

# Detection of $\text{Cu}^{2+}$ in Red Wines by EPR

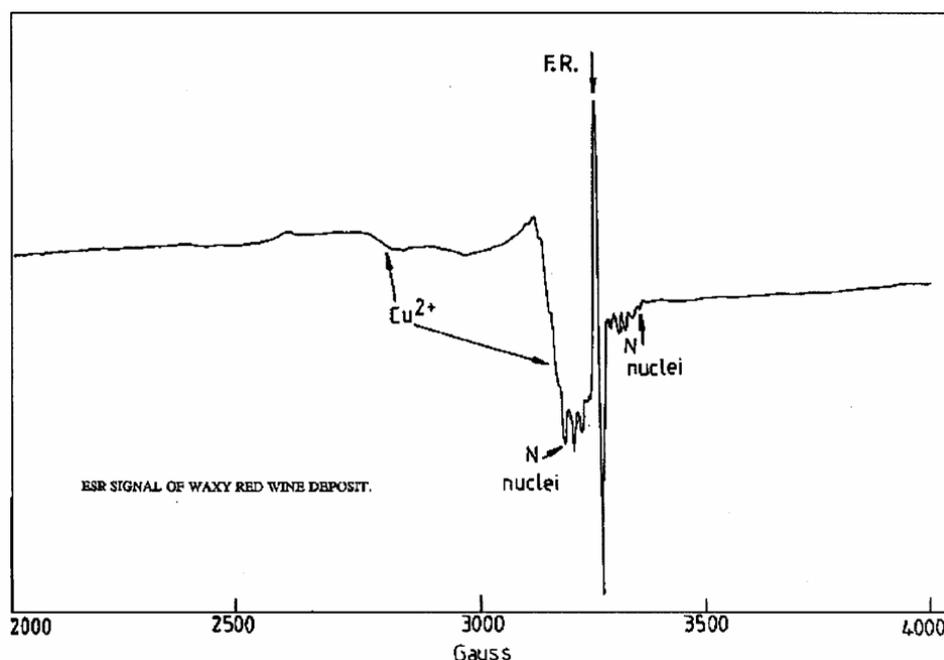
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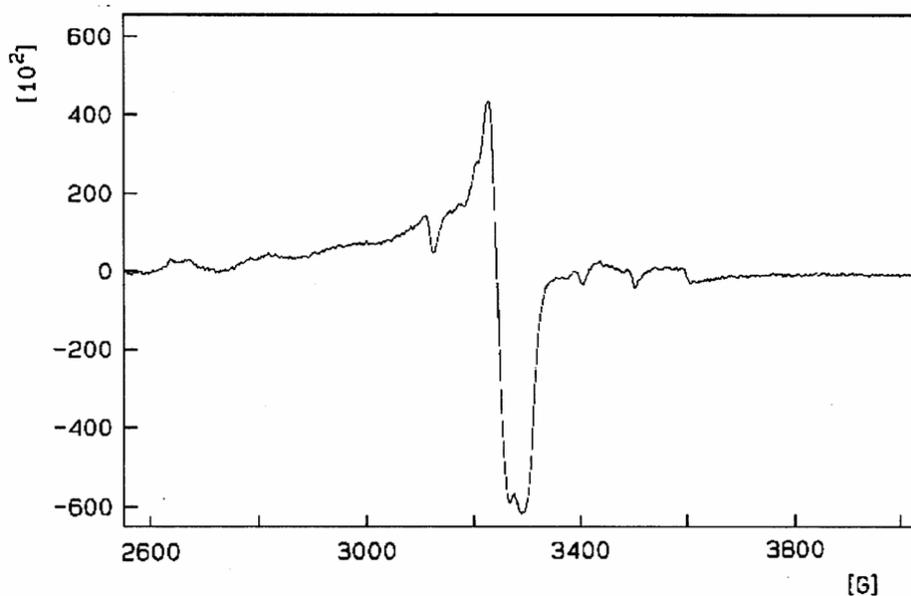
Until now,  $\text{Cu}^{2+}$  had not been detected by EPR in red wines, at room temperature (liquid) and temperatures close to  $-20\text{ }^\circ\text{C}$ . By working at  $\sim 120\text{ K}$ , increasing both microwave power and magnetic induction modulation amplitude, and using signal amplitude,  $\text{Cu}^{2+}$  has been detected. The signal has disappeared at temperatures close to  $-20\text{ }^\circ\text{C}$  because of thermal broadening.

## 1. Introduction

Cu is known to occur in both red and white wines [1], but had not been detected by EPR at temperatures close to  $-20\text{ }^\circ\text{C}$  [2] or at room temperature [3]. Fig.1 shows the  $\text{Cu}^{2+}$  EPR signal from the waxy red bottle deposit thrown by some South Australian red wines (Shiraz) [2]. Artificially aged white wine throws a fluffy brown precipitate which also contains  $\text{Cu}^{2+}$  detectable by EPR [2]. It was presumed therefore that Cu 'hid' from EPR as the singly charged ion which is not paramagnetic. But in the year 2000, a supposedly pure extract of procyanidin polyphenols from Shiraz grape seeds was discovered to give an EPR signal, attributable to  $\text{Cu}^{2+}$ , at temperatures in the region of 120 K, which disappeared as room temperature was approached, owing to thermal broadening [2]. Work with brandies [4] showed clearly where  $\text{Cu}^{2+}$  hyperfine lines would lie with respect to the  $\text{Mn}^{2+}$  EPR spectrum, which occurs in all wines. This is shown in fig.2, (note: the label on the horizontal axis, [G], is Gauss). So it was decided to attempt to detect  $\text{Cu}^{2+}$  by increasing the microwave power and the magnetic induction amplitude beyond that normally used in the free radical work, since metal ions give lines much broader than the free radicals, and which saturate at much higher power. Signal averaging was also available. Operation at 120 K was also to be used.



**Figure 1** EPR spectrum of the waxy red bottle deposit thrown by some red wines.



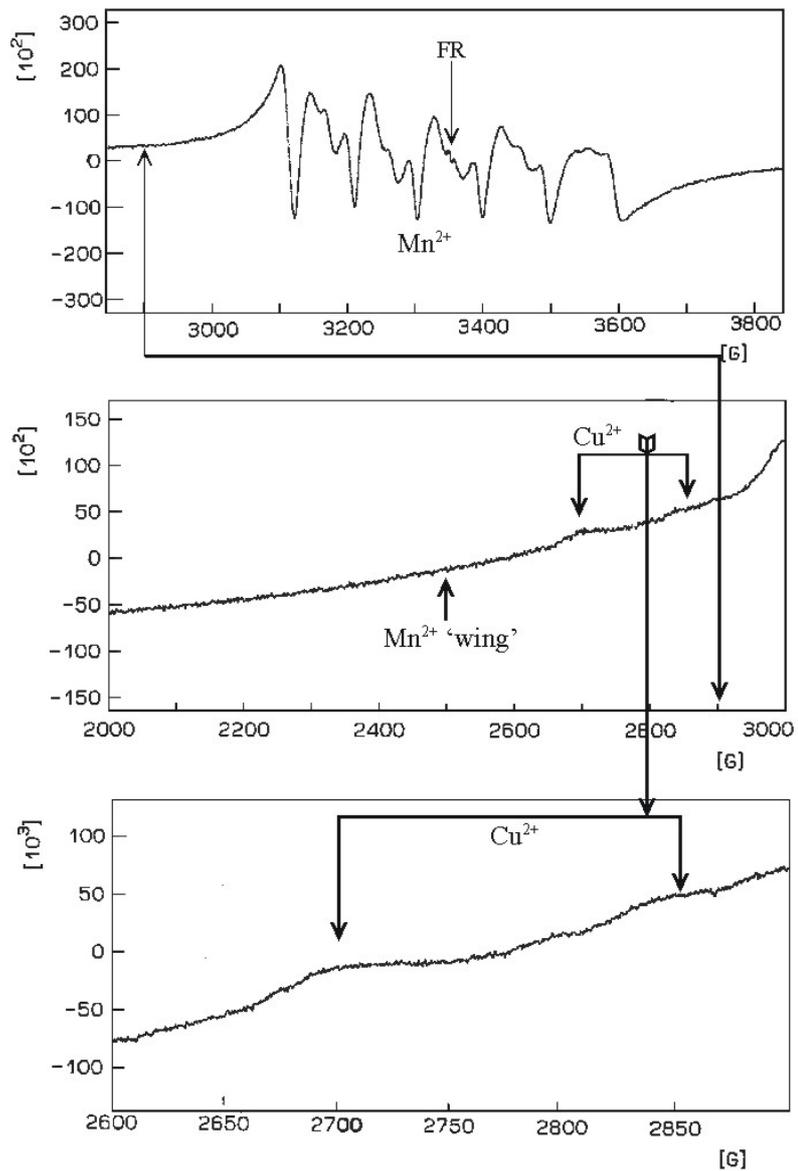
**Figure 2** A brandy EPR spectrum, showing both  $\text{Cu}^{2+}$  lines (the main central and broad ones) and  $\text{Mn}^{2+}$  lines (the sharper ones).

## 2. Sample preparation

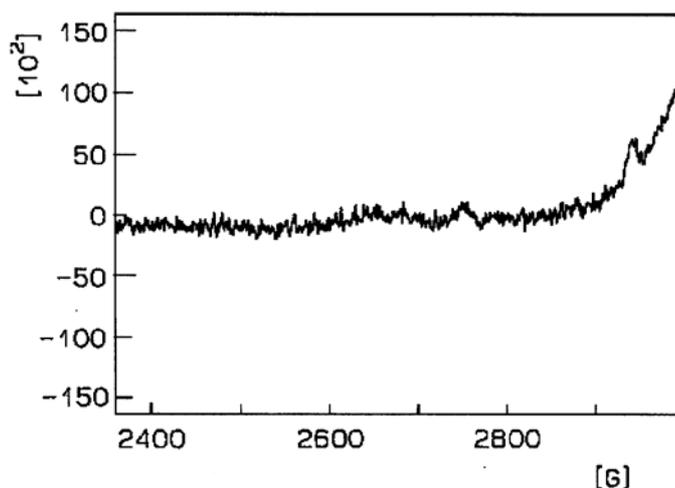
All samples for the figures 1-5 were placed in standard 2mm internal diameter quartz EPR tubes (Wilmad). All liquid samples were cold evaporated to one tenth of their original volume before being placed in the sample tubes. The Fig.1 spectrum was obtained with a Varian E12 EPR spectrometer, operating at  $\sim 9.1$  GHz, and at room temperature ( $20^\circ\text{C}$ ). All other spectra were obtained with a Bruker EPR spectrometer, operating at  $\sim 9.4$  GHz. The temperature for fig.2 was  $\sim -20^\circ\text{C}$ , and for all subsequent figs., 120 K. The microwave power for figs.1 and 2 was 1mW, and the modulation amplitude 4 G. For the remaining figs. the microwave power was 8 mW, and the modulation amplitude was 8 G.

## 3. Results

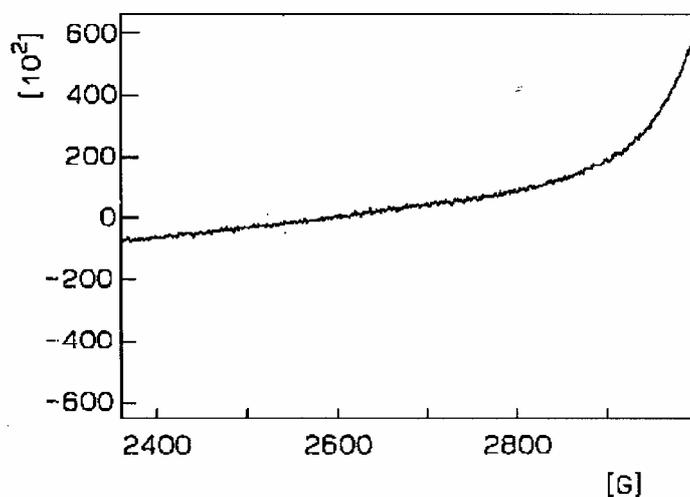
The first sample examined at 120 K was a Shiraz, since a  $\text{Cu}^{2+}$  spectrum had been discovered in Shiraz grapes. The results are shown in fig.3, where the hyperfine lines from the copper are seen in the low magnetic induction wing of the manganese spectrum, as expected from fig.2. Signal averaging was used to improve signal-to-noise ratio. The results from a Pinot Noir and from a Cabernet – Merlot blend are shown in figs. 4 and 5 respectively. The Mn concentration in the Cabernet Merlot is so great that it ‘takes over’ the signal display, a property of the Bruker spectrometer display system. If one looks along the registered line, one will see the Cu line, at very low signal to noise ratio!



**Figure 3** Top:  $Mn^{2+}$  spectrum, with wing to be examined arrowed. Middle: wing region, showing  $Cu^{2+}$  lines. Bottom: wing section expanded, and at higher gain.



**Figure 4** Pinot Noir  $\text{Cu}^{2+}$  line.



**Figure 5** Cabernet Merlot  $\text{Cu}^{2+}$  Line.

#### 4. Discussion

The amount of observable  $\text{Cu}^{2+}$  is clearly very much less than the amount of  $\text{Mn}^{2+}$ , and is not necessarily all of the Cu present in the wines, since some may be present as the singly charged ion. The amount of  $\text{Cu}^{2+}$  present will depend on the soil, whether the vines have been treated with a Cu compound to counteract diseases, and also on the grape type. But it is comforting to have finally detected  $\text{Cu}^{2+}$  in the wine itself, and not in what might be termed a 'product' of the wine, like the waxy red bottle deposit of fig.1.

#### Acknowledgments

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#### References

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