Undesirable and Harmful Metals in Wines—Determination and Removal

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ABSTRACT

A method is described for the lowering or removal of the metal content of wines. For this purpose, a chelating material is employed, formed from cellulose functionalized with iminodiacetic acid. Its use allows, first, a preconcentration of metals present at trace levels and, secondly, a lowering or removal of undesirable metals. Possible matrix effects, both by organic and inorganic components, have been considered and allowed for in the analytical determination.

INTRODUCTION

In trace metal analysis, efforts are generally devoted to increasing sensitive methods.

In recent years, techniques which employ chelating materials have found extensive and useful applications.

These methods generally pursue the goal of obtaining a preconcentration of the metals of interest. In this paper the use of chelating material previously investigated and characterized in our laboratory is described. The chelating unit is iminodiacetic acid, chemically bound to cellulose filters. The use of this material, which has shown good affinity and high capacity towards a large series of metal cations (Gennaro *et al.*, 1983), achieves two purposes. First, it allows preconcentration of trace metals present in a liquid sample, thus increasing sensitivity, as well as

characterisation and reduction of any matrix interference from both inorganic and organic components. Secondly, it allows the lowering or removal of undesirable metal contents in the treated samples.

The present paper deals with both purposes of trace metals determination and metal removal in oenology. This is important because the complex composition of wines affects the determination of metals and because of the need to lower the concentration of metals in view of their potential toxicity and their effects in reducing the physical stability of wines (precipitations).

Ca(II), Fe(II), Fe(III), Cu(II), Zn(II) and Pb(II) may be present in wines. They arise naturally from, grapes, as well as from unsuitable containers or conditions used in the steps of vinification and storage. Acid components present in wines, such as SO_2 and CO_2, may induce solubilization of metals from the containers; so, for example, Ca(II) and Fe(II) can pass into wines from cement tanks. Also, redox reactions can occur in wines with the formation of metal ions from metal; oxygen may be absorbed in the vinification steps. The metals which cause the greatest troubles if present in wines are Pb(II), Zn(II), Cu(II) and Fe(II). Pb(II) contamination may derive from ecological pollution, such as from car exhausts, as well as from the use, in the wine production processes, of unsuitable apparatus. Bronze equipment, for example, or lead paints, may pollute musts and wines. Because of its well known toxicity effect, the maximum Pb(II) content allowed in wines according to European legislation is, for example, $0.20\,mg\,litre^{-1}$ for Great Britain, or $0.30\,mg\,litre^{-1}$ for Italy, France and the Federal Republic of Germany.

The Zn(II) toxicity is lower; however, an ingestion over about 60 mg a day may induce gastric troubles; moreover, its presence at high levels affects the organoleptic properties of wine.

Cu(II) becomes toxic in amounts higher than 2–3 mg a day. Musts generally contain Cu(II) (1–4 ppm) due to pesticidal treatments. During the production processes, Cu(II) content may vary; it may be lowered due to the formation of insoluble precipitates (sulphides, hydroxocomplexes, tartrates ..), or it may increase, due to corrosion processes from the equipment.

Iron in wines is generally present in amounts up to $12\,mg\,litre^{-1}$, both as Fe(II) and Fe(III). Soluble complex species formed with wine organic acids, such as malic and tartaric may give rise, during the vinification processes, to insoluble precipitates (as phosphates) or colloidal forms which flocculate and give to the commercial product an undesirable turbid aspect. The presence of iron in wines is admitted; iron, in fact, is

not a toxic metal and, furthermore, it seems to be important in the development of red wine bright colour, during wine ageing.

Na(I), K(I), Ca(II) and Mg(II) are generally contained in wines in relevant amounts; their presence does not create toxicological problems but organoleptic ones in the commercial product. So, for example, Ca(II) may form insoluble precipitates, such as tartrates, whose precipitation rate is very slow. The high times and the low temperatures required in order to reach complete precipitation before the last filtration prior to marketing make the treatment very expensive.

In order to overcome the different problems caused by metals in wines, many techniques are generally employed in oenology. Vinification processes employ the addition of sodium potassium tartrates in order to favour the formation of soluble tartrate complexes of iron and copper, so preventing the formation of insoluble ferric phosphates and copper sulphides. The addition of tartrate ions may cause, as a collateral effect, the precipitation of Ca(II) and hydrogen potassium tartrates. In order to make the precipitation times shorter, sometimes flocculants are added. The use of Al(III) salts is reported, but the high toxicity of Al(III) has been recently documented (Berlin & Bennett, 1984).

A treatment very largely used in oenology is the addition of ferrocyanide, for the purpose of eliminating, as insoluble salts, Fe(III), Cu(II), Zn(II) and, in particular, the most toxic, Pb(II). Ferrocyanide must be added under very strict control: an excess must be avoided, taking into account that most wines show pH values around 3. Therefore, the precipitation of Pb(II), also taking into account the conditional solubility product value, is far from being quantitative.

We think that most of these operations, which all show collateral negative effects, might be replaced by the use of cellulose functionalized with iminodiacetic (IDA) groups. We propose, therefore, to perform an accurate measurement of all the metals contained in wine, to pass it through the functionalized material and to evaluate the fraction of retained metal. In order to perform an accurate metal measurement, all the possible matrix effects, both by organic and inorganic components, have to be taken into account.

EXPERIMENTAL

Commercial Whatman No. 41 cellulose discs were used as substrate material. The chelating agent is represented by iminodiacetic groups

chemically bound on cellulose. The preparation is described in detail in a previous work (Gennaro *et al.*, 1983). It involves essentially the chlorination reaction of cellulose, using dimethylformamide as solvent, with $POCl_3$ and the subsequent replacement of the chlorine groups with iminodiacetic groups, by reaction (105–110 °C) in a saturated solution of disodium iminodiacetate, in dimethylformamide.

A Millipore filtration system was employed to support the functionalized filter.

Metal stock standard solutions (1000·00 mg litre^{-1}) C. Erba for atomic absorption were diluted as required.

All chemicals were analytical grade reagents.

Water was doubly distilled (DDW) in quartz. All laboratory glassware, polyethylene and polypropylene equipment, were thoroughly cleaned by soaking in 6M HNO_3 and repeatedly rinsing with DDW.

A DC-plasma emission Spectraspan IV (SMI, Andover, MA, USA) was used for the emission measurements. Two-point calibration (high and low standards) was performed. The most suitable wavelength was chosen for the measurement of each metal, even when in mixtures.

pH measurements were performed on an Orion 811 pH meter equipped with a combined glass-calomel electrode. Adjustable Eppendorf pipettes and Micrometric Instrument precision syringes were used for solution preparation.

Samples of wines that were not treated by any demetalizing procedure were supplied by 'Fratelli Savigliano' Winemakers (Diano d'Alba).

RESULTS AND DISCUSSION

When dealing with the determination of metal content in a real sample, all the possible matrix interferences in the measurement have to be taken into account. No instrumental technique which may be used (such as anodic stripping voltammetry or emission and absorption spectroscopies) can be considered free from interference effects. These can be caused both by organic and inorganic components.

When plasma spectroscopy is used, interference effects may arise during sample nebulization, thermal decomposition and atomization processes in the flame, due to variations produced by the physical properties of the sample solution or by changes in the excitation conditions in the plasma caused by the matrix elements. Many reports

deal with interference effects on plasma emission spectroscopy both from organic (Florence, 1982; Thompson *et al.*, 1982; Malamas *et al.*, 1984) and inorganic components (Larson *et al.*, 1975; Rippetoe *et al.*, 1975; Boumans, 1976; Felkel & Pardue, 1978; Eastwood *et al.*, 1980; Blades & Horlick, 1981; Camerlynck *et al.*, 1982; Sanz-Medel *et al.*, 1983).

In particular, as it concerns the inorganic interference, it was always observed that there was an enhancement effect on the metal signal due to easily ionizable element emission: the largest effect was noticed on the emission of transition elements with unfilled d-shells. All the suggested mechanisms which may contribute to the enhancement of emission, such as ionization and volatilization equilibria and viscosity effects (Eastwood *et al.*, 1980; Blades & Horlick, 1981) cannot be considered as mutually exclusive. They depend both on the spectral bandwidth of the spectrometer and on the spectral characteristics of the elements so that they cannot, in any case, be predicted or evaluated *a priori.*

In order to overcome interference effects, it is suggested (Eastwood *et al.*, 1980; Felkel & Pardue, 1978) that an 'ionic buffer', which consists in the addition of a relatively large concentration of an easily ionizable metal to the metal standards, be used for the calibration. This 'buffer' should permit a levelling of the matrix inorganic interference to be achieved.

Some experiments performed on mixtures of Pb(II) (1·00 ppm) and Na(I) (varying amounts) showed that only when the same amount of Na(I) as in the sample is added in the Pb(II) standards, does the measurement become accurate; the error is positive when Na(I) in the standard is less than in the sample and otherwise is negative for higher Na(I) concentrations. It may be concluded that it is not possible to identify a minimum concentration of the interfering metal that may act as an 'ionic buffer' when added to the metal standards.

A series of measurements performed by plasma emission spectroscopy on solutions of different compositions allowed some general conclusions which may be useful when metal measurement on a real matrix is required. First, the interference degree, when present, is a function, not only of the analytical concentration of the interfering substance, but also of the molar ratio existing between the interfering substance and the metal to be measured. Cd(II), Co(II), Cu(II), Hg(II), Ni(II), Pb(II), Zn(II), Al(III) and Fe(III) do not mutually interfere at all and they do not affect the measurement of easily ionizable metal ions. Alkali and alkaline-earth metals, on the contrary, all interfere in the measurement of other cations, but to different extents. So, while 1000 ppm of K(I) produces an error,

always less than 5 %, in the measurement of Cu(II), Pb(II), Al(III), Na(I), Ca(II), Mg(II), Zn(II) and Fe(III) (at 1·00 ppm, respectively), the presence of 1000 ppm of Ca(II) or Mg(II), under the same conditions, produces interference errors often greater than 100 %. Also, Ca(II) and Mg(II) mutually interfere.

Furthermore, the magnitude of the interference produced by the same amount of easily ionizable metal in the measurements of different metal ions is different, just as the effects caused by the various interfering metals on the same metal are different.

In the light of these observations, it can be concluded that nothing may be predicted or projected about the measurement of metals in a matrix which contains easily ionizable metals, without knowing its composition. This is surely the situation present in a wine. A preliminary measurement of all the metals present is therefore necessary in order to perform an accurate interference study on a model solution, prepared at a composition very similar to the sample.

It was previously shown (Gennaro *et al.*, 1985) that accurate and reproducible metal measurements are obtained only when the metal standard solutions, with which the calibration is performed, contain the same organic composition as the sample or if the standard addition method is employed. Owing to the very complex composition of wine, the standard addition technique was employed in order to obtain a preliminary measurement of the metal concentrations (in particular Ca(II), Mg(II), Na(I) and K(I)) in two different wine samples.

From these indications, free from organic interference errors but not from inorganic ones, a model solution containing Fe(III), 5·00 ppm; Pb(II), 1·00 ppm; Cu(II), 1·00 ppm; Al(III), 1·50 ppm; Zn(II), 2·00 ppm; Na(I), 40·00 ppm; Ca(II), 80·00 ppm and Mg(II), 120·00 ppm, was prepared. As previously shown, the presence of Ca(II) and Mg(II) has to be taken into account. For K(I) some measurements, performed using concentrations close to those evaluated in wines (about 500 ppm), showed that it does not suffer from detectable interference, either active or passive. For Na(I) interference, measurements of all the other metals performed in the presence of up to 50 ppm of Na(I), showed an error of less than 2 %. Multi-element standards were prepared in the absence and in the presence of Ca(II) (120·00 ppm) and Mg(II) (80·00 ppm). The 'model' solution prepared was measured, for comparison, with two types of standard. The data obtained showed that the presence of Ca(II) and Mg(II) seriously affects measurements (an error about + 100 % is evident for Pb(II), and

about $+60\%$ for Al(III)), whilst their addition to the standard solutions reduces all the errors to levels (about 1%) acceptable for the purpose.

On the basis of the results obtained on the 'model' solutions, the measurements can now be performed on wine samples. As an example, Table 1 lists the results obtained for a red wine sample. The standard addition method was employed and the calibration standard solutions contained the same amounts of Ca(II) and Mg(II) as previously found.

TABLE 1

Metal Contents of a Red Wine, Before and After Metal Uptake with one IDA Filter

Cation	Metal present in wine (ppm)	Metal after filter uptake (ppm)	Metal recovered from filter (ppm)
Fe(III)	6.03 ± 0.02	5.12 ± 0.02	0.89 ± 0.01
Pb(II)	0.60 ± 0.01	0.10 ± 0.01	0.49 ± 0.01
Al(III)	1.19 ± 0.01	0.84 ± 0.01	0.34 ± 0.01
Zn(II)	1.67 ± 0.01	0.87 ± 0.01	0.82 ± 0.01
Cu(II)	0.74 ± 0.01	0.16 ± 0.01	0.59 ± 0.01
Na(I)	39.7 ± 0.05	40.0 ± 0.04	—
Ca(II)	90.3 ± 0.06	87.9 ± 0.05	2.71 ± 0.02
Mg(II)	124 ± 0.05	121 ± 0.05	2.94 ± 0.01

The IDA filter seems to be very useful in removing undesired metals from wines. Table 2 lists the capacities of the filter towards different cations. Some experiments were performed in order to evaluate the competition that can take place in a mixture of different metal cations when their total content is close to, or greater than, the filter capacity. As expected there was a greater affinity of the filter towards metal cations which show, with IDA in solution, a greater conditional formation constant, the alkali and alkali-earth metals being less easily fixed on the filter.

This behaviour does not affect possible application to wine demetalization; in fact, the complete removal of these cations is not required. Whilst lowering of K(I) and Mg(II) is irrelevant, a partial retainment of Ca(II) on the filter may be advantageous; a lower concentration in wine reduces the formation of insoluble precipitates. In contrast, the complete elimination of Cu(II), Pb(II) and Co(II) is required. The total metal content of the wines considered (Tables 1 and 3)

TABLE 2
Capacity Values, Expressed as μmoles of each Metal, Taken up
by 1 g of Fixing Material

| Cation | Capacity (μmol g^{-1}) | |
	IDA filter[a]	IDA cotton
Fe(III)	109	
Pb(II)	218	
Hg(II)	88	
Zn(II)	157	
Cu(II)	202	
Na(I)	111	
Ca(II)	105	2519
Mg(II)	182	
Cd(II)	171	
Co(II)	171	
Ni(II)	184	

[a] One filter = 0·165 g.

would demand greater than average capacity of one IDA filter. It is
therefore to be expected that most of the Ca(II), Mg(II), Na(I) and K(I),
since they are less easily retained and present in greater concentrations,
passes nearly wholly into the filtered solution. Therefore, only the metal
standards for the measurements of the filtered solutions were corrected
for Ca(II) and Mg(II).

The fixation of the metals on IDA filters proceeds predominantly by a
chelation mechanism. It is necessary, on the basis of this consideration, to
take into account the possibility that organic components may form
complex metal species in wine stronger than the corresponding species
with IDA; this situation would make impossible the retainment on the
filter.

The results obtained on filtered and eluted fractions showed
comparable metal contents between filtered and eluted solutions both in
wines and in the model solution (Tables 1, 3 and 4). The expected poor
retention of Ca(II) and Mg(II) was confirmed. Moreover, filtration
through one filter alone, due to its insufficient capacity, permitted only a
lowering of the metal content. In order to gain a complete removal of the
metals of interest, taking into account (Table 2) capacity values, as well as
total metal concentration, eight filters were placed in the Millipore
filtration system. A hundred millilitres of the model solution or the white
wine were used and the elution performed with 20 ml of 1·0N HCl. The

TABLE 3

Metal Contents of a White Wine, Before and After Metal Uptake with Eight IDA Filters in H^+ or in K^+ Form

Cation	Metal present in wine (ppm)	Metal after H filters uptake (ppm)	Metal recovered from H filters (ppm)	Metal after K filters uptake (ppm)	Metal recovered from K filters (ppm)
Fe(III)	9·34 ± 0·02	0·98 ± 0·01	8·23 ± 0·01	1·20 ± 0·01	8·10 ± 0·02
Pb(II)	0·82 ± 0·01	nd	0·83 ± 0·01	nd	0·82 ± 0·01
Al(III)	1·37 ± 0·01	0·12 ± 0·01	1·23 ± 0·01	0·13 ± 0·01	1·22 ± 0·01
Zn(II)	1·61 ± 0·01	0·19 ± 0·01	1·43 ± 0·01	0·20 ± 0·01	1·43 ± 0·01
Cu(II)	1·19 ± 0·01	nd	1·18 ± 0·01	nd	1·20 ± 0·01
Na(I)	28·7 ± 0·03	6·40 ± 0·02	22·9 ± 0·02	25·7 ± 0·02	3·12 ± 0·02
Ca(II)	96·0 ± 0·06	18·8 ± 0·03	76·7 ± 0·03	28·4 ± 0·03	67·4 ± 0·02
Mg(II)	299 ± 0·06	49·8 ± 0·02	249 ± 0·04	62·2 ± 0·04	236 ± 0·05
K(I)	515 ± 0·08	221 ± 0·03	293 ± 0·04	458 ± 0·05	58·8 ± 0·04

nd, not detected.

metal standard solutions were prepared after previous measurements of Ca(II) and Mg(II), both in filtered and eluted solutions. In Tables 3 and 4 all the data concerning the metals in the model solution and in the wine are listed. The data show that the complete removal of metals of interest is achieved with the use of eight filters.

It is worthy of note that the proposed method can be useful also for preconcentration purposes, when the concentration of a toxic metal in a wine is close to, or below, the instrumental sensitivity.

Certainly, before the method proposed for removing metals from wines may find practical applications, it is necessary to accurately evaluate whether it brings disadvantages or introduces any variation in typical wine properties. Aroma and taste do not appear different at all after the treatment. The brightness certainly improves.

In order to avoid pH variations during the demetalization of a wine sample, the following procedure is suggested.

The IDA filters are previously converted into the K^+ form by flowing through 100 ml of a solution of K^+ (1000 ppm, pH = 7·0). After repeated washings with DDW, the filter is ready to be used. The flowing of 100 ml of white wine through the K-IDA filter shows the same behaviour (see Table 3) as the starting IDA filters, for Cu(II), Pb(II), Zn(II) and Al(III) and a lower retention of Fe(III), Mg(II), Ca(II) and Na(I). In contrast, the use of IDA filters causes a significant lowering of pH: 100 ml

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TABLE 4

Measurement of Metals in a Multi-component Standard Wine Model Solution, Before and After Metal Uptake with one IDA Filter, Eight IDA Filters and IDA Cotton (3 g for 100 ml of Solution)

Cation	Metal added (ppm)	One IDA filter		Eight IDA filters		IDA cotton	
		Metal after uptake (ppm)	Metal recovered (ppm)	Metal after uptake (ppm)	Metal recovered (ppm)	Metal after uptake (ppm)	Metal recovered (ppm)
Fe(III)	5·00	4·22 ± 0·02	0·79 ± 0·01	nd	4·97 ± 0·02	nd	4·93 ± 0·01
Pb(II)	1·00	0·13 ± 0·01	0·87 ± 0·01	nd	0·99 ± 0·01	nd	0·97 ± 0·01
Al(III)	1·50	1·02 ± 0·01	0·47 ± 0·01	0·17 ± 0·01	1·35 ± 0·01	nd	1·47 ± 0·01
Zn(II)	2·00	0·98 ± 0·01	1·00 ± 0·01	0·12 ± 0·01	1·91 ± 0·01	0·10 ± 0·02	1·88 ± 0·01
Cu(II)	1·00	0·21 ± 0·01	0·78 ± 0·01	nd	0·97 ± 0·01	nd	0·98 ± 0·01
Na(I)	40·0	40·0 ± 0·05	nd	7·80 ± 0·02	32·8 ± 0·02	2·76 ± 0·02	37·7 ± 0·02
Ca(II)	80·0	77·7 ± 0·06	2·36 ± 0·02	16·7 ± 0·02	63·7 ± 0·04	nd	80·2 ± 0·03
Mg(II)	120	117 ± 0·05	2·88 ± 0·03	20·1 ± 0·03	100 ± 0·05	1·88 ± 0·01	119 ± 0·05

nd, not detected.

of the same wine, after treatment with H–IDA filters, showed, after metal uptake, a pH decrease from 3·14 to 2·87. This variation is due to the fact that, around pH 3, the IDA units are partially protonated and a proton transfer to the sample occurs upon metal uptake. Such pH decrease could be buffered with addition of $NaHCO_3$ (this is an allowed treatment) but the use of the filters in the K^+ form is simpler and does not need successive neutralization treatments.

The K(I) concentration obviously increased in the filtered wine; this must be due to the lower K(I) retention on the filter, as well as the displacement of K^+ ions by chelation. In any case, the K^+ final concentration was not greater than that originally present in the wine. The pH variation during the filtration treatment is negligible.

No variation in property of the wines should occur during treatment. Also, contamination, from IDA itself, can be excluded, if one considers that IDA is chemically bound on cellulose and that functionalized material always shows, after repeated use and regenerations with HCl, the same chelating ability.

The removal of metals could be of interest in a great variety of real samples. In addition to the synthesis of IDA functionalized cellulose, we have functionalized a sample of hydrophilic cotton with IDA groups, according to the procedures described above for the filters. The material obtained (in appearance very similar to the original one) was supported on a Millipore system and repeatedly washed with DDW. A hundred millilitres of the model solution were passed through. Table 4 shows the complete removal of Fe(III), Al(III), Cu(II), Pb(II) and Ca(II). A comparative treatment was performed by passing the same solution through the same quantity of non-functionalized cotton; no retention was observed.

The particular efficiency of this material in fixing metals suggested that its capacity should be tested for Ca(II). Three grams of functionalized cotton were able to fix up to 7557 μmol of Ca(II). Also, the cotton is regenerable with HCl. The good efficiency (Table 2) of this material and the rapidity of the technique could make it very interesting for practical applications.

In conclusion, the use of IDA functionalized cellulose appeared useful for the purpose of lowering and removing metals from liquid samples. In particular, in wines, it is possible to eliminate traces of Pb(II) and Cu(II) by a method which appears more practical, reliable and safe than the use of ferrocyanide.

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