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Radioactivity measurements applied to the dating and authentication of old wines

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Abstract

For many years the neutrino group in the CENBG has been involved in the development of low background γ-ray spectrometers, based on the use of HPGe crystals. When applied to radioactivity measurements of wine in bottles, it has been shown that besides the well-known isotope ^{40}K, the wine contains also trace amounts of ^{137}Cs (less than 1 Bq/l) with an activity depending on the vintage. This technique has thus led to the possibility to date the wine bottles of vintages between 1952 and ∼1980 and to verify the year written on the label or on the cork. Since the measurements do not require opening the bottle, the technique has also proved to be very useful for detecting counterfeit wines of the XIXth century and first half of the XXth century. ***To cite this article: Ph. Hubert et al., C. R. Physique 10 (2009).***

Résumé

Mesures de radioactivité appliquées à la datation et à l'authenticité des vins. Depuis maintenant de nombreuses années, le groupe neutrino du CENBG s'est fortement impliqué dans le développement de la spectrométrie gamma bas bruit de fond basée sur l'utilisation des cristaux de Ge hyper purs. Appliquée aux mesures de radioactivité du vin, il a été montré que le vin contenait, comme attendu, l'isotope ^{40}K, mais aussi des traces faibles de ^{137}Cs (<1 Bq/l) dont l'activité est dépendante du millésime. Par suite, la technique a ouvert la possibilité de dater les vins millésimés entre 1952 et ∼1980 et ainsi de vérifier les dates inscrites sur les étiquettes ou les bouchons. De plus, comme les mesures n'imposent pas nécessairement l'ouverture de la bouteille, la technique s'est aussi révélée très utile pour rechercher les fausses bouteilles datant du XIX^{e} siècle ou de la première moitié du XX^{e} siècle. ***Pour citer cet article : Ph. Hubert et al., C. R. Physique 10 (2009).***

Keywords: Radioactivity; Gamma spectrometry; ^{137}Cs; Wine dating; Authentication of old wines

Mots-clés : Radioactivité ; Spectrométrie gamma ; ^{137}Cs ; Datation du vin ; Authentification

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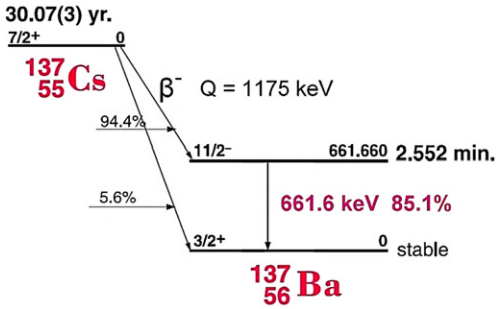

Fig. 1. Decay scheme of the ^{137}Cs nucleus to the daughter nucleus ^{137}Ba. A typical gamma ray of 661 keV is emitted in 85.1% of the decays.

1. Introduction

As is well known, the radioactivity process corresponds to the spontaneous transformation of a nucleus into a daughter nucleus with emission of a beta or alpha particle. Most of the time these decays are followed by one or several gamma rays whose energies are typical of the decaying nucleus. As an example, Fig. 1 gives the decay diagram of ^{137}Cs where it is shown that this nucleus decays by electron emission with 5.6% probability to the ground state of the daughter nucleus ^{137}Ba, and 94.4% to its first excited state. This excited state then decays to the ground state by emission of a well-known 661.7 keV gamma ray with an 85.1% probability. Another example is given by the ^{40}K nucleus which decays with a 10.7% probability by electronic capture to the first excited state of ^{40}Ar. This state then decays to the ground state by emission of a well-known 1460.8 keV gamma ray. The detection of these lines with a high energy resolution gamma spectrometer indicates the presence of these radioactive nuclei in the measured sample. Moreover, the intensities of the lines are directly related to the activity (in Bq/kg) or number of radioactive nuclei present in this sample.

In nature, every material contains some radioactivity. For example, pure water contains only a few Bq/l of tritium, a pure beta emitter with a low $Q_\beta = 18$ keV value (Q_β is the amount of energy released in the β decay), which is rather difficult to measure. On the contrary, 1 kg of dried sediment can contain a few hundred of Bq of U, Th or ^{40}K, depending on its geological location. There are mainly three different origins for the radioactivity:

(1) ^{238}U, ^{235}U, ^{232}Th and their daughters (Th, Ra, Bi, Pb and Po isotopes) and ^{40}K. Their half-life $T_{1/2}$ being of the order of the age of the Earth, they are naturally present in the soil or in the plants. The activities reflect generally the chemical and physical properties of the soil.
(2) Cosmic radiation which, when entering the Earth atmosphere, creates radioactive nuclei like ^{14}C, ^{7}Be, tritium, etc. Usually this activity is rather weak, in the mBq/kg range.
(3) Human activity like nuclear atmospheric tests, nuclear power plants, and all the radioisotopes used in industry or in medicine. Typical radio elements are the fission products ^{137}Cs, ^{90}Sr, ^{60}Co, etc.

Nowadays radioactivity measurements are of common use in various disciplines ranging from fundamental physics to medicine, industry, environmental sciences, archeology, and so on. In the present article we will show that the low background gamma-ray spectrometry technique can also be applied to dating and authentication of rare and expensive wines. Moreover, we will emphasize that these analyses can be carried out without opening the bottles and finally we will give a few examples where the technique has been successfully applied.

2. Wine forgery versus radioactivity measurements

Since the beginning of the 1980s the prices of old and fine wines have been continuously soaring, the world record being a bottle of Mouton-Rothschild 1787, supposed to have been ordered by Thomas Jefferson himself, which was sold in an auction for $ 156,000 in 1985 [1]. Of course, most of these bottles are not bought for drinking, but will join a museum, an exhibition or a private collection.

Nevertheless, even now, some old bottles mainly dating from the XIXth century or the beginning of the XXth century can reach a few thousand dollars. Most of the time these very high prices concern a limited number of

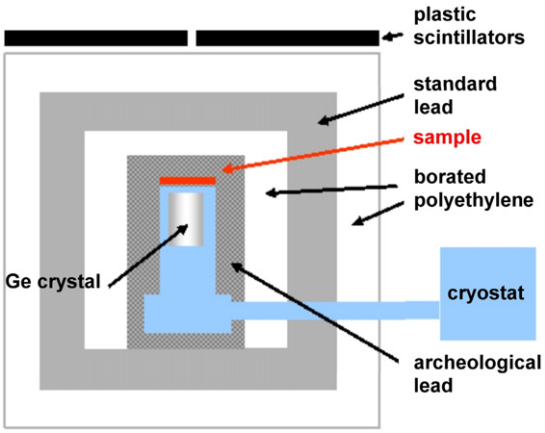

Fig. 2. Schematic drawing of the installation of a low background Ge spectrometer at the University of Bordeaux.

châteaux, like the world famous Pétrus in Pomerol, Yquem in Sauternes, Lafite-Rothschild and Mouton-Rothschild in Médoc, Romanée-Conti in Bourgogne and a few others. They are very often drunk during fancy wine tasting parties which gather critics, collectors and wine "amateurs".

As for any expensive material, it has been, or is still very tempting and valuable for some people to launch on the market a small number of fake bottles. Detecting these bottles is almost impossible, especially if the glass, the label, the cork and the capsule have been retrieved from an authentic bottle. The problem of fraud in wine has always been a concern for professionals. Since chemical analyses have revealed to be unsuccessful and wine tastings can lead to biased results, they thought to use radioactivity measurements where the main idea is to try to date the wine, since the decay period of a radioisotope can give a time parameter. Already in 1954 Kaufman and Libby used tritium ($T_{1/2} = 12.3$ y) to date several French and Italian wines [2]. About 25 years later, P. Martinière et al. [3] (see also B. Médina in Ref. [4]) used the ^{14}C isotope to date several Bordeaux wines. The procedure is based on the fact that the amount of ^{14}C in the atmosphere increased by about a factor of two after the atmospheric nuclear tests (1950–1963), and thereafter decayed regularly. Although successful, these techniques have some drawbacks, the first one being the necessity to open the bottles since these radioisotopes are pure beta emitters. And an opened bottle has no value, except for the wine taster himself! Then the preparation of a sample, usually from distillation, can be rather tedious. Moreover the tritium technique is nowadays more difficult due to the fallout from nuclear reactors, and the ^{14}C technique can give a wrong dating result where there has been the addition of a product such as sugar. Therefore it became quite important and urgent to try to find another technique, and we started to measure gamma activities in several bottles of wine.

3. The low background gamma spectrometry

Beside the tritium and ^{14}C, several other radioactive nuclei are currently encountered in nature (and in wine) most of them being also gamma emitters. Therefore arose the idea to measure wine samples through gamma spectrometry with HPGe crystals. The high energy resolution (∼0.2%) and good detection efficiency (a few % depending on the crystal volume and geometry) allow easy isotope identification and activity measurement. Moreover, our group at the University of Bordeaux has several years experience in the development of low background gamma-ray spectrometers. The expression "low background" in terms of sensitivity means being able to measure activities between 5 and 6 orders of magnitude less than the average level in nature, i.e., around 1 mBq/kg depending on the isotope and nature of the sample. In order to be able to measure these very low activities, the Ge spectrometer is generally placed in an underground laboratory; the cryostat is made with highly selected "non-radioactive" materials and is surrounded by heavy shielding [5]. The internal shield usually consists of 5 cm thick archeological or old lead which does not contain any ^{210}Pb activity, and the external one of 10 cm of standard lead (Fig. 2).

At the University of Bordeaux the Ge spectrometers are installed in the basement of a research building, i.e. with only ∼3 m water equivalent in protection against the cosmic rays. Therefore a 10 cm layer of borated polyethylene is introduced between the two lead layers in order to minimize the effect of neutrons, and finally an active veto made

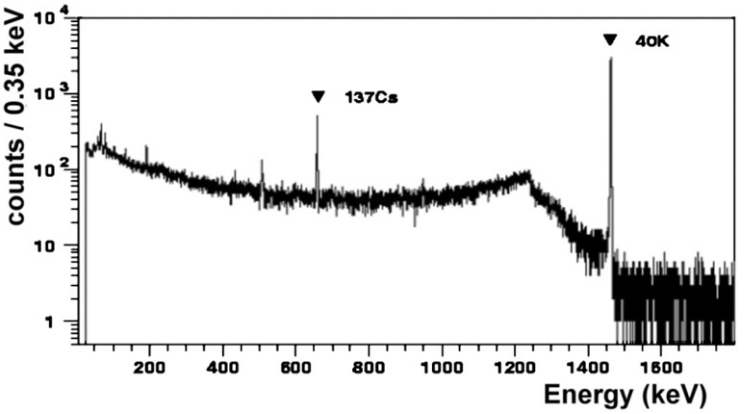

Fig. 3. Typical gamma energy spectrum of a wine sample after evaporation and reduction into ashes.

of several plastic scintillators coupled to photomultiplier tubes is added in order to minimize the effect of the cosmic rays. Under these experimental conditions the total counting rate of the spectrometer is around few counts/mn in the energy range 30 keV–3 MeV and the sensitivity around 1 mBq/kg depends on the isotope and of the nature of the sample (geometry, density, presence of ^{40}K, etc.), which is enough for our application.

After achievement of the low background gamma-ray spectrometry, we were asked few years ago by the DGCCRF[1] to look at the possibility of dating the bottles of wine using this technique.

4. Gamma spectrometry of Bordeaux red wines

Since at the beginning we did not have any idea about the type of radioactive isotopes and their activities to be encountered in a wine, it was decided to carry out the first measurements with the best available sensitivity. This implied reducing wine samples through evaporation and then burning the residue into ashes. Fig. 3 shows a typical gamma spectrum registered with a wine from the 1960s. As expected, the first results showed that wine essentially contains the isotope ^{40}K at the level of 30 Bq/l, which corresponds to about 0.9 g of natural potassium per liter of wine. Also, the presence of very weak lines at low energy (238 keV from ^{212}Pb and 351 keV from ^{214}Pb not shown in Fig. 3) is easily explained by the presence of radium isotopes at the mBq/l level. All these isotopes decay with very long periods and cannot be used for dating on a human scale. But far more surprising was the fact that certain bottles also contain weak (<1 Bq/l) but easily measurable ^{137}Cs ($T_{1/2} = 30$ y) activities. And even more interesting was the fact that these activities were found to vary as a function of the year. After these first encouraging results, we investigated the possibility to find a set of certified "*millésimes*" and to carry out their measurements. For easier convenience, we restricted our sample only to red Bordeaux wines. A reference curve was readily obtained [6] and the updated curve is displayed in Fig. 4. It shows that the ^{137}Cs activity starts to be observable in wines from the beginning of the 1950s, reaches a maximum in 1963, date of the signature of the Partial Test Ban Treaty limiting atmospheric nuclear tests, and then decays down to 1986, date of the Chernobyl accident.

The reservoir of the ^{137}Cs radioisotope is the upper atmosphere. With rain, aerosols, and dust the Cs nuclei fall not only on the soil, but also on the leaves and the grapes. Moreover, in the Bordeaux area, the ^{137}Cs activity on the surface of the soil ranges from $\sim$1 up to 10 Bq/kg depending on the location of the vineyard. Due to work in the wine fields with tractors and similar professional tools, some additional dust finds its way onto the grapes. Since the main reservoir is the upper atmosphere, we expect about the same ^{137}Cs behavior for all wines in the northern atmosphere, with the exception of the "Chernobyl" peak, since it is well known that the fallout after this accident was extremely dependent upon the geographical site. This point was checked with the measurement of a few wines from different areas and different vintages in France, and also of a few French 1986 bottles [6].

[1] *Direction Générale de la Concurrence, de la Consommation et de la Répression des Fraudes*, a French government agency charged with protecting consumers, assuring fair competition and preventing fraud.

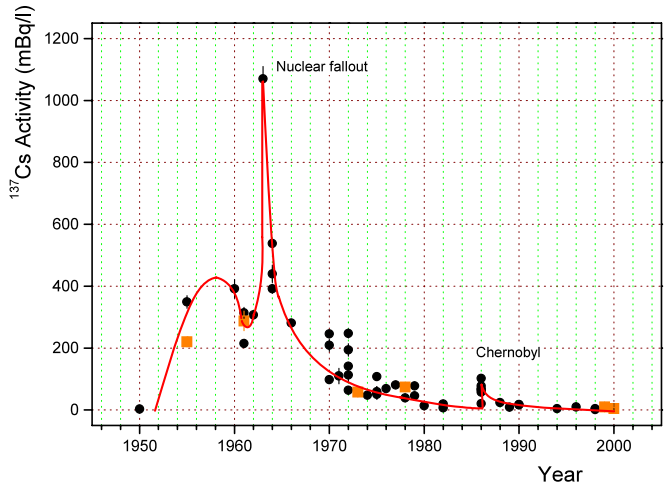

Fig. 4. Activity (mBq/l) of the ^{137}Cs radioactive isotope as a function of the wine vintage. All activities are for Bordeaux wines only, and are normalized to an arbitrary date, January 1st, 2000. The solid circles correspond to measurements after reduction of the wine into ashes, the orange squares correspond to nondestructive measurements, i.e., without opening the bottles (see text). Statistical errors are generally smaller than the dimension of the points.

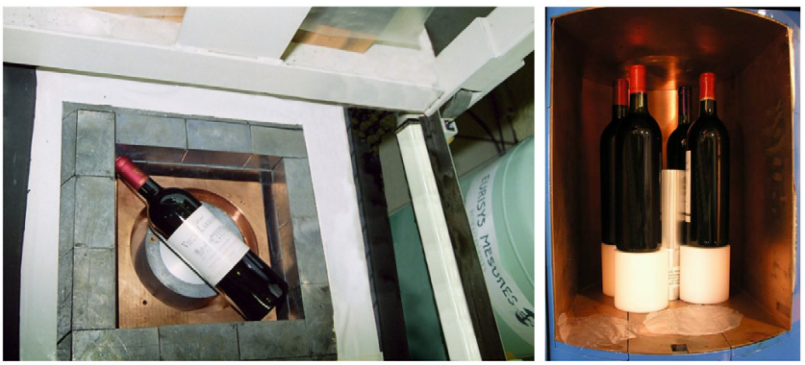

Fig. 5. Photographs of two different set-ups use for nondestructive gamma measurement of a bottle of wine.

Note that no ^{137}Cs activity has ever been found in the glass of the bottles, which is easily understood since Cs evaporates around 500 °C. Also, some very weak ^{137}Cs activity has been found in the cork, but too weak to explain the quantity observed in the wine. However, it has been used to prove that an old bottle has been re-corked more recently.

Evidently, this reference curve can be used to verify the wine vintage and also to look for counterfeit wines. For example a 1960 wine must contain around 400 mBq/l (normalized to January 1st, 2000) of ^{137}Cs. If the date 1960 is written on the label and/or the cork, and if we measure a ^{137}Cs activity around 50 mBq/l, this means that the wine is probably much younger, or has been mixed with a very young vintage. Also, it shows that any wine older than 1952 should not contain any ^{137}Cs activity. This point is very interesting since, as already pointed out above, most of the expensive wines are from the XIXth century or the first half of the XXth century, and most of the fake bottles appeared on the market after 1980, the time when the prices of wine started to soar.

Soon after having obtained the reference curve, we realized that the measurement could be carried out without opening the bottle, since the 661 keV gamma ray of the ^{137}Cs decay easily escapes the wine and crosses the glass before being detected (losses are only a few percent). Fig. 5 shows the photos of two different experimental set-ups used for our application and Fig. 6 gives an example of a gamma spectrum recorded in this way.

Comparison with Fig. 3 shows that in this case the spectrum contains many more lines due to the rather high level of radioactivity in the glass (^{40}K, U, Th, Ra and their daughters), but the ^{137}Cs line is still present. As a consequence

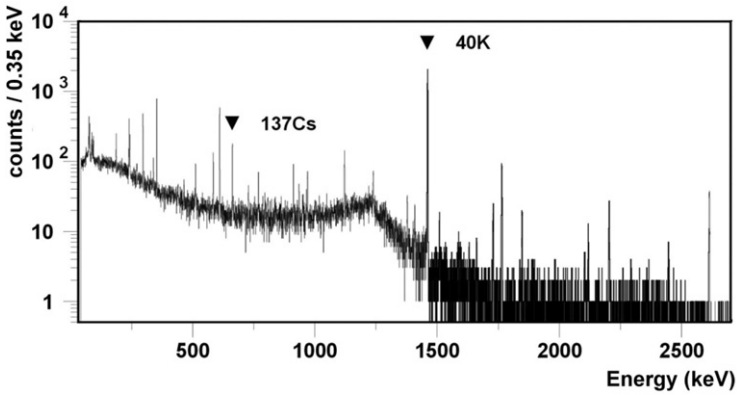

Fig. 6. Gamma spectrum of a bottle of wine in one of the geometries shown in Fig. 5. The Cs line is clearly seen, and all the other lines are mainly from the natural radioactivity of the glass.

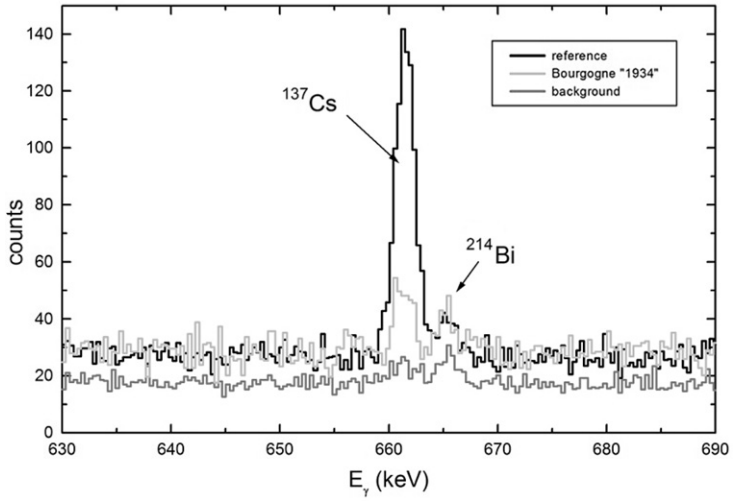

Fig. 7. Partial gamma spectra showing the ^{137}Cs line recorded with three different bottles: first with a 1963 Médoc used as a reference, second with a 2003 Bordeaux red wine for a background measurement, and third with a labeled 1934 Bourgogne. Note that the small line at 666 keV belongs to the ^{214}Bi, a daughter of the ^{226}Ra present in the glass of all bottles.

such a nondestructive measurement implies a serious loss of sensitivity, first because of the much larger solid angle of the source, and second because of the increase of the level of background below the ^{137}Cs line. Nevertheless a few new measurements were carried out under these experimental conditions, and the results are given as square points in Fig. 4. There is a rather good agreement between the destructive and nondestructive measurements.

5. Some examples of application

As a first example of an application of the technique, Fig. 7 shows the partial spectra recorded under three different conditions: first with a bottle of Médoc 1963 that we use for reference and which contains 1340 mBq/l (in 2008) of ^{137}Cs, second with a bottle of Bordeaux 2003 used for a background measurement and third with a red Bourgogne labeled 1934. The ^{137}Cs peak at 661 keV is clearly visible in the Bourgogne spectrum, showing immediately that this bottle is a counterfeit.

As a second example, Fig. 8 shows the measurement of three magnums of Bordeaux red wines. One is a Fronsac 1964 used as a reference; while the two others are supposed to be 1945 Bordeaux vintages. It is clear that one of these bottles is a counterfeit, while the other may be authentic.

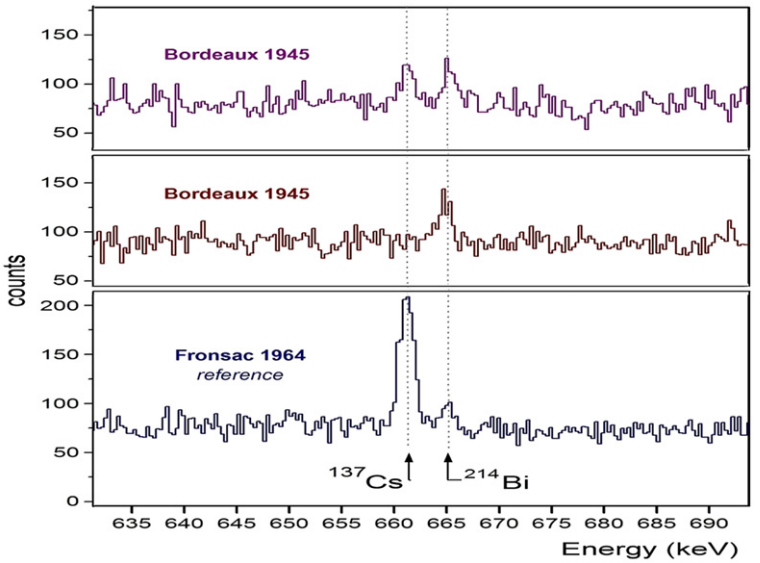

Fig. 8. Partial gamma spectra showing the ^{137}Cs line recorded with three different magnums: first with a magnum of Fronsac 1964 used as reference and second with two 1945 magnums of Bordeaux red wine. Clearly one is a counterfeit, while the other may be authentic.

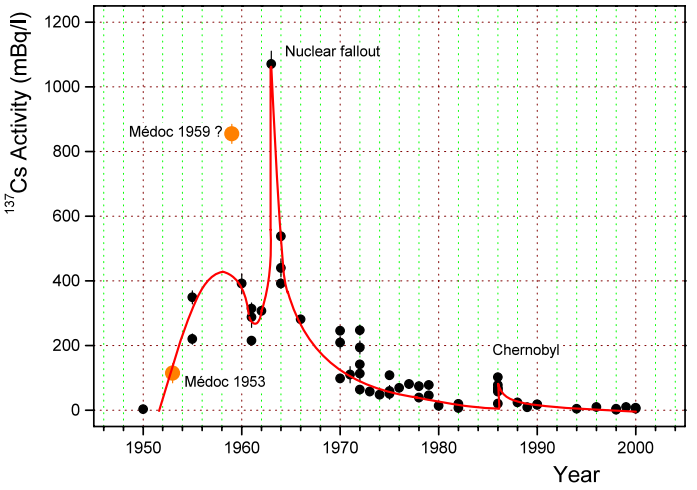

Fig. 9. ^{137}Cs activities measured in two magnums of Médoc with vintage 1953 and 1959 in comparison with the reference curve.

The third example (Fig. 9) is taken from the measurement of two magnum bottles of Médoc wines, one labeled with the vintage 1953, the second with the vintage 1959. From the gamma measurements the activity for the 1953 bottle is in a very good agreement with the reference curve, while for the 1959 bottle, its activity is found to be too strong by at least a factor of 2. Probably this latter bottle was bottled with a younger wine?

Finally, the last example concerns a series of bottles labeled Mouton-Rothschild and Lafite-Rothschild and with the same vintage, 1900. Among a series of six bottles of each of these "Grand Crus" collected by the French Justice, five of them have been measured by gamma spectrometry, without opening the bottles. As reported in Fig. 10, all the bottles contain some ^{137}Cs activity and are therefore counterfeits. Moreover, the activities are different from one bottle to the other, showing that probably different mixings have been done. Note that the bottles number 5 (absent in Fig. 10) were analyzed only through the ^{14}C technique. Their dating has been found in very good agreement with the ^{137}Cs results, i.e., vintages of the 1960s.

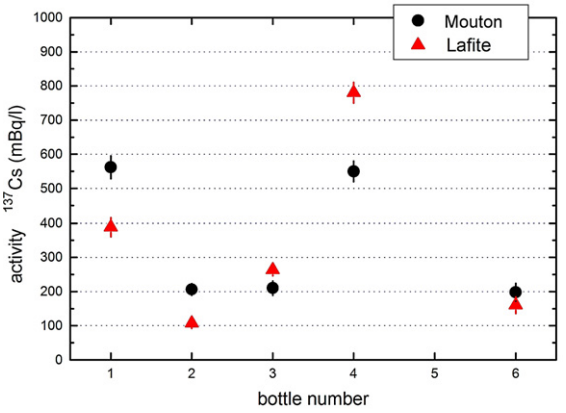

Fig. 10. Results of the gamma measurements of a series of bottles labeled Mouton-Rothschild and Lafite-Rothschild 1900. All these bottles contain measurable quantities of ^{137}Cs and are therefore counterfeit. Note that the activities (normalized to the same arbitrary date, January 1st, 2000) are different from one bottle to another, showing that different mixtures were made.

6. Conclusion

Using the low background gamma-ray technique it has been shown that a wine labeled from 1952 up to about 1990 contains some ^{137}Cs activity, rather weak (below 1 Bq/l) but measurable. Moreover, it has been shown, through some concrete examples, that the technique can be successful for wine dating and for counterfeit detection. The main advantage compared to the others possibilities of dating is that it does not require opening the bottle, albeit with a serious loss in the sensitivity of the measurements. We now consider that the method is validated, and as a consequence, it is currently used by the DGCCRF laboratory. With the help of the reference curve it is rather easy to calculate the amount of ^{137}Cs needed to forge a known vintage wine. However, other parameters can be used to detect fraudulent wines, like the radioactivity of the glass of the bottle and/or other radioactive isotopes naturally present in the wine.

In case of young wines where prices are not so expensive, or if the taste of old bottles is expected to be very bad, the bottle can be opened. After reduction of the wine into ashes, the sensitivity of the ^{137}Cs measurement becomes much better, down to few mBq/l. Also, in this case other analyses can be carried out, such as tritium, ^{14}C or even ^{210}Pb ($T_{1/2} = 22$ y) measurements. This latter one is particularly interesting because of its period close the age of a human generation. However, its activity is rather low (<100 mBq/l), the emitted gamma ray at 46 keV has a weak intensity (4%) and the ^{40}K nuclide in the wine induces a large background due (1) to the Bremsstrahlung of the beta decay to the ^{40}Ca nucleus, and (2) to the Compton of the 1460 keV gamma ray emitted in the decay to the ^{40}Ar nucleus. Anyway, it can be detected with the present sensitivity of our low background Ge spectrometers, but special developments have still to be done in order to improve the accuracy of the measurements and before validating this new possibility.

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References

[1] B. Wallace, The Billionaire's Vinegar, Crown, 2008.
[2] S. Kaufman, W.L. Libby, Phys. Rev. 6 (1954) 1337.
[3] P. Martinière, et al., Annales des falsifications, de l'expertise chimique et toxicologique 72 (1979) 263.
[4] B. Médina, Wine authenticity, in: P.R. Ashurst, M.J. Dennis (Eds.), Food Authentication, Blakie Academic & Professional, London, 1996, p. 60.
[5] R. Torrès, Développements et performances d'un spectromètre Ge bas bruit de fond au niveau de la mer, Thèse Université de Bordeaux 1, 1998.
[6] Ph. Hubert, et al., Annales des falsifications, de l'expertise chimique et toxicologique 94 (2001) 357.