Radioactivity and Heavy Metals Concentration in Italian (Calabrian) DOC Wines

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Abstract: Wine is an alcoholic drink, largely used to accompany food, with a key role in the protective effects on cardiovascular diseases. This study was developed to investigate radioisotopes and heavy metal content of twenty red, rose and white Italian wines, belonging to controlled origin denomination (DOC) geographic areas of the Calabria region, south of Italy. High Purity Germanium (HPGe) Gamma Spectrometry was employed to evaluate anthropogenic ($^{137}$Cs) and natural ($^{40}$K) radionuclides specific activity. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to assess any possible heavy metals contamination by a comparison between Cu, Zn, Pb, B, As and Cd concentrations with the limits set by the Italian Legislation. Calculated annual effective doses due to the ingestion of investigated samples are under allowable levels (1 mSv/year), thus excluding the risk of ionizing radiation effects on humans. Regarding to the metals concentration, experimental results show that they are lower than the contamination threshold values, thus excluding their presence as pollutants.

Keywords: wine; radioactivity concentration; metals contamination; High Purity Germanium (HPGe) Gamma Spectrometry; Inductively Coupled Plasma Mass Spectrometry (ICP-MS); effective dose; ingestion

1. Introduction

Humans are subjected to radiations coming from natural and artificial sources in their living environments [1].

Natural radioactivity is due to the presence of cosmogenic and primordial radionuclides in the Earth’s crust [2]. The first ones are produced by the interaction of cosmic-rays with atomic nuclei in the atmosphere, while the origin of the second ones goes back to the formation of the Earth, when they were produced by the process of nucleo-synthesis [3,4]. Artificial fallout radionuclides, such as $^{137}$Cs, are derived mainly from global nuclear tests conducted between the mid 1940s and the 1980s, as well as from nuclear accidents [5].

External gamma rays, inhalation of radionuclides and ingestion of radioisotopes through food and water are the three ways of exposure to ionizing radiations [6]. For the latter, in particular, the natural radioactivity comes mainly from $^{40}$K because nuclides of the uranium and thorium radioactive chains are usually present in traces [7,8]. Ingested or inhaled radionuclides are distributed among body organs with varying radio sensitivities [9].
Wine is an alcoholic drink, largely used to accompany food [10]. Italy is the first exporter of wine in the world, closely followed by Spain and France [11]. In particular, Calabria and Sicily are the Italian regions with the biggest wine growing acreages [12]. The quality assurance of wines needs well-defined investigations, e.g., determination of ethanol or sugar content, concentration of organic acids, minerals and trace elements concentrations (for their influence on wine technology as well as their toxic effects), etc. [13].

Contaminated wines consumption will increase the amount of radioactivity and chemical contamination inside a human being and therefore increases the health risks associated with radiation exposure and metals pollution. The exact health effects will depend on which radionuclides and metals have been ingested and, on their amount [14].

In this article twenty (in total) red, rose and white Italian wines, belonging to controlled origin denomination (DOC) geographic areas of the Calabria region, south of Italy, were analyzed to identify and quantify: natural (\(^{40}\)K) and artificial (\(^{137}\)Cs) gamma-emitting radionuclides, with HPGe gamma spectrometry, to evaluate any possible radioisotopes contamination and to estimate the effective dose due to the wine ingestion; heavy metals (Cu, Zn, Pb, B, As, Cd), with Inductively Coupled Plasma Mass Spectrometry (ICP-MS), to assess any possible chemical pollution.

From the geological point of view, the investigated area belongs to the “Calabrian-Peloritan arc”. Its rocks are acidic intrusive igneous (e.g., granites) and metamorphic of medium and high grade (e.g., gneiss) [15].

The investigated Calabrian wines have never been analyzed in terms of radioisotopes and heavy metals contamination: thus, the health risks for the population have never been evaluated.

2. Materials and Methods

2.1. Samples Collection and Description

The analyses were carried out on twenty Calabrian red, rose and white wines of the year 2016. The samples were kindly provided by the Italian Sommelier Association in the first months of 2019 as they are, without any treatment, stored in a 20 mL polyethylene plastic vial for subsequent experimental laboratory analyses.

Of the twenty samples, thirteen came from the same Calabrian geographic area in province of Crotone, the so-called “Cirò” DOC area. Of the other seven, five samples belonged to the “Terre di Cosenza” DOC area; one rose wine came from the “Sant’Anna di Isola di Capo Rizzuto” DOC area; one white wine belonged to the “Savuto” DOC area. A map of all Calabrian DOCs (in different colors), with the investigated areas of origin enclosed in a dotted line, is reported in Figure 1.

Investigated samples are reported in the Table 1, together their ID code and geographic area of provenance.

Ten samples of each wine were collected and analysed and the mean value of the detected parameters was reported.

| No | Sample ID | DOC Area of Provenance | Wine Typology |
|----|-----------|------------------------|---------------|
| 1  | S1        | Terre di Cosenza        | Red           |
| 2  | S2        |                        |               |
| 3  | S3        |                        | White         |
| 4  | S4        | Cirò                   |               |
| 5  | S5        |                        | Red           |
| 6  | S6        |                        |               |
| 7  | S7        |                        |               |
Table 1. Cont.

| No | Sample ID | DOC Area of Provenance | Wine Typology |
|----|-----------|------------------------|---------------|
| 8  | S8        |                        |               |
| 9  | S9        |                        |               |
| 10 | S10       |                        |               |
| 11 | S11       | Terre di Cosenza       | Rose          |
| 12 | S12       | S. Anna di Isola di Capo Rizzuto | Rose   |
| 13 | S13       | Cirò                   | White         |
| 14 | S14       | Terre di Cosenza       | White         |
| 15 | S15       |                        | Rose          |
| 16 | S16       | Cirò                   | Rose          |
| 17 | S17       |                        | White         |
| 18 | S18       | Savuto                 | White         |
| 19 | S19       | Terre di Cosenza       | White         |
| 20 | S20       |                        | White         |

Figure 1. A map of all Calabrian DOCs (in different colors), with the investigated areas of origin enclosed in a dotted line.
2.2. Gamma Spectrometry Analysis and Evaluation of Radiological Hazard Effects

In the laboratory, for the gamma spectrometry analysis, samples (packed in a 20 mL polyethylene plastic vial to reach geometric homogeneity around the detector) were counted for 70,000 s and spectra were analyzed in order to obtain the activity concentration of $^{137}\text{Cs}$ and $^{40}\text{K}$ through the evaluation of their $\gamma$-lines at 661.66 keV and 1460.81 keV, respectively.

The experimental setup was composed by two Ortec HPGe detectors, shielded from environmental background by using lead shields with copper, and tin lining and integrated digital electronics. The first was a negative biased detector (GMX) with FWHM of 1.94 keV, peak to Compton ratio of 65:1 and relative efficiency of 37.5% at 1.33 MeV ($^{60}\text{Co}$). The second one was a positive biased detector (GEM) with FWHM of 1.85 keV, peak to Compton ratio of 64:1 and relative efficiency of 40% at 1.33 MeV ($^{60}\text{Co}$). The ANGLE 4 code was employed for the efficiency transfer factors calculations to the 20 mL vial sample holder geometry [16].

The Gamma Vision (Ortec) software was used for data acquisition and analysis [17]. The quality of the measurements was also demonstrated through the participation in intercomparison exercises organized by international organizations [18]. The measurement result uncertainty, coverage factor $k = 2$, was calculated taking into account the following components: uncertainty of the counting estimation, of the calibration source, of the efficiency calibration, of the background subtraction and of the $\gamma$-branching ratio [17].

The evaluation of radiological hazard effects was made in terms of the annual effective dose for wine ingestion. It was calculated by the following [19]:

$$D_{\text{ing}} \left( \frac{Sv}{y} \right) = h_{\text{ing,K-40}} J_{\text{ing,K-40}}$$

where $h_{\text{ing,K-40}}$ is the coefficient of effective dose for the insertion unit, for the ingestion of $^{40}\text{K}$ (Sv/Bq) and $J_{\text{ing,K-40}}$ is the intake of $^{40}\text{K}$ (Bq/year) [19]. The latter value was obtained by multiplying the mean annual wine consumption for the activity concentration of the investigated radionuclide experimentally measured.

2.3. ICP-MS Analysis

The concentration of Cu (isotope $^{63}\text{Cu}$), Zn ($^{66}\text{Zn}$), Pb ($^{208}\text{Pb}$), B ($^{11}\text{B}$), As ($^{75}\text{As}$) and Cd ($^{111}\text{Cd}$) was obtained through Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis with a Thermo Scientific iCAP Qc ICP-MS. The limit of quantification (LOQ) is 5 µg/L, 10 µg/L, 0.5 µg/L, 10 µg/L, 1 µg/L and 0.1 µg/L for Cu, Zn, Pb, B, As and Cd, respectively.

The instrument operating parameters are reported in the Table 2.

| ICP-MS Operating Parameters | 1550 W |
|----------------------------|--------|
| Forward power              | 1550 W |
| Nebuliser gas              | 0.98 L/min |
| Auxiliary gas              | 0.8 L/min |
| Cool gas flow              | 14.0 L/min |
| Collision cell gas He      | 4.5 mL/min |
| Sample uptake/wash time    | 45 s each |
| Optimized dwell times per analyte | 0.01 s. |
| Point per peak             | One |
| Repeats per sample         | Three |

The ICP-MS was operated in a single collision cell mode, with kinetic energy discrimination (KED), using pure He as the collision gas [20]. For the analytes determination in wine where sample turbidity
was <1 NTU, the sample was considered ready for analysis by appropriate addition of Carlo Erba ultrapure nitric acid (67–69%). Sample material in solution was introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization and ionization. Ions were extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. Interferences relating to the technique were recognized and corrected through compensation for isobaric interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of the internal standard Ultra Scientific ICM-810 (Sc, Y, In, Tb, Bi at 100 ppm in 2% HNO₃) [21].

3. Results and Discussion

3.1. Radioactivity Analysis

The specific activity of $^{40}$K in the investigated wine samples is reported in the Table 3.

| Sample ID | $^{40}$K (Bq/L) | $^{137}$Cs (Bq/L) |
|-----------|----------------|------------------|
| S1        | 1784 ± 62      | <0.10            |
| S2        | 1826 ± 63      | <0.09            |
| S3        | 1758 ± 61      | <0.08            |
| S4        | 1837 ± 126     | <0.09            |
| S5        | 1794 ± 174     | <0.10            |
| S6        | 1798 ± 167     | <0.10            |
| S7        | 1670 ± 174     | <0.07            |
| S8        | 1825 ± 136     | <0.08            |
| S9        | 1724 ± 68      | <0.10            |
| S10       | 1830 ± 149     | <0.10            |
| S11       | 1714 ± 108     | <0.09            |
| S12       | 1709 ± 68      | <0.08            |
| S13       | 1776 ± 120     | <0.08            |
| S14       | 1679 ± 60      | <0.10            |
| S15       | 1623 ± 116     | <0.08            |
| S16       | 1697 ± 126     | <0.09            |
| S17       | 1717 ± 134     | <0.09            |
| S18       | 1595 ± 66      | <0.08            |
| S19       | 1723 ± 120     | <0.09            |
| S20       | 1712 ± 156     | <0.09            |

$^{40}$K levels ranged from a low 1595 Bq/L for S18 to a high of 1837 Bq/L for S4.

Potassium is a mineral element present in grapes and wine, also used as a fertilizer in the vineyard [22]. Much of the potassium in wine comes from potassium in the soil where the vines are grown. As the vines grow, they absorb the potassium in the soil; for this reason, many grape growers add potassium to the soil because it can produce a large crop of wine grapes [23]. Also, the potassium sorbate, used to preserve certain types of wine, can increase the potassium content [24]. The vinification process directly influences the amount of potassium kept in the alcoholic beverage [25]. Some processes, such as ion exchange in which potassium is exchanged with sodium, decrease the amount of potassium in the drink. Removal of potassium ions helps prevent crystallization [26].
Regarding $^{137}$Cs, its activity concentration in all analyzed samples was lower than the minimum detectable activity value, as reported in the Table 3, thus excluding an anthropogenic radioactive contamination of the investigated samples.

### 3.2. The Annual Effective Dose for Ingestion

To evaluate the human health risk, the estimation of the annual effective dose due to the ingestion of investigated samples, as calculated by Equation (1), for the age category higher than 18 years, was performed and experimental results are reported in the Table 4. Assuming an average yearly consumption in Italy of about 35 L [27], the annual effective dose due to the wine ingestion ranged from a low 0.346 mSv/y for S18 to a high of 0.399 mSv/y for S4.

**Table 4.** The annual effective dose due to the ingestion of investigated samples for the age category higher than 18 years.

| Sample ID | $D_{\text{ing}}$ (mSv/y) |
|-----------|--------------------------|
| S1        | 0.387                    |
| S2        | 0.396                    |
| S3        | 0.382                    |
| S4        | 0.399                    |
| S5        | 0.384                    |
| S6        | 0.387                    |
| S7        | 0.362                    |
| S8        | 0.395                    |
| S9        | 0.374                    |
| S10       | 0.397                    |
| S11       | 0.372                    |
| S12       | 0.371                    |
| S13       | 0.385                    |
| S14       | 0.364                    |
| S15       | 0.352                    |
| S16       | 0.368                    |
| S17       | 0.373                    |
| S18       | 0.346                    |
| S19       | 0.374                    |
| S20       | 0.372                    |

These values are under allowable levels (1 mSv/year) [28] for all investigated samples and therefore there is no risk of ionizing radiation effects on humans.

The evaluation of human health risk due to the ingestion of investigated samples for age categories lower than 18 years was not performed, because the ingestion of wine is not recommended in Italy [29].

### 3.3. Mineral Contents

Element concentrations, determined by ICP-MS in the twenty analyzed wine samples, are reported in the Table 5. The investigated elements in wine have very different origins: groundwater, fertilizers, air pollution, winemaking, aging, bottling. The amount of Zn and Cu comes naturally from the soil and can be also a consequence of pesticides addition. B content depends on the ground where the grapes are produced, fertilizers and equipment used during wine-making. The presence of As, Pb and Cd is due to the filtration process. The metals concentrations reported in the present article are in very good agreement with values reported in literature for European wines [30] and lower than the contamination threshold value reported in the Italian Legislation [31].
Table 5. Element contents, determined by ICP-MS in the twenty investigated wine samples.

| Sample ID | Cu (µg/L) | Zn (µg/L) | Pb (µg/L) | B (µg/L) | As (µg/L) | Cd (µg/L) |
|-----------|-----------|-----------|-----------|----------|-----------|-----------|
| S1        | 59        | 507       | 4         | 8443     | 2         | 0.17      |
| S2        | 53        | 672       | 59        | 8949     | 6         | 0.25      |
| S3        | 60        | 492       | 27        | 7685     | 9         | 0.23      |
| S4        | 43        | 967       | 42        | 7635     | 6         | 0.32      |
| S5        | 52        | 751       | 24        | 8600     | 17        | 0.34      |
| S6        | 85        | 826       | 29        | 8977     | 7         | 0.25      |
| S7        | 62        | 546       | 5         | 7751     | 5         | 0.22      |
| S8        | 81        | 473       | 44        | 9429     | 17        | 0.19      |
| S9        | 456       | 634       | 19        | 9489     | 35        | 3.7       |
| S10       | 137       | 547       | 18        | 7383     | 7         | 0.25      |
| S11       | 77        | 551       | 3         | 2696     | 2         | 0.34      |
| S12       | 14        | 289       | 5         | 4914     | 4         | 0.32      |
| S13       | 43        | 409       | 9         | 4773     | 13        | 0.30      |
| S14       | 37        | 478       | 14        | 7501     | 7         | 0.22      |
| S15       | 80        | 679       | 11        | 4326     | 9         | 0.32      |
| S16       | 19        | 371       | 7         | 3825     | 4         | 0.31      |
| S17       | 22        | 837       | 11        | 4532     | 6         | 0.37      |
| S18       | 187       | 560       | 5         | 4114     | 5         | 0.21      |
| S19       | 20        | 352       | 4         | 1995     | 3         | 1.06      |
| S20       | 54        | 590       | 3         | 4758     | 5         | 0.27      |

Contamination threshold 1000 5000 200 10,200 200 10

4. Conclusions

In this article authors evaluated the radioactivity and heavy metals amount in twenty different samples of Italian wines, belonging to controlled origin denomination (DOC) geographic areas of the Calabria region, south of Italy.

The activity concentration of the main natural radionuclide present, $^{40}$K, was measured using HpGe gamma spectrometry, with the aim to estimate the health risk, for the age category higher than 18 years, by the effective dose due to their ingestion. The coefficient of the effective dose for ingestion was reported by the Italian Legislative Decree 230/95 and successful modifications. The calculated annual effective dose was found to be under allowable levels (1 mSv/year), thus excluding the risk of ionizing radiation effects on human beings.

The anthropogenic radioactivity was evaluated through the $^{137}$Cs specific activity measurement. It was lower than the minimum detectable activity value, thus excluding its presence as a pollutant.

With regards to the metal’s concentration, it was lower than the contamination threshold value for Cu, Zn, Pb, B, As and Cd, thus excluding their presence as contaminants.

Author Contributions: F.C. performed gamma-spectrometry analysis, collected data, designed the study and drafted the manuscript; A.B. and M.D. contributed to perform gamma-spectrometry analysis; M.M. performed ICP-MS analysis; L.S. contributed to perform ICP-MS analysis; G.B. and D.P. supervised the study.

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