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Influence of different bentonites on the rare earth element concentrations of clarified Romanian wines

Victor G. Mihucz [a,b], Carla J. Done [c], Enikő Tatár [b,d], István Virág [d], Gyula Záray [a,b,d,*], Emil G. Baiulescu [c]

[a] *Joint Research Group of Environmental Chemistry of Hungarian Academy of Sciences & L. Eötvös University, P.O. Box 32, H-1518 Budapest, Hungary*
[b] *Hungarian Satellite Centre of Trace Elements Institute to UNESCO, P.O. Box 32, H-1518 Budapest, Hungary*
[c] *University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, Regina Elisabeta Blvd. 4-12, 030018 Bucharest-3, Romania*
[d] *Department of Inorganic and Analytical Chemistry, L. Eötvös University, P.O. Box 32, H-1518 Budapest, Hungary*

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Abstract

The rare earth element (REE) concentrations of 19 Romanian young wine samples originating from the Dealurile Moldovei viticulture area were determined by double focusing inductively coupled plasma mass spectrometry (DF-ICP-MS) after microwave-assisted digestion with nitric acid. The determination of Eu was hampered by the BaO molecular interference. Generally, the red wine samples were more concentrated for REEs than the white wine samples studied. The REE concentrations of the four bentonites (Gelbenton, Evergel, BW200, Tükrös) determined after their fusion were higher by three orders of magnitude than those of the wine samples. After a simulated wine purification process performed with these bentonite samples and a red and white pool samples, the REE concentrations of the clarified wine samples increased by 1.2–1.5 times for red, and 1.3–3 times for white wines in case of the fibrous bentonite sample (Gelbenton), by about 2–5 times in case of the bentonite containing ovalbumin, caseine and gelatine (Evergel), meanwhile this factor was about 20–25 for Na bentonite powder samples (BW200, Tükrös). On basis of the chemometric evaluation using the REE concentrations as input data, the majority of the Feteasca wines belonged to the same cluster as well as the two Cabernet Sauvignon to another subcluster. The adequate choice of the bentonite may allow the use of REEs as fingerprints for determining the wine provenance.

Keywords: Rare earth elements; Wines; Bentonites; ICP-MS; Cluster analysis

1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is a multi-element technique suitable for the analysis of young–finished, red–white, table–fortified wine and even sweet wines with over-ripe grape samples by (semi)quantitative mode providing high selectivity, sensitivity and lower detection limits than other multi-element techniques [1–3].

Wine is of a great economic importance, however, falsification, wrong declaration and blending of wines cause a serious financial shortage. Therefore, there is a strong need to develop fingerprint techniques assisted by mathematical statistical methods in order to determine the provenance of wines. The biggest restriction to the fingerprinting is the representative selection of the group of elements or compounds found in wine samples, which ideally should depend only on the soil composition, but not on the wine technology, transport or storage. Biology, soil mineralogy and solution geochemistry, can all contribute to controlling element uptake by plants [4].

Rare earth elements (REEs) would be ideal candidates for fingerprinting as they have similar chemical properties. The greatest risk for introducing REEs and other elements in wines represents the purification of wines by bentonites [3]. Therefore, up to now, volatile organic compounds like 1-hexanol and cyclohexane [5], amino acids [6,7] or anthocyanins [8] have been chosen for wine fingerprinting. Medina and Van Zeller [9] differentiated among red wines from different parts of France using volatile compounds, phenols, metals, anthocyanins and organic acids. Maarse et al. [10] and García-Jares et al. [11] used volatile

* Corresponding author at: Department of Inorganic and Analytical Chemistry, L. Eötvös University, P.O. Box 32, H-1518 Budapest, Hungary.
Tel.: +36 1 372 2607; fax: +36 1 372 2608.
E-mail address: zaray@ludens.elte.hu (G. Záray).

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compounds, organic acids, amino acids, and major and minor metals to distinguish between German wines from the Rhein-Pfalz and Mosel regions and between some white wines from Rias Baixas (Galicia), respectively. However, metals are the best to perform a differentiation according to the geographical origin due to the direct relationship with soil composition. This differentiation can be carried out by using major, trace and ultra-trace elements [12]. Cluster analysis is proved to be suitable for mathematical statistical evaluation of major and trace element concentrations of wine samples [13–20]. The initial assumption of this analysis is that the nearness of the objects, defined by their variables, reflects the similarity of their properties [21]. In case of Czech wine samples, differentiation was made by making a comparison with the vineyard soil composition for 27 major and trace elements, but not for REEs [13]. The authors concluded that both wine and soil samples were very well clustered according to their locality. However, the clustering of wines did not follow clustering of soils and it was possible that major and trace element fingerprints of wines reflect soil chemistry, pollution and wine manufacturing practices by individual producers.

An excellent way of comparing the REE concentration ratios for different matrices, consists of dividing the concentration of each element by the corresponding value for chondrite and then plotting their logarithm values versus the atomic mass of REEs [22]. Chondritic meteorites are regarded as a reference, because they contain REEs in their primitive relative abundance. The plotted curves obtained should have a smooth shape with the possible exceptions for Ce and Eu. The anomaly of Ce is due to the fact that Ce occurs in tetravalent form under oxidising condition, and that of Eu because Eu(III) can be reduced to Eu(II) causing fractionation relative to other REEs. A smooth profile can therefore be used as an additional assessment of analytical accuracy [23]. Hence, this curve can, for instance, reveal possible anthropogenic contamination; demonstrate that the environmental habitats were well protected from pollution [24]; or show the bioavailability of the low solubility REEs for living organisms [25,26].

The aim of the present work was to detect and quantitatively determine REEs in selected Romanian young white and red wine samples; to investigate the suitability of the REEs as a fingerprint for wine provenance by chemometric means; to evaluate the effect of wine purification by different types of (fibrous, powder, natural or natural gelling agents containing) bentonites on the fingerprinting attempt.

2. Experimental

2.1. Instrumentation

For the determination of rare earth elements (REEs), an Element2 DF-ICP-MS instrument (Thermo Finnigan, Germany) was used. The instrumental conditions of the DF-ICP-MS analytical procedure are summarised in Table 1. For the fusion of bentonites, a KMM6/1200 Kalória GMK (Hungary) temperature controlled furnace (Model LT-S/1200) and Pt crucibles were used. Microwave-assisted digestion of the wine samples was performed by using a Multiwave Paar Physica device (Paar, Austria). For this procedure, six HQ50 quartz bombs (Paar, Austria) were used simultaneously.

Table 1
Instrumental conditions of the DF-ICP-MS measurements for REE determination

Power (W)	1200
Ar gas carrier flow (dm^3/min)	16.0
Ar gas auxiliary flow (dm^3/min)	0.8
Ar nebuliser flow (dm^3/min)	1.1
Measurement mode	Low resolution ($R = 300$)
Acquisition mode	E-scan
No. scans	20 (5 runs, 4 passes)
Search window (%)	60
Integration window (%)	60
Calibration	External
Internal standard	50 pg cm^{-3} In
Points per peak	30
Isotopes	^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{173}Y, ^{175}Lu
Nebuliser	Meinhard
Spray chamber	Scott
Sampler cone	Ni, Ø 1.0 mm orifice
Skimmer cone	Ni, Ø 0.4 mm orifice

2.2. Reagents and materials

Throughout the experiments ion-exchanged water (Pur1te, UK) with a resistivity of 17 MΩ cm was used. Suprapure® 65% HNO_3 (Merck, Germany) was used for the microwave-assisted digestion of the samples. For tuning and mass calibration of the DF-ICP-MS instrument, an acidic (5% HNO_3) Merck Multi-element standard solution in concentration of 1 ng cm^{-3} for each element was employed. For the determination of REEs, a Spex Certi Prep Claritas ppt multi-element standard solution containing Ce, Dy, Er, Eu, Gd, Hf, La, Lu, Nd, Pr, Sc, Sm, Tb Tm, Yb each in a concentration of 10 μg cm^{-3} was applied. For internal standardisation, an acidic (0.5 mol dm^{-3} HNO_3) In Merck stock solution in a concentration of 1000 μg cm^{-3} was used. All solutions were prepared daily from their stock solutions by appropriate dilution with deionised water. The final HNO_3 concentration of the solutions was 5%. Four, commercially available bentonite samples, Gelbenton, Evergel, BW200 and Tükrös were used for wine clarifying without any further purification. Gelbenton and Evergel bentonites were produced in Italy. BW200 and Tükrös bentonites are originating from Germany and Hungary, respectively. Lithium metaborate ($LiBO_2$) and ammonium nitrate (NH_4NO_3), used for the fusion of the bentonite samples, were purchased by Spex.

2.3. Procedures

2.3.1. Wine selection and clarifying by bentonites

Nineteen young wine samples – 12 white and 7 red – of the 2003 vintage prepared according to the valid EU regulations were selected from the Dealurile Moldovei viticultural region, namely from the hills of Cotnari, Jassy (Copou, Uri-