



Possibility of wine dating using the natural Pb-210 radioactive isotope



Ph. Hubert ^a, M.S. Pravikoff ^{a,*}, J. Gaye ^b

^a Centre d'Études Nucléaires de Bordeaux-Gradignan (CENBG), IN2P3 and Université de Bordeaux, 19 Chemin du Solarium, F-33175 Gradignan Cedex, France

^b Service Commun des Laboratoires, Laboratoire de Bordeaux-Pessac de la DGCCRF, 3 avenue du Dr Albert Schweitzer, F-33600 Pessac, France

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ABSTRACT

To control the authenticity of an old wine without opening the bottle, we developed a few years ago a method based on the measurement of the ¹³⁷Cs activity. However, for recent vintages, the ¹³⁷Cs activity drops to far too low values (most of the time less than 10 mBq/L for a 10-year-old wine) for this method to perform correctly. In this paper we examine the possibility to date wines using the natural radioelement ²¹⁰Pb which has a 22-year period. This new method we propose implies the opening of the bottle and the follow-on destruction of the wine itself, which means that it can only be used for investigating non-expensive bottles or wine lots where there are multiple bottles of the same provenance. Uncertainties on the resulting ²¹⁰Pb radioactivity values are large, up to more than 50%, mainly due to local atmospheric variations, which prevents us to carry out precise dating. However it can be used to discriminate between an old wine (pre-1952) and a young wine (past-1990), an information that cannot be obtained with the other techniques based on other isotopes (¹³⁷Cs, ¹⁴C or tritium).

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1. Introduction

Almost 15 years ago it was shown that it is possible to date a wine through the activity measurement of the radioactive isotope ¹³⁷Cs ($T_{1/2} = 30$ y) using the low background gamma-ray spectrometry technique (Hubert et al., 2001, 2009). The method proves very useful for vintages from 1952 to 2000, 1952 being the year when the ¹³⁷Cs 661 keV gamma line was to be observed in a gamma-ray spectrum for the very first time. Going further onwards in time, from 2000 to present days, the ¹³⁷Cs activity is far too feeble to be observed in the gamma spectra. On the contrary, finding a ¹³⁷Cs signal in an assumed pre-1952 bottle is a definitive proof that one deals with a tampered wine.

This ¹³⁷Cs dating technique method gives insight into highly-priced allegedly vintage wines without opening the bottle, which is a prerequisite for avoiding costly investments. Its limitations regarding dating younger wines has triggered the idea to look for other isotopes. If one sticks to non-destructive methods, there is no other usable gamma-ray emitting radio-isotope. On the other hand, if opening a bottle of a young wine for tests is possible, candidates

are tritium (³H) ($T_{1/2} = 12$ y), ¹⁴C ($T_{1/2} = 5730$ y), ⁹⁰Sr ($T_{1/2} = 28$ y) and ²¹⁰Pb ($T_{1/2} = 22$ y).

Tritium was already used in 1954 (Kaufman and Libby, 1954) for wines younger than 25 years of age. Measurement of wine with ³H by Schönhofer was also performed in the early 1990s (Schönhofer, 1992). This method is applied nowadays in the case of alcohols like Cognac, Armagnac or Calvados. However, tritium measurements are hampered by nuclear fallouts and the spreadout of nuclear power plants.

Dating wines and alcohols with ¹⁴C dates back to 1970 when it was investigated by the Oenology Laboratory in Bordeaux (Martinière et al., 1979). It was performed in Austria with AMS (Accelerator Mass Spectrometry) in the 1990s (Schönhofer, 1992) and in Lyon, France with liquid scintillators (Centre de Datation par le RadioCarbone). The technique produces quite good results, the drawback is its complexity. Nonetheless, renewed interest for the authentication of red wine vintage using bomb-pulse ¹⁴C has emerged in the last few years (Asenstorfer et al., 2011). It still is not a straight-forward method, but a quite robust and reliable one according to the authors.

⁹⁰Sr, like ¹⁴C and tritium is a β -pure emitter and remains to be studied for wine dating. However, as also a fission product, the same behavior as for ¹³⁷Cs is expected.

What is left is ²¹⁰Pb with a half life of 22 years. As gamma-ray emitters, apart from ²¹⁰Pb, only two other radio-isotopes of

* Corresponding author. Tel.: +33 557 120 852.

E-mail address: pravikof@cenbg.in2p3.fr (M.S. Pravikoff).

natural origin, show up in wine measurements: ^{40}K , ^{226}Ra . The nuclide ^{40}K , although quite present at the level of 30–40 Bq/L is not useful because its half life is over one billion years. The ^{226}Ra activity is usually very weak, close or below the detection limit (<10 mBq/L). ^{210}Pb , as we will see later, is in clear excess compared to the level of ^{226}Ra (at secular equilibrium, the activity concentrations of ^{210}Pb and ^{226}Ra would be the same).

2. Material and method

The underlying concept of the ^{210}Pb dating method relies on the fact that normal air always contains a few Bq/m³ of radon gas (mainly ^{222}Rn , $T_{1/2} = 3.8$ d). Following its α -decay, the resulting nucleus ^{218}Po ($T_{1/2} = 3$ mn) is ionized and then agglomerates on the aerosols or dust particles. After several decays, what is left is the long-lived ^{210}Pb which ends up on the soil, and also on grapes and leaves, the rate of deposit being governed by local atmospheric conditions (Pietrzak-Flis and Skowronska-Smolak, 1995). ^{210}Pb is a β -emitter with a 16% branching to the ground state of ^{210}Bi ($Q_{\beta} = 63$ keV) and an 84% branching to the first excited state of ^{210}Bi , with the emission of a 46.5 keV γ -ray (total γ intensity 4.25%).

2.1. Description of the HP Ge detectors

The best apparatus for measuring the ^{210}Pb activity is a well-type, high-purity, high-efficiency low-background germanium detector like the ones at the PRISNA facility (Perrot et al., 2012). (PRISNA is an underground facility at CENBG dedicated to γ spectrometry with a shield of 5 m water equivalent made of concrete and soil.) All the materials used for the cryostat were carefully selected for zero or near zero levels of radioactivity. Moreover, the detectors are encased in a special shield made, from inside to outside, of 5 cm of Roman-time lead, 10 cm of borated polyethylene (against neutrons) and 10 cm of normal lead (against external γ -rays). On top of this setup, there is approximately 1 m² of 3 cm thick plastic scintillators acting as a cosmic veto. This combination of passive and active shields helps to lower the total counting rate between 30 keV and 3 MeV to a typical value of 10 counts/min. The detection efficiency for the 46 keV gamma for a sample set inside the well was measured experimentally with IAEA sources (Shakhashiro et al., 2012) and comforted by GEANT4 simulations (Geant4 Collaboration, 2003, 2006). It is around 60%.

2.2. Description of the ^{210}Pb extraction protocol

To reduce the amount of potassium present in the wine and the corresponding ^{40}K radioactivity contribution to the gamma spectra, we extracted the lead using an ion-exchange resin technique. The CHELEX 100 resin absorbs almost 100% of the lead under given conditions, notably a pH around 7.2. The preparation protocol was developed by the SCL (Service Commun des Laboratoires) of the DGCCRF (Direction Générale de la Concurrence, de la Consommation et de la Répression des Fraudes, a French government agency ensuring consumer protection, securing fair competition and preventing fraud) and involves opening the bottle. The main steps are given in the following paragraph. More information can be found in the corresponding bibliography (Bio-Rad, 2010; Paulson, 1986).

Lead-210 was extracted by a batch process, shaking the wine with a Chelex 100 ion-exchange resin. The extraction yield is inferred by determining lead before and after via atomic absorption spectrometry (Thermo Elemental spectrometer with GF 95 of the SCL L33 in Pessac) and stands around 90%. The procedure was:

- adjust the wine sample (between 500 and 750 mL) to a pH of 7.2 ± 0.2 with concentrated ammonia
- collect 5 mL for the before-treatment lead determination
- add to the sample 50 μg of lead (5 mL of a 10 mg/L lead solution)
- add the resin (5 g of resin for every 100 mL of sample) and stir for ~15 h
- vacuum filter the wine on an ash-less filter paper
- collect 5 mL of the filtrate for a lead determination
- oven-dry the resin for at least 5 h at 60 °C
- Insert the filter paper into the tube for the well-type germanium detector measurement.

This protocol has the advantage of extracting the ^{210}Pb content of 500–750 mL of wine into a 5 cm³ tube, enhancing de facto the sensitivity of the gamma-ray measurement.

3. Results and discussion

3.1. Direct measurements of ^{210}Pb in vine leaves and grapes

To get acquainted with the ^{210}Pb detection technique, we first measured dried vine leaves and found ^{210}Pb activities varying from few Bq/kg in May up to 100 Bq/kg at the beginning of November, right after the grape harvest and the usual rainy fall in Bordeaux. This emphasizes the atmospheric origin of the deposit. Then we reduced 360 g of grapes into ashes by heating up to 550 °C. After 4 days of gamma measurement we found a positive value for the ^{210}Pb (80 ± 25 mBq/kg) in a clear excess as compared to the ^{226}Ra activity (<5 mBq/kg). The large error on the ^{210}Pb activity is due to the high ^{40}K activity of 51 ± 5 Bq/kg (see next paragraph). Since we expected a surface deposit on the grapes, we collected 18.3 g of grape-skin sample that again we reduced to ash. The gamma measurement led us again to a positive ^{210}Pb activity of 0.87 ± 0.33 Bq/kg. Note that for this grape-skin sample, the ^{40}K activity was up to 420 ± 40 Bq/kg. From these results, it is not surprising that wine itself incorporates a certain amount of ^{210}Pb . As a result, dating wine with ^{210}Pb becomes a possibility, since once bottled, ^{210}Pb can only decrease exponentially with time according to its half-life value. However, there is concern that ^{210}Pb activity may be too dependent on the production sites and the atmospheric conditions of each year of harvest.

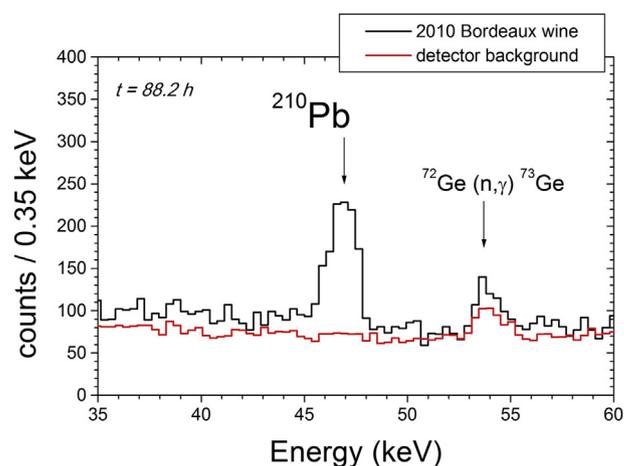


Fig. 1. Low energy part of the γ spectrum recorded for a red 2010 Bordeaux wine (690 mL) after the batch procedure described in §2.2. A 300 cm³ well type low background HPGe is used for the measurement, the time of statistics is 88.2 h and the deduced ^{210}Pb activity is 144 ± 13 mBq/L. The red curve is the background, measured for 314.3 h and scaled down to the same 88.2 h duration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

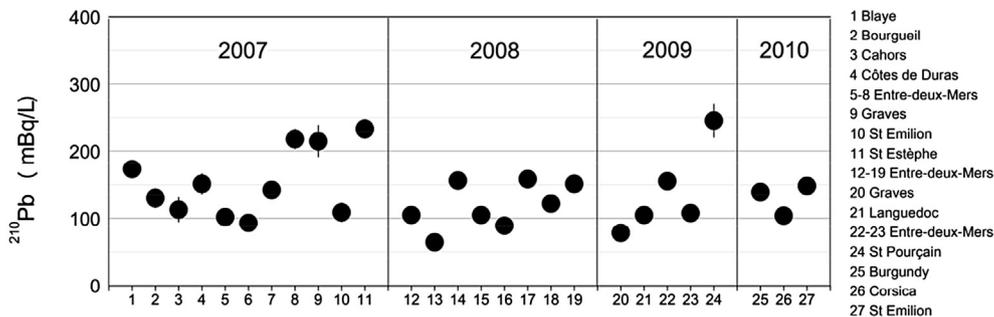


Fig. 2. Distribution of the ^{210}Pb activity in a series of 27 French red wines from vintages 2007 to 2010. The ordinate is the activity (mBq/L) calculated for the date October 1st of the year of the harvest (same year as vintage). Errors are at 1σ level and include statistics, uncertainty in the detection efficiency (5%) and in the ion-extraction yield of the lead (10%).

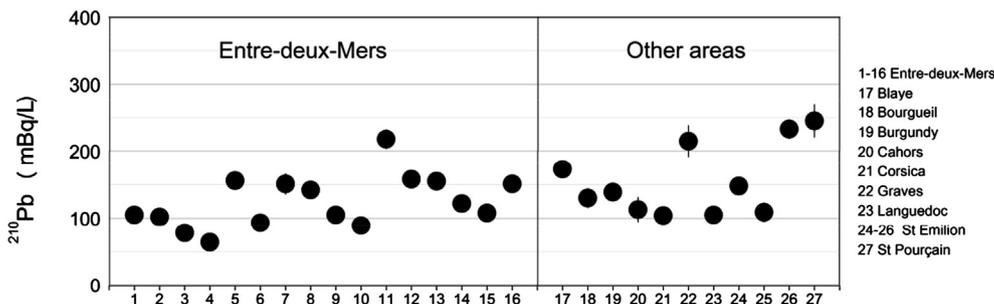


Fig. 3. Distribution of the ^{210}Pb activity in the same series of 27 French red wines as in Fig. 2, sorted by their origin: “Entre-deux-Mers” region on the left part and other wine areas on the right part.

3.2. Measurements of ^{210}Pb after ion exchange separation

These first ^{210}Pb activity measurements showed that the amount of ^{40}K in the samples severely reduces the sensitivity of the ^{210}Pb γ measurements. This naturally-occurring nucleus decays with a 10.8% branching ratio to the first excited state of ^{40}Ar , emitting the well-known 1460.8 keV γ -ray whose Compton scattering induces a rather high spectral background at low energy. Moreover, ^{40}K is also an 89.1% pure β -emitter to the ^{40}Ca nucleus ($Q_{\beta} = 1.3$ MeV), and the Bremsstrahlung of the electrons induces also a background component from low energy up to a few hundred keV. We then applied the ion-exchange resin technique to our wine samples. With this process the amount of potassium is reduced by a factor of ~ 30 . The yield of the ion exchange separation obtained by measuring the amount of lead in the wine before and after the batch operation was higher than 90%.

Fig. 1 shows the typical low energy part of a γ spectrum obtained for a 2010 red Bordeaux wine (690 mL) after 3.67 days (88.2 h) of data acquisition. In this example the amount of ^{210}Pb (measured in Feb. 2012) is 144 ± 13 mBq/L. The background (red curve) is due to the usual cosmic rays and neutrons and to the remaining ^{40}K (~ 1 Bq/kg) after the ion-exchange process. It was measured for 13.1 days (314.3 h) and shows no evidence of a line at 46 keV. For a long measurement of that duration, the limit of detection for a peak is 0.25 counts/hour, and the deduced detection sensitivity for ^{210}Pb in wines is of some 3 mBq/L.

For this study we measured a series of 40 Bordeaux red wines of different vintages and different areas (Graves, Médoc, Entre-deux-Mers, Saint-Émilion, etc.), a series of 9 French red wines from other regions (Burgundy, Corsica, Cahors, etc.) and a 1995 California wine. Most of the bottles were bought in local supermarkets. The oldest ones were obtained from private cellars. The youngest ones are from 2010 and the oldest one is a 1944 Médoc.

Fig. 2 shows the distribution of the ^{210}Pb activity for the vintages 2007 to 2010, independently of their geographical

origin. These activities are adjusted to the October 1st of the corresponding year, the usual harvest date for vine grapes. On the average, there is no strong dependence on the vintage. Within a given vintage the dispersion of the points is rather large with variations up to $\pm 50\%$. The minimum value (60 mBq/L) was for a wine produced in the “Entre-deux-Mers”, and the maximum value (238 mBq/L) for a wine coming from “Saint-Pourçain-sur-Sioule”, an area close to the “Massif Central”, known to be rather granitic with high levels of radon. But the effect of radon is not obvious: the 2010 Corsica wine has a rather low ^{210}Pb activity, even though Corsica is known to be also a high radon level area.

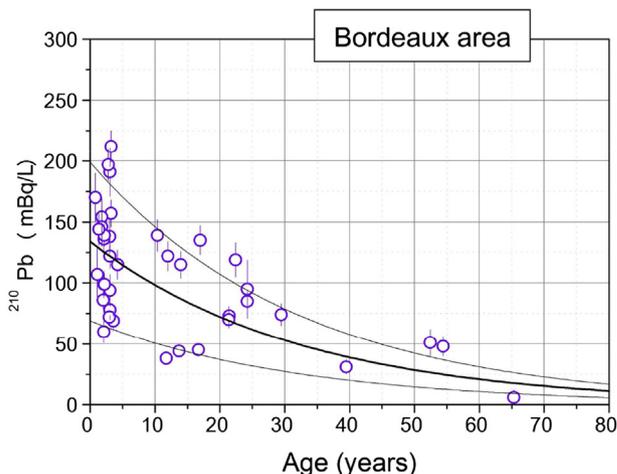


Fig. 4. Distribution of the ^{210}Pb activity in a series of 40 Bordeaux red wines as a function of the elapsed time between the date of the measurement and the year of the harvest. The last point at age 66 y is a limit of detection value. The solid lines are calculated assuming an initial activity of 134 ± 65 mBq/L and a 22.3 y half-life.

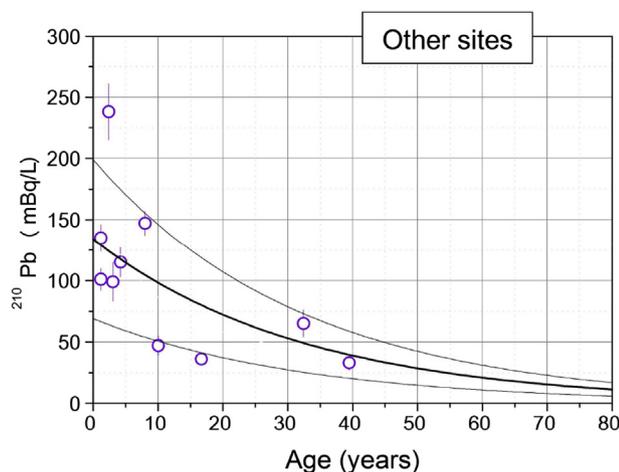


Fig. 5. Distribution of the ^{210}Pb activity in a series of 9 French red wines and the 1995 California wine as a function of the elapsed time between the date of the measurement and the year of the harvest. The solid lines are calculated assuming an initial activity of 134 ± 65 mBq/L and a 22.3 y half-life.

The left part of Fig. 3 shows again the ^{210}Pb activity distribution but just for red wines collected within the same area, namely the “Entre-deux-Mers”, independently of the vintage. On the right part is shown the same distribution but for wines collected in the 11 different geographical areas throughout France. There is no noticeable effect due to the production site.

The average A_0 value for those young red wine is 134 ± 65 mBq/L of ^{210}Pb , that is with a large dispersion which is probably connected to the variations of atmospheric conditions. As a consequence, dating a wine through the use of this isotope would prove to be rather difficult. This fact is further illustrated in Figs. 4 and 5 which show the ^{210}Pb activity as a function of the elapsed time between the date of the gamma measurement and the date of the harvest. Fig. 4 is plotted for only red Bordeaux wines whatever their vintage, while Fig. 5 is for all the other red wines.

The thick solid line is the decay curve calculated for ^{210}Pb half-life assuming an initial activity of 134 mBq/L while the two thin solid lines are the related $\pm 1\sigma$ curves. Even if most of the points fall in the area between the two thin lines, as already said above, a precise dating is not possible. However, activity measurement of this isotope is useful to decide if a wine is “young” or “old”. The best example is given by the last point in Fig. 4 which corresponds to a 1944 Médoc red wine. Its ^{137}Cs activity measured in a Marinelli geometry is less than 10 mBq/L, leading to a vintage older than 1952 or younger than 1990 according to the reference curve of Hubert et al. (2001, 2009). The fact that the ^{210}Pb activity is less than 12 mBq/L tells us immediately that this is an old bottle in agreement with the year on the label.

In that sense, activity measurement of the natural ^{210}Pb isotope is complementary to all the other techniques based on nuclear test fallouts (^{137}Cs , tritium, ^{14}C).

4. Conclusion

Gamma measurements of a series of 40 red wine bottles have shown that all of them contain a weak but measurable ^{210}Pb amount with the exception of the oldest vintage for which only a limit activity value is obtained. The origin of ^{210}Pb is natural and connected to the radon activity in the air. If our original idea was to use this isotope for dating young wines, the experimental results have shown that there exists a large dispersion in the ^{210}Pb activities, most probably connected to local atmospheric conditions. This large dispersion prevents us from using this isotope as a precise wine dating tool. However, we have shown that the ^{210}Pb activity measurement is useful to decide if a wine is a recent (around year 2000 or younger) or an old (pre-1952) vintage, which is an ambiguity not resolved by the former techniques based on ^{137}Cs , tritium or ^{14}C .

References

- Asenstorfer, R.E., Jones, G.P., Laurence, G., Zoppi, U., 2011. Authentication of red wine vintage using bomb-pulse ^{14}C . Progress in authentication of food and wine. ACS Symp. Ser. 1081 (6), 89–99.
- Bio-Rad Laboratories, 2010. Chelex 100 and Chelex 20 Chelating Ion Exchange Resin: Instruction Manual. Bio-Rad LIT200 Rev B.
- Geant4 Collaboration, 2003. Geant4, a simulation toolkit, nuclear instruments and methods in physics research section a: accelerators, spectrometers. Detect. Assoc. Equip. 506 (3), 250–303.
- Geant4 Collaboration, 2006. Geant4 developments and applications. IEEE Trans. Nucl. Sci. 53 (1), 270–278.
- Hubert, Ph., Hubert, F., Ohsumi, H., Gaye, J., Medina, B., Jouanneau, J.-M., 2001. Application de l'analyse par spectrométrie gamma bas bruit de fond à la datation des vins d'origine française. Ann. des Falsif. de l'expertise chimique Toxicol. 957, 357–368.
- Hubert, Ph., Perrot, F., Gaye, J., Medina, B., Pravikoff, M.S., 2009. Radioactivity measurements applied to the dating and authentication of old wines. C. R. Phys. 10, 622–629.
- Kaufman, S., Libby, W.F., 1954. The natural distribution of tritium. Phys. Rev. 93, 1337–1344.
- Martinière, P., Gaultier, J.-M., Sudraud, P., Severac, J., Caussanel, J.-L., 1979. Evolution de la radioactivité par le carbone 14 des vins de Gironde. In: Application à la recherche des millésimes, Annales des falsifications, de l'expertise chimique et toxicologique, vol. 72, pp. 263–274.
- Paulson, A.J., 1986. Effects of flow rate and pretreatment on the extraction of trace metals from estuarine and coastal seawater by Chelex-100. Anal. Chem. 58 (1), 183–187.
- Perrot, F., Hubert, Ph., Marquet, Ch., Pravikoff, M.S., Bourquin, P., Chiron, H., Guernion, P.-Y., Nachab, A., 2012. Evidence of ^{131}I and $^{134,137}\text{Cs}$ activities in Bordeaux, France due to the Fukushima nuclear accident. J. Environ. Radioact. 114, 61–65.
- Pietrzak-Flis, Z., Skowronska-Smolak, M., 1995. Transfer of ^{210}Pb and ^{218}Po to plants via root system and above-ground interception. Sci. Total Environ. 162, 139–147.
- Schönhofer, F., 1992. C-14 in Austrian wine and vinegar. Radiocarbon 34 (3), 768–771.
- Shakhashiro, A., Tarjan, S., Cecatelli, A., Kis-Benedek, G., Betti, M., 2012. IAEA-447: a new certified reference material for environmental radioactivity measurements. Appl. Radiat. Isot. 70 (8), 1632–1643.