The Removal of Copper and Iron from Wine Using a Chelating Resin[1]

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An insoluble polymer-supported absorbant, developed for the selective removal of excess copper and iron from wine was tested. Tests conducted on dry white wine with excessive copper and iron showed effective removal of 98% copper (II) and 82% iron (III). This treatment did not significantly affect the other wine constituents and therefore offers an appropriate alternative to the ferrocyanide treatment.

The presence of excess dissolved copper and iron can result in undesirable changes in the flavour and appearance of wine. The nature and composition of the clouding caused by excess iron and copper have been well studied and documented (Ribereau-Gayon, 1933; Berg, 1953; Kean & Marsh, 1956 a, b; Amerine & Joslyn, 1973; Amerine *et al.* 1979).

The catalytic action of both copper and iron in oxidation reactions (Ribereau-Gayon, 1933; Berg & Akiyoshi, 1956) as well as in reduction reactions (Berg, 1953) is known, and plays an important part in changing the flavour and colour of wine to the detriment of quality. Apart from the bitter metallic taste caused by the presence of excessive amounts of copper in wine, copper is classified as poisonous and a legal limit of 1 mg/l in wine has been recommended for both California (Amerine *et al.*, 1979) and Australia (Anon., 1982). The legal limit for copper in South African wine and spirits is 7,0 mg/l (Anon., 1980). Eschnauer (1966) placed the maximum limit for copper in German wines, to avoid clouding, at 2 mg/l. This is very high compared with a limit of 0,3 mg/l proposed by Amerine & Joslyn (1973) on Californian wines. Berg (1953) found the maximum acceptable iron content for wine to be 5 mg/l.

Amerine & Joslyn (1973) stated that under normal conditions of vinification, most of the iron is present in the ferrous state. The ratio of ferric to ferrous ions will depend on the state of oxidation of the wine. The removal of copper and iron during fermentation is well known and documented (Thoukis & Amerine, 1956; Hsia, Planck and Nagel, 1975), but with highly contaminated must the resulting wine sometimes still contains excessive amounts which must be removed.

Although it is sometimes necessary to remove excess copper and iron from wine the only method, to date, that found practical application is the ferrocyanide treatment, also called "blue fining". The potassium ferrocyanide treatment and variations thereof have been well studied and documented (Brown, 1932; Fessler, 1952; Joslyn & Lukton, 1953; Amerine *et al.*, 1979).

This treatment is potentially hazardous because although potassium ferrocyanide itself is not poisonous it may, when added to grape juice or wine, hydrolyse to form hydrocyanic acid which is poisonous (Brown, 1932). In some countries this treatment is legalised but subject to very strict control. In South Africa the treatment must be done under Government supervision.

When treating a wine with ferrocyanide special precautions must be taken which include, among others, the following:
  i) After treatment and filtration all equipment must be flushed with alkali to destroy any residue reagent.
 ii) Careful disposal of filter sheets and filter aid material.
iii) Special analyses are needed to ensure that no hydrogen cyanide or any unreacted ferrocyanide remains in the treated wine.
 iv) It sometimes happens that treated wines are excessively fined with bentonite to assure complete removal of ferrocyanide – protein complexes with an adverse effect on the quality of the wine.

Over the years alternative methods have constantly been sought but with little or no success.

The objective of this study was to develop an appropriate alternative to the "blue fining" process for the removal of heavy metals, and more specifically copper and iron, from wine. Specifications for such a treatment demand the specific and selective extraction of copper and iron from wines without altering, to any detectable extent, both analytically or organoleptically, the composition or quality of the wine. Of the alternatives considered, insoluble "polymer supported" absorbants held the most promise and were studied in detail.

MATERIALS AND METHODS

The development of a suitable chelating resin entails firstly, the selection of a suitable chelating group that will selectively absorb copper and iron without significantly absorbing any of the other constituents in wine. The second step required the study and optimisation of the reaction conditions needed for the attachment of

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the chelating group to a suitable insoluble polymer matrix. A ligand, 8-hydroxyquinoline, was selected and attached to a macroporous poly (styrene-co-divinylbenzene) co-polymer in bead form (Loubser, 1984).

The resin had a capacity of 1,2 mmol/g (dry resin) for copper (II), 0,5 mmol/g (dry resin) for iron (II) and 1,0 mmol/g (dry resin) for iron (III) at pH 3,5 with a water regain value of 1,15. The exchange kinetics of the resin proved adequate for the use of the resin in a column.

The beverage to be treated was passed down a 40 x 1 cm internal diameter column containing the insoluble polymer-supported absorbant at room temperature (ca 20°C) at a flow rate of either 5 or 10 bed volumes (BV) per hour. The column was packed with either 2 or 4 g (dry mass) moist resin.

The treatment schedule can be summarised as follows:

Beverage/ Alcohol content	Polymer dry mass (g)	Flow rate (BV/h)	Volume treated (ml)	Contamination level (mg/l)	
				Fe	Cu
1) Dry White Wine 12% (V/V)	4	5	2 000	21,0	5,8
2) Dry White Wine 12% (V/V)	4	10	2 000	21,0	5,8
3) Dry Red Wine 13% (V/V)	4	5	1 400	13,0	5,2
4) Grape Juice 0% (V/V)	2	5	1 000	13,6	6,2
5) Fortified Wine 16,5% (V/V)	2	5	600	16,0	7,8
6) Brandy 43% (V/V)	2	5	1 000	1,1	3,5
7) Sugar Cane Alcohol 43% (V/V)	2	5	1 000	6,0	7,3

The natural dry wines, prior to their use in all experiments, were protein stabilised with bentonite followed by tartrate stabilization at -4°C for 7 days. Excess iron and copper were added as iron (III) chloride hexahydrate or copper (II) sulphate pentahydrate, to all beverages.

The chelating polymer was regenerated with 50 ml 2M hydrochloric acid for every 1 g (dry mass) polymer used, at a flow rate of 10 BV per hour. The chemical stability of the chelating polymer was tested by treatment of the polymer for 24 hours at 90°C respectively with 8 M hydrochloric acid and 8 M sodium hydroxide followed by subsequent redetermination of capacity.

The pH of wines was measured using a Beckman model 3500 pH meter. Total acidity, total phenols and total nitrogen were determined by standard methods (Amerine & Ough, 1980). Total tartrates were measured using the method of Rebelein (1972). Optical density measurements were done on a Beckman ACTA CIII UV-visible spectrophotometer using 1,0 cm cuvettes at 420 nm and also 520 nm for red wines.

A Varian model 775 atomic absorption spectrophotometer was used for all metal analyses. The concentrations of copper and iron were determined with an air-acetylene flame, but as potassium and sodium are subject to ionization interference in the flame a more easily ionisable ion in the form of cesium was added (1 000 mg/l) (Caputi, Ueda & Ueda, 1967; Meredith, Baldwin & Andreasen, 1970; Lepage, 1978).

The determination of calcium and magnesium in wine posed problems since the wine constituents phosphates and sulphates, cause chemical interferences in an air-acetylene flame. The addition of lanthanum (1 500 mg/l) solved this problem for magnesium. This method has been prescribed for analysis of beer (Trachman, Gantz & Saletan, 1970; Lepage, 1980). It was necessary to use a nitrous oxide flame to prevent chemical interference in calcium determinations (Manning & Capacho – Delgado, 1966).

RESULTS AND DISCUSSIONS

Dry White Wine:

A natural dry white wine with added excess copper and iron was passed through a column containing the chelating polymer at 5 BV per hour and after regeneration a repeat run at double the latter flow rate (10 BV/h) was done.

Tables 1 and 2 give the results of analyses of the different fractions.

Tables 1 and 2 shows:
1. Treatment of 2 000 ml wine containing excessive concentrations of copper and iron resulted in 82% removal of iron and 98% removal of copper at 5 BV/h and 72% for iron and 95% for copper at 10 BV/h. These results are shown schematically in Figure 1.
2. The more effective removal of copper is to be expected since copper (II) forms a more stable complex with 8-hydroxyquinoline than iron (II) or iron (III).

TABLE 1

Analyses of a dry white wine after treatment at a flow rate of 5 BV/h

Volume treated (ml)	Fe (mg/l)	Cu (mg/l)	pH	Total Acidity (g/l)	Total Phenol (mg/l)	Total Tartrate (mg/l)	Optical Density 420 nm
Control	21,0	5,8	3,10	4,9	260	1 265	0,098[a]
200	0,6	0,05	2,84	3,7	83	551	0,020
400	1,2	0,05	3,06	5,0	91	1 307	0,030
600	0,9	0,04	3,09	5,0	107	1 355	0,030
800	1,0	0,04	3,08	5,0	109	1 329	0,030
1 000	1,4	0,04	3,20	4,9	126	1 298	0,030
1 400	3,9	0,09	3,15	4,9	149	1 276	0,035
1 800	8,0	0,20	3,07	5,0	156	1 254	0,040
2 000	8,4	0,23	3,09	5,0	160	1 276	0,048
Calculated bulk average	3,73	0,10	3,08	4,84	129	1 218	0,034
Removal	82%	98%					

a) Optical density of wine prior to contamination was 0,068

TABLE 2

Analyses of a dry white wine after treatment at a flow rate of 10 BV/h

Volume treated (ml)	Fe (mg/l)	Cu (mg/l)	pH	Total Acidity (g/l)	Total Phenol (mg/l)	Total Tartrate (mg/l)	Optical Density 420 nm
Control	21,0	5,8	3,10	4,9	260	1 265	0,098[a]
200	1,7	0,06	2,85	4,4	113	601	0,032
400	2,9	0,12	3,15	4,8	128	1 015	0,038
600	3,5	0,16	3,21	4,9	143	1 167	0,056
800	5,3	0,34	3,23	5,0	143	1 254	0,066
1 000	7,4	0,53	3,22	5,0	162	1 211	0,068
1 400	6,3	0,28	3,20	5,0	160	1 189	0,070
1 800	8,8	0,46	3,21	5,0	160	1 167	0,080
2 000	7,4	0,38	3,20	4,9	159	1 145	0,080
Calculated bulk average	5,8	0,31	3,17	4,9	149	1 111	0,064
Removal	72%	95%					

a) Optical density of wine prior to contamination was 0,068

3. Removal of both copper and iron is more efficient at the lower flow rates, while a higher rate led to higher leakage of iron than of copper. (Figure 1).

4. The concentrations of potassium, calcium, sodium, magnesium and total nitrogen of the wine were 620, 63, 49, 88 and 252 mg/l respectively and remained unchanged.

5. Apart from a definite drop of the pH in the first 200 ml sample, no significant change occured in that of the rest of the wine. This is believed to have been caused by elution of residual hydrogen ions, which are loosely associated with the basic sites on the polymer matrix or the 8-hydroxyquinoline ligand.

6. The optical density (colour) and total phenol content decreased markedly during the early stages of the treatment but increased very slowly as more wine was treated. Since the brown colour being measured is formed by oxidation of phenols, it is logical that optical density and phenol content should follow the same pattern. The decrease in colour and total phenol content could be due to the fact that the protonated amine sites on the polymer, as a consequence of preparation technique, could act as weak base anion exchange sites absorbing phenols (Helfferich, 1962). These effects are more pronounced at the lower flow rate.

7. The initial sharp decrease in the tartrate concentration could be the result of the ability of tartrate to associate with the exchange sites on both the ligand and the polymeric carrier as in the case of phenols, but with possibly less affinity.

The total and free sulphur dioxide contents were not monitored during these experiments because open-column systems were used. During a separate experiment in which a closed system was used (resin added to wine) definite decreases in both free and
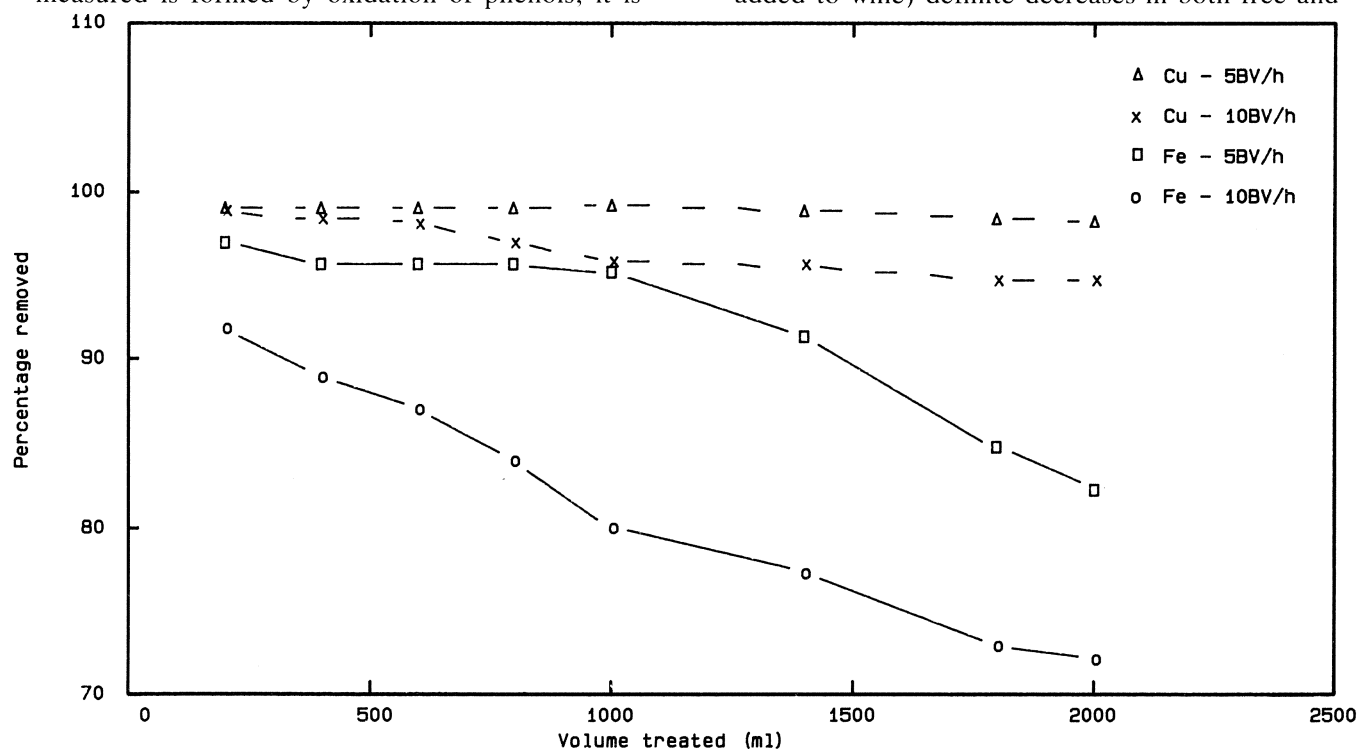

FIGURE 1

Percentage copper and iron removed from a dry white wine containing excessive copper and iron by a chelating polymer at flow rates of 5 and 10 BV/h.

TABLE 3

Analyses of a dry red wine after treatment at a flow rate of 5 BV/h

Volume treated (ml)	Fe (mg/l)	Cu (mg/l)	pH	Total Acidity (g/l)	Total Nitrogen (mg/l)	Total Phenol (mg/l)	Total Tartrate (mg/l)	Optical Density	
								420 nm	520 nm
Control	13,0	5,20	3,61	4,0	280	1 306	1 537	1,810	2,33
200	1,1	0,12	3,29	3,6	266	549	557	0,936	1,55
400	2,7	0,22	3,58	4,0	280	1 072	1 450	1,266	1,77
600	4,7	0,46	3,60	4,1	280	991	1 842	1,450	1,98
800	6,1	0,70	3,60	4,1	280	1 306	1 733	1,720	2,30
1 000	7,3	1,10	3,60	4,1	280	2 118	1 555	1,790	2,37
1 400	7,0	0,94	3,60	4,1	280	1 775	1 733	1,746	2,40
Calculated bulk average	5,1	0,64					1 522	1,522	2,11
Removal	61%	88%							

total sulphur dioxide of about 40% and 20%, respectively, were noted. In practice it will therefore be necessary to adjust sulphur dioxide levels immediately after treatment.

The relative amounts of iron (II) and iron (III) in wines depend on the state of oxidation of the wine, but under normal conditions of vinification most of the iron is expected to be in the form of iron (II) (Amerine & Joslyn, 1973). It could therefore be expected that iron (II) concentrations in naturally contaminated wines will be much higher compared to the wines under study where only iron (III) was added. This in turn could effect the efficiency of iron removal since the capacity of the chelating resin under study is appreciably higher (about 75%) for iron (III) than for iron (II) at pH 3,5 (Loubser, 1984).

To verify the above a dry white wine naturally high in iron (20 mg/l) was treated in precisely the same way at a flow rate of 5 BV/h. Results of this experiment indicated a slight reduction in the efficiency of iron removal from 91% where iron (III) was added to 88% for the wine naturally high in iron (1 400 ml wine treated).

Small-scale open column systems were used, which made sensory evaluation impossible. No adverse effects on wine quality can be envisaged as the functional group, 8-hydroxyquinoline, is chemically bound to an inert polymeric carrier, which is insoluble in aqueous or ethanolic solutions. Further studies should include statistical organoleptic tests.

Dry red wine:

Excess copper and iron (20 and 5 mg/l respectively) were added to a natural dry red wine, but after a few hours a haze developed. The haze, most probably an iron clouding ("casse") was filtered out and the wine treated with the chelating polymer. Analyses of the collected fractions are summarized in Table 3.

From table 3 it is evident that the reaction of the red wine is similar to that of the white wine. Concentrations of potassium, calcium, sodium and magnesium of the wine were 1 260, 57, 44 and 110 mg/l respectively and were not affected by this treatment. The first difference is that copper and iron are less effectively removed. After 1 400 ml of red wine had been eluted, 61% of the iron was removed compared with 91% for white wine, and 88% of the copper with 99% from the white wine.

A further difference was that after about 800 ml had been treated the colour remained stable compared to the continuous removal of colour, at 420 nm, for the white wine.

Possible explanations for these differences could be, firstly, that soluble complexes of these metal ions are formed with the phenolic compounds. Phenolics are present in red wine at appreciably higher concentrations than in white wine and metal ions may therefore be less readily available in red wines as exchangeable ions. Secondly, the available protonated amine sites can become saturated with the high concentration of colouring material which could reduce the metal complexing ability of the polymer. This could be due to interference with the free exchange of metal ions either by some unproved mechanism or by blocking of the fine pores of the polymer matrix. The collected colouring material proved to be removable from the polymer by passing 2 M sodium hydroxide through the column.

TABLE 4

Analyses of grape juice after treatment at a flow rate of 5 BV/h

Volume treated (ml)	Fe (mg/l)	Cu (mg/l)	Zn (mg/l)	pH	Total Acidity (g/l)	Reducing Sugar (g/l)	Total Nitrogen (mg/l)	Optical Density 420 nm
Control	13,6	6,20	0,32	3,28	5,3	184	350	0,060
200	1,8	0,11	0,18	3,27	5,0	189	308	0,026
400	2,2	0,07	0,19	3,26	5,2	189	308	0,026
600	3,6	0,14	0,21	3,24	5,2	°186	308	0,028
800	5,3	0,21	0,21	3,29	5,2	186	308	0,036
1 000	5,3	0,24	0,21	3,30	5,2	188	308	0,036
Calculated bulk average	3,64	0,15						0,030
Removal	73%	98%						

Grape Juice:

Grape juice (18°B, protein and tartrate-stable) containing excess copper and iron was treated with the chelating resin. Analyses of the collected fractions are summarized in Table 4.

It is clear that both copper and iron can be removed effectively by the chelating polymer from grape juice. The removal of copper was very effective and was practically the same as for wine. The removal of iron on the other hand, was less effective than from the wine (see Table 1).

Potassium, calcium, sodium, magnesium and manganese initial concentrations were 910, 56, 40, 77 and 0,5 mg/*l* respectively and remained unchanged.

High Alcohol beverages:

The removal of copper and iron from other beverages was also tested and the results are summarised in Table 5. Since no change in potassium, calcium, sodium, magnesium, ethanol or sugar contents could be detected, corresponding values are not included in the Table.

TABLE 5

Analyses of high alcohol beverages after treatment at flow rates of 5 BV/h

Volume treated (m*l*)	Fortified Wine		Brandy		Cane Spirit	
	Fe (mg/*l*)	Cu (mg/*l*)	Fe (mg/*l*)	Cu (mg/*l*)	Fe (mg/*l*)	Cu (mg/*l*)
Control	16,0	7,8	1,1	3,5	6,0	7,3
200	3,0	0,4				
400	4,4	0,4	0,6	0,6	2,2	1,0
600	7,5	0,85				
800			0,7	1,0	2,6	1,0
1 000			0,7	1,3	2,7	1,4
Calculated bulk average	4,97	0,55	0,66	0,9	2,46	1,08
Removal	69%	93%	40%	74%	59%	85%

Although the chelating polymer still achieves effective reduction of copper and iron, its lower efficiency in the higher alcohol beverages can only be as a result of the higher alcohol content. This is probably accounted for by a reduction of the stability constant of the complex in higher alcohol – water mixtures.

Repeated experiments with contaminated wines followed by regeneration of the chelating polymer proved that the polymer can be fully regenerated with hydrochloric acid or sulphuric acid. The chemical stability of the polymer also proved to be adequate when, after treatment with 8 M hydrochloric acid and 8 M sodium hydroxide, the capacity of the polymer for copper (II), iron (II) and iron (III) remained unchanged.

CONCLUSION

An insoluble polymer-supported absorbant, developed specifically to remove copper and iron from wine, was tested. It was proved that the reagent will remove copper and iron very effectively and selectively from wine. No significant changes in the composition of the tested wines were evident other than a tolerable loss of colour and decrease in phenol content.

The use of the ferrocyanide treatment undoubtedly harms the image of the wine industry, but since no alternative is available winemakers are forced to use it.

This investigation revealed an exciting new possibility but many aspects still need to be researched before it could find practical application. It is only large scale production of the chelating polymer followed by large scale treatment of wine that could give answers to questions such as costing, life span of polymer or its effect on wine quality.

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