FACTORS INFLUENCING UPTAKE OF COPPER FROM BRANDY BY ION-EXCHANGE RESINS

By B. C. RANKINE

Copper was efficiently removed from un-aged brandy by cation-exchange but not at all by anion-exchange. In aged brandy partial removal was obtained with both cation and anion resins.

Caramel and tannin both formed complexes with copper, and their stability increased with decrease in acidity. Very low removal of copper from these compounds was obtained at pH values above 5, and in some experiments copper was actually taken up from the cation-exchange resin.

Tasting tests indicated that ion-exchange treatment of brandies produced a slight reduction in quality.

Plastic tubing (P.V.C.) produced a permanent haze in brandy after dilution, and its use cannot be recommended.

The copper content of 33 representative Australian brandies was 0·7–12 p.p.m. with a mean value of 3·4 p.p.m.

Introduction

Excess copper is undesirable in brandy because it can cause a flocculent deposit,[1] and also because at least one state importing Australian brandy (Singapore) has recently imposed a legal limit of 5 p.p.m. on brandy in their 1957 Food and Drug Regulations.

Apart from this legal aspect, copper does not appear to play an important rôle in Australian brandy as deposition is not frequently encountered and copper is not toxic in the amounts present.

However as Singapore imports a considerable portion of Australian brandy exports it is important that more information should be obtained on copper in brandy and means of reducing it, if necessary.

It was thought that an investigation of the treatment of brandy with ion-exchange resins to remove copper would be fruitful, in view of the removal obtained in wine[2] and the anticipated absence of copper-complexing compounds in brandy. Rentschler & Tanner[3] and Garino-Canina[4] have reported removal of metals from brandy by ion-exchange.

Removal of copper by traditional fining methods is unsatisfactory, but Lafon & Couillaud[5] obtained satisfactory removal with carbon used as an ion-exchanger, followed by a milk fining. Negre & Cordonnier[6] found that calcium and sodium phytate could remove copper from brandy, although the removal was more effective under alkaline conditions.

In order to obtain more information on the copper content of Australian brandies generally, a survey of 33 representative samples was undertaken. These were obtained from the major licensed brandy distillers.

Experimental

Ion exchange

Two brandies were selected for investigation:

(1) a young acid brandy sampled shortly after distillation and not aged;
(2) an aged brandy consisting of a blend of 4-, 5- and 6-year brandies aged in 65-gal. oak casks and ready for sale.

Both brandies were double pot-distilled from wine made mainly from Doradillo grapes. Details of their composition, determined by methods described in the A.O.A.C.,[7] are shown in Table I. The young brandy was selected as an extreme example of copper contamination and in comparison with typical Australian brandies its acidity is very high.

Both brandies were brought to the laboratory and treated similarly by passing down columns of cation and anion resins. The cation resin was Zeo-Karb 225 (Permutit Co., London) which was sieved before use to obtain beads of 20–40 B.S.S. mesh size. The resin was used in both the sodium and hydrogen forms by regeneration with sodium chloride and HCl respectively. The anion resin (De-Acidite G, Permutit Co. Ltd., London) was sieved as above and used in the hydroxyl form by regeneration with aqueous ammonia.

Table I

Composition of brandies used in the ion-exchange investigation

	Young brandy	Old brandy
Ethanol, % by vol.	60	62
,, proof spirit	5 O.P.	8 O.P.
pH	2·8	4·0
Total acid, mequiv./l.	20	7
Fixed acid, ,,	1	2
Volatile acid, ,,	19	5
Aldehydes, mg./l.	81	88
Caramel, g./l.	1·5	1·5
Copper, mg./l.	26	4·8
Iron, ,,	0·5	0·8

Laboratory ion-exchange resin columns were prepared in 25-ml. burettes with the resin (10–13 ml.) resting on a pad of glass wool. The flow rate of brandy down the columns was adjusted to 18 resin volumes per h.

Samples were withdrawn every 22 bed volumes and analysed for pH by glass electrode, and copper by the colour developed with diethyldithiocarbamate measured spectrophotometrically after wet digestion with HNO_3, H_2SO_4 and perchloric acid. All analyses were carried out in duplicate.

Equilibration experiments were then carried out by shaking 80 ml. of brandy, or solutions of pure brandy components in 60% ethanol, at various pH values between 3 and 6 (HCl or KOH), in 100-ml. Jena glass reagent bottles with 5 g. of air-dried cation-exchange resin for 3 h. at 20 ± 2° C. This technique was used in a previous investigation[8] and the shaking time and resin quantity have been found adequate to ensure that equilibrium is reached.

After being shaken, the solutions were decanted from the resin and analysed for pH and copper content as above.

Copper content of Australian brandies

The 33 representative Australian brandies were analysed for copper and pH as described above, and for total acidity by the method described in the A.O.A.C.[7] The lead content was also measured and is reported elsewhere.[9]

Results and discussion

Column experiments

The progressive removal of copper was measured during passage through the ion-exchange resin columns. The results are shown in Table II, with the changes in pH.

Although 120 resin volumes of brandy were treated it was apparent that the resins were not exhausted of their exchange capacity but, as the progressive changes were considered of more importance, the actual volumes of brandy treated to the break-through point of the resins were not measured.

The interesting feature of the results in Table II is the difference shown between the young and the old brandy in the amount of copper removed by both resin types. The cation resin efficiently removed the copper in the young brandy in both the hydrogen and sodium form of the resin, whereas removal of copper by the anion resin was quite unsuccessful. In the old brandy efficient removal took place only with the cation resin in the hydrogen form.

Equilibration experiments

It was decided to study the influence of pH on the extent to which copper can be complexed, and also to investigate the nature of the complexing agents by using pure samples of brandy constituents. Rather than use column ion-exchange, which leads to greater difficulties in pH control and interpretation of results, batch equilibration experiments were used.

Consideration was given to the components of brandy which might complex copper and two were selected for testing: caramel, an additive used for colouring, and tannic acid, representing the tannic constituents which are extracted from wooden cooperage during maturation.

Table II

Progressive removal of copper from brandies by column ion-exchange

Resin volumes 10–13 ml. Cation resin : Zeo-Karb 225
Flow rate 18 resin volumes/h. Anion resin : De-Acidite G

Bed volumes	Cation exchange (Na)			Cation exchange (H)			Anion exchange (OH)		
	Cu, p.p.m.	% removed	pH	Cu, p.p.m.	% removed	pH	Cu, p.p.m.	% removed	pH
Young brandy									
Untreated	26	—	2·78	26	—	2·78	26	—	2·78
0–22	0·7	97	3·28	0·1	99	2·61	26	0	5·00
22–44	—	—	3·00	—	—	2·59	—	—	3·64
44–66	0·2	99	2·90	0·1	99	2·57	—	—	3·55
66–88	—	—	2·82	—	—	2·56	26	0	3·35
88–110	—	—	2·77	—	—	2·55	—	—	3·26
110–132	0·1	99	2·75	0·1	99	2·55	26	0	3·19
Mean	0·3	99	—	0·1	99	—	26	0	—
Old brandy									
Untreated	4·8	—	4·02	4·8	—	4·02	4·8	—	4·02
0–22	1·3	75	4·27	0·1	98	3·15	2·3	52	5·53
22–44	1·1	77	4·08	—	—	3·06	—	—	5·43
44–66	—	—	4·05	0·1	98	3·05	2·7	44	5·34
66–88	1·0	79	4·04	—	—	3·03	—	—	5·16
88–110	—	—	4·03	—	—	3·02	—	—	5·12
110–132	1·2	76	4·02	0·1	98	3·00	2·7	44	5·06
Mean	1·1	77	—	0·1	98	—	2·6	46	—

Acetic acid was also tested as a check on the experimental procedure, because it is an important constituent of brandy and is unable to complex copper.

A number of experiments were carried out with solutions of caramel and tannic acid in ethanol and also as additions to brandy, and the results of these experiments have been brought together in Table III. Each of the solutions shown was divided into several 80-ml. samples and each sample was adjusted to a different pH value in the range pH 3–6, which is the extreme pH range of brandy. The sodium form of the cation resin was used so that the pH change produced by contact with the resin was minimised.

The results obtained with pure solutions showed that copper was completely removed from 60% ethanol both in the absence and presence of 13 mequiv./l. of acetic acid (approaching the quantity present in the young brandy).

Caramel, however, exerted a binding action on copper, which was dependent on pH, and, in view of the experiments in which caramel was added to the young brandy, accounts for the behaviour of the latter. The old brandy showed a considerably stronger binding action for copper particularly above about pH 5–5·5. It is apparent that the presence of caramel can account for binding of copper in the young brandy, but only partially account for the strong binding action exerted by the old brandy.

In view of the results of the experiments in Table III the significant difference in composition between the young and the old brandy is wood age. During maturation in small oak cooperage various tannin constituents are known to be extracted into the brandy. These tannin constituents are of indefinite and complex composition, but to test whether they exerted a binding action on copper experiments with Merck reagent grade tannic acid (the purest form of tannic acid available) were carried out.

The results indicated that above about pH 5–5·5 tannin exerts a significant binding action on copper as shown by its addition to the young brandy.

It would appear that the strong binding action of the old brandy on copper is due to the presence of caramel and wood extractives. One important finding is the strength by which copper is bound at pH values above about pH 5·5, where copper was actually removed from the ion-exchange resin and taken up by the brandy. (An analysis of the resin after several thorough regenerations showed that it contained 35 p.p.m. of copper presumably present as an impurity.)

Table III

Influence of pH and certain brandy components on removal of copper from brandy by cation-exchange resin

80 ml. of solution, 5 g. Zeo-Karb 225(Na) shaken 3 h. at 20 ± 2°

Solutions	pH at equilibrium	Copper, p.p.m.		Cu removed, %	Solutions	pH at equilibrium	Copper, p.p.m.		Cu removed, %
		Before shaking	After shaking				Before shaking	After shaking	
Ethanol 60% (v/v)	3·76	4·8	0	100	Young brandy	3·37	26	0·4	98
	4·63	4·8	0	100		4·21	26	1·7	93
	5·18	4·8	0	100		5·38	26	5·7	78
	5·44	4·8	0	100		5·98	26	10·2	61
Ethanol 60% (v/v) + 13 mequiv./l. acetic acid	3·66	4·8	0	100	Young brandy + 0·1% tannic acid (Merck)	3·94	26	1·5	94
	4·52	4·8	0	100		4·78	26	3·0	88
	4·93	4·8	0	100		5·67	26	17·1	34
	5·84	4·8	0	100					
Ethanol 60% (v/v) + 1·5 g. of caramel/l.	3·80	4·8	0	100	Young brandy + 1·5 g. of caramel/l.	3·40	26	1·0	96
	4·78	4·8	0·4	92		4·19	26	3·1	88
	5·41	4·8	0·9	91		4·99	26	5·9	77
	5·86	4·8	1·2	75		6·05	26	12·0	54
Ethanol 60% + 1·5 g. of caramel/l. and 0·1% tannic acid (Merck)	4·65	4·8	0·2	96	Old brandy	3·71	4·8	0·6	88
	5·08	4·8	0·4	92		4·50	4·8	1·0	79
	5·88	4·8	1·2	75		5·24	4·8	2·7	44
						6·20	4·8	7·7	−60*
As above but with 0·5% tannic acid	4·58	4·8	0·2	96	Old brandy + 0·1% tannic acid	4·22	4·8	0·9	81
	5·19	4·8	0·4	92		4·82	4·8	1·8	63
	5·97	4·8	2·2	54		5·59	4·8	3·9	19
					Old brandy + 1·5 g. of caramel/l.	4·44	4·8	1·9	60
						5·22	4·8	3·9	19
						5·94	4·8	7·3	−52*

* Negative value implying that copper was removed from the ion-exchange resin

In view of the complex and indefinite composition of both caramel and tannin no attempt was made to elucidate the nature of the complex formed between these constituents and copper.

Influence of ion-exchange treatments on taste

The brandy samples which were passed through the ion-exchange columns were compared with the control samples by a panel of four tasters. The general comment was that the treatments seemed to produce a reduction in quality, and in the old brandy a loss of wood character was observed.

However, should brandy need to be treated by ion-exchange resins the results of this investigation show that the treatment should be carried out soon after distillation before addition of caramel or contact with wood, and accordingly the action of ion-exchange treatment in reducing the 'aged-in-wood' character would not apply.

Haze produced by plastic tubing

An interesting side effect was observed after brandy was passed through plastic tubing into ion-exchange columns. After passage through the columns the brandy was quite clear, but on dilution to normal bottling strength of 39% ethanol by volume (32° under proof) a heavy and permanent haze was formed.

It was found that the haze only formed after the brandy had passed through P.V.C. (polyvinyl chloride) plastic tubing and was not related to the ion-exchange process. Tests of several samples of P.V.C. tubing, both beverage-grade and otherwise, gave similar results, and indicated the undesirability of using P.V.C. plastic tubing for handling spirits.

Discussion with plastic technologists revealed that flexible plastics of the P.V.C. type contain plasticisers and stabilisers which may sometimes be dissolved by the appropriate solvents.

The inference from the observations and tests was that brandy containing 60% ethanol by volume dissolved out some constituent of the plastic tubing to form a stable clear solution, but on diluting the brandy to bottling strength the lowered solvent concentration precipitated the plastic constituent which remained as a heavy stable opalescent haze, consisting under the microscope of very small particles a fraction of 1 μ in diameter.

Nature of copper in brandy

Whilst the investigation was designed to study the factors influencing uptake of copper from brandy by ion-exchange resins, some information may be inferred on the nature of copper in brandy.

Table IV

Copper content (p.p.m.) of Australian brandies

Distiller	Age in years	Alcoholic strength		Total acid, mequiv./l.	pH	Cu, p.p.m.
		Proof spirit (British)	% (v/v)			
A	3	34 U.P.	38	5·3	3·42	4·0
	4	29 U.P.	40	9·1	3·22	4·6
B	4	33 U.P.	38	3·6	4·04	2·7
	4	15 O.P.	66	4·4	4·24	2·5
C	3	33 U.P.	38	2·7	4·20	0·8
	Blend 5, 6, 14	32 U.P.	39	4·2	4·25	0·7
D	Blend 4, 5, 7 & 9			2·6	4·57	1·0
E	3	30 U.P.	40	4·6	3·58	3·2
F	3	34 U.P.	38	2·7	4·00	0·8
G	2	30 U.P.	40	4·6	4·22	0·8
H	—	32 U.P.	39	3·5	4·35	0·9
I	3	33 U.P.	38	5·3	3·30	5·3
	5	33 U.P.	38	5·8	3·43	3·7
J	—	31 U.P.	39	3·0	4·10	4·9
K	3	6 O.P.	61	9·5	3·47	8·5
	—	32 U.P.	39	8·4	3·68	7·3
L	1	10 O.P.	63	2·5	4·01	6·6
	2	10 O.P.	63	2·1	4·60	0·8
	3	9 O.P.	63	3·0	4·58	1·7
	6	33 U.P.	38	2·8	4·24	7·0
	14	25 U.P.	43	8·0	4·28	12·0
M	4	33 U.P.	38	2·8	4·04	2·3
	5	25 U.P.	43	4·9	4·08	1·6
N	1	0·4 O.P.	57	1·7	4·39	1·0
O	3	32 U.P.	39	2·6	4·14	1·1
	5	30 U.P.	40	4·3	4·01	1·9
	15	30 U.P.	40	7·5	3·92	1·7
P	3	31 U.P.	39	4·8	3·60	6·5
	4	25 U.P.	43	9·3	3·77	6·9
Q	3	21 U.P.	45	2·4	4·06	0·7
	4	20 U.P.	46	3·1	4·13	1·1

Range of values: 0·7–12; mean 3·4

Samples obtained from United Kingdom

P	—	30 U.P.	40	7·9	3·51	4·2
	—	10 O.P.	63	7·6	3·89	3·7
Distilled water		—	—	—	—	0·0
R	—	31 U.P.	39	4·7	4·05	0·9
	—	10 O.P.	63	6·1	4·52	1·4
Distilled water		—	—	—	—	0·0

It would appear that in un-aged brandy without addition of caramel, copper is present as a simple cation, as it can be readily removed with a cation-exchange resin but not at all with an anion-exchange resin. When caramel is added a copper–caramel complex is formed, the stability of which depends on pH. After the brandy is aged in wood the complex tannin materials further complex copper and make its removal with cation-exchange resin more difficult. The complex formed is partly anionic since it is partly taken up by an anion resin, and the copper remaining can be mainly removed by subsequent passage through a cation-exchange resin.

Entry of copper into brandy

Considerable information is available on the methods of entry of copper into cognac from the work of Lafon & Couillaud,[5] who found that all the copper entered as contamination during and subsequent to distillation, and the copper content of the wine being distilled was not important, because copper is not entrained in the vapour.

Contamination mainly occurred from copper condensers on the stills, particularly if not properly cleaned, and the extent of contamination varied during distillation, being high initially, low during most of the distillation and very high in the ' queue ', or the relatively high-boiling fraction (tails) distilling after most of the ethanol, and containing a high proportion of volatile acid.

Subsequent cellar handling with brass equipment, such as pumps, produced an increase in copper content, e.g., 1 l. of cognac left in a brass pump for 24 h. increased in copper content by 150 p.p.m.

After brandy has been placed in wooden maturation casks the copper content does not remain stationary. The copper–tannin combination forms and is removed from solution as a flocculent brown precipitate. This reaction is dependent on pH and is most complete above pH 4·2, progressively less so between pH 4·2 and 2·5 and does not occur below pH 2·5. The results reported above serve to support and amplify this finding.

As brandy matures in wood its acidity increases, due mainly to extraction of acidic compounds from the wood, the copper–tannin precipitate slowly redissolves with time and the copper content gradually increases.

Copper content of Australian brandies

The results of the analyses are shown in Table IV. The range of values from 0·7 to 12 p.p.m. is considerable and it is interesting to observe that eight of the samples exceed the limit set by the State of Singapore (5 p.p.m.).

The United Kingdom samples were obtained from two of the principal Australian exporters. Most of the brandy is exported in bulk and broken down with distilled water and bottled in England, and accordingly samples of the bulk brandy and distilled water were also obtained.

As a matter of interest the copper content of the brandies was compared with the total acidity and a highly significant correlation was observed (the correlation coefficient with 29 degrees of freedom was 0·62), indicating that the extent of copper contamination is closely related to the total acidity of the brandy.

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LEAD CONTENT OF AUSTRALIAN BRANDIES

By B. C. RANKINE

The lead contents of 37 Australian brandies ranged, with one exception (0·25 p.p.m.), from <0·01 to 0·06 p.p.m. with a mean of 0·029 p.p.m. These included samples of Australian brandies bottled in the United Kingdom.

The significance of the results in view of the proposed British legal limit of 0·5 p.p.m. is discussed.

Introduction

For many years lead has been known to be a cumulative poison and its maximum content in foods and beverages has been subject to legislation. Apparently lead is one of the most toxic of the trace elements and serves no beneficial function in human metabolism.

In 1954 the British Ministry of Food recommended revised limits of 1·0 p.p.m. for lead in wines, and recently a limit of 0·5 p.p.m. for spirits has been proposed.

As the United Kingdom is one of Australia's export markets for brandy, a limit of lead in brandy is of importance to the Australian industry, and consequently this investigation of Australian brandies was made at the request of the Australian Wine Board, which represents the export interests of the wine industry.

Experimental

Collection of brandies

With the co-operation of the Australian Wine Board, a total of 31 samples was obtained from 17 licensed distillers and, as far as possible, each sample represented the finished product as sold. Consequently the samples are probably a representative cross-section of Australian brandies available for sale at present. Information on age of the brandy, type of still, alcohol content and other relevant data was obtained with most samples.

In addition samples of Australian brandy from two shippers were obtained from the United Kingdom. These comprised samples from high-strength bulk brandy as shipped (most brandy is shipped in bulk to U.K.), samples of the bulk brandy broken down to bottling strength with distilled water and also samples of the distilled water used for dilution.

Method of analysis

The method of analysis was that described by the Analytical Methods Committee of the Society for Analytical Chemistry.[1] Care was taken to purify the reagents as described in the method, and in addition all acids were purified by distillation through Pyrex glass or silica.

The organic matter in the brandy aliquots (100 ml.) was destroyed by wet digestion with HNO_3 and H_2SO_4 and method A was used for the separation of lead. All analyses were carried out in duplicate. The recovery of added lead was found to be 95–98% and replicate analyses on the same sample agreed to within 0·3 μg. in a 100-ml. brandy sample, corresponding to 0·003 p.p.m.

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