The Control of Redox Potential Using Air During Wine Fermentations.

Roger Boulton

Emeritus Professor of Enology and of Chemical Engineering,

University of California, Davis

2022 Oregon Wine Symposium

Topic: Techniques and Cellar Practices for the Use of Oxygen in Winemaking

Thursday 17th February 2022

Outline

- What is the Redox Potential (aka Electrode Potential, Oxidation-Reduction Potential, ORP)?
- Why is it important during wine fermentations?
- How is the potential measured in fermentation systems?
- How can it be controlled by aeration during red or white fermentations?
- What target values should it be controlled at during fermentation?
- Some examples of research and commercial-scale fermentations.
- Why is it the more useful control variable than dissolved oxygen during wine fermentation?

Some Background

Oxygen does not (cannot) oxidize anything until it is *activated* by components in solution (*iron and copper* tartrate complexes) or temperature or light…to *hydrogen peroxide*.

The *extent to which oxygen can be activated* is determined primarily by the available iron(II) tartrate complex in wine. Half of the iron (II) is in this complex form and half is in the free iron(II) form at resting juice (and wine) potentials.

The iron content would be 30 uM, if the wine contains 5 mg/L of total iron. Most wines will be 1 to 3 mg/L in total iron, 6 to 18 uM.

Typical hydrogen peroxide formation is between 5 to 10 uM. The amount of oxygen consumed by this is at most 10 uM, or about 0.3 mg/L of dissolved oxygen. No more is needed (*or can react*) at each addition.

The major reactions of hydrogen peroxide are *with free* SO_2 to form sulfate, *with iron (III)* to reform iron (II) for the next round, and *with glutathione*, *GSH* to form oxidized glutathione, GSSG.

In the presence of ethanol, the hydrogen peroxide forms the hydroxyethyl radical, *which is the real oxidizing agent* in wine.

No dihydroxy phenols (or tannins) were oxidized (or used) during these reactions. They play no role in redox potential.

Why is it important in Wine Fermentations

Prevents formation of H_2S from elemental Sulphur

Prevents the formation of certain sulfur components by Yeast

Affects yeast viability and fermentation activity once yeast growth has ceased

This prevents sluggish and stuck fermentations

How is it measured?

Has liquid filling solution,
Needs to be mounted vertical
or at 45 degrees

We prefer 45 degrees on side of the
Fermentor Wall, no obstruction for skins

Cleaned after each Fermentation,
Calibrated in Lab against Reference Solution
Installed in Fermentor prior to filling

https://www.hamiltoncompany.com/process-analytics/sensors/ph-and-orp-probes/pre-pressurized-ph-and-orp-sensors/easyferm-plus-orp-sensors/easyferm-plus-orp-sensors-arc


CR
FlexiFit TC 50-
P/N 237341/01
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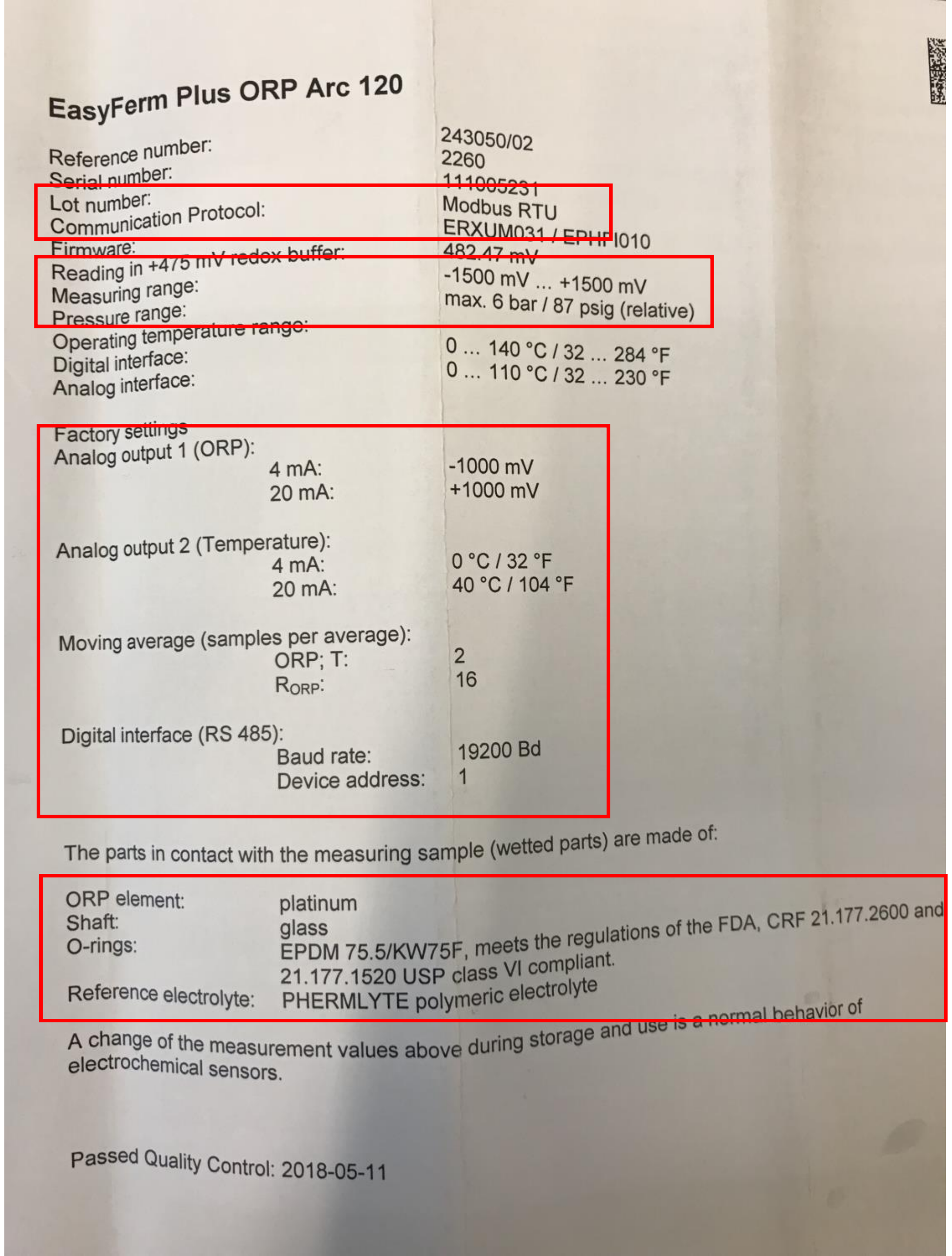
HAMILTON



EasyFerm Plus ORP Arc 120

Reference number:	243050/02 2260
Serial number:	111005231
Lot number:	Modbus RTU
Communication Protocol:	ERXUM031 / EPHFI010
Firmware:	482.47 mV
Reading in +475 mV redox buffer:	-1500 mV ... +1500 mV
Measuring range:	max. 6 bar / 87 psig (relative)
Pressure range:	
Operating temperature range:	0 ... 140 °C / 32 ... 284 °F
Digital interface:	0 ... 110 °C / 32 ... 230 °F
Analog interface:	

Factory settings

Analog output 1 (ORP):		
	4 mA:	-1000 mV
	20 mA:	+1000 mV
Analog output 2 (Temperature):		
	4 mA:	0 °C / 32 °F
	20 mA:	40 °C / 104 °F
Moving average (samples per average):		
	ORP; T:	2
	R_{ORP}:	16
Digital interface (RS 485):		
	Baud rate:	19200 Bd
	Device address:	1

The parts in contact with the measuring sample (wetted parts) are made of:

ORP element:	platinum
Shaft:	glass
O-rings:	EPDM 75.5/KW75F, meets the regulations of the FDA, CRF 21.177.2600 and 21.177.1520 USP class VI compliant.
Reference electrolyte:	PHERMLYTE polymeric electrolyte

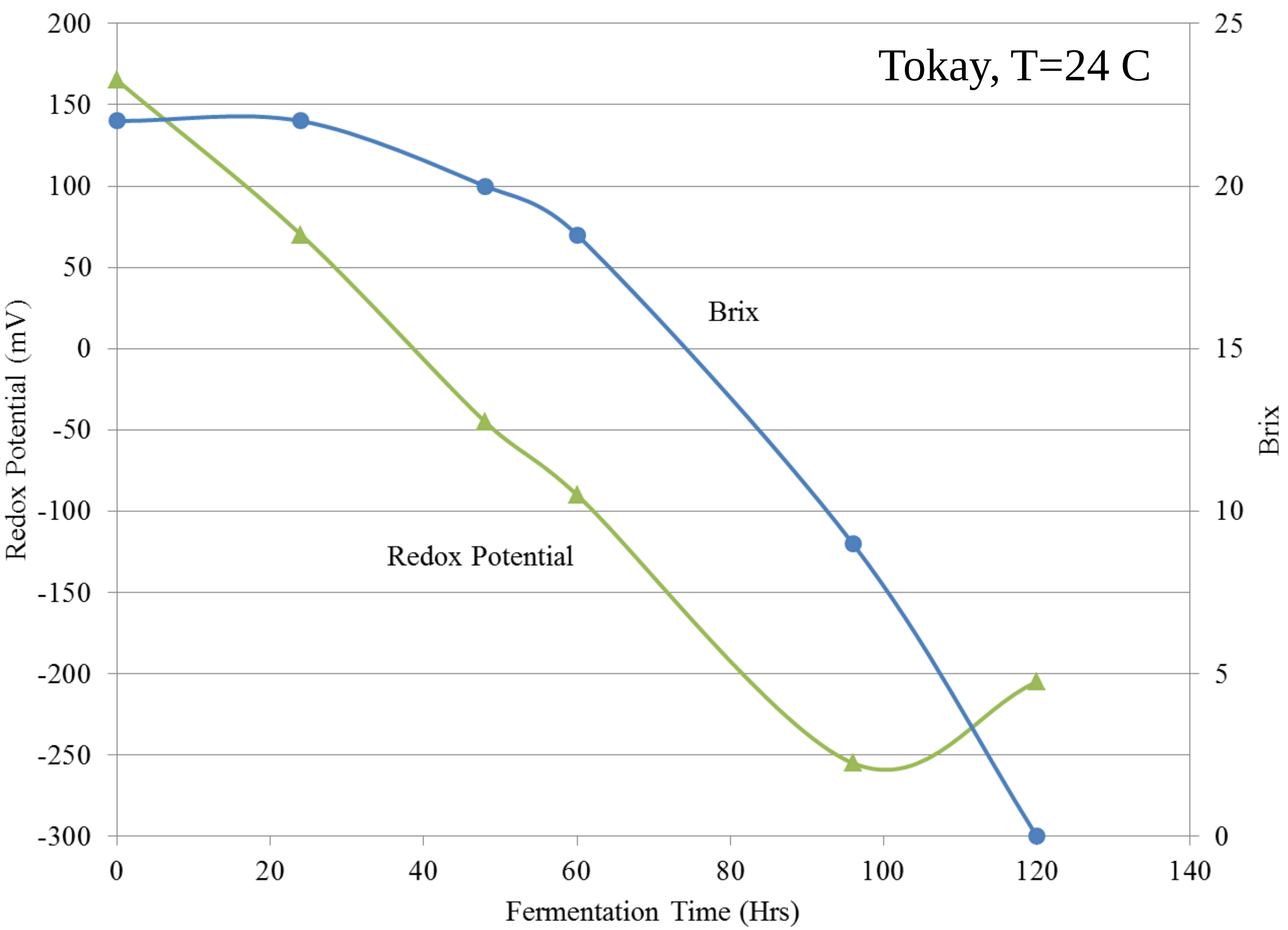
A change of the measurement values above during storage and use is a normal behavior of electrochemical sensors.

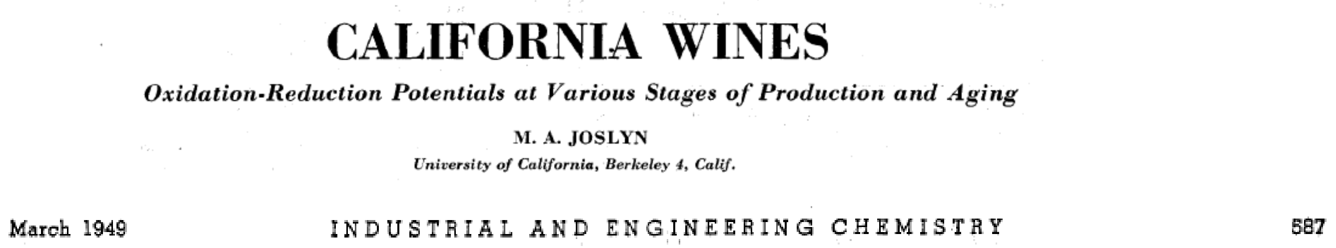
Passed Quality Control: 2018-05-11


PanelView Plus 1500
AB
TIT-40
07-01
Y MANAGER IF E_STOP ACTIVATED
TEMP SETTINGS NEED TO BE RESET
EMERGENCY

Some Wine Fermentation Examples of Redox Potential

Joslyn 1949
Schanderl 1959
Rankine 1963
Berovic 2002





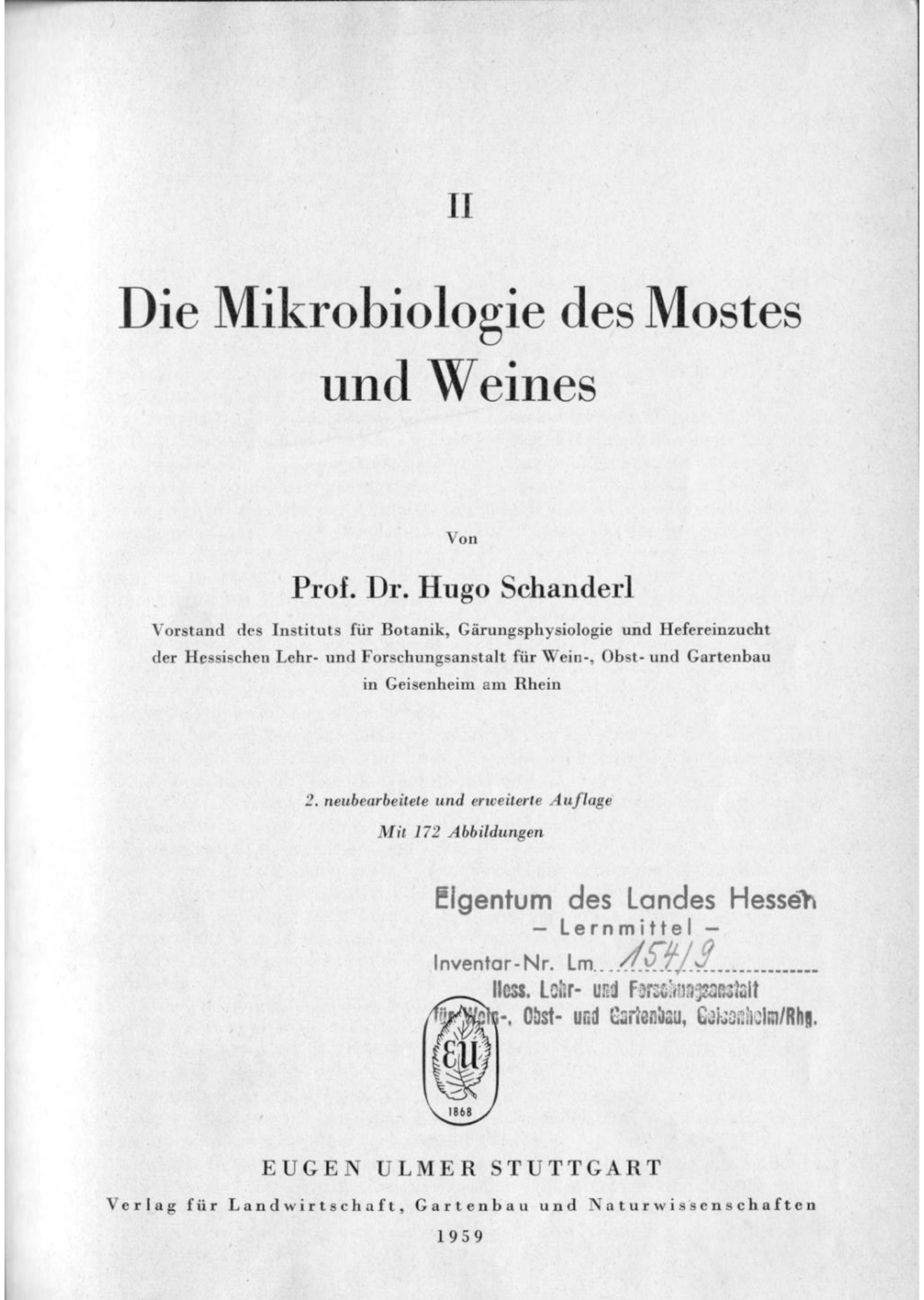
CALIFORNIA WINES

Oxidation-Reduction Potentials at Various Stages of Production and Aging

M. A. JOSLYN

University of California, Berkeley 4, Calif.

March 1949 INDUSTRIAL AND ENGINEERING CHEMISTRY 587



II

Die Mikrobiologie des Mostes und Weines

Von

Prof. Dr. Hugo Schanderl

Vorstand des Instituts für Botanik, Gärungsphysiologie und Hefereinzucht
der Hessischen Lehr- und Forschungsanstalt für Wein-, Obst- und Gartenbau
in Geisenheim am Rhein

2. neubearbeitete und erweiterte Auflage
Mit 172 Abbildungen

EUGEN ULMER STUTTGART
Verlag für Landwirtschaft, Gartenbau und Naturwissenschaften
1959

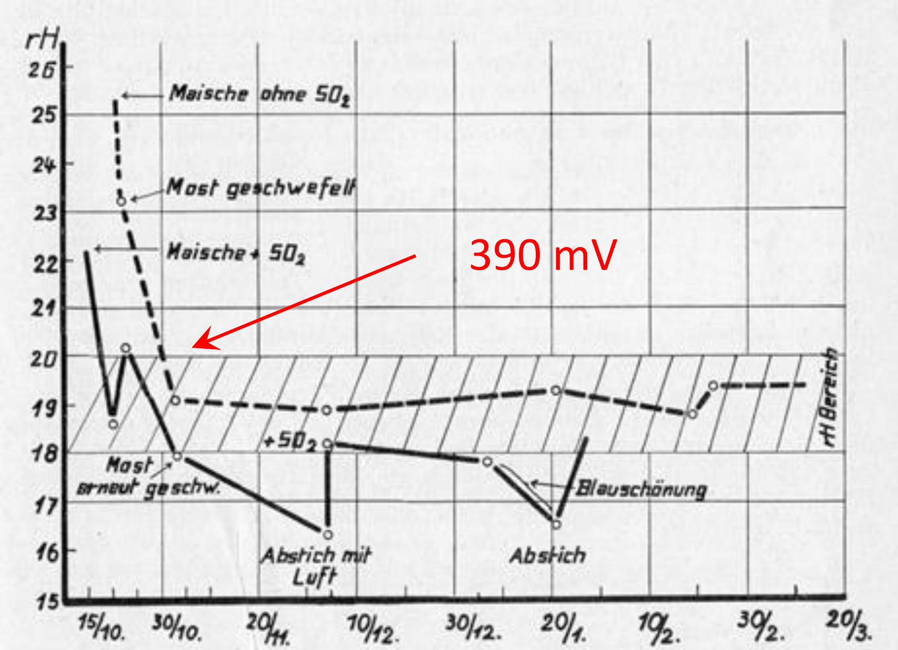


Abb. 123. Die Verfolgung der r_H-Zahlen zweier 1947er Rheingauer Weine im Halbstückfaß. Die ausgezogene Kurve schildert den r_H-Verlauf eines schon in der Maische geschwefelten Mostes, die gestrichelte Kurve den eines Mostes, der erst nach der Kelterung geschwefelt worden war. Man sieht, daß der Wein aus der geschwefelten Maische die ganze Beobachtungszeit hindurch „reduktiver" war als der andere. Man beachte weiterhin den Einfluß des Abstiches mit Luft auf die r_H-Zahl!

$$\mathrm{rH} = \frac{E_{\mathrm{H^+/H_2}}}{0.03} + 2\mathrm{pH}$$

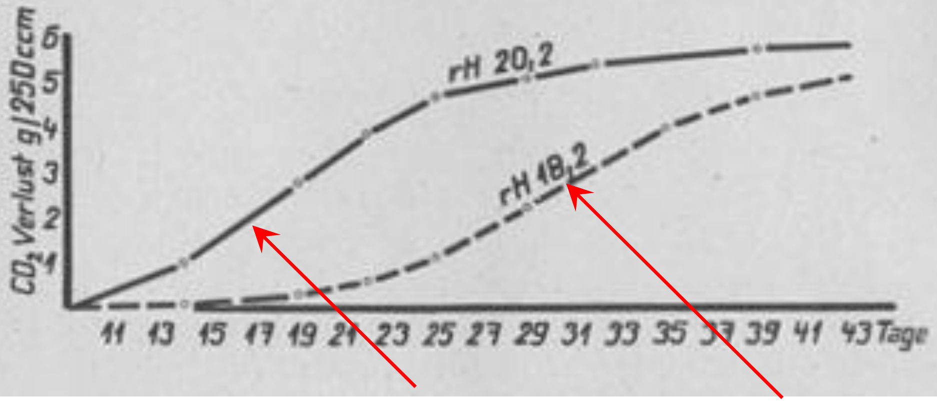
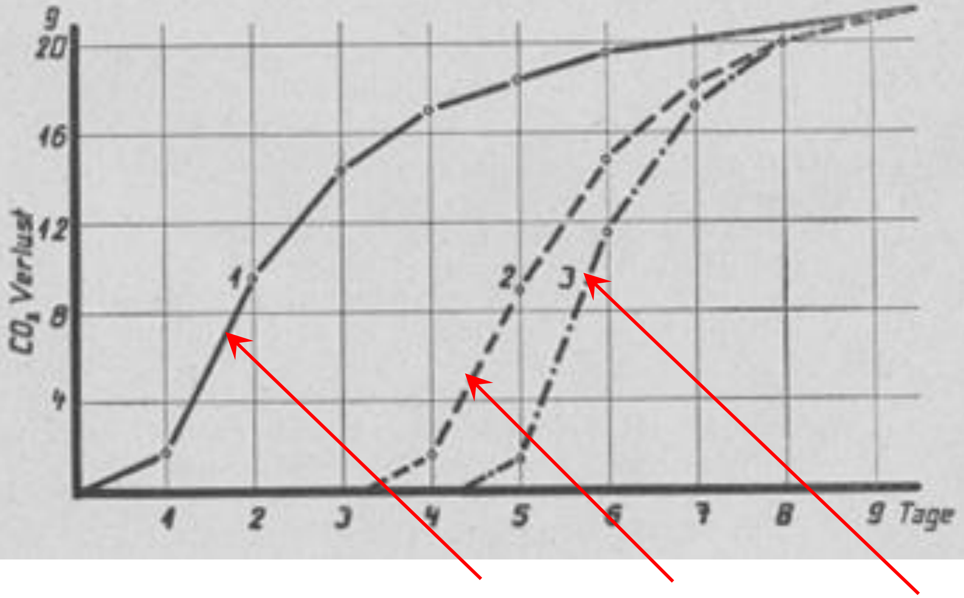


Abb. 81. Der Verlauf einer Gärung von 2 verschiedenen Anfangsredoxstufen aus. Der Most mit einer höheren Anfangsredoxstufe gärt früher und schneller.

390 mV

330 mV

Abb. 82. Die Anfangsredoxstufe wurde durch Zugabe von Ascorbinsäure (Vitamin C) gesenkt, 1 = Kontrolle, 2 = Anfangs-rH = 18,0, 3 = Anfangsredoxstufe = 16,1; die Hefe reagiert darauf, wie wenn der Most geschwefelt worden wäre.



391 mV

326 mV

269 mV

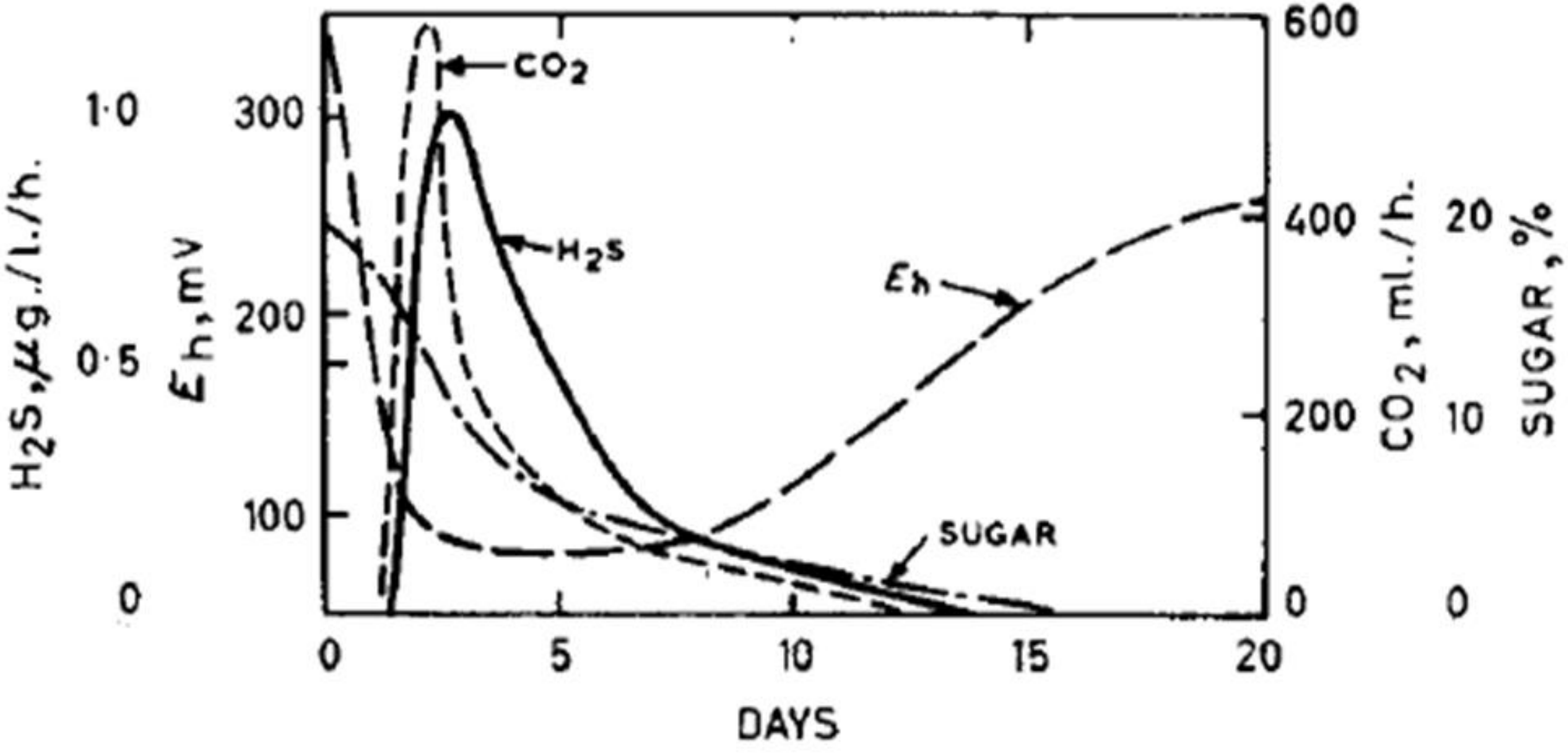
Schanderl, H. Mikrobiologie des Weines (1959)

H_2S Formation from Elemental Sulphur During Fermentation

Rankine (1963)

Maximum H_2S Formation is at the Redox Potential Minimum

Spontaneous Formation of H2S from Elemental Sulphur at Potentials below 150 mV



NATURE, ORIGIN AND PREVENTION OF HYDROGEN SULPHIDE AROMA IN WINES

By B. C. RANKINE

J. Sci. Food. Agric. (1963) 14:79-91

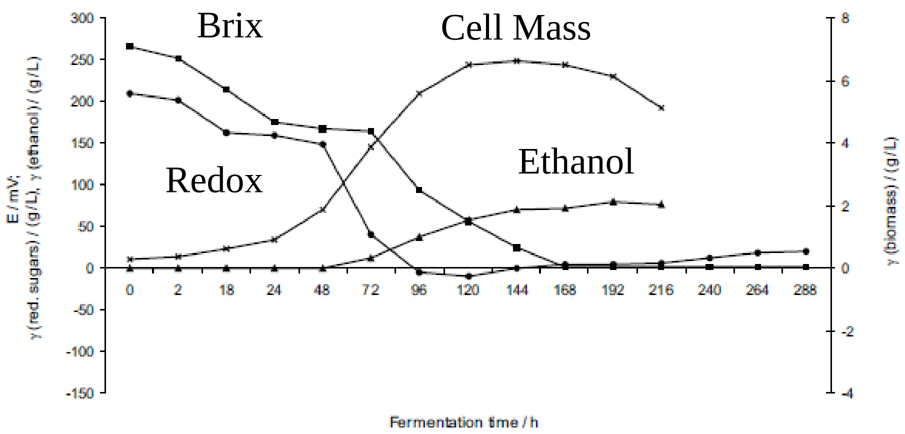


Fig. 1. Time dependence of redox potential (●), reductive sugar concentration γ / (g/L) (■), ethanol concentration γ / (g/L) (▲) (at the left ordinate) and biomass growth concentration γ / (g/L) (×) (at the right ordinate) at fermentation temperature 15 °C

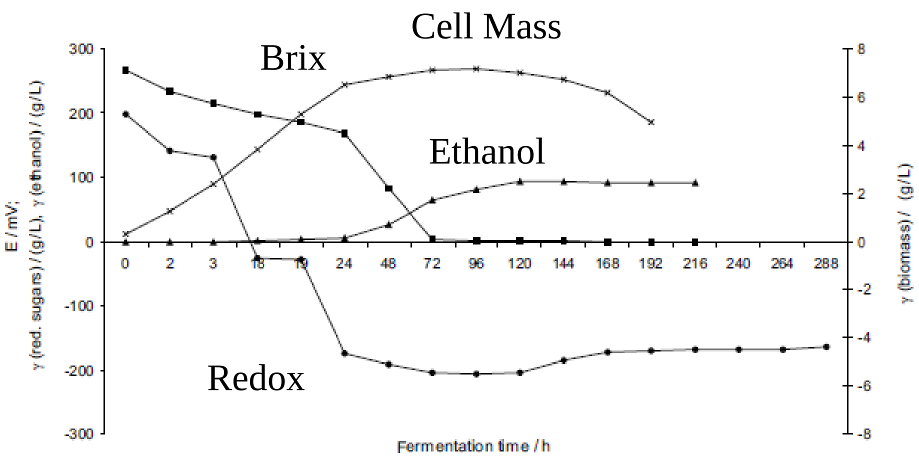


Fig. 3. Time dependence of redox potential (●), reductive sugar concentration γ / (g/L) (■), ethanol concentration γ / (g/L) (▲)(at the left ordinate) and biomass growth γ / (g/L) (×) (at the right ordinate) at fermentation temperature 24 °C

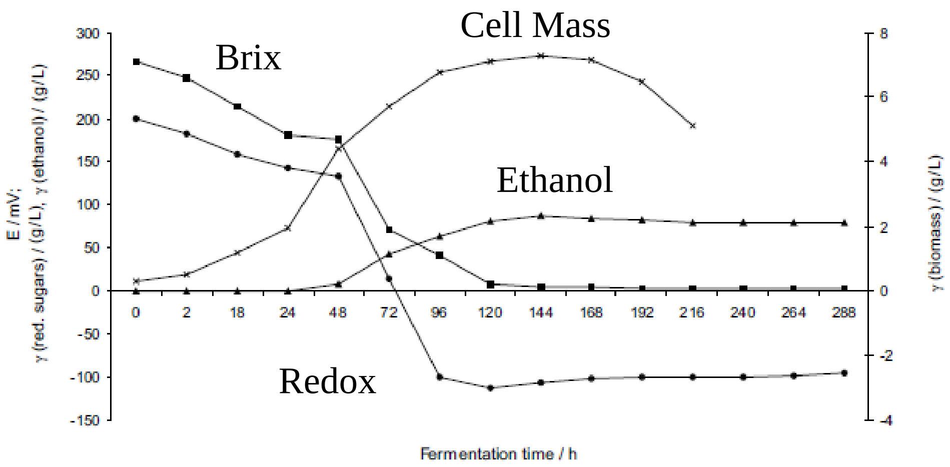


Fig. 2. Time dependence of redox potential (●), reductive sugar concentration γ / (g/L) (■), ethanol concentration γ / (g/L) (▲) (at the left ordinate) and biomass growth concentration γ / (g/L) (×) (at the right ordinate) at fermentation temperature 18 °C

The Role of On-line Redox Potential Measurement in *Sauvignon blanc* Fermentation

Aleksandra Kukec[1], Marin Berovič[2], Štefan Čelan[1], Mojmir Wondra[3]*

Redox Potential Measurement in *Sauvignon blanc* Fermentation, *Food Technol. Biotechnol.* 40 (1) 49–55 (2002)

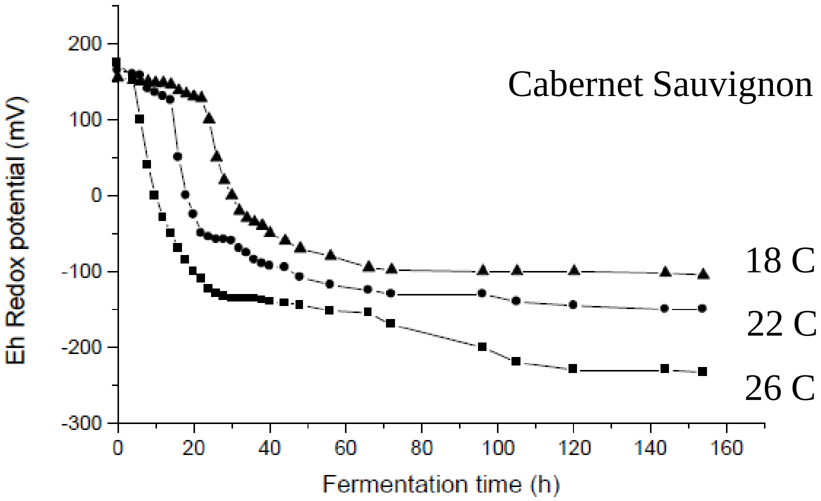


Fig.1. Redox potential temperature dependence in *Cabernet sauvignon* must.
Fermentation temperatures ▲18, ●22 and ■26 °C

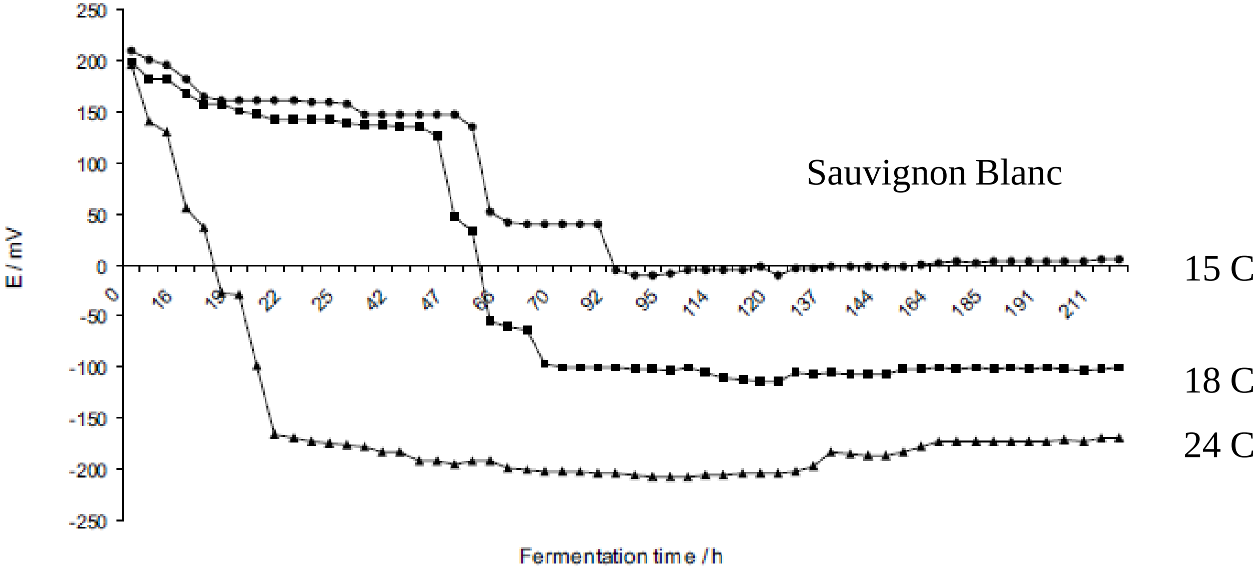


Fig. 4. Effect of time on redox potential values measured on-line during wine fermentation at different temperatures; 15 (●), 18 (■), 24 °C (▲).

Controlled Redox Potential Trials

Research Scale, Red Wine, 100 L, 2017 Harvest

Commercial, Surface Measurement, White Wine, 20 KL, 2018 Harvest

Commercial, Wall Mounted, Red Wine, 10 KL, 2020 Harvest

Commercial, Floating in skin cap, Open top-Punch down Red Wine, 300 L, 2020 Harvest

Scaled Fermentation, Red Wine, 100 L, 1 KL, 10 KL, 2021 Harvest

How is it Controlled During Fermentation?

Controlling Fermentation above a specific level, say 200 mV

Controlling Fermentation in a specific range, say between 150 and 250 mV

Killeen et al. (2018).

ORP
Electrode

Air

Solenoid
Valve

Air

Control to
Solenoid

Versa Star
Meter

RS-232/UART

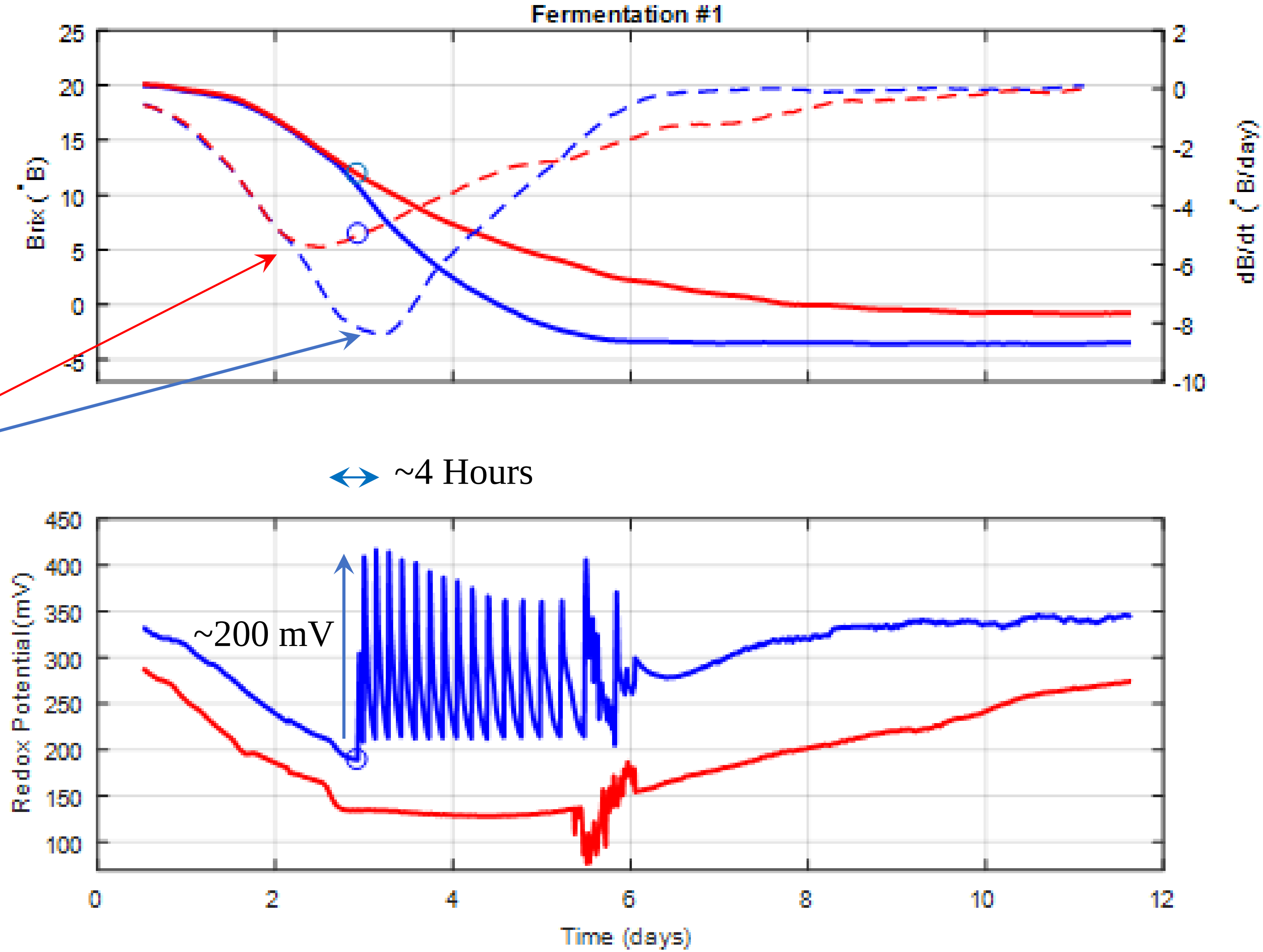
Control
Board

Advanced Monitoring and Control of Redox Potential in Wine Fermentation

David J. Killeen, Roger Boulton, André Knoesen

Am J Enol Vitic. October 2018 69: 394-399; published ahead of print May 29, 2018 ; **DOI:** 10.5344/ajev.2018.17063

Maximum
Fermentation
Rate



Rise in mV is almost immediate,
if well-mixed, 20 to 30 minutes

Reaction decay is approx. 3 to 4 hours

Air addition at 4 to 8
times per day

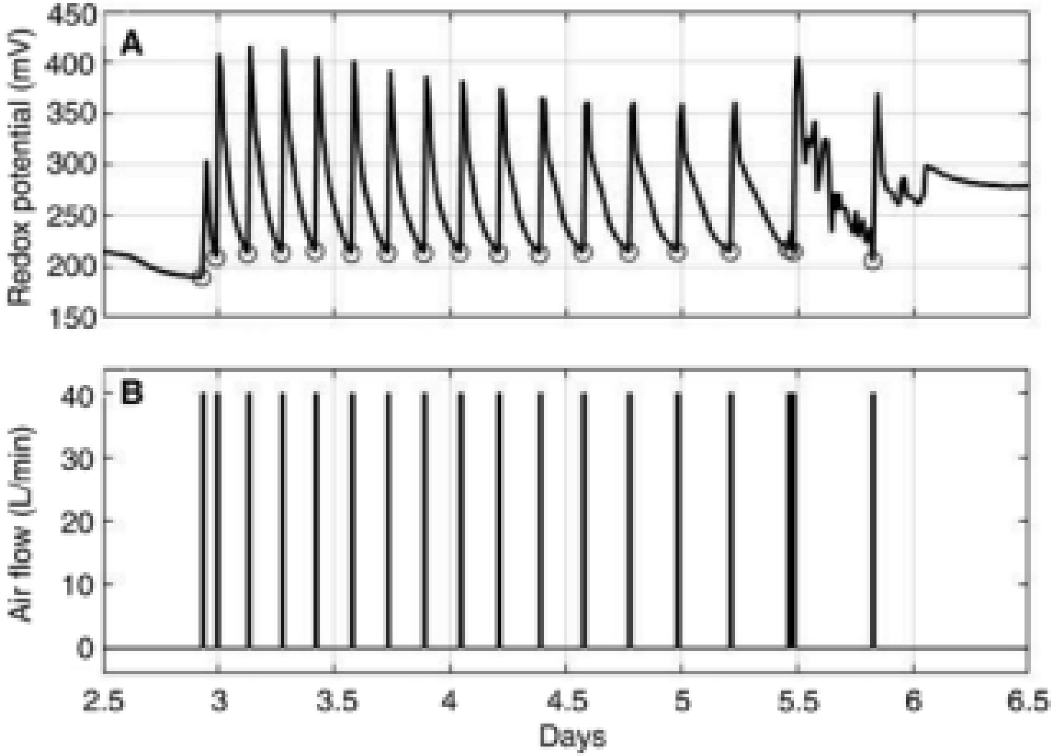
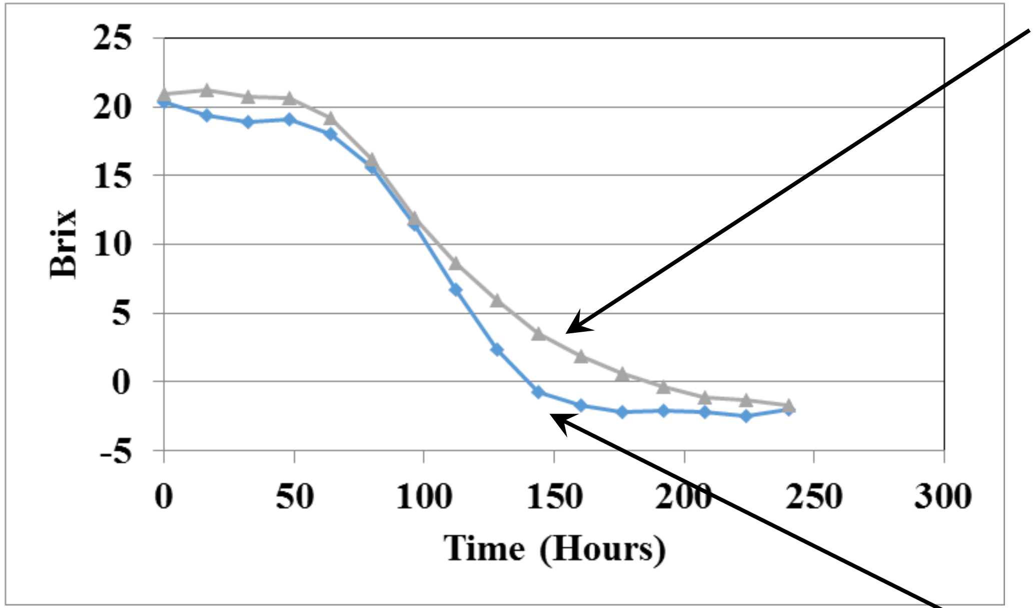
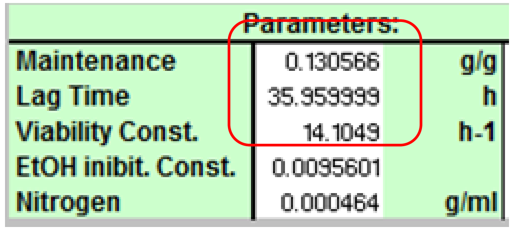


Figure 6 (**A**) Demonstration of redox potential control during mid-fermentation, and (**B**) the airflow input from fermentation set 1.

Fermentation Model Parameters

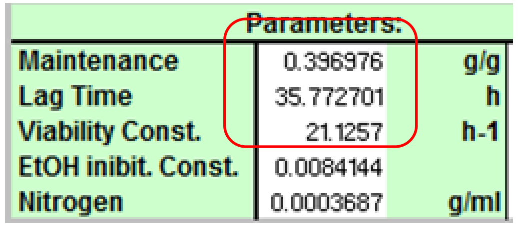


Higher Maintenance Rate
and higher Cell Viability



Parameters:		
Maintenance	0.130566	g/g
Lag Time	35.959999	h
Viability Const.	14.1049	h-1
EtOH inibit. Const.	0.0095601	
Nitrogen	0.000464	g/ml

No Redox Control



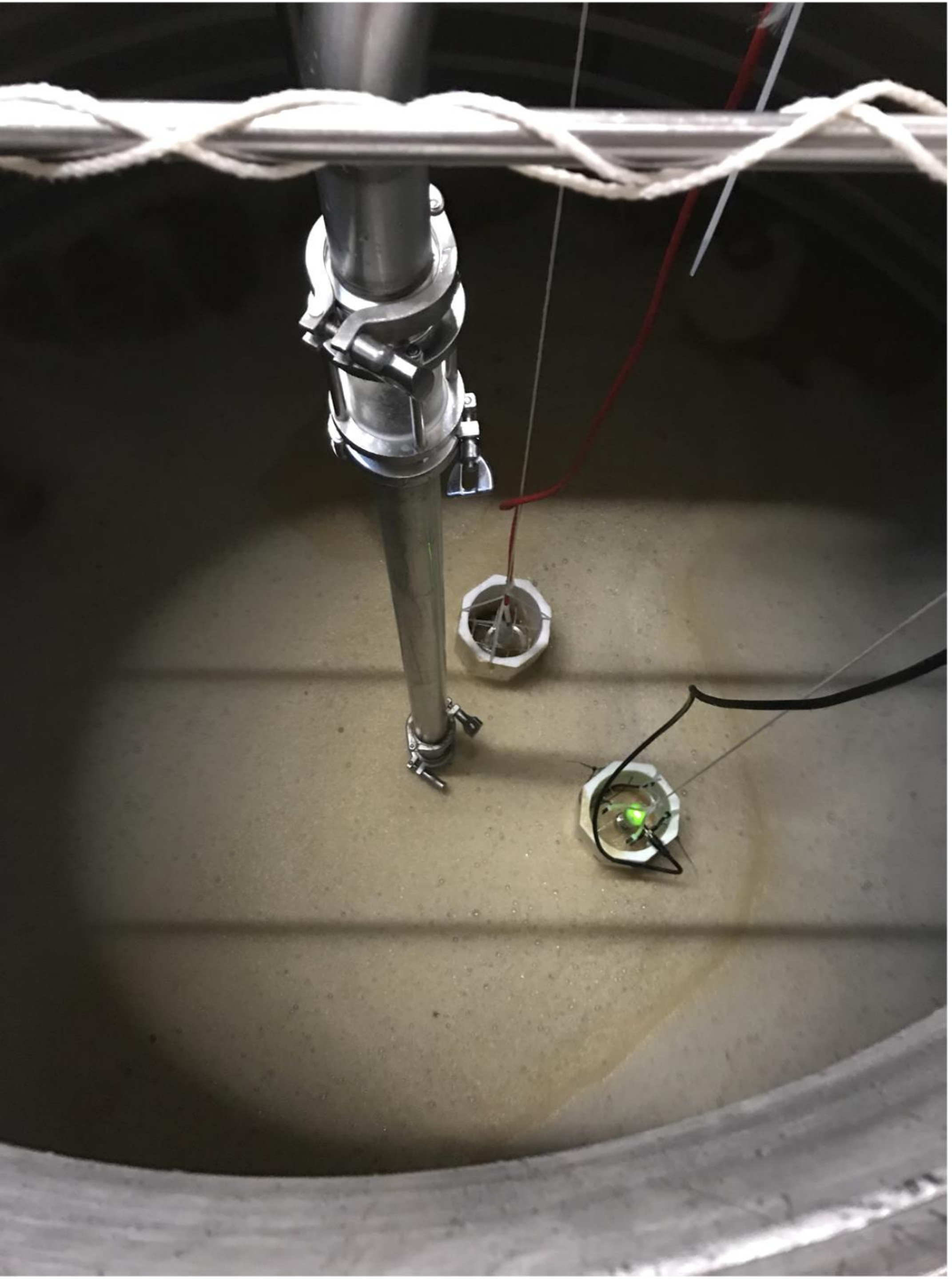
Parameters:		
Maintenance	0.396976	g/g
Lag Time	35.772701	h
Viability Const.	21.1257	h-1
EtOH inibit. Const.	0.0084144	
Nitrogen	0.0003687	g/ml

With Redox Control

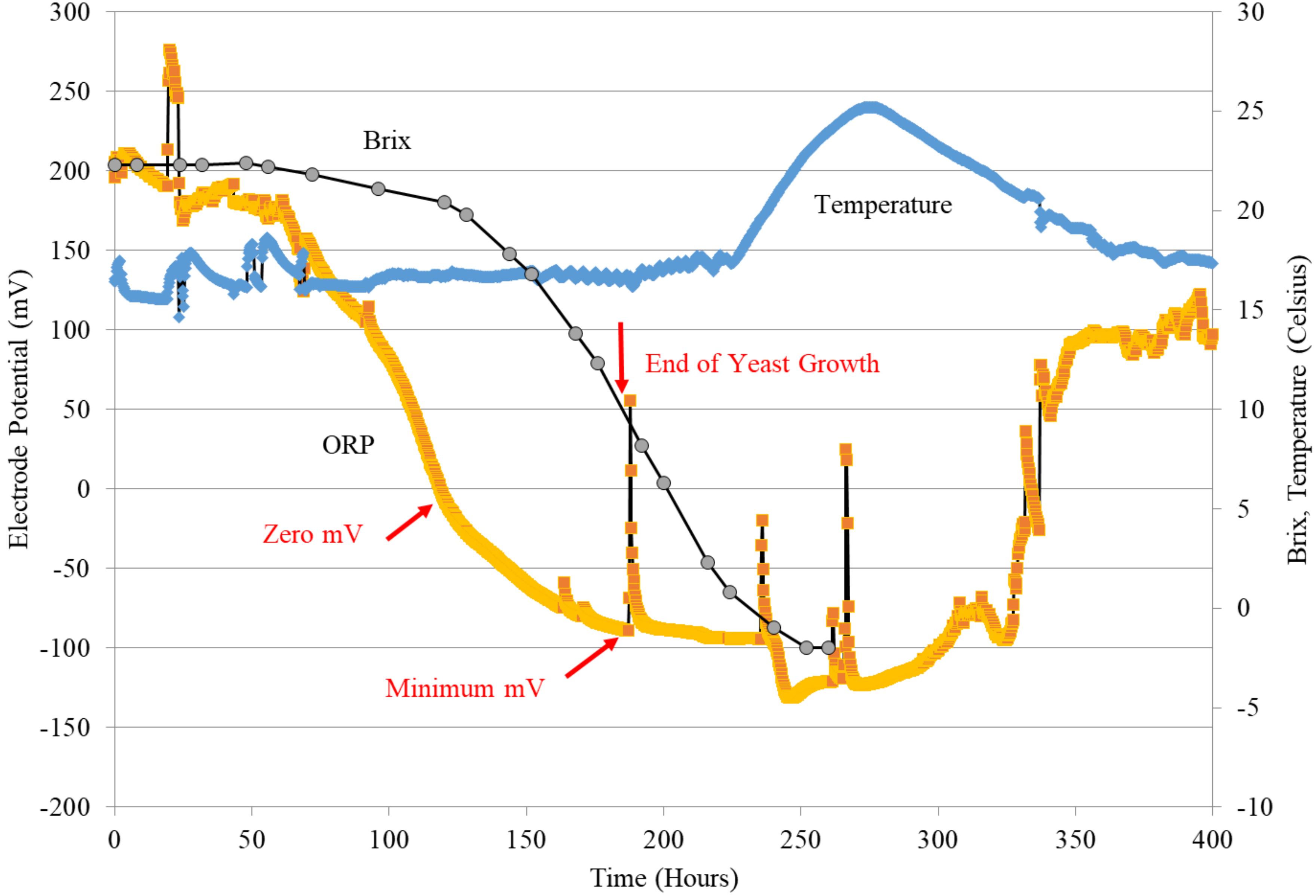
Commercial Scale Fermentation

White Trial, Surface Float Location, 2018 post Harvest

Hamilton Probe, Reconstituted Juice, 16 C



White Wine Example, 20KL

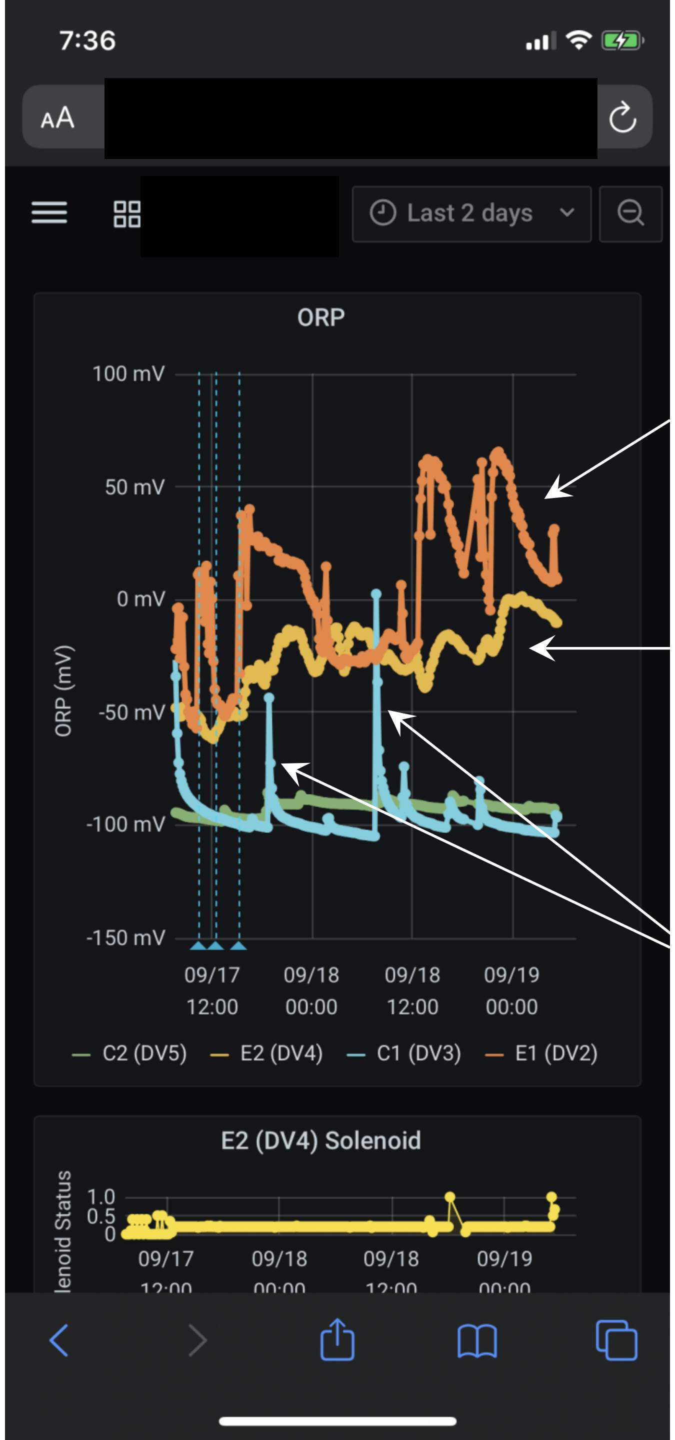


Commercial Scale Fermentation

Sensor floating in skin cap, Open top-Punch down, Red Wine, 300 L, 2020 Harvest

Open Top,
Cold Soak,
Punch Down,
Pinot Noir.

Floating Epoxy Sensor,
Air Tube on the floor



Note the Redox Potential held between -50 and +60 mV*

Note the Redox Potential held between -50 and zero mV*

Note the decline in Redox Potential after each punch down

* mV on the relative scale, add 240 for the absolute scale

Scaled Fermentation 2021

Scaled Fermentation, Red Wine,
Same Grapes at 100 L (3x), 1 KL, (UC Davis) 10 KL (Commercial)
Control to above 150 mV
Results yet to be Published


Recognizing the generosity of
Cakebread Cellars
DANGER


DANGER
CONFINED SPACE
ENTER BY
PERMIT ONLY

Why is it more useful than Dissolved Oxygen?

It is difficult to get oxygen dissolved into wine, 2 to 4 mg/L at best

Most the dissolved oxygen is unreactive

Only the first 0.5 mg/L is active, after that it is independent of the DO level

Closing Comments

Less than 1 mg/L of DO is required to get a 100 to 200 mV rise.

The effect is short lived, so frequent or controlled additions are required.

An open tube is adequate, no need for spargers or membranes.

Mixing within the fermentor is important to get this result

The effect of Punch-down or Pump-over is real, but short lived.

Acknowledgements

Stephen Sinclair Scott Endowment

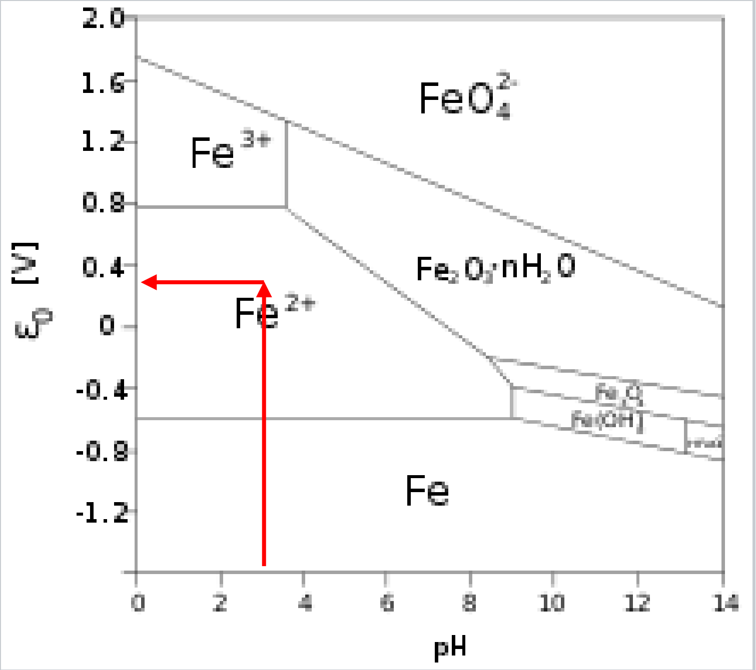
T.J. Rodgers Fellowships

Jordan Vineyard & Winery
DANGER
PERMIT REQUIRED
CONFINED SPACE
DO NOT ENTER

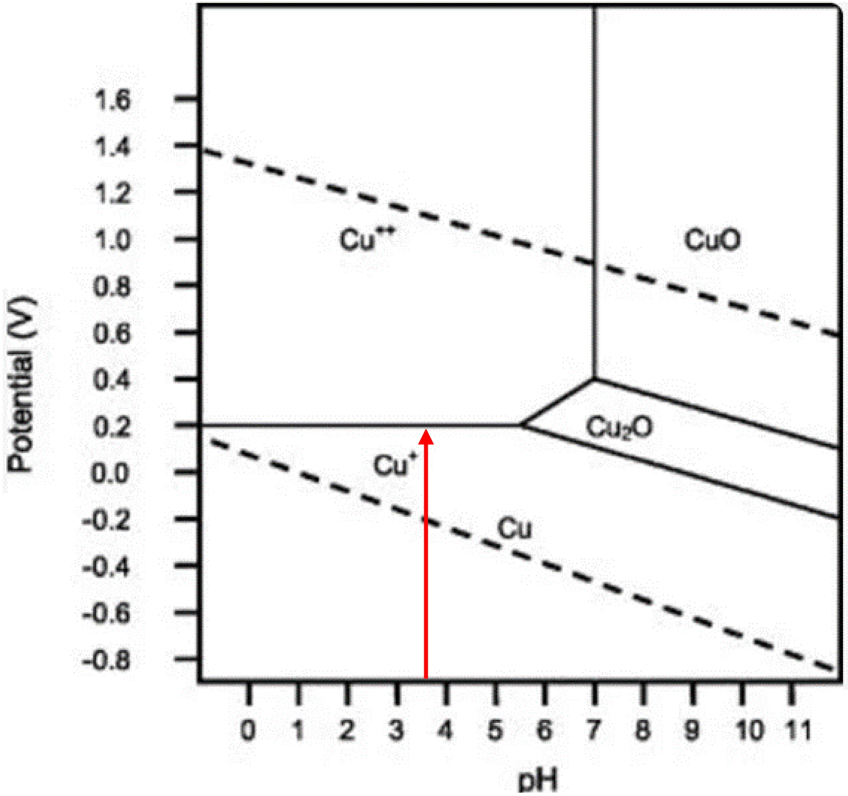
J. Lohr Vineyards & Wines
P14
P13
DANGER

Redox Potential and Iron, Copper

Fe(II) and Fe(III) pair
Cu(I) and Cu(II) pair
Copper sulfides and Elemental Sulphur
Iron and Copper Tartrate Complexes



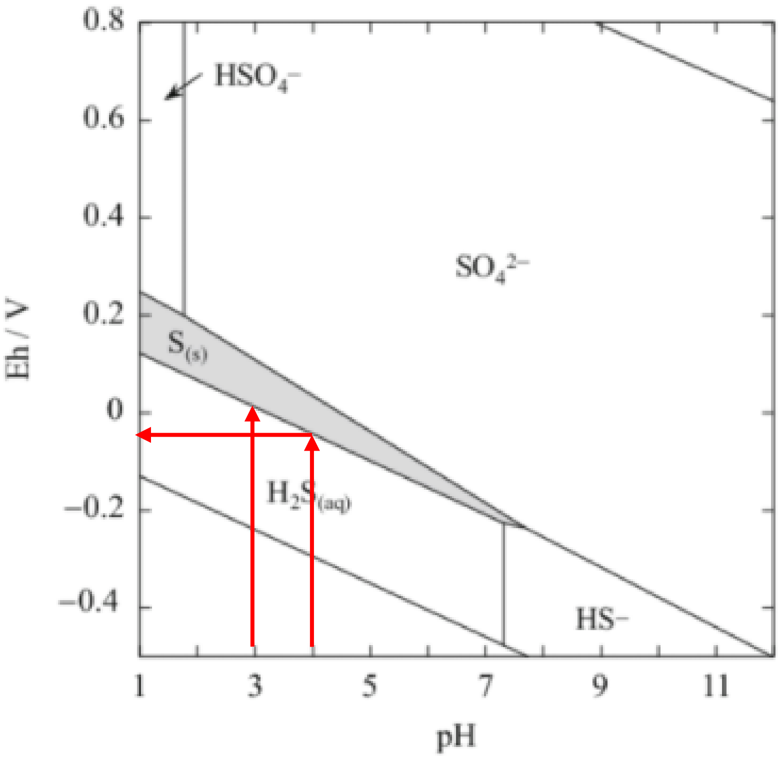
Pourbaix diagram of iron.[1]



https://en.wikipedia.org/wiki/Pourbaix_diagram

https://www.physicsforums.com/threads/copper-pourbaix-diagram.870540/

https://www.researchgate.net/figure/Eh-pH-diagrams-for-sulfur-and-selenium-species-at-5-C-and-150-bar-total-pressure-The-30_fig5_283837484



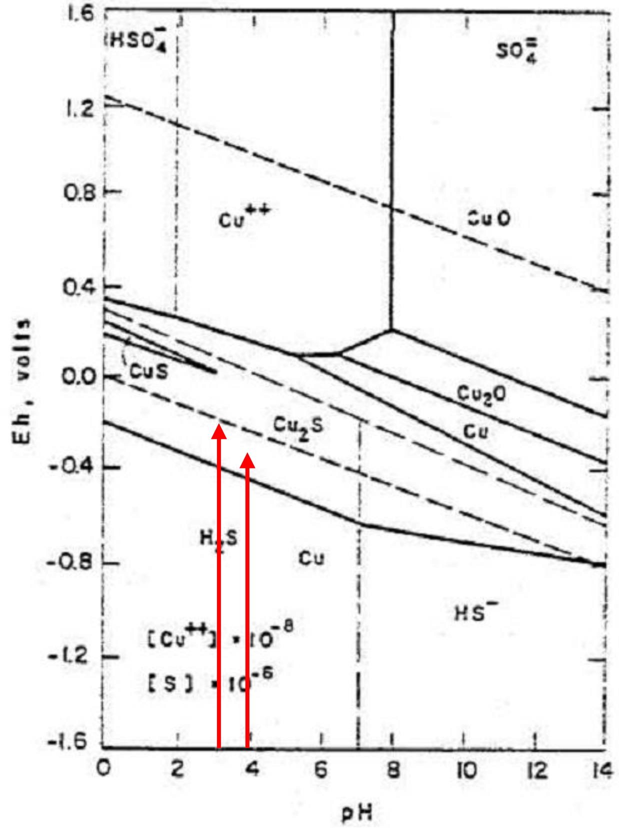
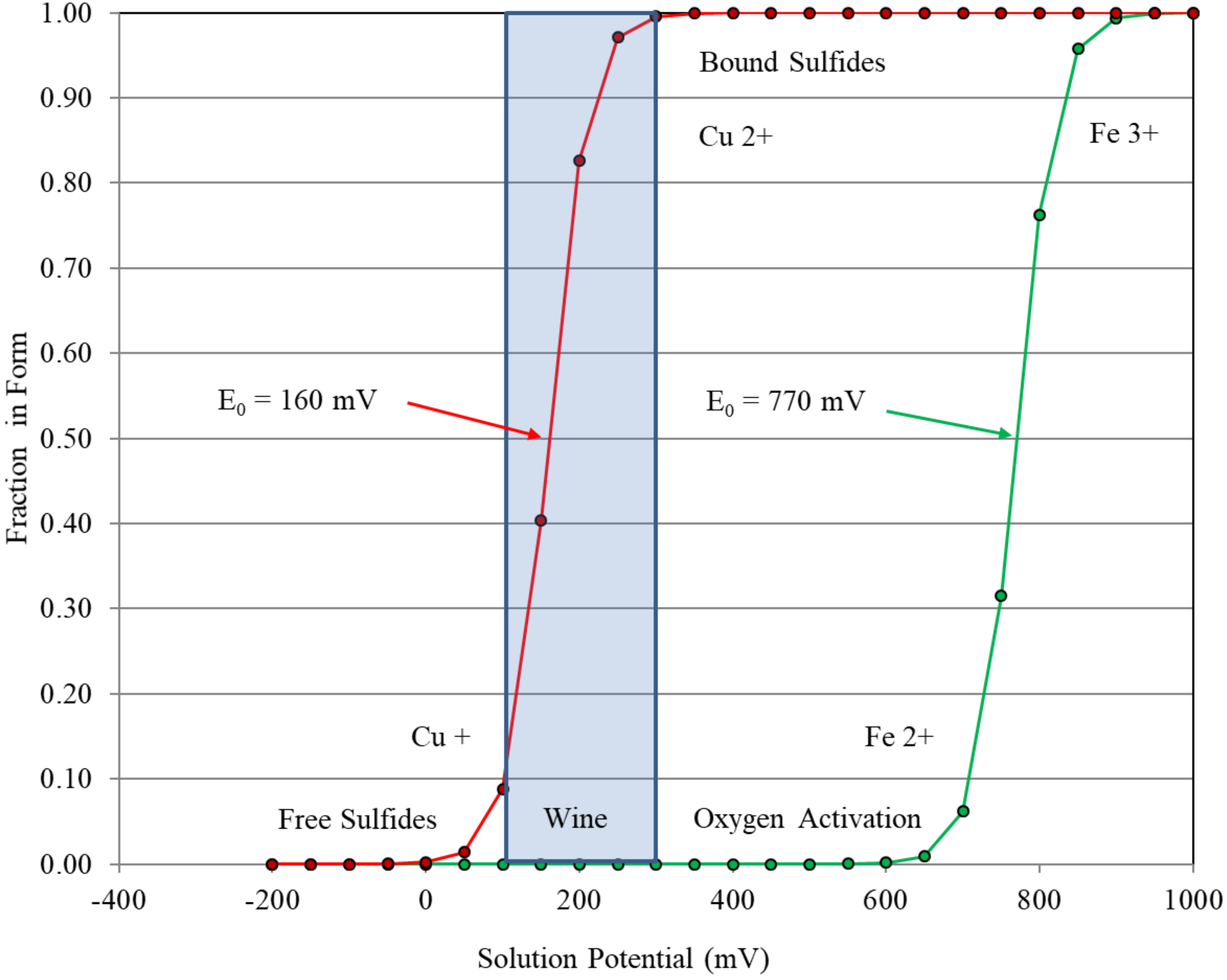


Figure 5. The Eh-pH diagram for copper sulfides

https://www.911metallurgist.com/oxidation-reduction-effects-depression-sulfide-minerals/



Fraction in Form
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
-400
-200
0
200
400
600
800
1000
Solution Potential (mV)
Bound Sulfides
Cu 2+
Fe 3+
E_0 = 160 mV
E_0 = 770 mV
Cu +
Fe 2+
Free Sulfides
Wine
Oxygen Activation

The Nernst Equation

$$aA + bB + n[e^-] + h[H^+] = cC + dD$$

$$E_h = E_0 + \frac{0.05916}{n}\log\left(\frac{\{A\}^a\{B\}^b}{\{C\}^c\{D\}^d}\right) - \frac{0.05916h}{n}\mathrm{pH}$$

$$E_h = E_0 + \frac{0.0592}{n}\log\frac{[\mathrm{Oxidized}]}{[\mathrm{Reduced}]} - \frac{0.0592}{n}h\,\mathrm{pH}$$

$$E_h = E_0 + \frac{0.0592}{n}\log\frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}]}$$

$n= 1, h=0$

$$E_h = E_0 + \frac{0.0592}{n}\log\frac{[\mathrm{Cu}^{2+}]}{[\mathrm{Cu}^{+}]}$$

$n= 1, h=0$

$$E_h = E_0 + \frac{0.0592}{n}\log\frac{[\mathrm{GSSG}]}{[\mathrm{GSH}]} - \frac{0.0592}{n}h\,\mathrm{pH}$$

$n= 2, h=2$

Measured Redox Potential and Other scales

$$E_h = E_0 + \frac{0.0592}{n} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$E_h = E_0 + \frac{0.0592}{n} \log \frac{[Cu^{2+}]}{[Cu^{+}]}$$

$$E_h = E_m + E_{ref}$$

$$E_h = E_0 + \frac{0.0592}{n} \log \frac{[GSSG]}{[GSH]} - \frac{0.0592}{n} h \, pH$$

Biology: pH 7
$E_{h7} = E_{07}$

Chemistry: pH 0
$E_{h0} = E_0$

$$E_{\text{complex}} = E_{\text{aqua}} - \frac{RT}{nF} \ln \frac{\beta^{\text{III}}}{\beta^{\text{II}}} \, .$$

Tartrate
Malate
Glutathione
Cysteine

Metal Binding Constants

$M + H + L = MHL$ $\beta_{111} = [MHL]/[M]/[H]/[L]$

$M + H + 2L = MHL_2$ $\beta_{112} = [MHL_2]/[M]/[H]/[L]^2$

$Fe(II) + Ta = Fe(II)Ta$ $\beta_{101}^{II} = [Fe(II)Ta]/[Fe(II)]/[Ta]$

$\beta_{101}^{II} = 2.61$

$Fe(III) + Ta = Fe(III)Ta$ $\beta_{101}^{III} = [Fe(III)Ta]/[Fe(III)]/[Ta]$

$\beta_{101}^{III} = 13.55$

$$E_{\mathrm{complex}} = E_{\mathrm{aqua}} - \frac{RT}{nF} \ln \frac{\beta^{III}}{\beta^{II}} .$$

R =8.314 J K-1mol-1

F = 9.648 x 10^4 C mol-1

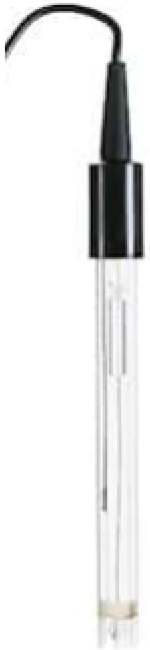
$E_{\mathrm{Fe(III)/Fe(II)}} = 0.77 – 0.59*\mathrm{Ln}(13.55/2.61) = +348$ mV

Measuring Electrode Potential in Wines

Nitrogen sparging, Removal of Free SO_2 and Dissolved Oxygen
Well-Stirred, Constant Temperature, 20 C
20 to 30 minutes to equilibrate solution and electrode
Record pH as well

1. Nitrogen Sparger

2. Oxidation Reduction Potential
(ORP) Electrode



Jacketed 3 Arm Flask

3. Temperature Probe

Round Bottom Stir Bar

Magnetic Stir Plate

pH mV meter