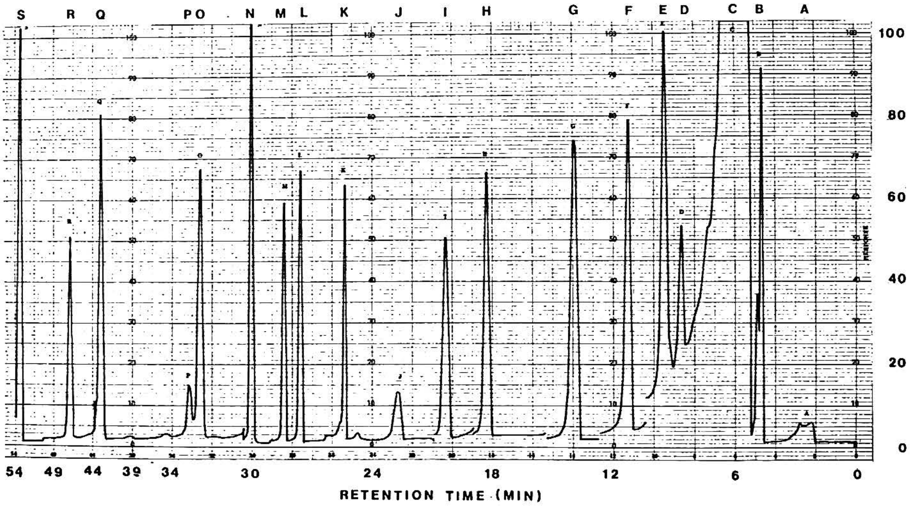
Table 2

Gas chromatographic determination of esters and higher alcohols, in duplicate, in a CS_2 extract of wine

Gaschromatographische Bestimmung von Estern und höheren Alkoholen in einem CS_2-Extrakt von Wein; doppelte Analyse

Components	1976 Colombard mg/l		1976 Chenin blanc I mg/l		1976 Chenin blanc II mg/l		1974 Pinotage mg/l		C %	S mg/l
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)		
Ethyl acetate	46,36	45,72	88,86	87,32	55,14	57,32	45,57	47,57	2,39	1,3053
Ethyl butyrate	0,19	0,18	0,26	0,26	0,31	0,29	0,20	0,19	2,45	0,0087
i-Butanol	26,86	26,93	47,70	46,83	10,80	9,78	53,46	56,42	3,74	1,1491
i-Amyl acetate	2,35	2,36	4,77	4,73	5,63	5,49	0,27	0,26	1,45	0,0514
Amyl alcohols	246,40	249,82	226,82	221,42	142,23	137,06	168,53	162,36	1,64	3,6434
Ethyl caproate	1,25	1,22	1,18	1,20	1,10	1,05	0,19	0,18	2,29	0,0217
Hexyl acetate	0,08	0,09	0,18	0,18	0,48	0,51	—	—	4,26	0,0129
Hexanol	1,53	1,59	1,34	1,35	1,82	1,95	2,52	2,52	2,29	0,0507
Ethyl caprylate	1,56	1,60	1,81	1,83	1,39	1,44	0,25	0,25	1,23	0,0234
Ethyl caprate	0,41	0,44	0,63	0,65	0,48	0,48	0,08	0,08	2,61	0,0127
Diethyl succinate	0,30	0,28	0,57	0,60	0,32	0,28	6,26	6,43	3,56	0,0628
β-Phenyl ethyl acetate	0,97	0,96	1,09	1,06	0,26	0,28	0,03	0,03	2,51	0,0132
β-Phenyl ethanol	82,72	83,53	43,75	42,53	15,60	15,09	29,65	28,87	1,44	0,6136
Octanoic acid	18,83	19,16	20,90	20,65	16,51	17,24	3,05	2,96	2,08	0,2984

(i), (ii): Duplicate analysis.
Chenin blanc I, II: Wines of different origins.
C: Coefficient of variation.
S: Standard deviation.



Chromatogram of CS_2 extract of a Chenin blanc wine. A = CS_2 (attenuator 5 × 10^3); B = Ethyl acetate (att. 5 × 10^3); C = Ethanol (att. 5 × 10^3); D = Ethyl butyrate (att. 2 × 10^2); E = i-Butyl acetate (att. 2 × 10^2); F = i-Butanol (att. 5 × 10^2); G = i-Amyl acetate (att. 2 ×10^2); H = Amyl alcohols (att. 1 × 10^4); I = Ethyl caproate (att. 1 × 10^3); J = Hexyl acetate (att. 5 × 10^2); K = Hexanol (att. 5 × 10^2); L = Ethyl caprylate (att. 2 × 10^3); M = i-Octanol, internal standard (att. 5 × 10^3); N = Ethyl nonanoate, int. std. (att. 2 × 10^3); O = Ethyl caprate (att. 5 × 10^2); P = Di-ethyl succinate (att. 5 × 10^2); Q = β-Phenyl ethyl acetate (att. 5 × 10^2); R = β-Phenyl ethyl alcohol (att. 1 × 10^3); S = Octanoic acid (att. 1 × 10^3).

Chromatogramm des CS_2-Extraktes eines Weines der Sorte Chenin blanc. A = CS_2 (Abschwächung 5 × 10^3); B = Äthylacetat (Abschw. 5 × 10^3); C = Äthanol (Abschw. 5 × 10^3); D = Äthylbutyrat (Abschw. 2 × 10^2); E = i-Butylacetat (Abschw. 2 × 10^2); F = i-Butanol (Abschw. 5 × 10^2); G = i-Amylacetat (Abschw. 2 × 10^2); H = Amylalkohole (Abschw. 1 × 10^4); I = Äthylcapronat (Abschw. 1 × 10^3); J = Hexylacetat (Abschw. 5 × 10^2); K = Hexanol (Abschw. 5 × 10^2); L = Äthylcaprylat (Abschw. 2 × 10^3); M = i-Octanol, innerer Standard (Abschw. 5 × 10^3); N = Äthylpelargonat, i. Std. (Abschw. 2 × 10^3); O = Äthylcaprinat (Abschw. 5 × 10^2); P = Diäthylsuccinat (Abschw. 5 × 10^2); Q = β-Phenyläthylacetat (Abschw. 5 × 10^2); R = β-Phenyläthanol (Abschw. 1 × 10^3); S = Caprylsäure (Abschw. 1 × 10^3).

Literature cited

Gruss, R., Kleber, K. und Zürcher, Ch., 1975: Gaschromatographische Bestimmung höherer Alkohole und Ester aus mit Schwefelkohlenstoff extrahierten Bierdestillaten. Monatsschr. Brauerei 12, 293—299.

KOCH, J., HESS, D. und GRUSS, R., 1971: Gaschromatographische Bestimmung der höheren Ester in Weindestillat, Weinbrand, Brennwein und Wein. Z. Lebensmitt.-Untersuch. -Forsch. 147, 207—213.

Eingegangen am 31. 5. 1977

J. P. SNYMAN
Oenological and Viticultural Research Institute
Private Bag X5026
Stellenbosch 7600
Republic of South Africa