Platinum and Rhodium in wines

Santino Orecchio[a], Diana Amorello[a], Salvatore Barreca[b], Elisa Gulli

a) Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche. Università di Palermo, Viale delle Scienze, I-90128, Palermo, Italy. E-mail: santino.orecchio@unipa.it
b) ARPA, Lombardia, Milano

Over the last decades, the increasing industrial demand of platinum and rhodium, has caused their anthropogenic emissions and spread in all the environmental matrices. Nowadays, vehicles catalysts contain different combinations of PGE in order to achieve optimum performance characteristics and to further reduce the emissions of contaminants. Pt and Rh emitted by vehicles exhausts are deposited along roadways, on adjacent vegetation.

This paper is the first analytical approach to quantify the two heavy metals in alcoholic beverages. In this study a total of 40 different wine samples produced in Italy and Malta, a vodka and a brandy were investigated. In particular, the main intention of this work was to develop a reliable method for the quantification of Pt and Rh in complexes matrices, as wine, because they cannot be readily measured using conventional techniques employed in most laboratories, in particular, the ICP techniques due to matrix and spectra interferences.




About 10-50 mL of sample, in an oven, was dried at 105°C for one night. The dried sample material was ashed in a muffle at 600°C (5 hours). After cooling, the ashes were digested in 5 mL of concentrated HCl and filtered on 0,45 micron filters. After treatment was completed, the clear, colorless solution was transferred into a volumetric flask and brought to volume with Milli-Q water.

Differential Pulse Voltammetry (Pt)
Adsorptive Stripping Voltammetry (Rh)

Parameter	Pt	Rh
Initial potential (mV)	-300	-900
Final potential (mV)	-1000	-1200
Current range	Automatic	Automatic
Potential scan rate (mV s^{-1})	50	10
Potential of deposition (mV)	-	-700
Cycle n°	1	1
Deposition time (s)	-	30
Stirring rate (r.p.m.)	300	300
Size of the drop (a.u.)	60	60
Delay time before potential sweep (s)	10	10
Working electrode	Hanging mercury drop electrode	
Auxiliary electrode	Glassy carbon	
Reference electrode	Ag/AgCl/KCl (sat)	
Flowing gas	Nitrogen (99.998%)	

Analytical methods

Pt determinations were carried out by Differential Pulse Voltammetry (DPV/a) in H_2SO_4 1 M as supporting electrolyte, in the presence of 1.2 mM hydrazine sulphate and 0.6 mM formaldehyde. Formaldehyde and hydrazine condense in situ to produce the corresponding hydrazone, which forms a complex with Pt. Subsequently, a potential varying from -0.3 to -1.0 V, in the differential pulse mode, was applied to the working electrode, and the catalytic current of the hydrogen formation was measured at -0.85 V (versus Ag/AgCl); its intensity being proportional to platinum concentration. The catalytic effect of Pt makes this determination extremely sensitive.

Rhodium quantifications were carried out by Adsorptive Stripping Voltammetry. This technique is known to give an incomparable sensitivity for several trace metals at a mercury electrode (film or drop); it involves complexation of metals with definite ligands and adsorption of the resulting complex on the mercury surface. The adsorbed complex is electrochemically removed by scanning the electrode potential in a reductive direction.

Samples

Samples of white and red wines were kindly provided by the Istituto Regionale Vini e Oli della Sicilia (Palermo, Italy). In particular, 27 samples were wines from different parts of Sicily, 8 samples from northern Italy and 22 from Malta and Gozo. We also analyzed a vodka and a brandy samples.

Results

Considering all the wine samples, concentrations of Pt and Rh vary in the ranges from 3 to 470 $\mu g\ L^{-1}$ and from 0.0006 to 0.36 $\mu g\ L^{-1}$ respectively. In all the samples, platinum is always more abundant than rhodium. Among the samples analyzed, it is worth noting the very low concentrations of Pt and Rh found on a sample of vodka. This result is in agreement with our expectations because vodka is a beverage obtained from at least 3 distillation.

The lowest Pt concentrations were measured in the Sicilian red wines; the mean Pt concentration of the Sicilian red wines is 50±58 $\mu g\ L^{-1}$, while that of the Maltese red wine samples is 115±52 $\mu g\ L^{-1}$.

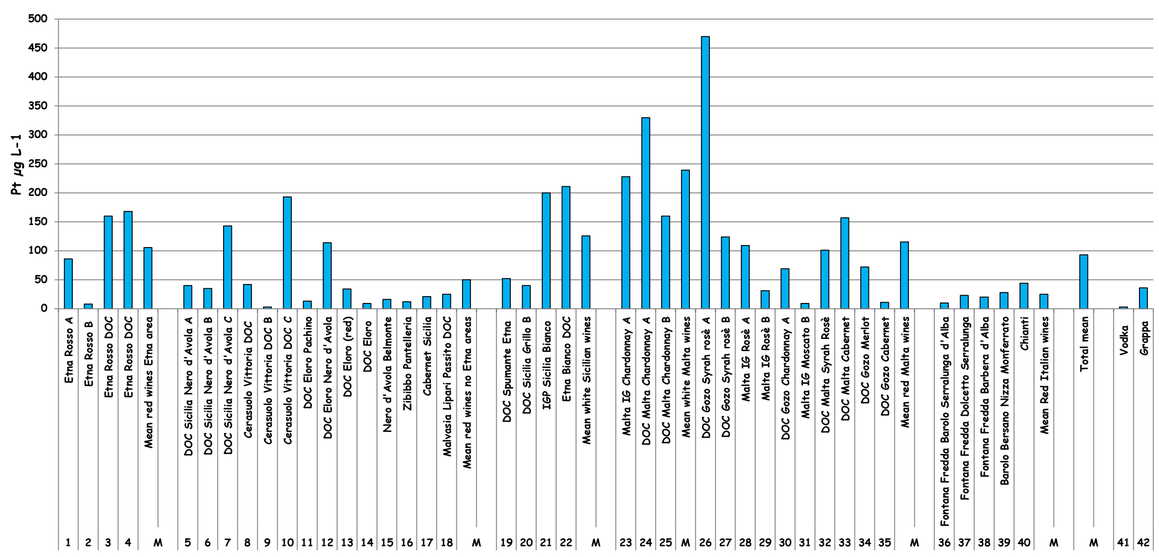
The higher amounts of Pt were detected in white wine samples of Malta and Gozo (mean = 239±86 $\mu g\ L^{-1}$), while the mean value of white Sicilian samples is 126±92 $\mu g\ L^{-1}$. A notable difference is found between the Pt concentrations of the wines produced in the area of Etna (106±75 $\mu g\ L^{-1}$) than those obtained in areas far from the volcano (50±58 $\mu g\ L^{-1}$).

The lowest Rh concentrations were measured in the Malta red wines; the mean Pt concentration of the Malta red wines is 0.013$\mu g\ L^{-1}$, while that of the Etna red wine samples is 0.083 $\mu g\ L^{-1}$. The higher amount of Rh were detected in the Malvasia Lipari Passito sample (0.36 $\mu g\ L^{-1}$), a fortified wine made in Lipari (a Sicilian island) from grapes partially dried in the sun.

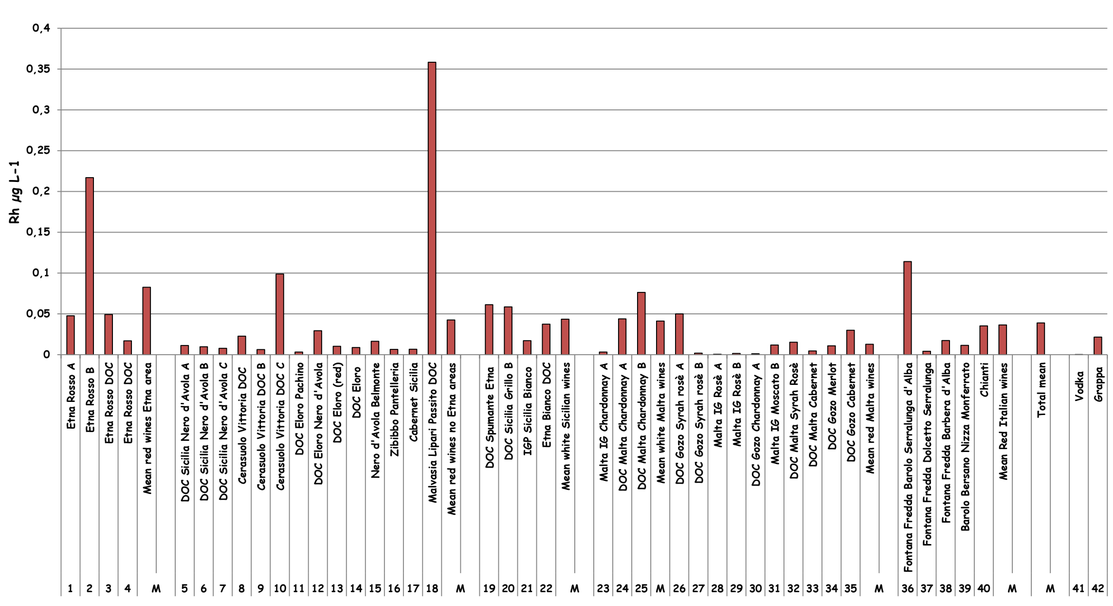
Considering the great variability of the results, it does not allow, by means of statistical methods, geographical origin (Sicilian or Maltese) of the samples.

We found a Pt/Rh ratios ranged from 37 to 180000, in quite disagreement with the ratio in catalytic converters of the type utilized. Unlike other matrices investigated, the concentrations of Pt and Rh are not correlated, suggesting that the grape or the plant (vitis vinifera) treated the two metals very differently.

Platinum concentrations in µg/L (average of three analysis) measured on wine samples



Rhodium concentrations in µg/L (average of three analysis) measured on wine samples



Conclusions

The advantages about the use of these techniques are the high sensitivity that improved the limits of quantification levels for the two elements that are presents at low levels in some samples, simplicity, speed and low costs. Wine samples analyzed contain levels of Pt and Rh under the recommended levels by international organisms for other food. In our case, for wine consumers the estimated intake of Pt and Rh through the studied beverage was lower than the reported values. It is not to ignore the fact that, in Italy and in other European countries, many people consume daily amounts of wine ten times greater than those we have assumed.