Redox Potentials during Fermentation and Aging: Yeast, Nutrients and Metals.

Roger Boulton
Stephen Scott Professor of Enology and Chemical Engineering
Department of Viticulture and Enology
University of California, Davis, CA, USA

New Zealand Society for Viticulture and Oenology Workshop
Blenheim, New Zealand
27th January 2019

Outline

- Redox Potentials vs Dissolved Oxygen
  - Fermentation and Aging
  - Role of Yeast and Juice Composition
  - Role of Added Nutrients and Temperature
- Control of Potentials during Fermentation
- Changes in Potentials during Wine Aging
  - Metals, Phenols and Additives
  - Sulfide and Thiol Liberation With Time

Oxidation-Reduction Reaction	Electrons n	Protons h	h/n	Slope 2.3RT/F /n*h*pH	Eh pH0 0.00	Eh pH3 3.00	Eh pH3.5 3.5	Eh pH4 4.00	Eh pH7 7.00
FeO4= + 8H+ + 3 e = Fe3+ + 4H2O	3	8	2.67	-0.158	2.20	1.73	1.65	1.57	1.09
O3(g) + 2 H+ + 2 e = O2(g) + H2O	2	2	1.00	-0.059	2.08	1.90	1.87	1.84	1.66
S2O8= + 2 e = 2 SO4=	2	0	0.00	0.000	2.01	2.01	2.01	2.01	2.01
H2O2 + 2H+ + 2e = 2H2O	2	2	1.00	-0.059	1.78	1.60	1.57	1.54	1.37
Ce4+ + 1e = Ce3+	1	0	0.00	0.000	1.61	1.61	1.61	1.61	1.61
MnO4- + 8H+ + 5e = Mn2+ + 4H2O	5	8	1.60	-0.095	1.51	1.23	1.18	1.13	0.85
HOO2. + H+ + 1e = H2O2	1	1	1.00	-0.059	1.51	1.33	1.30	1.27	1.10
Cr2O7= + 14H+ + 6e = 2Cr3+ + 7H2O	6	14	2.33	-0.138	1.33	0.92	0.85	0.78	0.36
O2 + 4H+ + 4e = 2H2O	4	4	1.00	-0.059	1.23	1.05	1.02	0.99	0.82
2IO3- + 12H+ + 10e = I2(s) + 6H20	10	12	1.20	-0.071	1.20	0.98	0.95	0.91	0.70
O2•$^{-}$ + 2H + 1e = H2O2	1	2	2.00	-0.118	0.94	0.58	0.67	0.47	0.11
o-Quinone +2H+ + 2e = Catechol	2	2	1.00	-0.059	0.84	0.66	0.63	0.60	0.43
Fe3+ + 1e = Fe2+	1	0	0.00	0.000	0.77	0.77	0.77	0.77	0.77
O2 + 2H+ + 2e = H2O2	2	2	1.00	-0.059	0.70	0.52	0.49	0.46	0.29
MeBlu + 2H+ 2e = LeucoMethBlu	2	2	1.00	-0.059	0.52	0.34	0.31	0.28	0.11
Dehydro + 2H+ + 2e = Ascorb	2	2	1.00	-0.059	0.47	0.29	0.26	0.23	0.06
0-Quinone + 2H+ + 2e = Caffeic Acid	2	2	1.00	-0.059	0.46	0.28	0.25	0.22	0.05
Fumarate + 2H+ + 2e = Succinate	2	2	1.00	-0.059	0.44	0.26	0.23	0.20	0.03
[Fe(CN)6]3- + 1e = [Fe(CN)6]4-	1	0	0.00	0.000	0.36	0.36	0.36	0.36	0.36
Indigo Carmine + 2H+ + 2e = Red Indigo Carmine	2	2	1.00	-0.059	0.29	0.11	0.08	0.05	-0.13
Pyruvate + 2H+ 2e = Lactate	2	2	1.00	-0.059	0.23	0.05	0.02	-0.01	-0.18
Acetaldehyde + 2H+ + 2e = Ethanol	2	2	1.00	-0.059	0.22	0.04	0.01	-0.02	-0.19
SO4= + 4H+ + 2e = SO2(aq) + 2H2O	2	4	2.00	-0.118	0.20	-0.16	-0.21	-0.27	-0.63
GSSG + 2H+ + 2e = 2 GSH	2	2	1.00	-0.059	0.18	0.00	-0.03	-0.06	-0.23
Cu++ + 1e = Cu+	1	0	0.00	0.000	0.16	0.16	0.16	0.16	0.16
S + 2H+ + 2e = H2S	2	2	1.00	-0.059	0.14	-0.04	-0.07	-0.10	-0.27
SO4= + 10H+ + 8e = H2S + 4H2O	10	8	0.8	-0.047	0.12	-0.02	-0.05	-0.07	-0.21
Cystine + 2H+ + 2e = Cysteine	2	2	1.00	-0.059	0.07	-0.11	-0.14	-0.17	-0.34
2H+ + 2e = H2(g)	2	2	1.00	-0.059	0.00	-0.18	-0.21	-0.24	-0.41
CO2 + 4H+ + 4e = 1/6*Glucose + H2O	4	4	1.00	-0.059	-0.02	-0.20	-0.23	-0.26	-0.43
HCOOH(aq) + 2 H+ + 2 e = HCHO(aq) + H2O	2	4	2.00	-0.118	-0.03	-0.39	-0.44	-0.50	-0.86
NAD+ + H+ + 2e = NADH	2	1	0.50	-0.030	-0.12	-0.20	-0.22	-0.23	-0.32
NADP+ + H+ + 2e = NADPH	2	1	0.50	-0.030	-0.12	-0.20	-0.22	-0.23	-0.32
O2(g) + H+ + 1e = HO2•(aq)	1	1	1.00	-0.059	-0.13	-0.31	-0.34	-0.37	-0.54
O2 + 1e = O2•$^{-}$	1	0	0.00	0.000	-0.33	-0.33	-0.33	-0.33	-0.33
Cr3+ + 1e = Cr2+	1	0	0.00	0.000	-0.42	-0.42	-0.42	-0.42	-0.42

Redox Potential and Microbial Growth

Hewitt (1930)
Joslyn (1949)
Schanderl (1949, 1959)
Ribereau-Gayon and Peynaud (1961)
Rankine (1963)

OXIDATION-REDUCTION POTENTIALS IN BACTERIOLOGY AND BIOCHEMISTRY

By

L. F. HEWITT

PH.D., B.SC., F.R.I.C.

Director,

Serum Research Institute, Medical Research Council

Carshalton, Surrey

Typical curves relating the electrode potentials of aerobic cultures of hæmolytic streptococci and *C. diphtheriæ* (Hewitt, 1930, 2) at various stages of development are given in fig. 20. A small inoculum of hæmolytic streptococci was made into sterile peptone-infusion broth and even after 30 minutes the E_h had commenced to fall, a minimum value (− 0·16 volt) being reached in 12 hours: this is approximately the duration of the logarithmic phase of growth and is characterised, as can be seen, by intense reducing activities. After this period the death rate of the

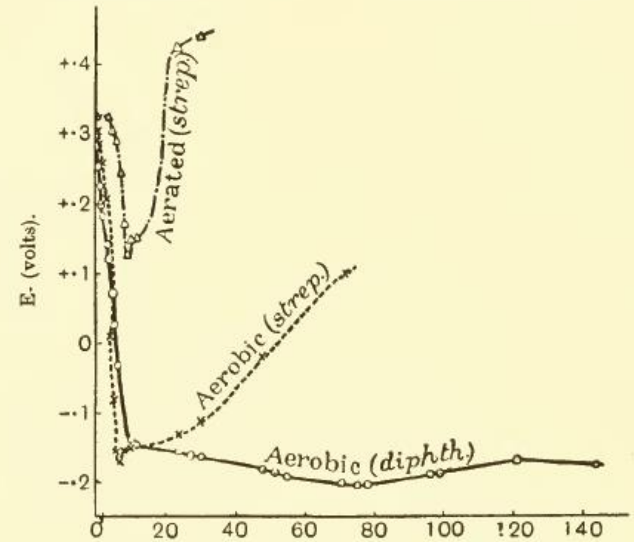


FIG. 20

Electrode potential : time curves of infusion broth cultures of hæmolytic streptococci and *C. diphtheriæ*

organisms becomes appreciable and the potential rises. Reducing conditions are not maintained under aerobic conditions when the organisms have ceased actively to proliferate. This increase in potential after the cessation of active multiplication is not, however, a general phenomenon exhibited by all organisms. In the case of *C. diphtheriæ*, for example, of which the corresponding curve is given in the same figure the potential falls to − 0·2 volt, rather more slowly than with hæmolytic streptococci, but this level is maintained for some days.

When cultures are aerated, it is found, as would be anticipated, that the generous supply of oxygen prevents to some extent the establishment of intense reducing conditions. Thus in the case of hæmolytic streptococci (top curves in fig. 20) the potential in ordinary aerobic cultures falls to − 0·16 volt, whilst in specially aerated cultures it does not fall below + 0·1 volt, and a marked effect is seen after the phase of active proliferation. In the aerated culture, the potential rises rapidly and reaches + 0·45 volt, a highly oxidising level, and peroxide may be detected in the culture.

STUDIES ON OXIDATION-REDUCTION IN MILK

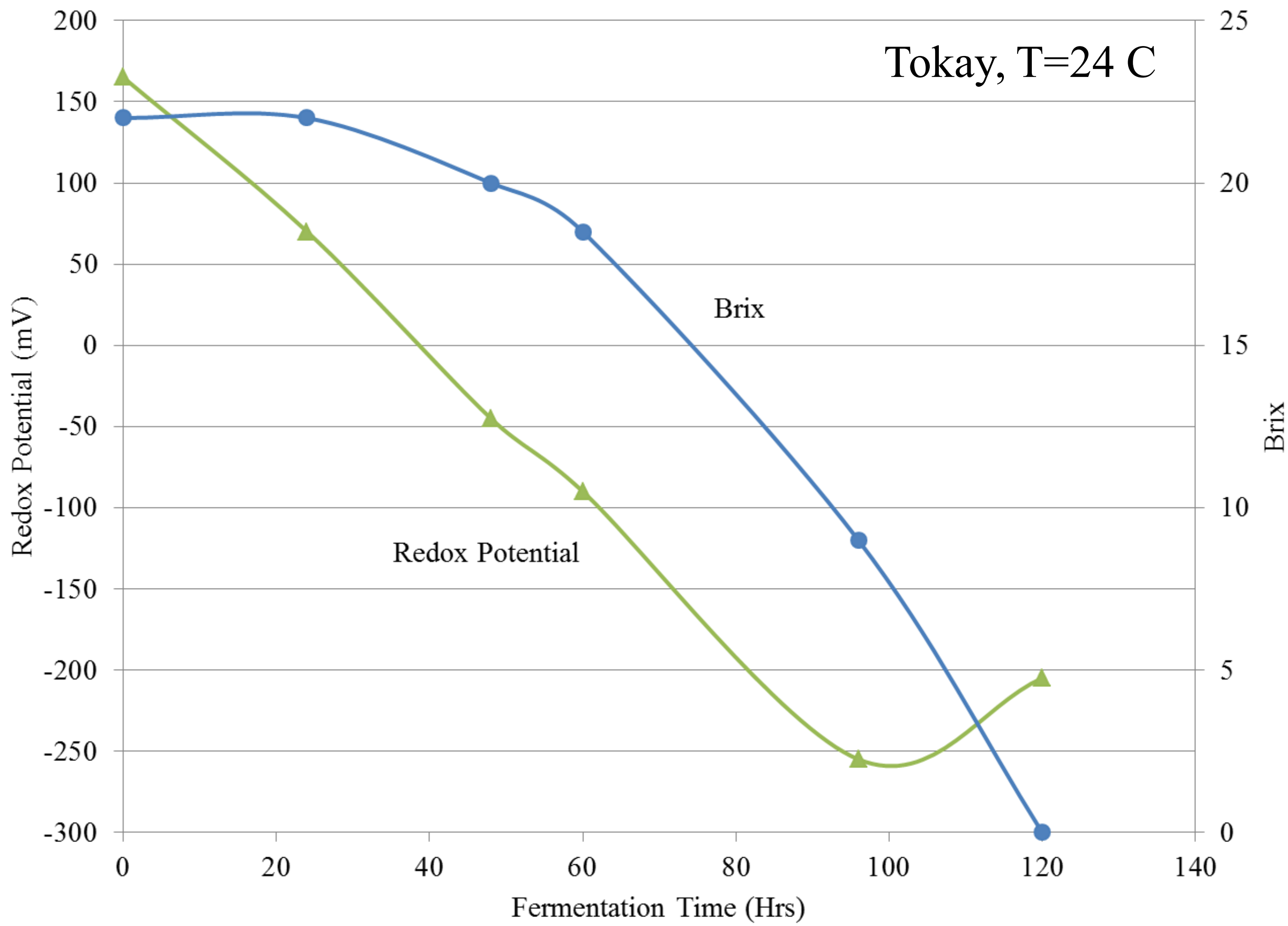
I. OXIDATION-REDUCTION POTENTIALS AND THE MECHANISM OF REDUCTION[1]

H. R. THORNTON AND E. G. HASTINGS

Department of Agricultural Bacteriology, University of Wisconsin

Received for publication June 20, 1929

of compounds which have been called "metabolites." Hopkins (1921) believes glutathione to be the hydrogen donator and acceptor in oxidation-reduction processes in animal tissues. He states that glutathione is a compound of cysteine and glutamic acid with a free S–H group.



CALIFORNIA WINES

Oxidation-Reduction Potentials at Various Stages of Production and Aging

M. A. JOSLYN

University of California, Berkeley 4, Calif.

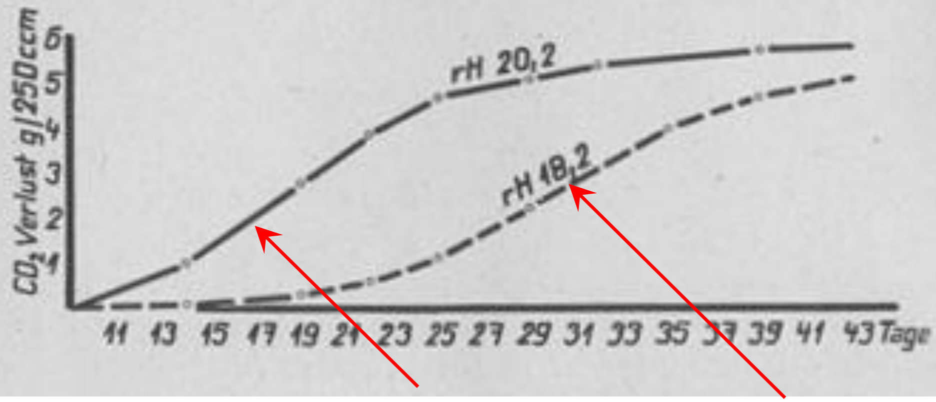


Abb. 81. Der Verlauf einer Gärung von 2 verschiedenen Anfangsredoxstufen aus. Der Most mit einer höheren Anfangsredoxstufe gärt früher und schneller.

435 mV 375 mV

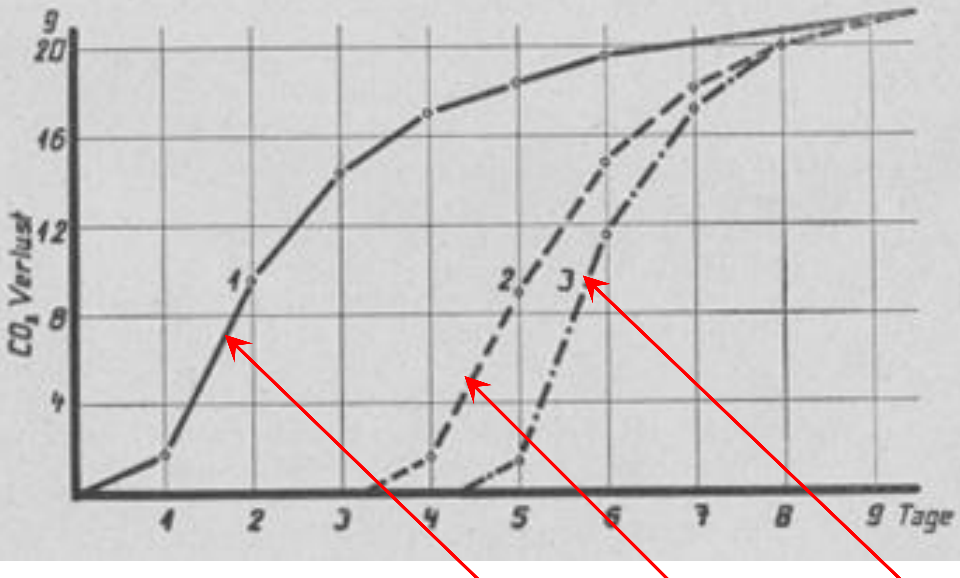
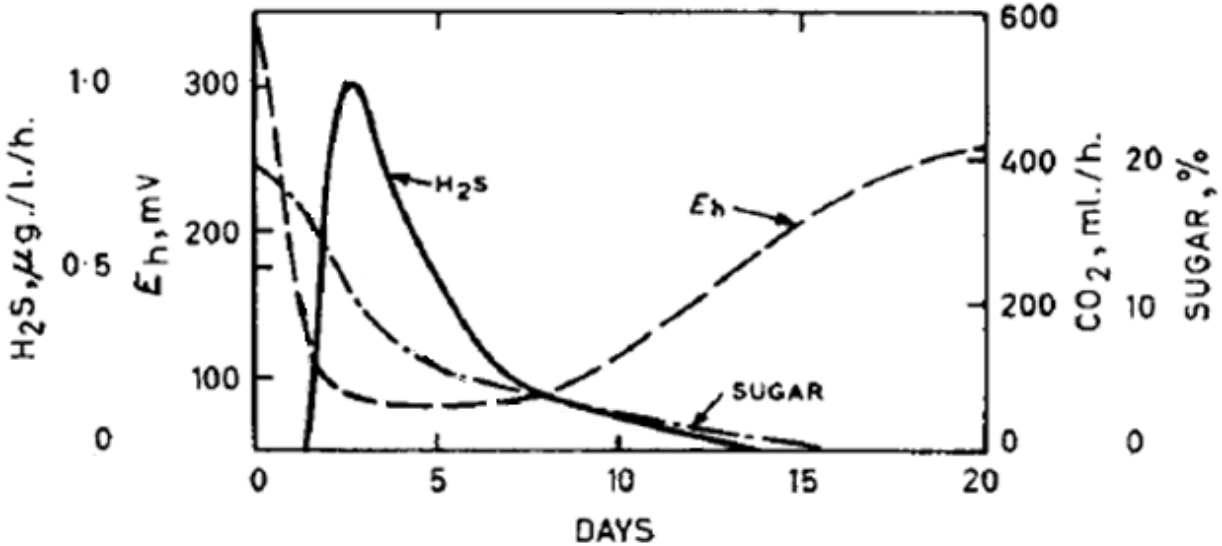
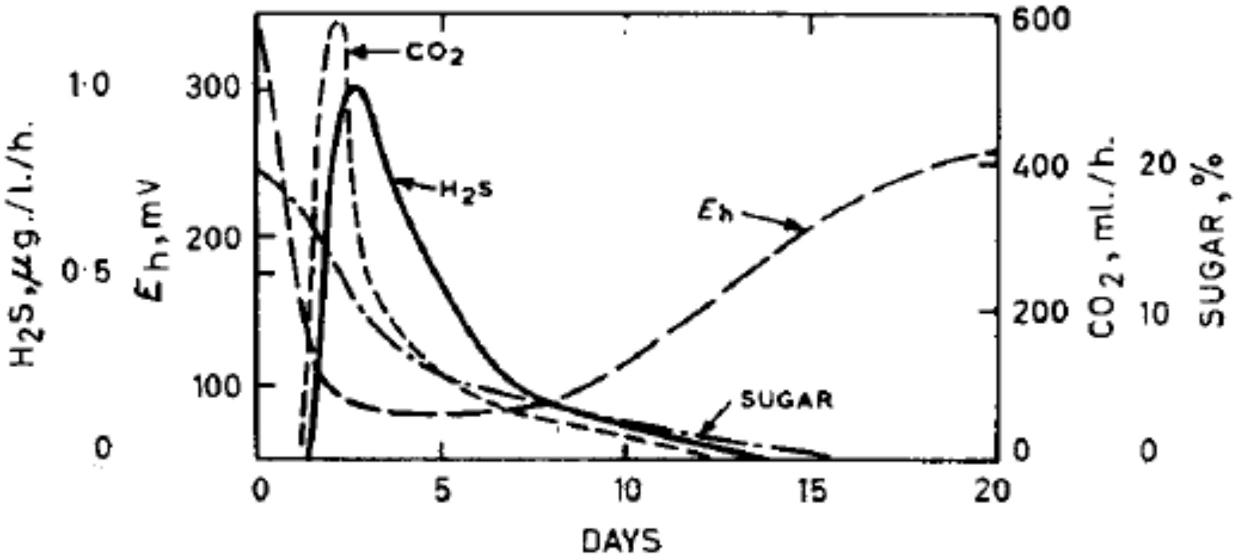


Abb. 82. Die Anfangsredoxstufe wurde durch Zugabe von Ascorbinsäure (Vitamin C) gesenkt, 1 = Kontrolle, 2 = Anfangs-rH = 18,0, 3 = Anfangsredoxstufe = 16,1; die Hefe reagiert darauf, wie wenn der Most geschwefelt worden wäre.

435 mV 370 mV 313 mV

Schanderl, H. Mikrobiologie des Weines (1959)





Rankine, B. C. Nature, Origin and prevention of Hydrogen Sulfide in Wines.
J. Sci. Food. Agric. (1963) 14:79-91

Malolactic Fermentation

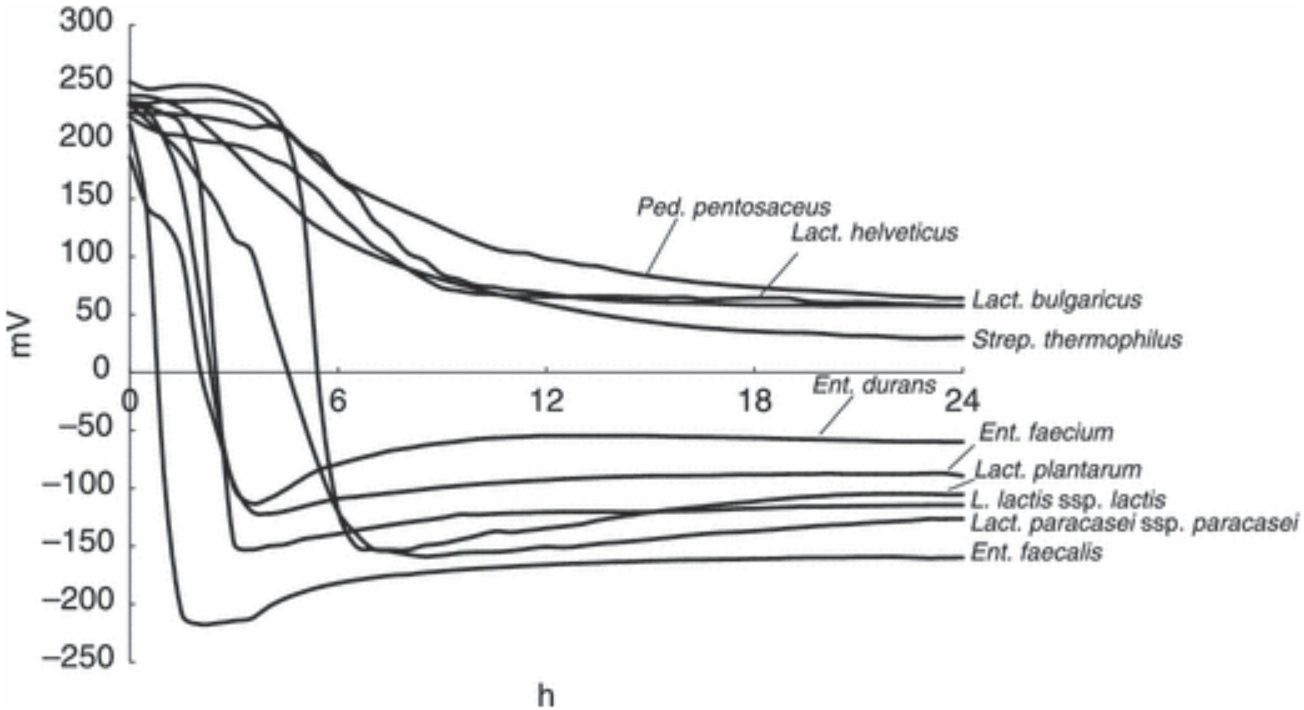
RELATION ENTRE LE POTENTIEL D'OXYDO-RÉDUCTION
ET LA FERMENTATION MALOLACTIQUE

D'après CHARPENTIÉ (18)

Évolution observée au douzième jour après l'ensemencement

		Aérobiose continue		Anaérobiose progressive		Anaérobiose absolue	
		Potentiel mV	Diminution d'acidité méq	Potentiel mV	Diminution d'acidité méq	Potentiel mV	Diminution d'acidité méq
*p*H 3,45	Avant	460		460		300	
	Après	420	11	285	9	300	1
*p*H 3,82	Avant	450		460		260	
	Après	470	11	260	11	270	6

Traite d'Oenologie, Vol II. Ribereau-Gayon, J. and Peynaud, E. (1961). p 492.



Journal of Applied Microbiology

Explore this journal >

ORIGINAL ARTICLE

Redox potential to discriminate among species of lactic acid bacteria

M. Brasca, S. Morandi, R. Lodi, A. Tamburini

First published: 19 June 2007 Full publication history

DOI: 10.1111/j.1365-2672.2007.03392.x View/save citation

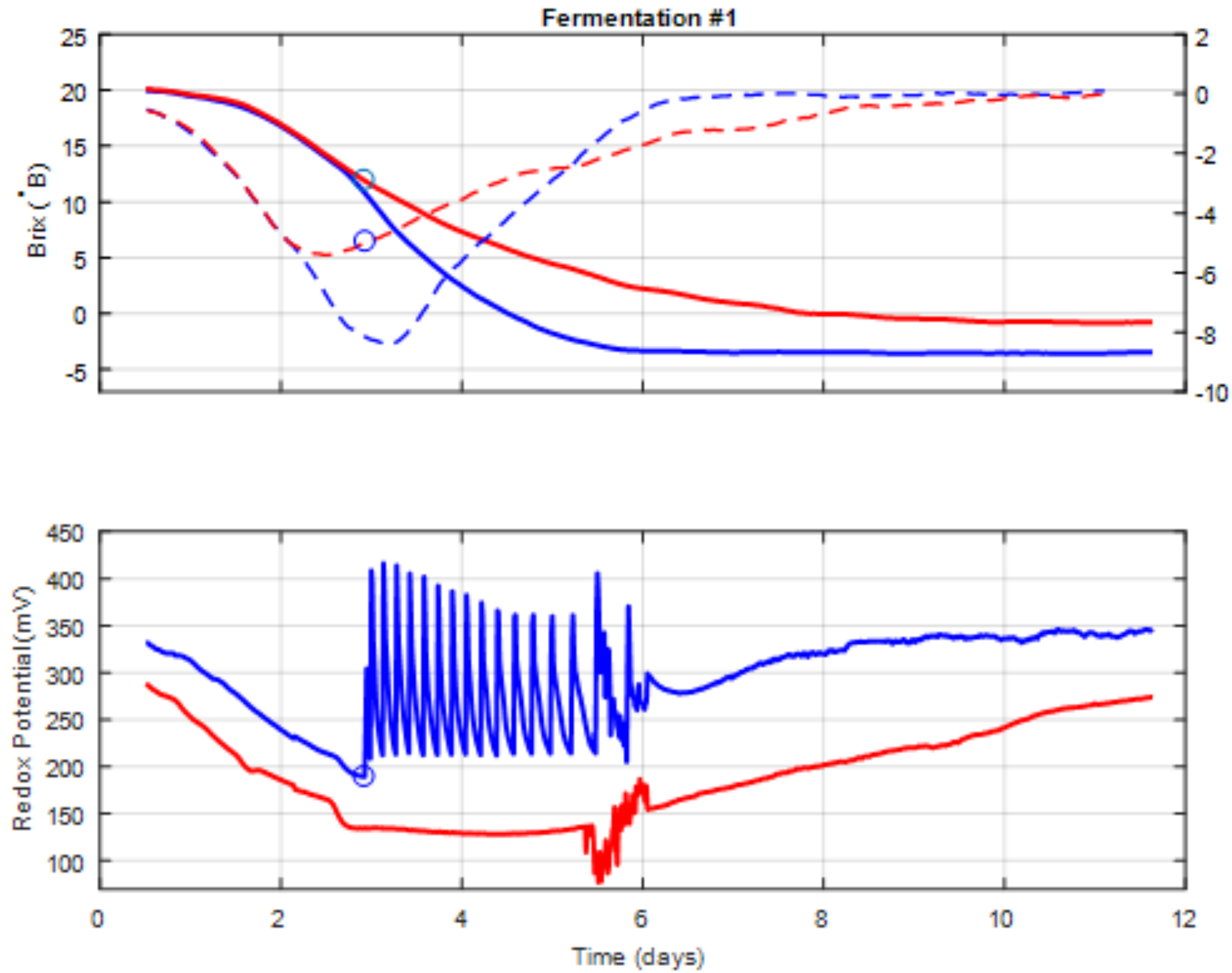
View issue TOC
Volume 103, Issue 5
November 2007
Pages 1516–1524

Controlled Redox Potential During Fermentation

Advanced Monitoring and Control of Redox Potential in Wine Fermentation

David J. Killeen,[1] Roger Boulton,[2*] and André Knoesen[1]

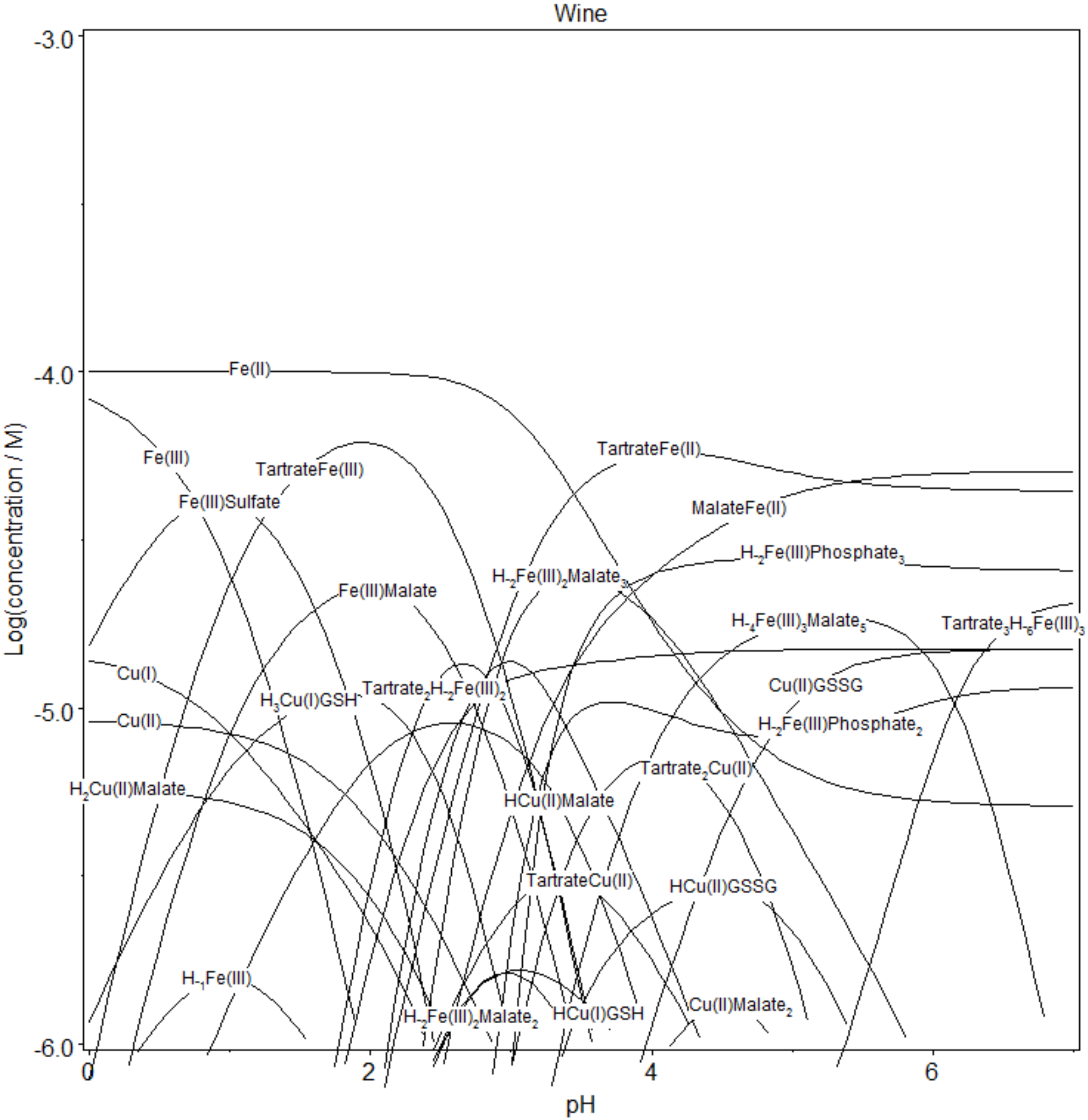
Am. J. Enol. Vitic. 69:4 (2018) 394-399

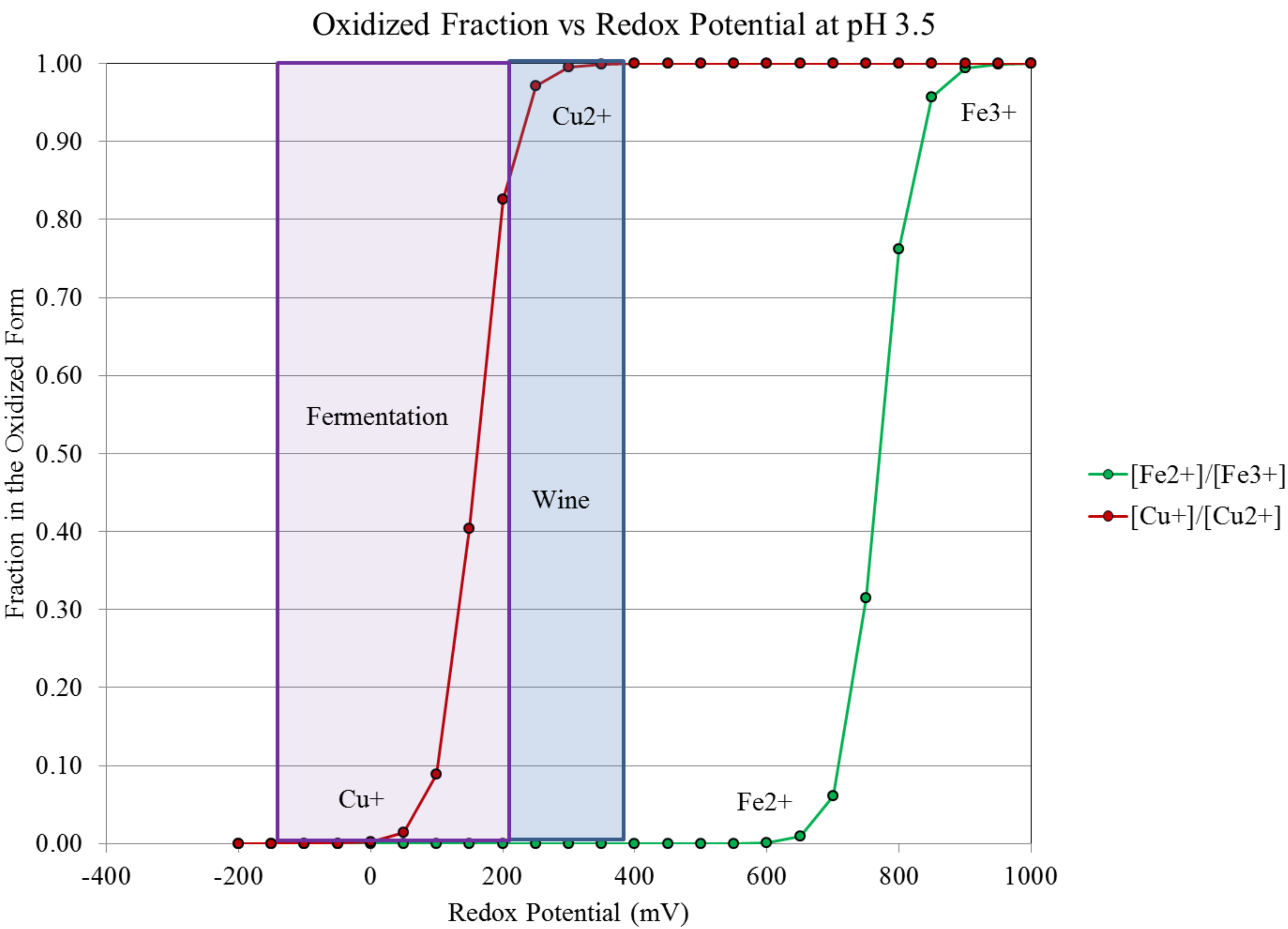


Am. J. Enol. Vitic. 69:4 (2018) 394-399

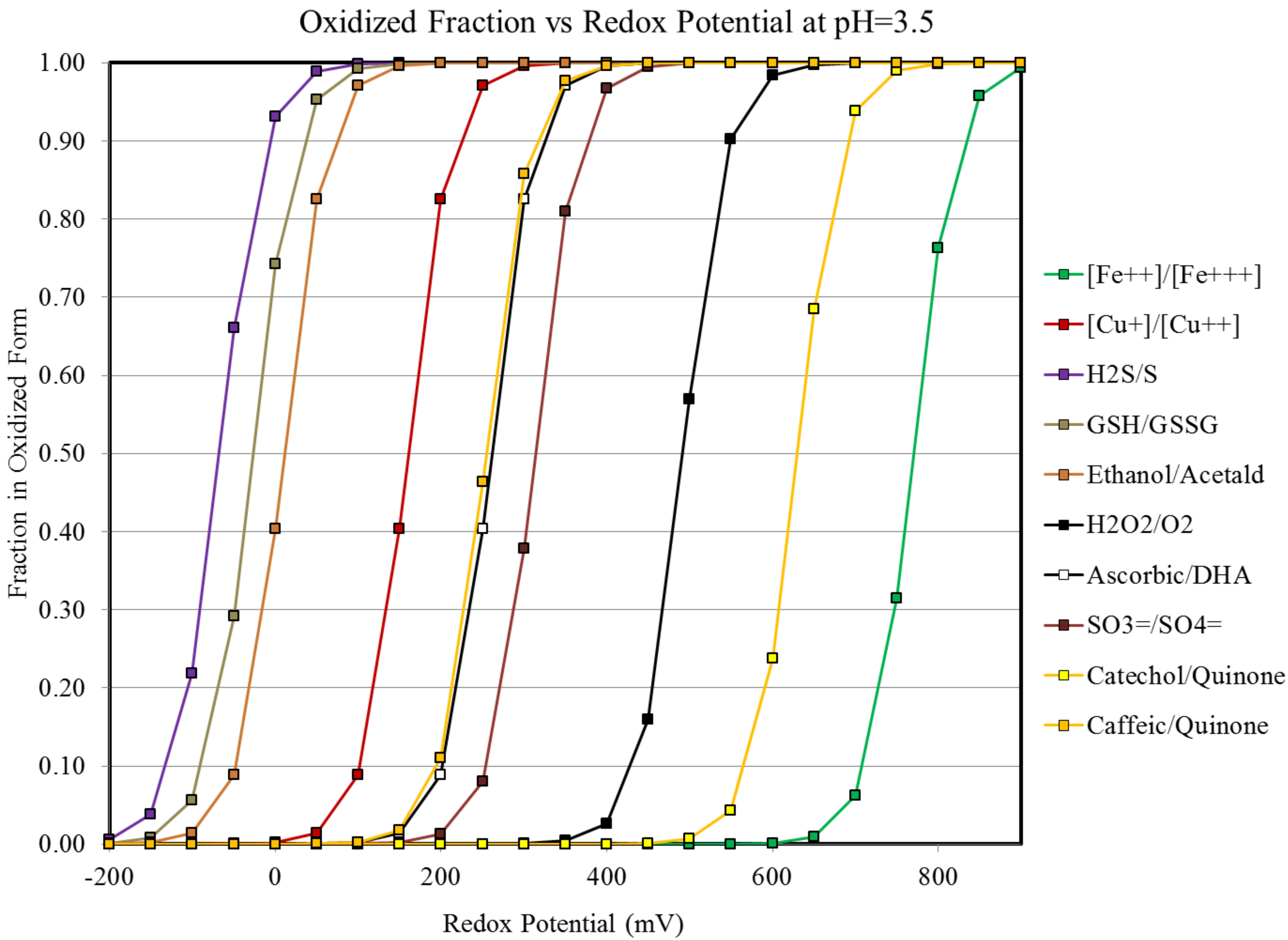
Free and Complexed Forms of Iron and Copper

Fe(II), Fe(III) and Cu(I), Cu(II)

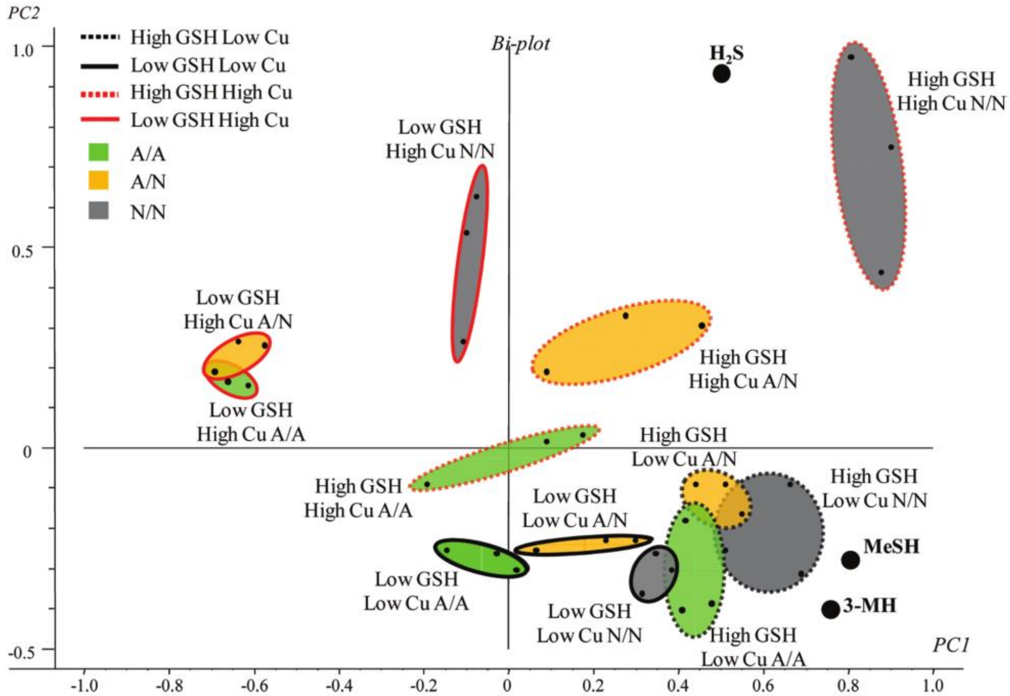

Wine
-3.0
-4.0
-5.0
-6.0
0
2
4
6
pH
Log(concentration / M)
Fe(II)
Fe(III)
TartrateFe(III)
Fe(III)Sulfate
TartrateFe(II)
MalateFe(II)
$H_{-2}Fe(III)Phosphate_3$
$H_{-2}Fe(III)_2Malate_3$
Fe(III)Malate
$H_{-4}Fe(III)_3Malate_5$
$Tartrate_3H_{-6}Fe(III)_3$
Cu(I)
Cu(II)GSSG
$H_3Cu(I)GSH$
$Tartrate_2H_{-2}Fe(III)_2$
Cu(II)
$H_{-2}Fe(III)Phosphate_2$
$H_2Cu(II)Malate$
$Tartrate_2Cu(II)$
HCu(II)Malate
TartrateCu(II)
HCu(II)GSSG
$H_{-1}Fe(III)$
$Cu(II)Malate_2$
$H_{-2}Fe(III)_2Malate_2$
HCu(I)GSH

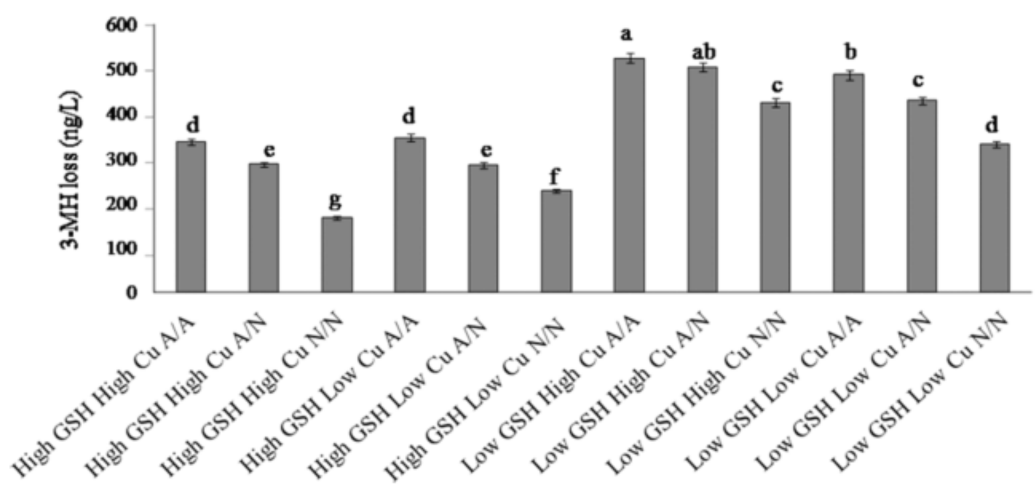


Oxidized Fraction vs Redox Potential at pH 3.5
Fraction in the Oxidized Form
Redox Potential (mV)
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
-400
-200
0
200
400
600
800
1000
Fermentation
Wine
Cu2+
Cu+
Fe3+
Fe2+
[Fe2+]/[Fe3+]
[Cu+]/[Cu2+]



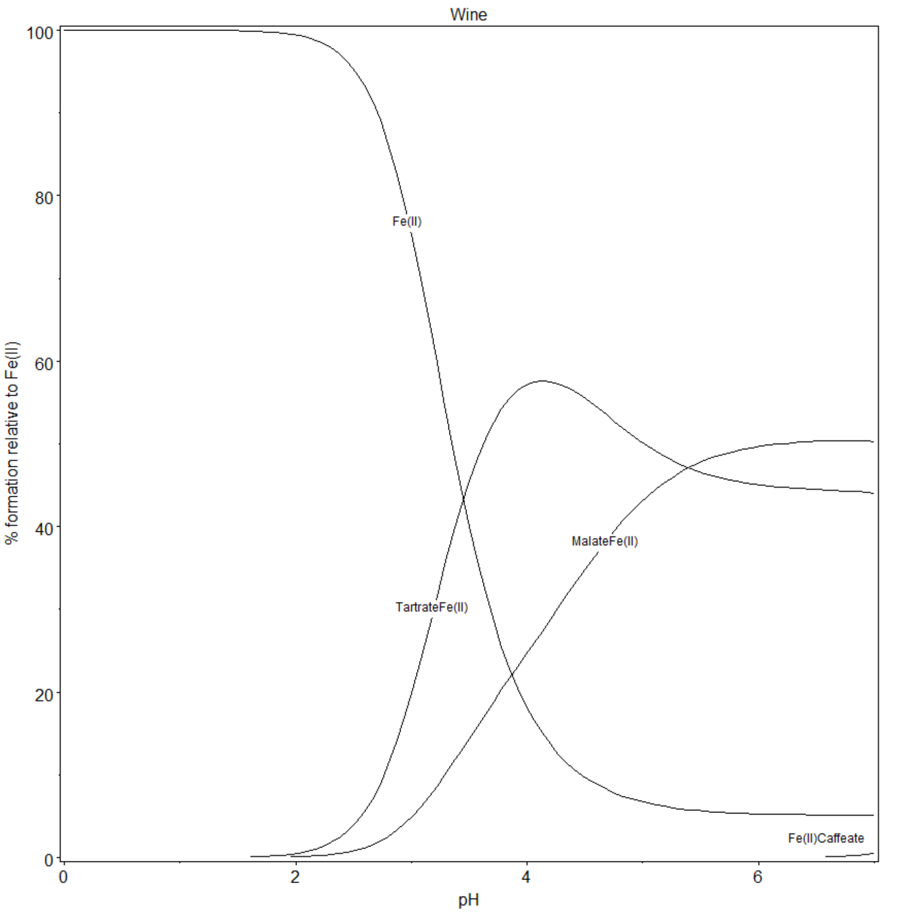
Oxidized Fraction vs Redox Potential at pH=3.5
Fraction in Oxidized Form
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
-200
0
200
400
600
800
Redox Potential (mV)
[Fe++]/[Fe+++]
[Cu+]/[Cu++]
H2S/S
GSH/GSSG
Ethanol/Acetald
H2O2/O2
Ascorbic/DHA
SO3=/SO4=
Catechol/Quinone
Caffeic/Quinone

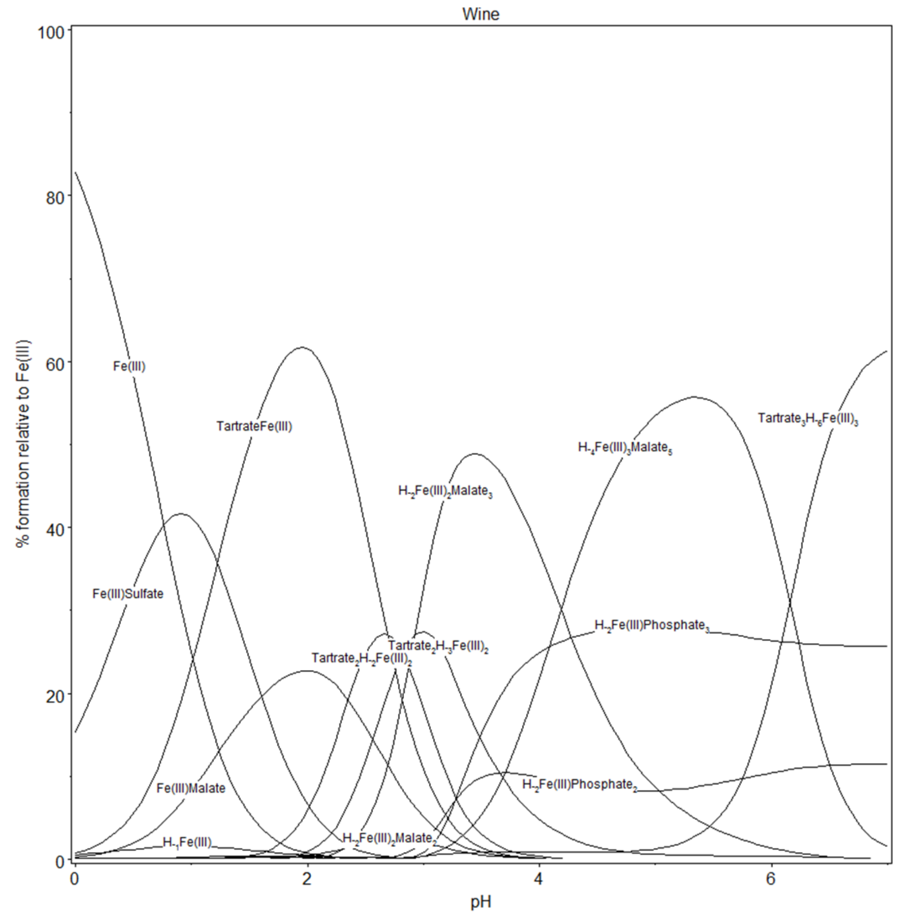


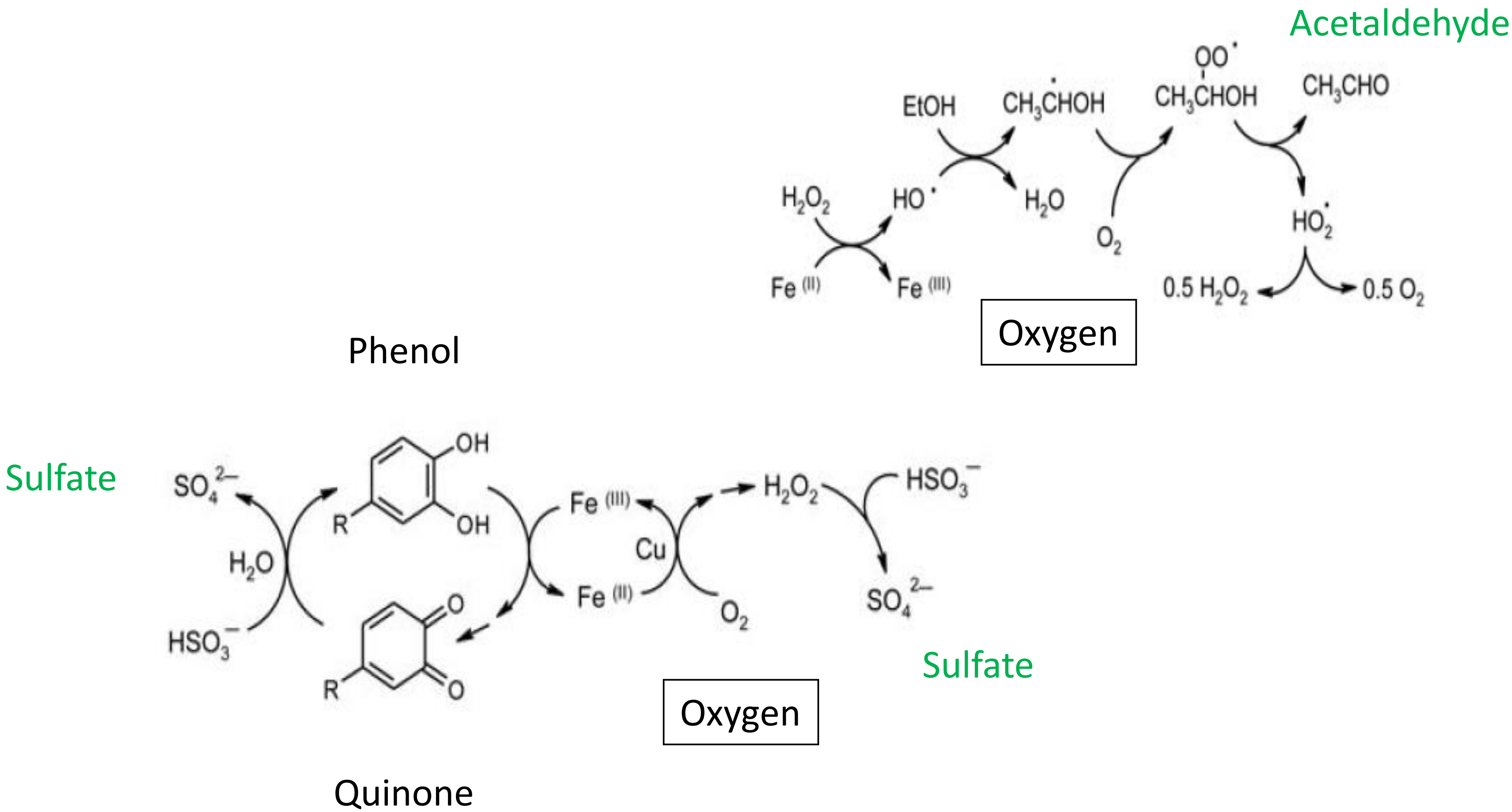


J. Agric. Food Chem. 2011, 59, 2564–2572

The Fe(II) and Fe(III) Complexes


Wine
100
80
60
40
20
0
% formation relative to Fe(II)
0
2
4
6
pH
Fe(II)
TartrateFe(II)
MalateFe(II)
Fe(II)Caffeate


Wine
100
80
60
40
20
0
% formation relative to Fe(III)
0
2
4
6
pH
Fe(III)
TartrateFe(III)
Fe(III)Sulfate
Fe(III)Malate
$H_{-1}Fe(III)$
$H_{-2}Fe(III)_2Malate_3$
$Tartrate_2H_{-2}Fe(III)_2$
$Tartrate_2H_{-3}Fe(III)_2$
$H_{-2}Fe(III)_2Malate_2$
$H_{-4}Fe(III)_3Malate_5$
$H_{-2}Fe(III)Phosphate_3$
$H_{-2}Fe(III)Phosphate_2$
$Tartrate_3H_{-6}Fe(III)_3$

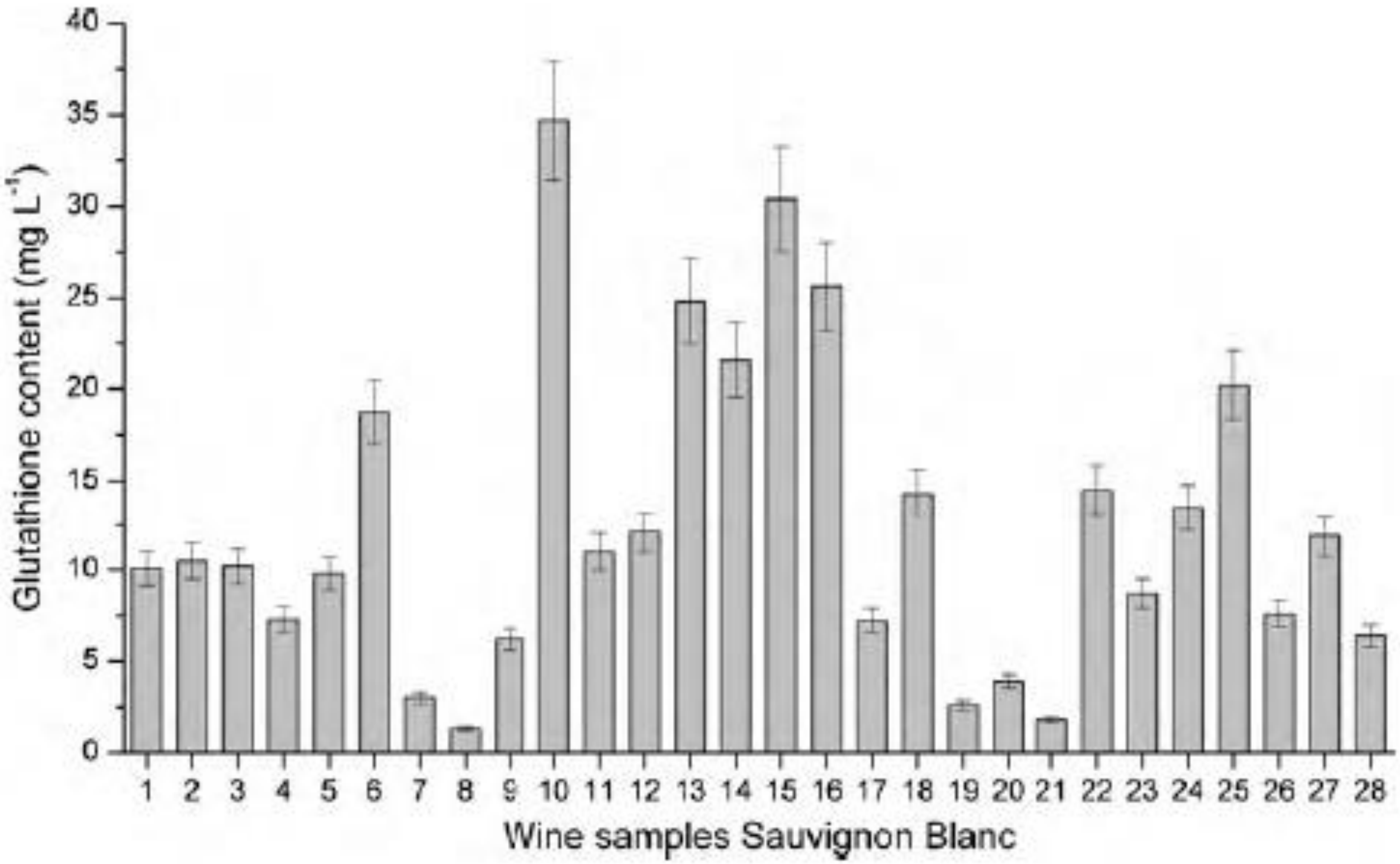


Danilewicz, J. C. (2011). Mechanism of autoxidation of polyphenols and participation of sulfite in wine: Key role of iron. Am. J. Enol. Vitic. 62:319-328.

“Antioxidant” Additions

Glutathione

Ascorbic Acid, Caffeic Acid



Analytica Chimica Acta 674 (2010) 239–242

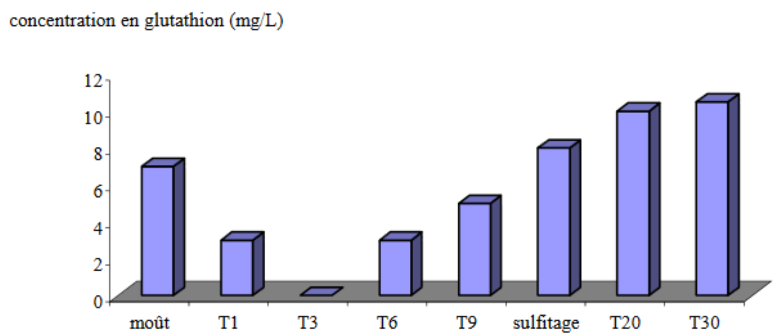


Figure 1: Evolution of the glutathione level in musts during fermentation

THE ROLE OF GLUTATHIONE ON THE AROMATIC EVOLUTION OF DRY WHITE WINE

Denis DUBOURDIEU* and Valérie LAVIGNE-CRUEGE**

VINIDEA.NET WINE INTERNET TECHNICAL JOURNAL, 02 2004, N°2 1-9

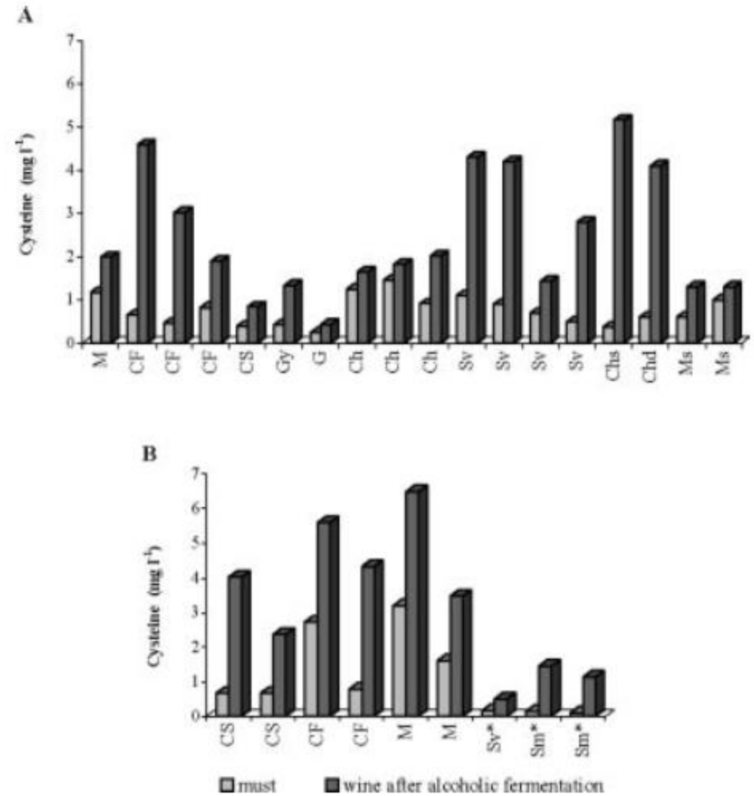


Figure 4. Influence of grape variety and alcoholic fermentation on cysteine levels (1999 vintage, *2000 vintage): A, Loire region; B, Bordeaux region. White grape varieties: Ch, Chenin; Chd, Chardonnay; Chs, Chasselas; Ms, Muscadet (Melon); Sv, Sauvignon; Sm, Sémillon. Red grape varieties: CF, Cabernet Franc; CS, Cabernet Sauvignon; Gy, Gamay; G, Grolleau; M, Merlot.

J Sci Food Agric 81:731–738 (online: 2001)

	Wine	Wine with added glutathione (10mg/L)
OD 420	0, 203	0, 136

Table 8: Measurement of the yellow tint after 3 years in bottle.

It is clear that the addition of glutathione at bottling reduces significantly the yellowing of wine. These results confirm the capacity of glutathione to help inhibit the enzymatic and non enzymatic browning phenomena of fruit juices (Molnar- Perl and Freidman, 1990 ; Freidman, 1994, 1996).

In the presence of glutathione the fruity aroma of the young wine, assessed with the 3-MH measurement, is also better preserved (Table 9).

	Wine	Wine with added glutathione (10m/L)
3-MH (ng/L)	320	445

Table 9: Level of 3-mercapto-hexanol in wines after 3 years in bottle..

Redox Potential Changes with Light

Redox Change and Thiol Release

Champagne Example

Redox Potential changes with different wavelengths of light exposure

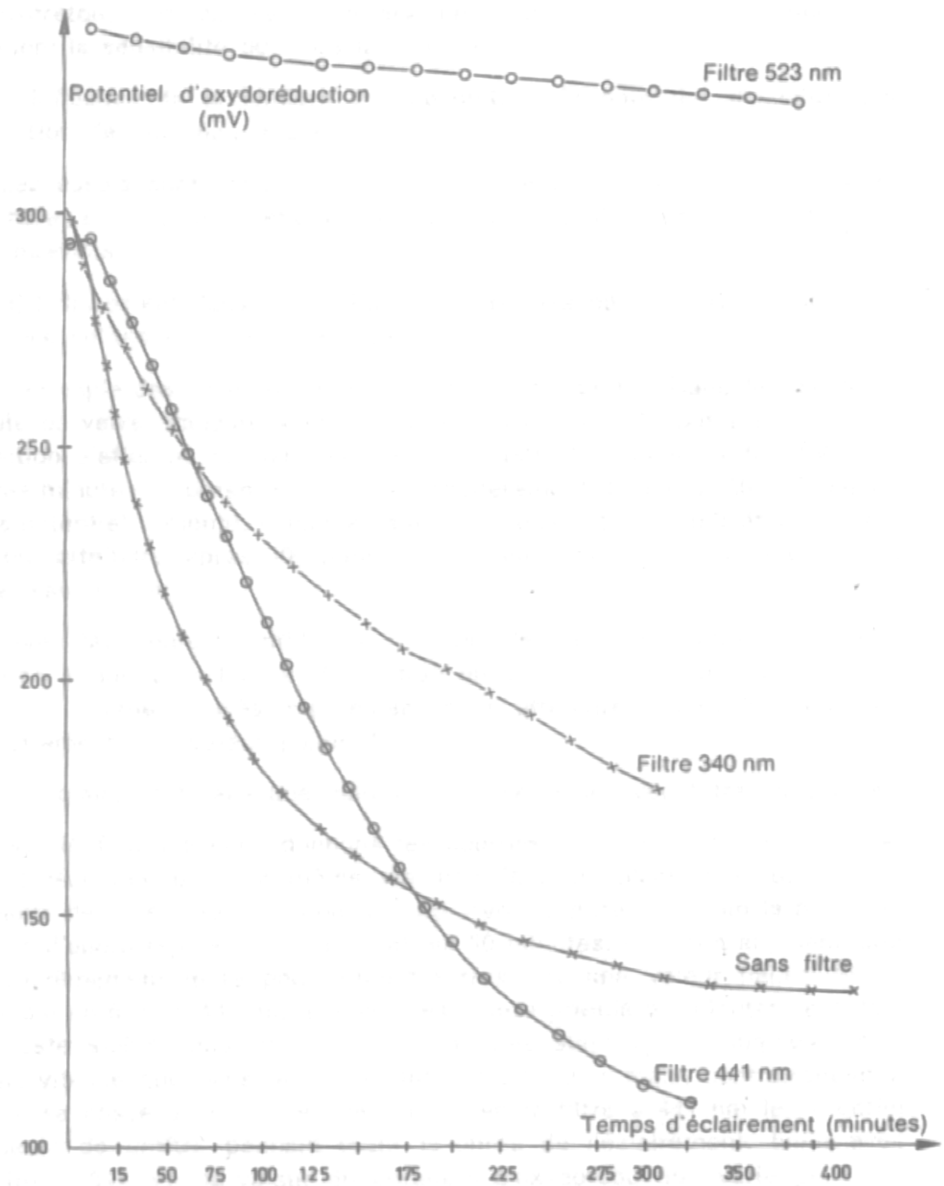


Fig. 3. — Evolution du potentiel d'oxydoréduction d'un vin dégorgé éclairé, à travers différents filtres, dans une cellule en verre banc.

Maujean, A., Haye, M. and Feuillat,M.

Conn. Vigne et Vin (1978) 12(4) 277-290.

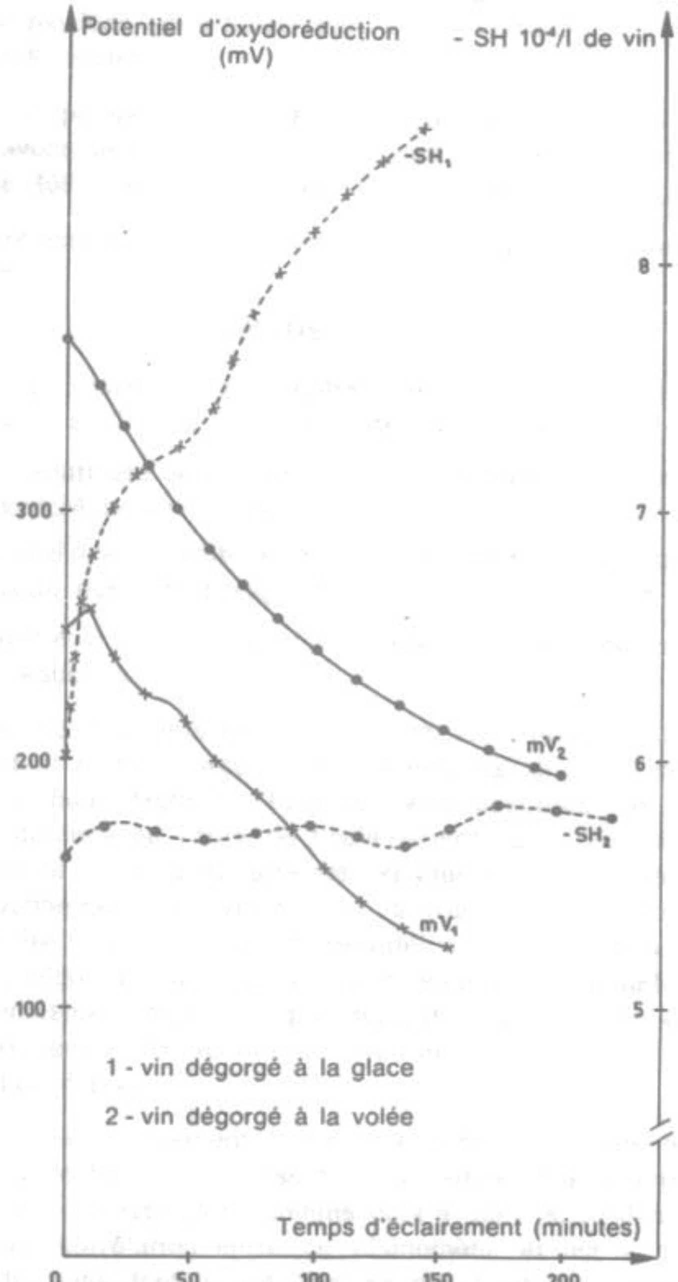


Fig. 6. — Evolution du potentiel d'oxydoréduction et du nombre de groupements SH d'un vin dégorgé à la glace et d'un vin dégorgé à la volée éclairés dans une cellule en verre standard « champenois ».

Redox Potential changes with different wavelengths of light exposure

Maujean, A., Haye, M. and Feuillat,M. Conn. Vigne et Vin (1978) 12(4) 277-290.

Acknowledgement

Organizing Committee of this Workshop

Stephen Sinclair Scott Endowment

University of California, Davis

My Students and Colleagues

Coming up: Nikolai St George