

Determination of Lead Concentrations in Wines of Different Origins in the Western Cape, South Africa, Produced between 1986 and 2013

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Abstract

South Africa is producing a substantial amount of wine to be consumed locally and abroad. However, lead content in wine is one of the main challenges that wine industries need to control in order to keep it under the recommended limit. Sixty one wine samples from different wine origins in the Western Cape with vintages from 1986 to 2013 were obtained and analysed. Only dry red wines were analysed since they can be stored and matured over a long period. The lead content in old wine from 1986 to 1999 ranged from 0,0394 to 1,22 mg/L with a mean value of 0,058 mg/L. The newer wines from 2000 to 2013 showed a comparatively lower lead content from 0 (< 0,008 mg/L detectable) to 0,033 mg/L with the median of 0,017 mg/L.

Keywords: South Africa; origins; dry red wine; lead; modifier

INTRODUCTION

Wine is one of the most widely and popularly consumed beverages in the world and has been around since the early periods of civilisation (Ajtony et al. **2008**). Recently, global world wine production and consumption has increased drastically (Insel **2014**). The evaluation of quality and food safety aspects of wine is of great importance to the producers and consumers of wine, and is also imperative for international trade in this commodity. Wine is regarded as a complex matrix that contains varying quantities of inorganic and organic compounds. Table 1 provides an illustration of some of the main compounds found in wine (Grindlay et al. **2011**).

Table 1. Main components found in wine

Wine composition	Classes	Chemical components	Concentration
Non-volatile organics	Volatile organics	Glycerol, butylethylglycol	8-19% (v/v)
	Non-volatile alcohols	Glucose, fructose, galactose, mannose	1-10 g/L
	Sugars	Tartaric, malic, citric, acetic	1-200 g/L
	Organic acids/salts	Aminoacids, polyphenols, flavonoids, etc	1-8 g/L
	Other substances	Cl ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ , SO ₃ ²⁻	<1 g/L
		Na, Mg, K, Ca	>10 mg/L
		B, Al, Mn, Fe, Cu, Zn, Sr, Rb	>10 mg/L
			0,1 mg/L

Over the years, studies have shown that a moderate consumption of wine, especially red wine, improves health and longevity when it is combined with a balanced diet and that it is known to reduce the effects of coronary diseases (Guilford & Pezzuto **2011**). Wine, being a natural product, is known to contain a wide range of heavy metals, most of which is the result of root uptake from the soil (Nour et al. **2009**). The soil composition of the vineyards contributes to the uptake of heavy metals through the grapevine roots and grapes provide a larger part of the ions present in the wine

(Pessanha et al. **2010**).

To regulate the metal content in wine, South Africa has set the limit of some metals in wine as shown in Table 2 (Tariba et al. **2011**). The use of pesticides, fertilisers and fungicides containing heavy metals in the vineyards during the growth of the grapes increase the concentration of metals in the soil. Metals are accumulative and eventually lead to contamination in the grape fruit during uptake (Fiket et al. **2011**). During the wine-making process, wine is exposed to long contact with the materials such as brass, aluminum, glass, stainless steel and wood from which wine-making machinery, pipes, casks and barrels used for handling and storing wine are made (Wani et al. **2015**).

Table 2. The recommended limits of concentrations of some heavy metals in wine in South Africa.

Name of substance	Maximum extent to which substance may be contained (mg/L)
Arsenic	0.2
Cadmium	0.01
Copper	1.0
Iron	10.0
Lead	0.2 (in wine produced after 31 December 1997)
Mercury	0.05
Zinc	5.0

Lead contamination in wine existed even in ancient times. Historical records indicate that the earliest winemaking in Mesopotamia and Caucasus was in 6000 BC. This led to the spread of cultivation of vineyards in the regions surrounding the Mediterranean Sea by the Romans (De Villiers et al. **2012**). The Romans at the time realised that the presence of lead in wines prevented it from turning sour and also made it taste sweeter (Robinson **1999**). This food sweetener was added to wine in the form of lead (II) acetate (Wani et al. **2015**). However, this caused lead poisoning and was believed to have been the primary reason for the collapse of the Roman Empire.

Prolonged storage of wine in lead crystal decanters and the use of tin-lead capsules to cover the bottle lead to a slow seepage of lead metal into wine (Jackson **2000**).

Exposure to trace levels of heavy metals in wine is a potential threat to the health of consumers (Ajtony et al. **2008**; Jackson **2000**). Lead can remain passive in the human body and accumulate over a number of years and is known to have adverse effects on

the male reproductive system (Telisman et al. **2000**). A study showed that lead (Pb) exposure to children under the age of 7 years had an effect on their intellectual development (Wasserman et al. **1997**).

The present study aimed to determine the levels of Pb in different brands of wines in South Africa from 1980s to 2013 using graphite furnace atomic absorption. Phosphoric acid and EDTA modifiers were also assessed in order to select the most efficient for the determination of lead from South African wine.

MATERIALS AND METHODS

Equipment

Analysis of lead was carried out with a Thermo Scientific CE 3000 series atomic absorption spectrometer equipped with a GFS Graphite furnace and GFS autosampler. The background correction was performed using a continuous deuterium source and for atomisers, pyrolytically coated graphite tubes with integrated L'vov platform were used. Lead determinations were performed at 283,3 nm with a 0,5 nm bandpass. All the samples were injected automatically by a GFS autosampler. Argon gas of purity 99,99% was used to purge the graphite tubes with a flow rate of 0,2 L/min. The samples were atomised for lead determinations using the graphite heating programme as illustrated in Table 3.

Table 3. Graphite furnace heating programme for the determination of lead in wine.

Phase	Temperature (°C)	Time (sec)	Ramp (°C/sec)	Gas type	Gas flow (L/min)
Drying	120	20,0	20	2	0,2
Ashing	800	30,0	200	2	0,2
Ashing	800	1,0	0	2	Off
Atomization	1500	2,5	0	2	Off
Cleaning	2500	1,0	0	2	0,2

Reagents and standard preparation

All the solutions and standards were prepared with deionised water of resistivity of 18 hM (Millipore) obtained by filtering water through a Milli-Q purification system before use. The concentration of 0.5% v/v nitric acid solution was prepared by transferring 25 mL of concentrated nitric acid (Merck) to a 5 L volumetric flask and made to the mark with de-ionized water. To prepare the 2% phosphoric acid, 2 mL of concentrated

phosphoric acid (Merck) was transferred into a 100 mL volumetric flask, and diluted to the mark with 0.5% v/v nitric acid solution. A commercially available 1000mg/L lead standard solution (Fluka, Sigma Aldrich) was used to prepare a working standard solution of 100 mg/L. Standard solutions ranging from 0 µg/L (blank) to 50 µg/L were prepared from the working standard by adding the appropriate amount and making to the mark with the mixture of 0.5% nitric acid and deionised water.

Wine Samples

Sixty one wine samples from different wine origins in the Western Cape with vintages from 1986 to 2013 were obtained and analysed. Only dry red wines were analysed since they can be stored and matured over a long period.

Sample preparation

Before the analysis was done, vintage samples were diluted to 10X with 0.5% nitric acid and 0.9 µL of sample was mixed with 0.1 µL of 2% phosphoric acid (chemical modifier). In order to eliminate the loss of volatile compound formation, chemical modifiers are used (Ajtony et al. **2008**; Kim **2004**). These chemical modifiers react with the sample to form stable compound of higher ashing temperature. Several modifiers such as EDTA, phosphoric acid, sucrose, ammonium phosphate salts, ascorbic acid and tartaric acid can be used for Pb analysis. In the present study, EDTA and phosphoric acid were compared and the atomisation parameters are shown in Table 4. A sample of 1 µL was transferred into a sample cup and analysed on the Graphite furnace. Three replicate measurements were performed for each sample, blank and standards.

RESULTS AND DISCUSSION

Method validation

Efficiency of modifiers

A dry red wine sample was diluted (1:1) with 50 ppm standards. The sample was analysed without modifier (water), with EDTA modifier and phosphoric acid modifiers and temperature for the ashing and atomisation phase were recorded. The results for determination of efficient modifier are indicate in Figure 1. It was shown that in the sample with no modifier (water) and with EDTA as modifier, Pb was stable up to 500 °C; whilst the sample with phosphoric acid was stable up to 900 °C ashing temperature. During the atomization phase at temperature 1500 °C, the phosphoric acid modifier obtained the best sensitivity while the sample without modifier obtained the optimum at 1400 °C and the EDTA modifier obtained optimum sensitivity at 1300 °C (Tariba et

al. 2011; Ajtony et al. 2008). Based on these results, phosphoric acid was used as the modifier for the determination of Pb in wines with ashing temperature of 900 °C and atomisation temperature of 1500 °C.

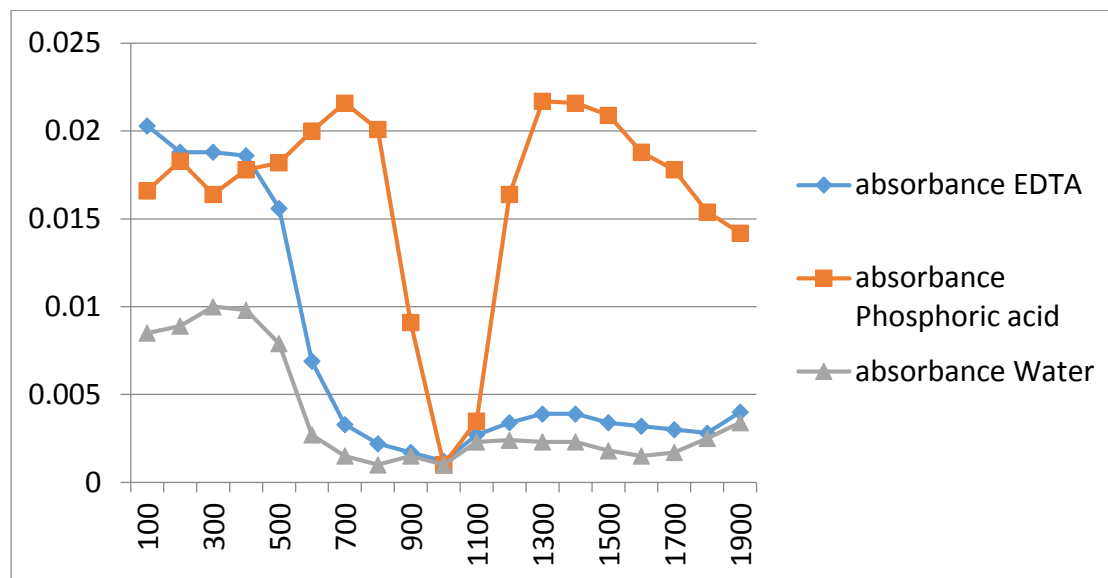


Figure 1: Ashing and atomisation graph for phosphoric acid and EDTA modifiers.

Analysis of wine samples

The concentration of Pb in wine samples of the older vintage (1986 to 1999) ranged from 0,0394 to 1,22 mg/L with a mean value of 0,058 mg/L (Table 5).

Table 4. Pb concentration of older wines.

Vintage	Origin	Cultivar	Producer	Pb capsule	Cork intacted	Pb concentration mg/L	Absorpti on
1986	Coastal region	Cabernet sauvignon	Kwv	yes	no	0,05844	0,0346
1987	Estate wine	Paul sauer	Kanonkop	yes	yes	0,06412	0,0426
1987	Constantia	Cabernet sauvignon	Klein constantia	yes	no	0,08582	0,0128
1987	Stellenbosch	Shiraz	Rust en vrede	yes	no	58,5440	0,0396
1987	Overgaauw	Tria corda	Overgaauw	yes	no	0,1496	0,0165
1987	Coastal region	Pinotage	Fleur du cap	yes	yes	0,06754	0,0119
1987	Stellenbosch	Cabernet sauvignon	Alphen	yes	no	0,05683	0,0113
1987	Stellenbosch	Shiraz	Spier	yes	no	0,07266	0,0122

1988	Coastal region	Baronne	Nederburg	yes	no	0,1056	0,0143
1988	Stellenbosch	Rustenburg	Rustenburg	yes	no	305,5519	0,0717
1988	Franschhoek	Shiraz	La maison du roi	yes	no	0,5921	0,0443
1988	Stellenbosch	Cabernet sauvignon	Alphen	yes	no	21,5484	0,0186
1989	Paarl	Cabernet sauvignon	Nederburg	yes	no	0,06213	0,0114
1989	Stellenbosch	Cabernet sauvignon	Zonnebloem	yes	no	0,1158	0,0152
1989	Constantia	Pinotage	Groot contantia	yes	yes	0,06934	0,0123
1989	Stellenbosch	Shiraz	Nassau	yes	no	0,04345	0,0106
1989	Paarl	Cabernet sauvignon	Fairview estate	yes	no	0,04184	0,0105
1990	Paarl	Cabernet sauvignon	Villiera estate wine	yes	yes	0,1057	0,0147
1990	Coastal region	Cabernet sauvignon	Kwv	no (plastic)	yes	0,09589	0,0141
1990	Paarl	Shiraz	Fairview estate	yes	yes	0,03924	0,0106
1992	Stellenbosch	Pinotage	Kanonkop	no (Tin imitation)	no	0,04521	0,0111
1999	Stellenbosch	Pinotage	Nietvoorbij	no (plastic)	yes	0,05298	0,0116

Out of the 22 samples analysed only 9% were found to be higher than the recommended limit of (0, 30 mg/L) (pre 1994) (Table 4). This was an indication that at least 91% of the sampled wine industry in South Africa complied with the regulatory authority on lead content in wines

Table 5. South African regulation on Pb limit levels in wines.

Regulations Pb limits	Concentration (mg/L)
pre 1994	0,3
1994 - 1997	0,25
1997 – to date	0,2

Table. 5 summarises the results of concentration of lead in the newer vintages. The concentration range of lead in wines was significantly reduced in the newer vintage. The concentration of lead in wines ranged from 0 (< 0,008 mg/L detectable) to 0,033

mg/L with the median of 0,017 mg/L when compared with the older wine. The significant reduction of lead content from older wines to newer wines could be attributed to better storage methods such as the use of stainless steel containers instead of concrete containers (Stockley et al. 2003).

Table 6. Pb concentration of newer wines

Origin	Cultivar	Type	Producer	Vintage	Lead concentration mg/L
Paarl	Shiraz	Dry red	Ayama	2000	0,013
Stellenbosch	Cabernet sauvignon	Dry red	Distell	2000	0,019
Simonvlei	Pinotage	Dry red	Simonvlei	2001	0,027
Stellenbosch	Pinotgris	Dry red	The Vineyards	2001	0,035
Stellenbosch	Shiraz	Dry red	Amani Vineyards	2002	0,019
Stellenbosch	Shiraz	Dry red	Asara	2002	0,033
Stellenbosch	Pinotage	Dry red	Spier	2003	0,018
Stellenbosch	Cabernet sauvignon	Dry red	Delheim	2003	0,024
Stellenbosch	Cabernet sauvignon	Dry red	Van Loveren	2004	0,015
Wellington	Pinot noir	Dry red	Bosman	2004	0,015
Clan williams	Shiraz	Dry red	Cederberg Cellars	2004	0,027
Robertsons	Merlot	Dry red	Robertson winery	2005	0,014
Stellenbosch	Shiraz	Dry red	Vergelegen	2005	0,018
Paarl	Merlot	Dry red	Boland Winery	2005	0,033
Paarl	Shiraz	Dry red	DGB	2005	0,035
Wellington	Cabernet sauvignon	Dry red	Napier	2006	0,014
Stellenbosch	Shiraz	Dry red	Lanzerac	2006	0,018
Wellington	Cabernet sauvignon	Dry red	L'ormarins	2006	0,023
Stellenbosch	Pinotage	Dry red	Distell	2006	0,024
Mulmesburry	Shiraz	Dry red	Swartland winery	2006	0,03
Walker bay	Pinot noir	Dry red	Walker Bay	2007	ND
Stellenbosch	Pinotage	Dry red	Distell	2007	0,012

Wellington	Cabernet sauvignon	Dry red	Napier	2007	0,019
Robertsons	Pinot noir	Dry red	Rooiberg Winery	2007	0,021
Stellenbosch	Shiraz	Dry red	Spier	2008	0,013
Stellenbosch	Cabernet sauvignon	Dry red	Amarez	2008	0,021
Tulbagh	Shiraz	Dry red	Saronsberg	2008	0,024
Stellenbosch	Shiraz	Dry red	Amarez	2008	0,025
Stellenbosch	Pinotage	Dry red	Distell	2009	ND
Stellenbosch	Cabernet sauvignon	Dry red	Amika	2009	0,019
Stellenbosch	Cabernet sauvignon	Dry red	Lanzerac	2009	0,024
Wellington	Shiraz	Dry red	Eastern produce cape	2010	ND
Coastal region	Merlot	Dry red	Graham Beck	2010	0,022
Swartland	Pinotage	Dry red	Painted Wolf	2010	0,023
Stellenbosch	Merlot	Dry red	Zonnebloem	2011	ND
Coastal region	Cabernet sauvignon	Dry red	Guardian Peak	2011	0,019
Stellenbosch	Cabernet sauvignon	Dry red	Distell	2011	0,02
Wellington	Pinot noir	Dry red	Doolhos wine estate	2012	ND
Stellenbosch	Pinotage	Dry red	Distell	2012	ND
Swartland	Shiraz	Dry red	Babylon's Peak	2012	0,013
Tulbagh	Shiraz	Dry red	Saronsberg	2012	0,016
Stellenbosch	Pinotage	Dry red	Distell	2013	ND

ND - not detected

CONCLUSION

Sixty one samples of both old (1986-1990) and new (2000- 2013) red wines from different region of South Africa were analysed for lead content. The results showed that only 9% of the sampled older wines had a lead content higher than the recommended limit, and 91% of wine samples contained lead content which was within the limit. The lead content in older wine from 1986 to 1990 ranged from 0,0394 to 1,22 mg/L with a mean value of 0,058 mg/L. The newer wines showed a comparatively lower lead content from 0 (< 0,008 mg/L detectable) to 0,033 mg/L with the median of 0,017 mg/L.

The determination of lead was performed after assessing the efficiency of the phosphoric acid and EDTA, for which phosphoric acid was found to have been effective.

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