# DETERMINATION OF IRON, COPPER, MANGANESE AND ZINC IN THE SOILS, GRAPES AND WINES OF THE AZORES

# DOSAGE DU FER, DU CUIVRE DU MANGANÈSE ET DU ZINC DANS LES SOLS, LES RAISINS ET LES VINS DES AÇORES

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**Résumé** : This paper describes the determination of iron, copper, manganese and zinc in the soils, grapes and wines of the three viticultural regions of the Azores. Iron, copper and zinc were determined by flame atomic absorption spectrometry and manganese by graphite furnace atomic absorption. The concentrations of the four elements differed in soils of the three regions; there was no difference in the concentration in grapes, whereas significant differences were observed for the wines as regards the amounts of iron, manganese and zinc. The concentrations of these four elements in wine correspond with the mean values observed for other European regions.

**Résumé** : Quatre oligo-éléments, le fer, le cuivre, le manganèse et le zinc ont été recherchés dans le sol, les raisins et le vin des trois régions viticoles des Açores, à cause de leur importance dans les différents métabolismes humaines mais encore pour leur rôle dans la stabilité physico-chimique du vin. Leur dosage a été réalisé par spectrophotométrie d'absorption atomique en flamme pour le fer, le cuivre et le zinc, et en spectrophotométrie d'absorption atomique sans flamme pour le manganèse. Tous les dosages ont été testés par rapport à un matériel de référence. Pour les sols, les trois régions étudiées ont des teneurs différentes pour les quatre oligo-éléments, le cuivre dominant nettement; pour le raisins il n'y avait pas de différence entre les régions et pour le vin il y a des différences significatives entre régions pour le fer, le manganèse et le zinc, mais pas pour le cuivre. Par comparaison à d'autres régions européennes, quel que soit la richesse du sol, les vins se situent pour ces quatre éléments dans les teneurs moyennes.

**Key words**: Oligo-elements; soils, grapes; wines, atomic absorption.

**Mots clés** : Oligo-éléments; sols, raisins, vins, absorption atomique

## INTRODUCTION

The Azores archipelago situated in the center of the Atlantic ocean comprises nine very different islands, though it is only on the islands of Terceira-Biscoitos, Graciosa and Pico that vines are cultivated. Given the isolated geographical situation of these islands, the volcanic nature of their soils and the unique manner in which vines are cultivated, we considered it interesting to study the mineral content of the soils, grapes and wines of this region.

Oligo-elements play a significant role in the biochemistry and physiology of plants and animals and may be divided into two categories, the essential (MALJOURND *et al.*, 1980) and the non-essential oligo-elements. The former are so-called as they are essential for life by virtue of their physiological role in living organisms. Since oligo-elements are obtained from the diet, it is of interest to determine the levels of these elements in the grapes and wines of given regions. The choice of oligo-elements for this study was based not only on the significance of the element itself, but also on its behavior in different matrices. It therefore seemed obvious to study iron, an essential oligo-element and copper not only for their roles in human physiology, but also in view of their role in the chemical stability of wine. Manganese was chosen for its importance in plant physiology in the formation of chlorophyll (MCHARGUE, 1922), and also for the part it is known

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*J. Int. Sci. Vigne Vin*, 2004, **38**, n°2, 109-118

**Table I - Operating conditions for flame atomic absorption spectrometry**

**Conditions opératoires pour absorption atomique en flamme.**

| Element Air/C2H2 | Lamp current mA | Wavelength nm | Slit width nm |
|---|---|---|---|
| Iron oxidant | 6 | 248.3 | 0.2 |
| Copper oxidant | 4 | 324.7 | 0.5 |
| Zinc oxidant | 5 | 213.9 | 0.5 |

**Table II - Operating conditions for graphite furnace absorption spectrometry**

**Conditions opératoires pour absorption atomique sans flamme**

| Lamp current mA | Wavelength nm | Slit width nm | Injection |
|---|---|---|---|
| 6 mA | 279.5 | 0.2 | 15µl sample/std + 5 µl 2 %$HNO_3$ |

to play in the activation of enzyme complexes that regulate the malo-lactic fermentation. Zinc was selected since it is one of the principal oligo-elements essential to man due to its presence in some 200 enzymes (SCTRRICK, 1991), and for the fact that it is essential to plant growth. The maximum concentration of zinc in wine has been set at 5 mg/l (OIV 1999) in view of the astringent character of zinc salts.

## MATERIALS AND METHODS

### I - INSTRUMENTATION AND OPERATING CONDITIONS

Iron, copper and zinc were determined by flame atomic absorption on a Varian GBC 3606 AA apparatus. The operating conditions for the analyses are given in table I. Manganese was determined by graphite furnace atomic absorption spectrometry (GFAAS) with a Varian series AA-1275 AA spectrophotometer equipped with a Varian series GTA 95 graphite tube atomiser, using nitrogen as the carrier gas. The operating conditions for the GFAAS analyses are given in table II.

The organic matrix was digested using a Maxidigest Mx350 instrument supplied by Prolabo, France. Two different digestion programs were used depending on the type of matrix (table III).

### II - REAGENTS AND SOLUTIONS

All glassware and material were first steeped in boiling technical grade nitric acid for 30 minutes, then rinsed with doubly distilled distilled water. Supra-fine® (Merck, France) chemicals and reagents were used throughout. Individual stock solutions were prepared each containing 1g/l of either of $FeCl_3$, $Cu(NO_3)_2$, $Mn(NO_3)_2$ or $Zn(NO_3)_2$ in bi-distilled water. The matrix modifier used for the determination of manganese was 2 % (v/v) $HNO_3$ in bi-distilled water. The methods was applied to the analysis of a certified reference material (Tort-2, Lobster hepatopancreas for trace metals) supplied by the National Research Council of Canada.

### III - ETHYLENEDIAMINE COMPLEXATION TECHNIQUE

The concentration of free metals in soils was determined by complexation with ethylenediamine tetra-acetate (EDTA). A solution was prepared by dissolving 14.6 g of EDTA in approximately 950 ml of bi-distilled water containing 8 ml of 35 % ammonia, the pH was adjusted to 7 and the volume of the solution adjusted to 7. Ten g of soil were mixed with 50 ml of this solution, the mixture was agitated by magnetic stirring at 125 rpm for 60 minutes and then filtered on ash-free paper.

### IV - CALIBRATION AND QUANTITATION

Working solutions in the concentration range 1-5 mg/l (iron), 0.25-2 mg/l (copper and zinc) and 1-4 µg/l (manganese) were freshly prepared daily in doubly distilled water by appropriate dilution of the stock solution. In each case four calibration points were prepared and each standard was analyzed in duplicate (flame AA) or in triplicate (GFAA).

### V - SAMPLE PREPARATION

Wines were analyzed directly following dilution to bring them within the calibration range. Grape samples (15 g) soil samples (0.5 g) were digested using the program described in table III and the digest was brought to a final volume of 50 ml with doubly distilled water. Soils were also extracted using the EDTA complexation technique described above in order to determine the amounts of metals directly assimilatable by the plant. The samples were analyzed in duplicate

### VI - DATA ANALYSIS

Statistical analysis was performed using the Statgraphics® software package. A one-way analysis of variance was carried out for each element in soils, grapes and wine. The statistical significance of the difference between the mean concentrations obtained by region were determined for $P < 0.05$.

## RESULTS

Before starting the analyses, the methods (including the digestion step) were verified using a standard reference material specifically designed for trace metals. The material derived from Lobster hepatopancreas contains certified concentrations based on results of determina-

tions by at least two independent methods of analysis. The material contains 105 ± 13 µg/g iron, 106 ± 10 µg/g copper, 180 ± 6 µg/g zinc and 13.6 ± 1.2 µg/g of manganese. Analysis of the material following digestion gave mean (n = 5) concentrations of 106, 100, 183 and 11.5 µg/g for iron, copper, zinc and manganese, respectively which are in excellent agreement with the stated values for the certified reference material.

The concentrations found of the four elements in soils, grapes and wines are given by region in tables IV, V and VI and VII and the results of the statistical analysis are presented in tables VIII, IX and X. Average concentrations for each region and each matrix (total and soluble soil content, grape and wine concentration) are shown in figure 1. An ANOVA was first carried out for soils to determine whether there was a statistically significant difference between the concentration of the four elements at two different sampling depths, above or below 20 cm. As the test did not reveal a significant difference between the two depths, the remainder of the study was carried out using samples taken from either depth.

Analysis of the soils reveal a significant difference ($p < 10\text{-}4$) between the soils of the three different regions for each of the four elements (table VIII); these observations apply to both the total metal content (following digestion) and the assimilatable or solubilisable content

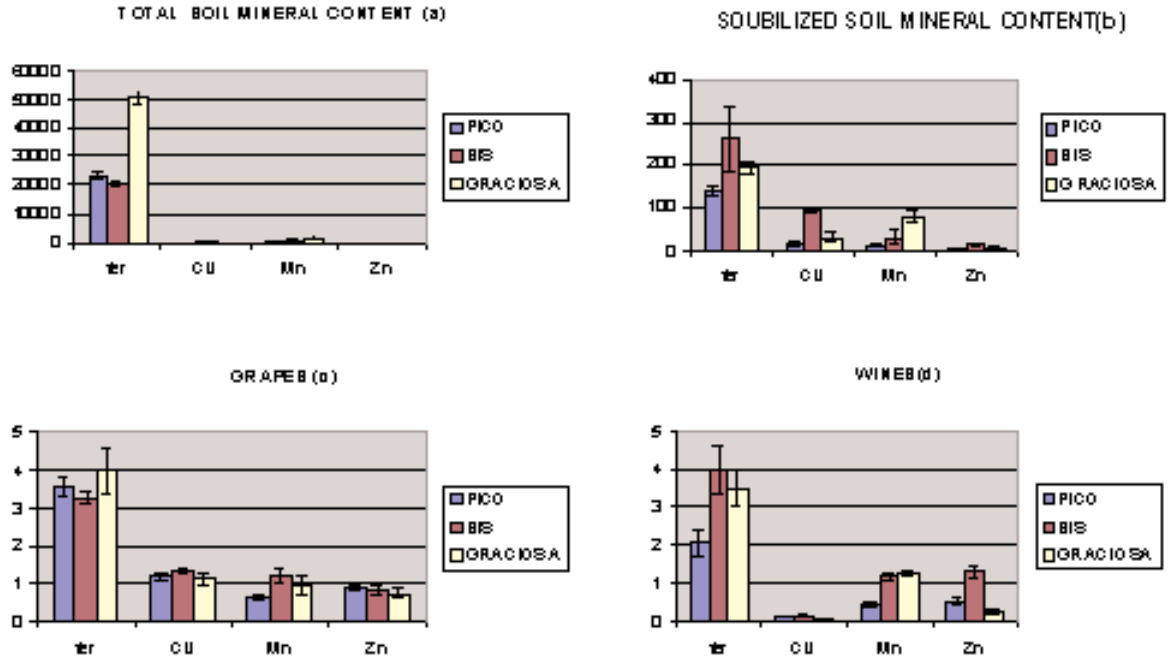


**Figure 1 - Mean concentrations of oligoelements by region**

(a) total mineral content mg/Kg; (b) solubilised mineral content mg/Kg; (c) grape concentration mg/Kg (d) wines (mg/l)

**Teneurs moyennes des oligo-éléments par région**

(a) teneurs totales sols, (mg/Kg; (b) teneurs solubilisées sols, mg/Kg; teneurs raisins, mg/Kg: (d) teneurs vins

**Table III - Program for the digestion of grapes and soils (TEISSEDRE *et al.*, 1993)**

**Programme pour la minéralisation de raisins et de sols (TEISSEDRE *et al.*, 1993)**

| Grapes | | | | |
|---|---|---|---|---|
| Step | Reagent | Volume (ml) | Microwave power (%) | Time (min) |
| 1 | HNO3, 65 % | 25 | 60 | 1 |
| 2 | 0 | 0 | 30 | 10 |
| 3 | H2O2, 35 % | 3 | 15 | 3 |
| 4 | HClO4 | 3 | 40 | 15 |
| | | Soils | | |
| 1 | HNO3, 65 % | 20 | 60 | 1 |
| 2 | 0 | 30 | 10 | |
| 3 | H2O2, 35 % | 3 | 15 | 3 |
| 4 | 0 | 40 | 15 | |

**Table IV – Concentrations of Iron in the Soils, Grapes and Wines of the Azores**

**Teneurs en fer pour les échantillons de sols, raisins et vins des régions des Açores**

| Geographical area | Soil (mg/Kg) | | | | Grapes (mg/Kg) | | Wines (mg/l) | |
|---|---|---|---|---|---|---|---|---|
| | Total content | | Soluble content | | | | | |
| | Depth[a] 10-20 cm | Depth 20-40cm | Depth 10-20 cm | Depth 20-40cm | Varieties | Amount found | Varieties | Amount found |
| Pico | 21720 | 22590 | 144 | 142 | Rio Grande (w) | 3 | Rio Grande (w) | 3 |
| | 14150 | 22810 | 54 | 199 | Periquita ( r) | 3 | Periquita (r) | 2 |
| | 23030 | 22890 | 200 | 113 | Saborinho ( r) | 4 | Saborinho (r) | 2 |
| | 22890 | 23140 | 165 | 237 | Generosa (w) | 3 | Generosa ( r) | 2 |
| | 29310 | 22080 | 135 | 128 | Arinto (w) | 3 | - | - |
| | 16870 | 19780 | 75 | 113 | Rufete (r ) | 4 | - | - |
| | 31410 | 34970 | 112 | 87 | Verdelho (w) | 4 | Verdelho (w) | 1 |
| | 30960 | 28730 | 90 | 119 | C. Sauvignon (r ) | 4 | C. Sauvignon ( r) | 2 |
| | 17010 | 24370 | 116 | 236 | Agronómica (r) | 3 | Agronómican ( r) | 2 |
| | 15410 | 22110 | 51 | 192 | Seara Nova (w) | 5 | Seara Nova (w) | 1 |
| | | | | | Verdelho (w) | 6 | *Verdelho (w) | |
| | | | | | Arinto (w) | 3 | Arinto (w) | 2 |
| | | | | | Terrantês (w) | 3 | Terrantês (w) | |
| | | | | | Seara Nova (w) | 2 | *Seara Nova (w) | |
| | | | | | Generosa (w) | 3 | Generosa (w) | 1 |
| | | | | | Rio Grande (w) | 3 | Rio Grande (w) | |
| | | | | | Agronómica (r) | 3 | *Agronómica (r) | 5 |
| | | | | | Periquita ( r) | 6 | Periquita ( r) | |
| | Depth 15-20 cm | | Depth 15-20 cm | | | | | |
| | 18910 | - | 62 | - | Verdelho (w) | 4 | Verdelho (w) | 2 |
| | 21473 | - | 454 | - | Arinto (w) | 4 | Arinto (w) | 7 |
| | | | | | Terrantês (w) | 3 | Terrantês (w) | 4 |
| Terceira-Biscoitos | | | | | | | Periquita (r ) | 5 |
| | 22489 | - | 180 | - | Verdelho (w) | 3 | Verdelho (w) | 3 |
| | 19930 | - | 418 | - | Verdelho (w) | 3 | Verdelho (w) | 4 |
| | 19712 | - | 189 | - | Verdelho (w) | 3 | *Verdelho (w) | 3 |
| | | | | | Terrantês (w) | 3 | Terrantês (w) | |
| | Depth 20 cm | Depth 50 cm | Depth 20 cm | Depth 50 cm | | | *Arinto (w) | |
| | | | | | | | Verdelho (w) (SS)** | 3 |
| | 45570 | 44778 | 249 | 220 | Arinto (w) | 4 | Boal (w) | |
| | 49677 | 56701 | 261 | 228 | Verdelho (w) | 6 | Terrantês (w) | |
| | 53845 | 50465 | 172 | 175 | Boal (w) | 3 | | |
| Graciosa | | | | | Terrantês (w) | 3 | *Arinto (w) | |
| | | | | | | | Verdelho (w) (oak)*** | 4 |
| | | | | | | | Boal (w) | |
| | | | | | | | Terrantês (w) | |
| | 45346 | 64047 | 176 | 229 | Boal (w) | 4 | - | - |
| | 39253 | 62560 | 125 | 122 | Tália (w) | 4 | - | - |

a – Depth ; w - white; r- red; nd – not detectable;*Blends of different grape varieties; ** Wine aged in stainless steel;
***Wine aged in oak barrels

**Table V – Concentrations of Copper in the Soils. Grapes and Wines of the Azores**

**Teneurs en cuivre pour les échantillons de sols, raisins et vins des régions des Açores**

| Geographical area | Soil (mg/Kg) | | | | Grapes (mg/Kg) | | Wines (mg/l) | |
|---|---|---|---|---|---|---|---|---|
| | Total content | | Soluble content | | | | | |
| Pico | Depth[a] 10-20 cm | Depth 20-40cm | Depth 10-20 cm | Depth 20-40cm | Varieties | Amount found | Varieties | Amount found |
| | 49 | 54 | 7 | 10 | Rio Grande (w) | 1.1 | Rio Grande (w) | 0.1 |
| | 37 | 50 | 2 | 7 | Periquita ( r) | 0.9 | Periquita ( r) | 0.1 |
| | 44 | 43 | 5 | 4 | Saborinho ( r) | 1.0 | Saborinho ( r) | 0.1 |
| | 37 | 41 | 6 | 6 | Generosa (w) | 0.7 | Generosa (w) | 0.1 |
| | 155 | 70 | 64 | 25 | Arinto (w) | 1.0 | | |
| | 34 | 42 | 3 | 5 | Rufete (r ) | 1.4 | | |
| | 100 | 131 | 30 | 47 | Verdelho (w) | 1.2 | Verdelho (w) | 0.3 |
| | 119 | 85 | 43 | 32 | C. Sauvignon (r ) | 0.9 | C. Sauvignon ( r) | 0.1 |
| | 37 | 44 | 6 | 8 | Agronómica (r) | 0.9 | Agronómica ( r) | 0.1 |
| | 30 | 38 | 2 | 1 | Seara Nova (w) | 1.0 | Seara Nova (w) | 0.1 |
| | | | | | Verdelho (w) | 1.7 | *Verdelho (w) | |
| | | | | | Arinto (w) | 1.8 | Arinto (w) | 0.1 |
| | | | | | Terrantês (w) | 1.7 | Terrantês (w) | |
| | | | | | Seara Nova (w) | 0.7 | *Seara Nova (w) | |
| | | | | | Generosa (w) | 2.2 | Generosa (w) | 0.1 |
| | | | | | Rio Grande (w) | 1.2 | Rio Grande (w) | |
| | | | | | Agronómica (r) | 1.0 | *Agronómica (r) | 0.1 |
| | | | | | Periquita ( r) | 1.0 | Periquita ( r) | |
| Terceira-Biscoitos | Depth 15-20 cm | | Depth 15-20 cm | | | | | |
| | 188 | - | 71 | - | Verdelho (w) | 1.250 | Verdelho (w) | 0.1 |
| | 1534 | - | 107 | | Arinto (w) | 1.2 | Arinto (w) | 0.1 |
| | | | | | Terrantês (w) | 1.2 | Terrantês (w) | 0.1 |
| | | | | | - | - | Periquita (r ) | 0.03 |
| | 426 | - | 85 | - | Verdelho (w) | 1.6 | Verdelho (w) | 0.1 |
| | 1359 | - | 108 | - | Verdelho (w) | 1.7 | Verdelho (w) | 0.5 |
| | 541 | - | 90 | - | Verdelho (w) | 1.2 | *Verdelho (w) | 0.2 |
| | | | | | Terrantês (w) | 1.3 | Terrantês (w) | |
| Graciosa | Depth 20 cm | Depth 50 cm | Depth 20 cm | Depth 50 cm | | | *Arinto (w) | |
| | | | | | | | Verdelho (w) (SS)** | 0.1 |
| | 366 | 163 | 82 | 51 | Arinto (w) | 1.1 | Boal (w) | |
| | 95 | 34 | 38 | 8 | Verdelho (w) | 0.9 | Terrantês (w) | |
| | 197 | 61 | 75 | 18 | Boal (w) | 0.7 | | |
| | | | | | Terrantês (w) | 0.8 | *Arinto (w) | |
| | | | | | | | Verdelho (w) (oak)*** | 0.1 |
| | | | | | | | Boal (w) | |
| | | | | | | | Terrantês (w) | |
| | 31 | 31 | 4 | 2 | Boal (w) | 1.9 | - | - |
| | 85 | 62 | 12 | 4 | Tália (w) | 1.4 | - | - |

a – Depth ; w - white; r- red; nd – not detectable; *Blends of different grape varieties; ** Wine aged in stainless steel; ***Wine aged in oak barrels

**Table VI – Concentrations of Manganese in the Soils, Grapes and Wines of the Azores**

**Teneurs en manganèse pour les échantillons de sols, raisins et vins des régions des Açores**

| Soil (mg/Kg) | | | | | Grapes (mg/Kg) | | Wines (mg/l) | |
|---|---|---|---|---|---|---|---|---|
| Geographical area | Total content | | Soluble content | | Varieties | Amount found | Varieties | Amount found |
| | Depth[a] 10-20 cm | Depth 20-40cm | Depth 10-20 cm | Depth 20-40cm | | | | |
| Pico | 586 | 566 | 12 | 10 | Rio Grande (w) | 0.4 | Rio Grande(w) | 0.4 |
| | 263 | 560 | 3 | 14 | Periquita ( r) | 0.5 | Periquita ( r) | 0.4 |
| | 607 | 566 | 18 | 9 | Saborinho ( r) | 0.5 | Saborinho ( r) | 0.4 |
| | 534 | 711 | 12 | 21 | Generosa (w) | 0.4 | Generosa (w) | 0.5 |
| | 1421 | 945 | 32 | 30 | Arinto (w) | 0.7 | - | - |
| | 339 | 471 | 6 | 9 | Rufete (r ) | 0.6 | - | |
| | 1134 | 754 | 6 | 10 | Verdelho (w) | 0.6 | Verdelho (w) | 0.5 |
| | 1147 | 1107 | 3 | 6 | C. Sauvignon (r ) | 0.5 | C. Sauvignon ( r) | 0.4 |
| | 432 | 687 | 8 | 6 | Agronómica (r) | 0.6 | Agronómica ( r) | 0.7 |
| | 293 | 727 | 5 | 33 | Seara Nova (w) | 0.8 | Seara Nova (w) | 0.2 |
| | | | | | Verdelho (w) | 1.1 | *Verdelho (w) | |
| | | | | | Arinto (w) | 1.5 | Arinto (w) | 0.7 |
| | | | | | Terrantês (w) | 0.9 | Terrantês (w) | |
| | | | | | Seara Nova (w) | 0.5 | *Seara Nova (w) | |
| | | | | | Generosa (w) | 0.9 | Generosa (w) | 0.6 |
| | | | | | Rio Grande (w) | 0.4 | Rio Grande (w) | |
| | | | | | Agronómica (r) | 0.7 | *Agronómica (r) | 0.4 |
| | | | | | Periquita ( r) | 0.3 | Periquita ( r) | |
| Terceira-Biscoitos | Depth 15-20 cm | | Depth 15-20 cm | | | | | |
| | 828 | - | 9 | - | Verdelho (w) | 1.9 | Verdelho (w) | 1.6 |
| | 2104 | - | 33 | - | Arinto (w) | 1.4 | Arinto (w) | 1.2 |
| | | | | | Terrantês (w) | 1.5 | Terrantês (w) | 1.2 |
| | | | | | - | - | Periquita (r ) | 1.0 |
| | 701 | - | 18 | - | Verdelho (w) | 1.7 | Verdelho (w) | 1.5 |
| | 721 | - | 86 | - | Verdelho (w) | 0.8 | Verdelho (w) | 1.1 |
| | 765 | - | 12 | - | Verdelho (w) | 0.7 | *Verdelho (w) | 0.8 |
| | | | | | Terrantês (w) | 0.6 | Terrantês (w) | |
| Graciosa | Depth 20 cm | Depth 50 cm | Depth 20 cm | Depth 50 cm | | | *Arinto (w) | |
| | | | | | | | Verdelho (w) (SS)** | 1.3 |
| | 2579 | 3270 | 124 | 82 | Arinto (w) | 1.7 | Boal (w) | |
| | 1490 | 2223 | 165 | 86 | Verdelho (w) | 0.8 | Terrantês (w) | |
| | 1871 | 2292 | 8 | 98 | Boal (w) | 0.5 | | |
| | | | | | Terrantês (w) | 0.5 | *Arinto (w) | |
| | | | | | | | Verdelho (w) (oak)*** | 1.2 |
| | | | | | | | Boal (w) | |
| | | | | | | | Terrantês (w) | |
| | 1509 | 1494 | 97 | 67 | Boal (w) | 0.9 | - | - |
| | 2083 | 1605 | 34 | 16 | Tália (w) | 1.5 | - | - |

**Table VII – Concentrations of Zinc in the Soils, Grapes and Wines of the Azores**

**Teneurs en zinc pour les échantillons de sols, raisins et vins des régions des Açores**

| Geographical area | Sols (mg/kg) | | | | Raisins (mg/kg) | | Wines (mg/l) | |
|---|---|---|---|---|---|---|---|---|
| | Total content | | Soluble content | | | | | |
| | Deptha 10-20 cm | Depth 20-40cm | Depth 10-20 cm | Depth20-40 cm | Varieties | Amount found | Varieties | Amount found |
| Pico | 53 | 52 | 4 | 4 | Rio Grande (w) | 0.9 | Rio Grande (w) | 0.6 |
| | 30 | 45 | 1 | 5 | Periquita ( r) | 0.6 | Periquita ( r) | 0.3 |
| | 59 | 45 | 8 | 2 | Saborinho ( r) | 0.6 | Saborinho ( r) | 0.2 |
| | 43 | 57 | 3 | 5 | Generosa (w) | 0.9 | Generosa (w) | 1.0 |
| | 120 | 71 | 13 | 11 | Arinto (w) | 1.0 | - | - |
| | 29 | 46 | 1 | 4 | Rufete (r ) | 1.2 | - | - |
| | 95 | 145 | 11 | 15 | Verdelho (w) | 0.7 | Verdelho (w) | 1.1 |
| | 115 | 88 | 13 | 12 | C. Sauvignon (r ) | 1.0 | C. Sauvignon ( r) | 0.2 |
| | 37 | 65 | 2 | 6 | Agronómica (r) | 0.9 | Agronómica ( r) | 1.0 |
| | 17 | 43 | 1 | 4 | Seara Nova (w) | 0.8 | Seara Nova (w) | 0.8 |
| | | | | | Verdelho (w) | 0.8 | *Verdelho (w) | |
| | | | | | Arinto (w) | 0.7 | Arinto (w) | 0.2 |
| | | | | | Terrantês (w) | 1.0 | Terrantês (w) | |
| | | | | | Seara Nova (w) | 0.6 | *Seara Nova (w) | |
| | | | | | Generosa (w) | 0.8 | Generosa (w) | 0.4 |
| | | | | | Rio Grande (w) | 0.7 | Rio Grande (w) | |
| | | | | | Agronómica (r) | 1.2 | *Agronómica (r) | 0.3 |
| | | | | | Periquita ( r) | 1.9 | Periquita ( r) | |
| Terceira-Biscoitos | Depth 15-20 cm | | Depth 15-20 cm | | | | | |
| | 85 | - | 11 | - | Verdelho (w) | 0.7 | Verdelho (w) | 1.1 |
| | 114 | - | 16 | - | Arinto (w) | 1.2 | Arinto (w) | 1.4 |
| | | | | | Terrantês (w) | 1.0 | Terrantês (w) | 1.9 |
| | | | | | - | - | Periquita (r ) | 1.8 |
| | 114 | | 13 | - | Verdelho (w) | 1.0 | Verdelho (w) | 0.9 |
| | 121 | | 17 | - | Verdelho (w) | 0.6 | Verdelho (w) | 0.4 |
| | 76 | | 12 | - | Verdelho (w) | 0.6 | *Verdelho (w) | 1.7 |
| | | | | | Terrantês (w) | 0.8 | *Terrantês (w) | |
| Graciosa | Depth 20 cm | Depth 50 cm | Depth 20 cm | Depth 50 cm | | | *Arinto (w) | |
| | | | | | | | *Verdelho (w) (SS)** | 0.3 |
| | 210 | 261 | 15 | 15 | Arinto (w) | 1.0 | *Boal (w) | |
| | 128 | 105 | 9 | 5 | Verdelho (w) | 0.7 | *Terrantês (w) | |
| | 151 | 138 | 12 | 7 | Boal (w) | 0.6 | | |
| | | | | | Terrantês (w) | 0.7 | Arinto (w) | |
| | | | | | | | Verdelho (w) (oak)*** | 0.2 |
| | | | | | | | Boal (w) | |
| | | | | | | | Terrantês (w) | |
| | 84 | 83 | 2 | 2 | Boal (w) | 0.7 | - | - |
| | 162 | 114 | 4 | 1 | Tália (w) | 1.0 | - | - |

a – Depth ; w - white; r- red; nd – not detectable; *Blends of different grape varieties; ** Wine aged in stainless steel; ***Wine aged in oak barrels

**Table VIII- Statistical results for iron, copper, manganese and zinc content of soils**

**Résultats statistiques pour le fer, le cuivre, le manganèse et le zinc dans les sols**

| | | Total soil mineral content mg/kg | | | | Solubilized soil mineral content mg/kg | | | |
|---|---|---|---|---|---|---|---|---|---|
| Region | | Pico | Biscoitos | Graciosa | | Pico | Biscoitos | Gracios | |
| N° of samples | | 20 | 5 | 10 | P | 20 | 5 | 10 | P |
| Fe | m | 23311,5 | 20502,8 | 511224,2 | $< 10^{-4}$ | 135,4 | 260,6 | 195,7 | 0,005 |
| | esm | 1228,2 | 647,1 | 2547,65 | 12,2 | 75,2 | 15,5 | | |
| Cu | m | 62,0 | 809,6 | 112,5 | $< 10^{-4}$ | 15,7 | 92,2 | 29,4 | $< 10^{-4}$ |
| | esm | 8,1 | 267,6 | 33,2 | 4,0 | 7,0 | 9,6 | | |
| Mn | m | 692,5 | 1023,8 | 2041,6 | $< 10^{-4}$ | 12,7 | 31,6 | 77,7 | $< 10^{-4}$ |
| | esm | 69,8 | 270,9 | 182,7 | | | 2,1 | 14,2 | 15,4 |
| Zn | m | 62,8 | 102,0 | 143,6 | 0,0001 | 6,3 | 13,8 | 7,2 | 0,019 |
| | esm | 7,5 | 9,017,8 | 1,0 | 1,2 | 1,7 | | | |

**Table IX- Statistical results for iron, copper, manganese and zinc content of grapes**

**Résultats statistiques pour le fer, le cuivre, le manganèse et le zinc dans les raisins**

| | | Mineral content mg/kg | | | |
|---|---|---|---|---|---|
| Region | | Pico | Biscoitos | Graciosa | |
| N° of samples | | 18 | 7 | 6 | P |
| Fe | m | 3.61 | 3.28 | 4.00 | 0,44 |
| | esm | 0.26 | 0.18 | 0.62 | |
| Cu | m | 1.19 | 1.34 | 1.13 | 0,55 |
| | esm | 0.09 | 0.08 | 0.18 | |
| Mn | m | 0.66 | 1.23 | 0.98 | 0,01 |
| | esm | 0.07 | 0.20 | 0.21 | |
| Zn | m | 0.90 | 0.84 | 0.78 | 0,62 |
| | esm | 0.07 | 0.08 | 0.07 | |

m: mean; esm: standard error; p: level of significance of difference between the three regions

**Table X- Statistical results for iron, copper, manganese and zinc content of wines**

**Résultats statistiques pour le fer, le cuivre, le manganèse et le zinc dans les vins**

| | | Mineral content mg/kg | | | |
|---|---|---|---|---|---|
| Region | | Pico | Biscoitos | Graciosa | |
| N° of samples | | 11 | 7 | 2 | *P* |
| Fe | m | 2.09 | 4.00 | 3.50 | 0,02 |
| | esm | 0.34 | 0.50 | 0.61 | |
| Cu | m | 0.12 | 0.16 | 0.10 | 0,63 |
| | esm | 0.02 | 0.06 | 0.0 | |
| Mn | m | 0.47 | 1.20 | 0.10 | $< 10^{-4}$ |
| | esm | 0.04 | 0.10 | 0.07 | |
| Zn | m | $< 10^{-4}$ | 1.3 | 0.25 | 0,003 |
| | esm | 0.11 | 0.20 | 0.05 | |

m: mean; esm: standard error; p: level of significance of difference between the three regions

**Table XI - Comparison of minerals in wines between the Azores and continental Europe**

**Comparaison entre les teneurs en éléments minéraux des vins des Açores et des vins de l,Europe continentale.**

| | Element (mg/l) | | | |
|---|---|---|---|---|
| | Iron | Copper | Manganese | Zinc |
| Portugal | 8.5 | 0.59 | | |
| Spain | 7 | 0.07 | 1.04 | 1.87 |
| Greece | 3.12 | | 0.86 | |
| France | 4 | 0.12 | 1.5 | 0.9 |
| Azores* | 3.2 | 0.13 | 0.97 | 0.71 |

*Present study

determined by EDTA complexation. The Graciosa region is richest in total iron, total and soluble manganese and in total zinc ($P < 10^{-4}$). The Biscoitos region (of Terceira island) is richest in soluble iron, ($P < 10^{-3}$) total and soluble copper and in soluble zinc ($P < 0.02$).

As regards the grapes (table IX) a significant difference is observed between the three regions in terms of manganese ($P < 0.01$); the Biscoitos region was found to have the highest concentration. Significant differences in the concentrations of the elements were not observed between the three regions.

For wines, (table X) significant differences between the three regions are observed for iron, manganese and zinc, but not for copper. Concentrations of iron and zinc are highest for wines in Biscoitos whereas wine from Graciosa has the highest concentration of manganese.

## DISCUSSION AND CONCLUSION

According to GALET (1976) all oligo-elements are present in soils at low concentrations, for example iron 1-5 %; copper 0.0008-0.005 %, manganese 0.02-1 % and zinc 0.001-0.01 % (g/100 g). If the mean values of the oligo-elements found in this study (see table VIII – total soil mineral content) are compared with the above figures, it may be seen that the values for iron fall within these levels; only the Graciosa region appears to have a higher concentration of this element. All three regions, but especially the Biscoitos region, appear to be rich in copper; manganese levels correspond to the average values given by Galet and for zinc, only the island of Graciosa has a slightly higher concentration. Significantly higher levels of iron (as much as 25.3 g/100 g) and manganese (as much as 0.8 g/100g) were reported by MADRUGA (1995) in the soils of the Azores.

Only a small fraction of the metals was found to exist in soluble form (capable of being absorbed by the plant): average values obtained by EDTA extraction for the three regions were 0.7 % of iron, 20.8 % copper 9.5 % zinc and 2.9 % manganese. Iron, the soluble fraction of which is the lowest, is essentially present in soil in the form of stable complexes or as insoluble salts such as ferric phosphate. Copper most likely occurs as a more dissociable and soluble form. The differences observed from one region to another would indicate the presence of another phenomenon. Biscoitos has the highest amounts of soluble fractions of iron (1.27 %), zinc (13.5 %) and manganese (3.09 %), but has the lowest amount of soluble copper fraction (11.4 %) compared to the two other regions (Pico (25 %) and Graciosa (26 %).

It was observed that the amounts of iron, copper and zinc in grapes was similar in the three regions, regardless of their concentrations in soils. This would suggest that the vine only absorbs only the amount of oligo-elements necessary for its requirements regardless of their concentrations in the soil. Only for manganese does the concentration differ in the grapes from one region to another: 0.66 mg/Kg (Pico), 1.23 mg/Kg (Biscoitos) and 0.98 mg/Kg (Graciosa). These observations concur with those of FREGONI (1999) who found in a study in Italy that acidic soil pH favors the absorption of micro-elements, manganese in particular, and in the present study the pH of the Biscoitos region has the most acidic soil (pH = 5.3).

Comparison of figure 1c ad 1d (mean concentration of oligoelements by region) in grapes and wines, respectively shows than the concentration of copper is significantly lower in wine that in grapes; this is most likely due to the fact that copper is eliminated with the lees in the form of insoluble copper sulfide.

The values found in the wines of the Azores were compared with those found in wines from mainland Europe. Values were previously reported for Portugal (CURVELO-GARCIA and GHIRA, 1978, 1979a, b, 1987), Spain (GONZALES-LARRAINA *et al.*, 1978 ; GARCIA, 1993, HERNANDEZ, 1994), Greece (VOULGAROPOULOS and SOULIS, 1987) and France (CABANIS *et al.*, 1998). The values found in this study and by these authors for iron, copper, manganese and zinc are summarized in table XI, which shows that the values obtained in the wines in this study correspond to those reported for mainland Europe, in spite of varying concentrations of these ele-

ments in soils. Iron and copper levels were determined in an earlier study of the wines of the Azores (RIBEREIO de LIMA, 1992 and MARQUES, 1997), the mean concentrations reported in these studies were in the region of 4.6 mg/l for iron and 0.88 mg/l for copper. The fact that the concentrations found in the present study are lower, particularly for copper, attests to the fact that in this region viticultural practices have improved to include lower levels of copper treatments and oenological practices have seen the installation of stainless steel equipment in place of existing iron- and copper-based materials.

## REFERENCES


CABANIS J-C., CABANIS M.T, CHEYNIER V., TEISSEDRE, P.L.. 1998. Tables de composition, 315-336. *In: Œnologie, Fondements Scientifiques et Technologiques*. C. Flanzy (Ed.) . Lavoisier, Tec & Doc., London, New York, Paris.

CURVELO-GARCIA A.S., 1978. Caracterização Enologica de Região Demarcada de Dão. De Vinea et Vino, *Portugaliae Documenta*, **2**, 2-14.

CURVELO-GARCIA A.S, Ghira, J., 1979a. *Caracterização Enologica das Principais Regiões Viticolas do Pais, II. Região do Oeste*. Instituto Nacional de Investição Agrária. Dois Portos.

CURVELO-GARCIA A.S, Ghira, J.. 1979b. *Caracterização Enologica das Principais Regiões Viticolas do Pais, III. Região do Cartaxo*. Instituto Nacional de Investição Agrária. Dois Portos

CURVELO-GARCIA A.S, GHIRA J., 1987. *Caracterização Enologica das Principais Regiões Viticolas do Pais, IV. Região de Pinhel*. Instituto da Vinha e do Vinho. Sacav_.

FREGONI M. and BAVARESCO L., 1999. *First international symposium of viticulture on acidic soils*. CNRS, France.

GALET P., 1976. *Précis de Viticulture*, 3rd Ed., Dehan, Montpellier, France

GARCIA M.M.P., 1993. *Caracterizacion de los vinos tintos de la Comarca Tacaronte-Acentejo*. Trabajo de Licenciatura, Universidade de La Laguna, La Laguna.

GONZALES-LARRAINA M., GONZALEZ A. et MEDINA B, 1987. Les ions métalliques dans la différenciation des vins rouges des trois régions d'appellation d'origine Rioja. *Connaissance Vigne Vin,* **21**, 127-140.

HERNANDEZ G.G., 1994. Caracterizacion, fisicoquimica y sensorial de los mostos y vinos tintos de la parte oriental de la demoninacion de origen Tacaronte-Acentejo de Tenerife. *Doctoral Thesis*, Universidad de la Laguna, La Laguna.

MADRUGA, J. 1995. Caracterização e constituiçcão dos horizontes plácicos em solos do Arquipélage dos Açores. *Tese de Doutoramento*, Univerisdade dos Açores, Angra do Heris.

MALJOIURNAL, B., Cecoux, G., Favier, A., Lafond, J.L. 1980. Les oligo-éléments essentiels. Rôle Biologique. *Gaz. Med. France*, **87**, 2243-2254.

MARQUES, T.S.C.L. 1997. Contribuição para a caracterização fisicoquimica y sensorialdo vinho Licorose do Pico. *Thèse de Licence*. Universidade dos Açcores, Angra do Herosimo.

MCHARGUE, J., 1922. The role of manganese in plants. *J. Am. Chem. Soc.*, **44**, 1592-1600.

OIV 1999. *Compendium of International Methods of Analysis of Wines and Musts*. OIV Publications, Paris.

RIBEIRO DE LIMA, M.T. 1992. Caracterização fisicoquimica do vinho «Verdelho do Pico», tipo aperitivo. Trabalho de sintese para as provas de aptidão pedagogica e capacidade cientifica, Universidade dos Açcores, Angra do Herosimo.

SCTRICK L., 1991. L'oligothérapie exactement, Editions Roger Jollois, Limoges, France.

TEISSEDRE P-L., CABANIS M.T. et CABANIS J.C., 1993. Comparison de deux méthodes de minéralisation en vue du dosage du plomb par spectrométrie d'absorption atomique electrothermique. Application à des échantillons de sols, feuilles de vignes, raisins, mouts, marcs et lies. *Analusis magazine*, **21**, 249-254.

VOULGAROPOULOS A. and SOULIS A. 1978. Teneurs de certains vins grecs du commerce in lithium, potassium, sodium, magnesium, calcium, strontium, baryum, manganèse, fer et aluminium. *Connaissance Vigne Vin*, **21**, 23-31.


*Manuscrit reçu le 23 octobre 2003 ; accepté pour publication, après modifications le 1er décembre 2003*