Neutrino, wine and fraudulent business practices

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Abstract
The search for the neutrino and its properties, to find if it is a Dirac or Majorana particle, has kept physicists and engineers busy for a long time. The Neutrino Ettore Majorana Observatory (NEMO) experiment and its latest demonstrator, SuperNEMO, demanded the development of high-purity low-background γ-ray detectors to select radioactive-free components for the demonstrator. A spin-off of these detectors is inter-disciplinary measurements, and it led to the establishment of a reference curve to date wines. In turn, this proved to be an effective method to fight against wine counterfeiters.

1 Introduction

Over the last few decades, demand for fine wines has soared tremendously. Especially some particular vintages, notably from famous wine areas, lead to stupendous market prices, be it between private collectors as well as through wine merchants and/or auction houses. The love of wine was not and is still not the main factor in this uprising business: wine has become or maybe always was a financial asset. No surprise that this lured many people to try to make huge and easy profit by forging counterfeited bottles of the most prestigious - and expensive - "Grands Crus". But for old or very old fine wines, experts are at loss because of the complexity of a wine, the lack of traceability and so on. By measuring the minute quantity of radioactivity contained in the wine without opening the bottle, a method has been developed to counteract counterfeiters in most cases. And the origin of this method lies in the study of the neutrino...

2 The Neutrino Ettore Majorana Observatory (NEMO) experiment and PRISNA (Plateforme Régionale Interdisciplinaire de Spectrométrie Nucléaire en Aquitaine)

In a typical double beta decay, two neutrons in the nucleus are converted to protons, and two electrons and two electron antineutrinos are emitted. This is the $2\beta2\nu$ process. The Neutrino Ettore Majorana Observatory (NEMO) experiment, which is running in the Modane Underground Laboratory (LSM aka Laboratoire Souterrain de Modane), located in the Traforo del Frejus between Italy and France, is looking for a very rare process of the natural radioactivity, called the neutrinoless double beta decay, in which a nucleus emits two electrons simultaneously and no neutrino. The expected half-life being so large (> 10^{26} years), few counts per year are expected, which implies that all the background components must be reduced by few orders of magnitude. Cosmic rays, external γ-rays, natural β emitters, neutrons and radon are a nuisance and have to be suppressed or dampened. Fig. 1 shows the challenge of detecting the $2\beta0\nu$ signal.

The SuperNEMO detector (6 m long, 2 m wide, 4 m high) is partly built out of materials containing no measurable radioactive isotopes such as U, Th, Ra and their progeny. In Fig. 2 we see the assembly of the different parts of the demonstrator: a source foil sandwiched between tracker (to reconstruct the electron trajectories) and calorimeter (to record the energy) walls. Since most of the natural radioactive isotopes are γ-emitters, to select and control the radio-purity of all materials, we had to develop ultra-low background γ-ray spectrometers on the basis of HPGe (High Purity Germanium) crystals. Four

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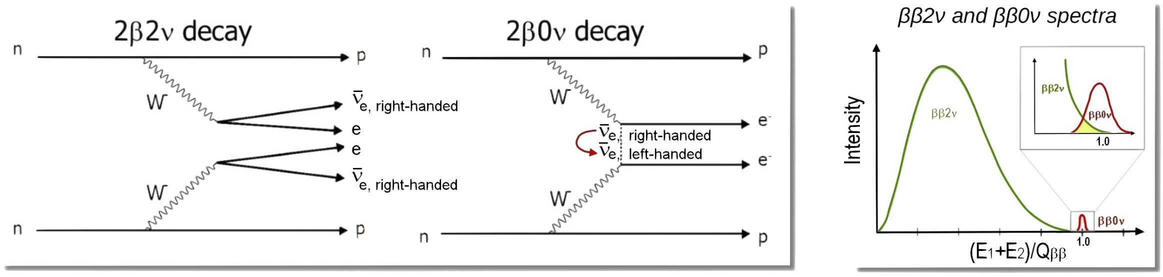

Fig. 1: Double Beta Decay with or without neutrino emission. [left] The two double-beta decay modes. [right] The aim is to measure the tiny $2\beta 0\nu$ signal despite the overlap due to the most common $2\beta 2\nu$ process.

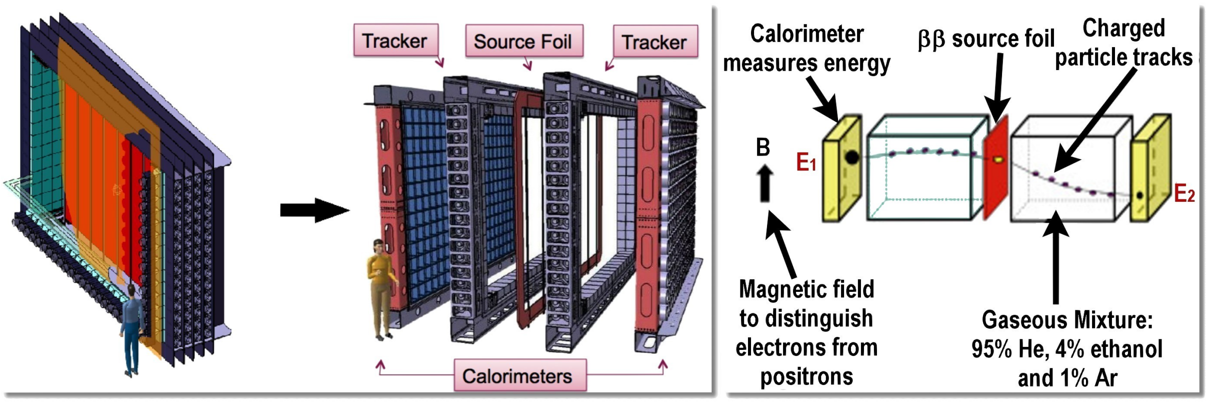

Fig. 2: SuperNEMO demonstrator. [left] From left to right, calorimeter, tracker, 2β source foil, tracker, calorimeter. [right] Schematic principle of the particle identification.

such spectrometers are hosted in the low-background environment PRISNA platform at our Institute in Bordeaux (Fig. 3). Their aim is to make a selection of the materials which, when validated, are measured for a final test by two similar detectors we have in the Modane Underground Laboratory.

3 From the neutrino to wine dating

Dating a wine through its radioactivity is an old idea. In 1954, Nobel Prize W.F. Libby proved one could date wines thanks to their Tritium content [1]. In the 1970s, P. Martinière et al. did the same with ^{14}C. And in 2001, the Centre d'Etudes Nucléaires de Bordeaux-Gradignan (CENBG), because of its expertise in very weak radioactivity measurements for the neutrino research, teamed with the French State local Agency for Consumer Protection (now Service Commun des Laboratoires). The initial goal was to infer if there was some possibility of dating wines in the frame of fraud fighting [2].

Our expertise in measuring low-background γ-ray emission, several orders of magnitude lower than natural radioactivity, is already applied to several inter-disciplinary research domains: characterisation of the geographic origin of edible foods (cocoa, plums, salt flowers, etc.), dating animal bones mostly in a fraud-fighting approach together with the French Bureau of Consumer Protection [3], inquiring the role of natural radioactivity in the set-on of neurodegenerative diseases [4]. But thanks to media, our best research program known to the public is dating wine by measuring its radioactivity, and the subsequent fraud affairs. Two approaches have been investigated, both involving γ-ray measurement of ^{137}Cs and ^{210}Pb resp. The former is a formidable answer to the challenge of dating a wine without opening the bottle. The latter, a destructive method, can be used in a few undetermined cases.

Fig. 3: PRISNA facility [left] and its protection against muons and related interactions [right]

Fig. 4: γ-ray measurement. [left] Bottle laying flat on a Ge detector. [right] 2 bottles shown against the Germanium detector just for illustration purpose.

3.1 Low background gamma-ray spectrometry

Most of the radioactive nuclei found in Nature, whether natural occurring ones like ^{40}K, Uranium and Thorium natural radioactive families, or anthropogenous ones like ^{137}Cs, are γ emitters. To detect and measure very weak activity levels, the detectors cryostats are made of the lowest radioactive possible materials. They are enclosed in lead shielding, the innermost part being made of archaeological lead, i.e. at least a few centuries-old lead, which is free of ^{210}Pb ($T_{1/2}$ = 22.2 y). Borated polyethylene is added to prevent neutrons reaching the Ge crystal. Plastic scintillators are placed on top of the spectrometers to veto to cosmic radiation which may interfere with the data taking by reacting with the matter surrounding the detectors. To further decrease those parasitic events, the spectrometers are installed in a special facility called PRISNA (Plate-forme Régionale Interdisciplinaire de Spectrométrie Nucléaire en Aquitaine) (Fig. 3), a building devoted to the measurement of very low radioactive samples with dampened outside radioactive background. Its specificity lies in the fact that it lays under 2.5 m of concrete and dirt (6 m water equivalent), that the walls, the roof and the floor inside the 70 m^2 are covered by radon-stopping foils. The climate environment control is set to have a residual radon content in the air equal or lower to the one outside the building.

Depending on the sample and the looked-after γ-ray isotope, sensitivity can reach values as low

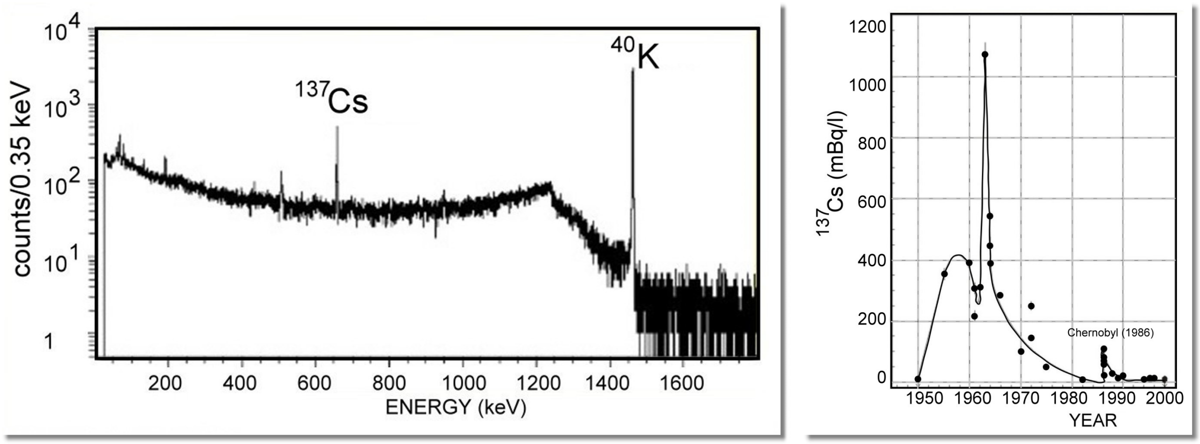

Fig. 5: Vintage spectrum and dating curve as measured by P. Hubert et al. in 2001. The γ-ray spectrum on the left shows the presence of ^{40}K and ^{137}Cs in the wine. On the Cs-137 Activity vs Year, all points are normalised to activities on Jan. 1st, 2000. Therefore, the maximum value in the 1960's was at that time a little more than twice the plotted value.

as 20 mBq/kg.

3.2 Wine data taking

^{137}Cs, with a half-life of 30 years is a man-made isotope. Its main origin comes from the numerous above ground atom bomb tests during the 1950's and 1960's with still some contributions in the the 1970's. The Chernobyl (1986) and Fukushima (2011) incidents have their share. The released activities were spread worldwide, then deposited on earth. The amount of subsequent ^{137}Cs radioactivity found at ground level is an almost perfect remembrance of the amount released, and it is different for each year since the early 1950's. When making wine, grapevines collect the activity coming from the fall-outs, and after bottling, each year harvest "records" that particular vintage radioactivity. We established therefore a reference curve ^{137}Cs activity vs vintage". Until our study, with pre-existing γ spectrometers, the limit of detection was not low enough to infer the existence of such a curve or even to detect whatsoever.

In a first attempt in 2001, 29 Bordeaux wines spanning the years 1950 to 1998 were burned to ashes at 500°C. The ashes were put in plastic boxes on top of the Germanium detectors. In Fig. 5 we see on the left side the corresponding spectrum with two main γ lines at Eγ = 661 keV (^{137}Cs) and Eγ = 1461 keV (^{40}K). The ^{137}Cs activity values are plotted as a function of the vintage year on the right-hand side of Fig. 5. It revealed a strong dependence of the activity and the year the wine was made and bottled. Note that in this representation, P. Hubert et al decided to normalise all values to Jan. 1st, 2000, taking into account the half-life of ^{137}Cs (30.1 y). This means that the maximum activity recorded for a 1964 wine was a little bit more than double the value shown on the plot.

This was a remarkable result, but it meant destroying the bottle content, which is hardly the best authentication method for valuable wines. The idea was then to let the bottle untouched and to measure it directly. Fig. 4 shows the two possibilities of doing so. On the right, a bottle (0.75 l) and a magnum (1.5 l) are shown together to emphasise the fact that different bottle sizes can be examined. By lowering the floor shielding, one can measure even Imperial bottles (6 l). For the real experiment, only one bottle is measured at a time. Another possible setup is to lay horizontally the bottle on top of the detector. This method has the advantage that the bottle and the wine remain intact. A drawback are that the glass itself, although not thick enough to stop the γ-ray of ^{137}Cs, is radioactive: ^{40}K and U/Th/Ra which induce a rise in the background of the spectrum. Another fact is that, because of geometry reasons, the detection efficiency is de facto lower than with a small vessel containing ashes.

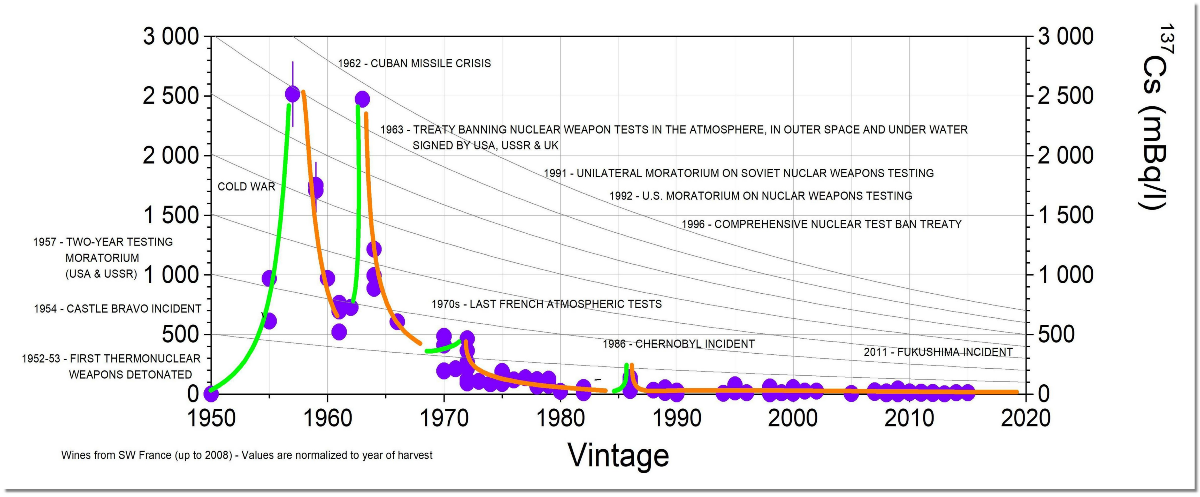

Fig. 6: Cs-137 content in wines from years 1950 to 2016. All activity values are for the corresponding vintage year. Green and orange lines are line-guides for the respective growth and decay tendencies. Comments on the figure report to above-ground tests, incidents and relevant political events.

Wines from 1929 to nowadays have been since measured this way. The latest, updated, curve is shown in Fig. 6. To stay away from normalising the data points at a given date, all reported and plotted values are now given for the respective vintages. Abacus curves allow one to take into account ^{137}Cs decay along the passing years. Relevant political events and incidents like the Castle Bravo and the Chernobyl ones are indicated on the plot. The rise and fall of the curve is a very good remembrance of those events. Fig. 6 is for the Northern Hemisphere. Just a couple of bottles from the Southern Hemisphere has been measured, but there is some renewed interest in doing the same work notably for Australia(e.g. for wines from the Barossa Valley) where fall-outs were a result of British tests above ground in the 1950s.

In 1986, the Chernobyl incident lead to a surge of the radioactivity levels. The closest the wine region was from Chernobyl, the greater was the increase. Fig. 6 is mainly based on SW France wines, and the "Chernobyl" peak is somewhat small. But we have measured French wines from Alsace and Corsica, two French regions several hundred miles east of Bordeaux with values of the order of 1 Bq/l instead of 0.1 Bq/l.

In 2011, the Fukushima incident released radioactive elements in the environment. The "cloud" crossed the Pacific Ocean all the way to Northern California. The nuclides deposition on the Weast Coast was minute. Nonetheless it was interesting to see if we could measure any variation of the ^{137}Cs level in California wines at that time. First measurements with unopened bottles were not conclusive and could only give limits of detection. But returning to the ash-producing methods allowed to see some increase of ^{137}Cs content for wines from 2011 and 2012. This is very preliminary and needs further investigation to confirm or not these findings [5].

3.3 Limits of the ^{137}Cs dating method

In some cases, dating a wine by the measurement of the ^{137}Cs content is out-of-reach. One cannot date this way young wines and wines from before the time of nuclear tests above the ground. For pre-1950 wine, there should be no ^{137}Cs in the wine and therefore no way to date it. For the recent wines, one can check if the alleged vintage year is compatible with the radioactivity content. In both cases one needs added tests, using other radionuclides like ^{210}Pb, ^{14}C, Tritium or even ^{90}Sr.

Fig. 7: [left] 1787-1789 "Thomas Jefferson bottles" (fake, measured at the LSM). [middle] Series of 1900 Château Lafitte bottles which had various levels of ^{137}Cs activity. [right] A magnum bottle of 1945 Mouton-Rothschild being investigated.

4 A Tool to Fight Counterfeited Wines

Since a wine dating from the pre-atomic era cannot contain ^{137}Cs, finding traces of this radioisotope in a bottle of wine assumed to be from before the 1950s has only one explanation: the wine has been tampered and younger or much younger wine has been poured in the bottle. This is being used to fight counterfeiters who brought to the market alleged vintage wines which are fake ones. These crooks have been very efficient have been on the market for the last 30 years, while famous rare wines reached astronomical prices in prestigious auction sales as well as through wine outlets. We have worked with several investigators, private and public, and testimonied as experts at the New York Court of Justice. To state a few cases, one involved the four so-called "Thomas Jefferson" bottles (Fig. 7). The complete story is to be found at Ref. [6]. Others cases stemmed from the sudden profusion of fine 1945 Mouton Rothschild bottles and magnums, as well as from other vineyards, on auction sales worldwide.

In Fig. 8 we see some examples of γ-ray spectra of fine wines. In all cases, since the bottles are untouched, the spectra combine the measured radioactivities of bot the glass of the bottle and the wine. Therefore, at 665 keV one always have a lline due to ^{214}Bi which is contained in the glass. On the left side, two bottles of 1942 Petrus wine: ^{137}Cs is present in one case, not in the other. Clearly the former is a counterfeited wine. Underneath, a 1964 Fronsac red wine exhibits a large ^{137}Cs line as expected and it is used as a reference bottle. On the right part of Fig. 8, four bottles of red Mouton wine from the 19^{th} Century (from 1853 to 1896) have been tampered with...

Since 2009, we have service-delivery activities performed at PRISNA by a Technical Unit (PRISNA Prestations) which benefits from technology transfers from our proof-of-concept studies, and has a wide panel of public and private clients. This has allowed to clean up the market and to encourage the actors in this domain to engage a quality approach including traceability. PRISNA Prestations is equipped with its own high-purity low-background Germanium detector and can deliver results in the frame of several European legal accreditations.

5 A last word

The amount of radiation present in all the wine tested is too small to harm a person's health. For more details on the original work which lead to ^{137}Cs dating method, please refer to [7, 8].

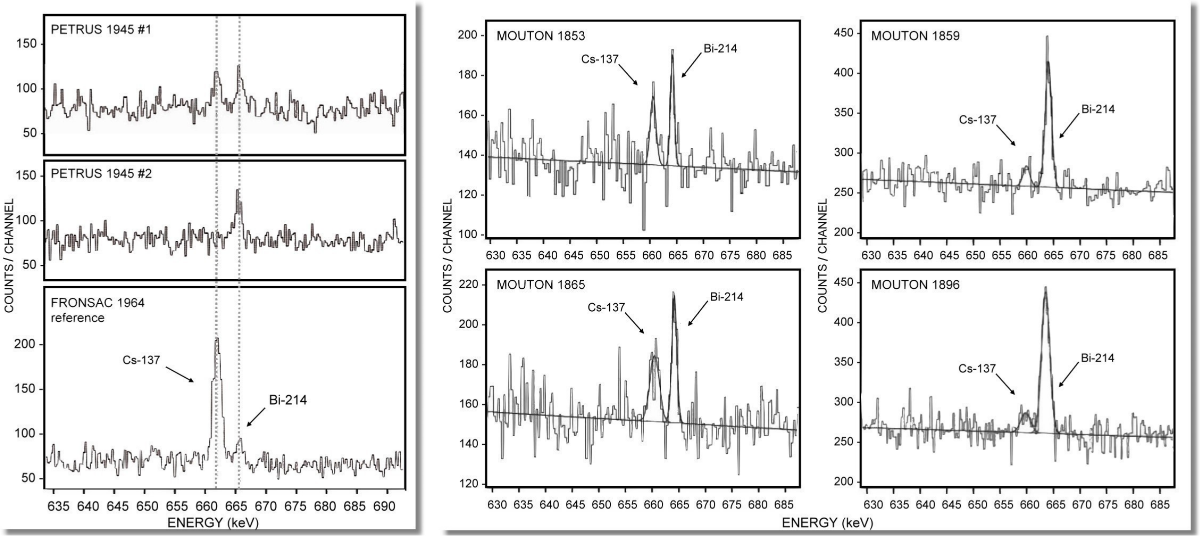

Fig. 8: [left] Two Petrus 1945 bottles from the same year: one is fake, one is genuine. The Fronsac 1964 bottle is used as a reference. [right] A series of 19th Century Mouton bottles, wines dating between 50 and 100 years before man-made ^{137}Cs appeared on Earth! These are fake wines. As usual, ^{214}Bi is always present and stems from the glass of the bottle.

Acknowledgments

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