# In Scotch Whisky, From Where are the $Fe^{3+}$ and $Cu^{2+}$ Ions Sourced?

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The distillate which becomes Single Malt Scotch Whisky has an Electron Paramagnetic Resonance (EPR) signal attributable to $Cu^{2+}$ but no $Fe^{3+}$ signal. After aging in used oak sherry barrels, the bottled product contains an additional $Fe^{3+}$ signal at g ~ 4 appears. Spectra of the same product aged for different lengths of time were very similar. Are the barrels or the metals in the distilling apparatus the source? What happens with Brandy?

## 1. Introduction

A previous EPR study of Scotch whiskies [1] showed $Fe^{3+}$ and $Cu^{2+}$ signals, each whisky having a unique spectrum. The $Fe^{3+}$ and $Cu^{2+}$ have previously been attributed to the metals in the distilling vessels [1]. To check the consistency of a particular spectrum from different years, the present study compared specimens of the distillate (from 2008) before transfer to the aging process and of the aged whisky (before bottling) from two different years (1960 and 1970). Since once of us has also previously investigated brandies by EPR [2], we obtained similar specimens of two brandies for comparison. The consistency of the aged whisky spectra was good. The most interesting observations, however, were that $Fe^{3+}$ and $Mn^{2+}$ were detectable by EPR in final aged product but not in the distillate and that the $Cu^{2+}$ ligand environment changed upon aging.

## 2. Methods and Sample Preparations

Double distilled brandy and whisky undergo similar preparations. The 'first' process is distilling the filtered liquid from the must/mash at least twice in a pot still, usually made of copper, or copper and stainless steel. Then the liquor was again twice distilled, and the final product placed in old oak sherry barrels (whisky) or old oak wine barrels (brandy). We examined the following specimens: (1) a 1960 and a 1970 whisky sample from each aging barrel and a 2008 final distillate prior to barrel ageing; (2) a 'first' (double) and 'second' (double) distillate for brandy.

Accurate metal concentration analysis was analysed by inductively-coupled plasma mass spectrometry (ICP-MS). Continuous-wave EPR spectra were obtained at X-band (9.45 GHz) using a Bruker E500 spectrometer fitted with a Bruker super-high-Q probe-head and a quartz cold finger insert (Wilmad, WG-816-B-Q). To increase the strength of the EPR signal, specimens were cold evaporated to dryness, then redissolved in a minimal volume of DMF. Samples were then transferred to 4 mm OD quartz sample tubes (Wilmad). The spectra are plotted as the usual first derivative of the microwave absorption. Unless otherwise indicated, experimental conditions were as follows: microwave power, 5 mW; magnetic field modulation amplitude, 4 G; field modulation frequency, 100 kHz; receiver time constant, 164 ms; sweep rate, 6.67 $G.s^{-1}$. Background correction was performed by subtraction of a third order polynomial.

**Figure 1.** Concentration of selected metal ions in distillate and aged whiskies produced in 1960 and 1970 from the same still.
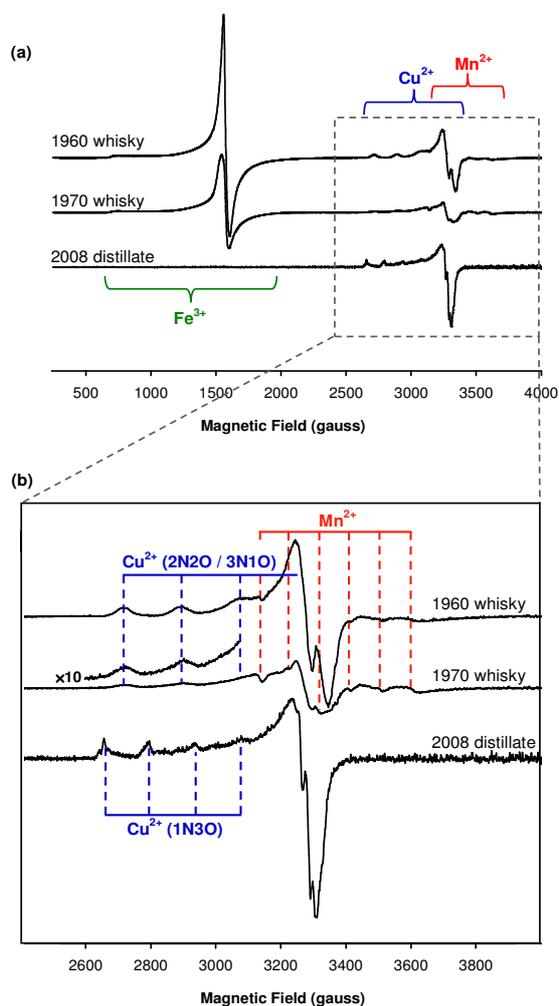


**Figure 2.** EPR spectra of a 2008 distillate and as-bottled aged whiskies from 1960 and 1970. The distillate shows no $Fe^{3+}$ (500–2000 gauss) or $Mn^{2+}$ (500–2000 gauss) signals, while the aged whiskies exhibit features characteristic of high-spin $Fe^{3+}$. Panel (b) is the same as panel (a) but with an expanded field scale. The spectrum of the 1970 whisky in the range 2600–3000 gauss is shown with an expanded intensity scale to enable clearer comparison with of the $Cu^{2+}$ features. Dashed vertical lines are a guide to the eye to highlight the approximate positions of key spectral features of each

metal-bound species. The predicted number of nitrogen and oxygen ligands in each $Cu^{2+}$ complex is indicated in parentheses. All spectra are normalised with the same intensity scale.
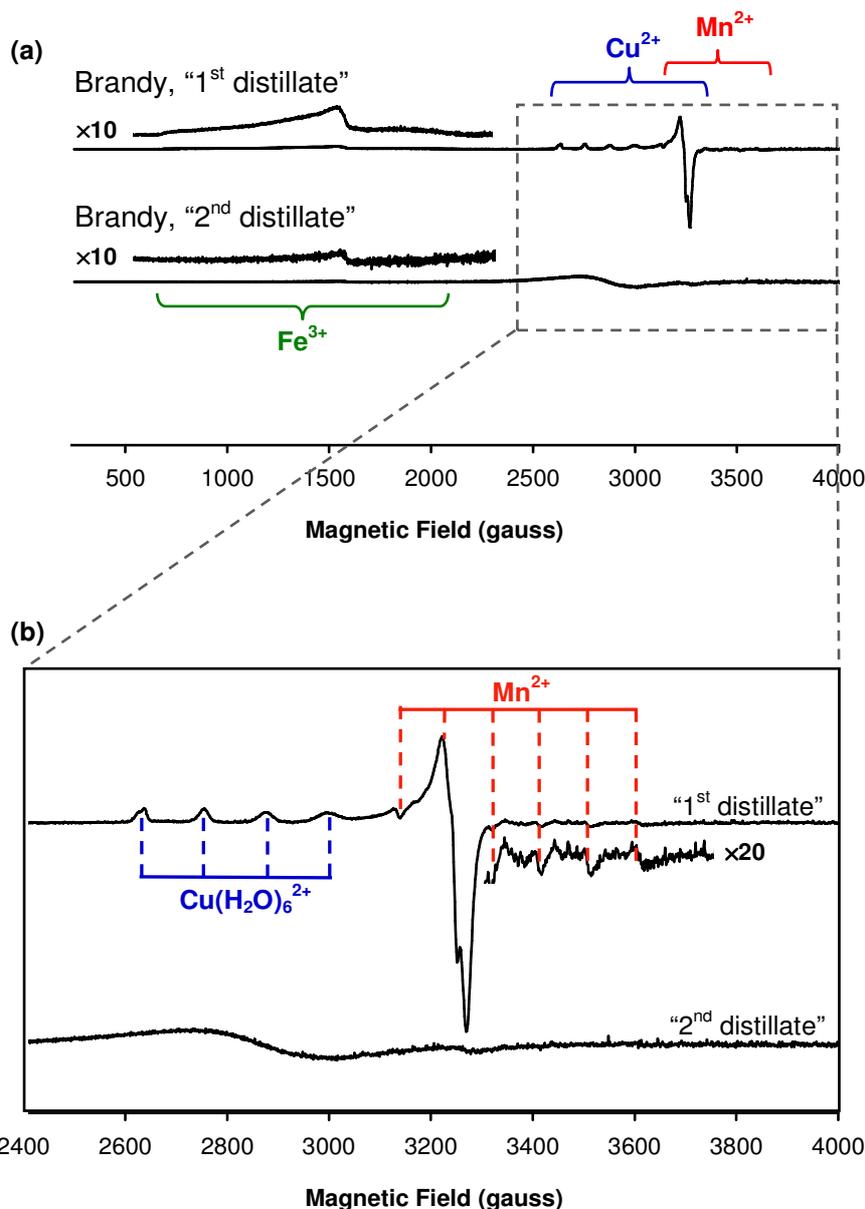


**Figure 3.** EPR spectra of a 'first' (double) and 'second' (double) distillate of brandy. Both distillates show relatively weak high-spin $Fe^{3+}$ (500–2000 gauss) and $Mn^{2+}$ (500–2000 gauss) signals. Panel (b) is the same as panel (a) but with an expanded field scale. Spectra are shown with expanded intensity scales as indicated to enable clearer identification of various features. Dashed vertical lines are a guide to the eye to highlight the approximate positions of key spectral features of each metal-bound species. The predicted number of nitrogen and oxygen ligands in each $Cu^{2+}$ complex is indicated in parentheses. All spectra are normalised with the same intensity scale.

## 3. Results and Discussion

The ICP-MS analysis indicated substantial differences between the metal levels of the distillate and the final aged products; levels of copper in the distillate were 2–3 times higher than the aged products, whilst the levels of iron and manganese were greater than 20 times and 5 times lower, respectively (Fig. 1). Comparing the final aged products, the total zinc, iron and manganese levels were 20–30% higher in the 1960 whisky as compared with the

1970 whisky, whereas its copper levels were around 30% lower (Fig. 1). However, the relative intensity of the $Cu^{2+}$ EPR spectra appeared to indicate the reverse (Fig. 2). Since any aqueous $Cu^+$ and $Fe^{2+}$ iron originating from the pot still would be oxidised to $Cu^{2+}$ and $Fe^{3+}$ upon exposure to an aerobic environment, this difference was unlikely due to the presence of "EPR-silent" $Cu^+$ in solution. A close inspection of the $Cu^{2+}$ spectral features indicated broader linewidths in the 1970 whisky sample (Fig. 2b), which would result in an apparent reduction in signal intensity (the EPR intensity depicts the first derivative of the microwave absorption, wherein narrower lines may appear more intense, although a true intensity comparison can only made after double-integration of the spectra). It is also possible that residual insoluble (and EPR-silent) metal-hydroxides were present in the dried films prior to reconstitution in DMF.

Referring to EPR spectra in Fig. 2b, the distillate exhibited a $Cu^{2+}$ spectrum characteristic of square planar or tetragonal coordination by 1 nitrogen and three oxygen ligands (1N3O), whereas the aged whiskies contain $Cu^{2+}$ in 2N2O or 3N1O coordination spheres [4]. The aged whisky spectra were very similar but subtly different. Due to the interference from the $Cu^{2+}$ spectra, it was not possible to conclusively determine whether any significant spectral differences due to $Mn^{2+}$ coordination were present in the aged whiskies. The relative intensity of the $Fe^{3+}$ EPR spectra (Fig. 2a) was consistent with the total Fe levels measured by ICP-MS (Fig. 1). Both of the aged whiskies exhibited resonances at effective $g$-values in the range $g \sim 4$–9 (field values between ~500–2000 gauss), consistent with one or more high-spin $Fe^{3+}$ centres possessing large zero-field splitting and a high rhombic distortion [5]. Some differences in linewidth were evident (eg. the strong feature near 1500 gauss in Fig. 2a) due to microheterogeneity of the $Fe^{3+}$ coordination sphere and/or due to a combination of adventitious and bound high spin $Fe^{3+}$, whose EPR signatures are difficult to distinguish [5,6]. The lack of detectable $Fe^{3+}$ and $Mn^{2+}$ by EPR in the distillate was consistent with the relatively low total iron and manganese levels measured by ICP-MS (Fig. 1).

In the case of the two brandies, the same (low) copper and manganese levels were measured by ICP-MS (Fig. 1). Total iron and zinc levels were both >2 times higher in the 'first' (double) distillate compared with the 'second' (double) distillate. The EPR spectra (Fig.3) indicated that $Cu^{2+}$ was unbound (aqueous) in the 'first' distillate [4], whereas only a broad, mostly featureless feature between 2000–4000 gauss was present in the spectrum of the 'second' distillate, possibly due to an insoluble $Cu^{2+}$ species. The presence of $Mn^{2+}$ could be identified in the 'first' distillate by EPR but not in the second. The $Fe^{3+}$ spectra of both distillates were both characteristic of high-spin $Fe^{3+}$, although they appeared as almost pure absorption spectra rather than first-derivative due to rapid-passage effects. For similar reasons to above, it was not possible to identify clear spectral differences in $Fe^{3+}$ coordination between the two distillates.

## Acknowledgments

## References

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