LIQUID SCINTILLATION SPECTROSCOPY (FSS)

1.1 Introduction

There are several natural radioactive isotopes in our environment. The most well-known ones are the uranium and the thorium that can be found in the soil everywhere, and their daughter products. The half-lives of the most abundant isotopes of the uranium and the thorium are 4.4 billion and 10 billion years. These are longer than the age of the Earth. At the creation of the material of our Earth there were several radioactive atoms but most are decayed into stable isotopes already a long time ago. The long half-life isotopes such as ²³⁵U, ²³⁸U, ²³²Th, ⁴⁰K, to mention the most important ones, survived. These isotopes are in several types of rocks, and they appear in every kind of soil. Their concentrations are sometimes small, but sometimes can be higher, too. These are the first group of natural radioactivity. But there are other radioactive atoms in our environment, different from these ones. The reason how the others can appear is that those are produced continuously. The main source of it is the cosmic radiation. The fast protons coming from the Sun can enter the upper atmosphere and they can collide to the nuclei of nitrogen and oxygen atoms that are available in O₂ and N₂ molecules. If the energy of the colliding proton is not very high in the collision, the protons and the neutrons will be the participants. The proton can hit a neutron out of a nucleus for example, that will make a neutron flux at the upper atmosphere. Several reactions can happen and many isotopes are produced. If their half-lives are long enough, those can mix up in the whole atmosphere taking part in the great circulations, and then these isotopes can spill out from the air to the ground with the precipitation. These isotopes can accumulate homogeneously in the atmosphere. Their equilibrium concentration is determined by their production rate namely the cross section of those reactions and their half-life.

The third group of naturally occurring ionizing radiation consists of the cosmic showers. The cosmic protons have many times higher energy than a typical energy of a nuclear physics reaction. In this case particle physics will govern a process. The protons can interact to a smaller part of the colliding nucleus. The quarks inside will be the participants of the reactions. In these reactions new particles can appear. In a proton nucleus collision a new particle, for example a pion, can be created. The pions then will decay into muons. The muons are like the electrons, are elementary particles but they have about 200 times larger mass. These muons will go through the atmosphere and reach the surface even though they enter the ground and will slow down there. During these processes new photons and electrons can be produced in a cascade process. These are the cosmic showers. Their extent can be several hundred meters on the surface.

1.2 The radiocarbon and the tritium in our environment

1.2.1 The origin of the tritium and the radiocarbon

We saw that neutrons can be produced in the upper layer of the atmosphere. These neutrons hit another atomic nucleus. Mainly oxygen and nitrogen nuclei are available. If a neutron hits a ¹⁴N nucleus it can hit out a proton and it can build into the place of the proton.

${}^{14}N + n \rightarrow {}^{14}C + p \, .$

The short description of this reaction according to the nuclear physics tradition: ${}^{14}N(n,p){}^{14}C$. This is the way in which the radiocarbon (the radioactive isotope of the carbon element) appears in the Earth, first in the upper layer. But its half-life is 5730 years and this time is very long compared to the time scales of the circulation and the diffusion, convection that happens in the atmosphere. This radiocarbon will be built into the live organisms, cells. For example the photosynthesis builds the CO₂ into the body of the plants, so they put ${}^{14}C$ into the plant. The animals will eat that and in the food chain these isotopes can be mixed into every kind of living object. The radiocarbon is present in its equilibrium concentration in, for example, trees or in the human body as well. Although the radiocarbon decays in the bodies but while those are living they will take it also from the environment. At last an equilibrium concentration will be reached. This equilibrium level has not been time independent for the last 50 years due to the artificial production of the ${}^{14}C$ as a result of the nuclear weapon tests. However, as a good approximation one can use the ratio, that is ${}^{14}C/{}^{12}C=10^{-12}$.

The neutron in the upper atmosphere can collide to the nuclei in different ways, too. They can hit the same ¹⁴N nucleus but it can pull a proton and a neutron out with itself. Several other reaction mechanisms can be imagined, but these two have the highest probability, because in these very stable nuclei will be formed. In these reactions the electric charge and the number of nucleons (proton number and the neutron number) are conserved. Before the reaction there were a ¹⁴N nucleus and a neutron present, where the sum of the electric charge is 7 times the elementary charge, and the sum of the nucleon number is 15. After the reaction the carbon has only 6 elementary charges and the tritium has one. The nucleon numbers are 3 in the tritium and therefore the A=12 isotope of the carbon will be formed, which is very stable isotope.

$^{14}N + n \rightarrow ^{12}C + ^{3}H$

The atomic nucleus which consists of 1 proton + 2 neutrons is called triton (this is the nucleus of the element tritium). This is the A=3 isotope of the hydrogen. Its half-life is 12,3 years, which is long enough to participate in the environmental processes. This can be built into the live bodies similarly to the ¹⁴C, and there is an equilibrium concentration of it. The tritium can appear in the water molecules mostly, but not exclusively. It can reach the surface waters like ocean, rivers, and lakes. But the subsurface hydrogeological flows have so long time scale (more than thousands of years), so in those the tritium will decay to zero. This is a big difference, and a possible method to determine whether the water sample comes from a long hydrogeological flow or its origin is instead from a fresh precipitation. The equilibrium ³H concentration of the surface rivers and rains is less than this for the ¹⁴C, since the tritium decays faster. Its ³H/H ratio is 10^{-18} .

1.2.2 Environmental activities of tritium and radiocarbon

In subsurface water flow the tritium activities are falling according to the exponential decay law. After 12.3 years the surface equilibrium concentration will be only the half of it and there is no way to supply it. Generally after *t* time the initial activity A_0 will fall to:

$$A(t) = A_0 \cdot 2^{-t/T} = A_0 \cdot e^{-(\ln 2/T) \cdot t}$$

where T is the half-life of the tritium. There is no supply alike the case of the subsurface flow, if we close the water into a bottle. In this way the natural equilibrium concentration that is formed in grapes and surface waters will be smaller and smaller as the time goes by. Therefore when the wines are closed in a bottle the tritium activity falls according to the rule above. If we determine the tritium activity on the other hand, we can tell the age of the wine

in a time scale of 1-50 years. The older liquids generally contain so little amount of tritium that only with expensive precision methods can its concentration be successfully determined.

For the radiocarbon the equilibrium activity concentration e.g. in a tree is 0.154 Bq/kg. If the tree dies the radiocarbon activity starts to fall exponentially, since there is no supply. This is how the age of a tree can be determined besides the counting of the annual rings. In the last 60 years the nuclear tests modified these radioactivity concentrations, unfortunately.

The radiocarbon chronology is good in the time range of thousand years, until about 30 000 - 40 000 years. Therefore the radiocarbon chronology gives information about the age of historical events.

The tritium and the radiocarbon are present in the human body according to the mentioned equilibrium activity. Therefore everyone is slightly radioactive. In the radioactive decay of these isotopes small energy electrons leave the decaying nuclei, and these electrons will be stopped in some micrometer. The cells absorb ionizing dose in this process, many molecules in the cell will be ionized. This radiation will not leave the body. Since the origin is from inside the body it is called inside dose. This has been going on for millions of years since the life appeared on Earth, and it is a part of the functioning of the body. The civilizations although are capable to increase this natural level of radioactivity. Therefore there are strict rules for the allowed radioactivity concentrations in water. This is also a check for illegal nuclear activities around the world. The International Atomic Energy Agency runs a worldwide monitoring system that checks the radioactive levels continuously.

1.2.3 The decay of the tritium and the radiocarbon

The triton and the radiocarbon as we already mentioned decays by beta-minus-decay. In both nuclei there are more neutrons than protons, and there are more neutrons than in the most stable isotope of the element. In the stable hydrogen the nucleus is a single proton. In the tritium there are 2 more neutrons. The most stable carbon has 6 neutrons, while the radiocarbon has 8. In the beta-decays of these isotopes 1 neutron will transform to a proton in a beta decay that is governed by the weak interaction. The weak interaction is one of nature's elementary interactions. In this process an electron (or its antiparticle the positron) and one kind of neutrino will participate. In the beta-minus-decay the neutron is converted to proton and the nuclear structure will be more effective, the final nucleus has larger binding energy after the neutrons and the protons realign. During the neutron \rightarrow proton conversion the mass number of the nucleus will not be changed, but the atomic number increases by one, since there will be one more proton. (In the other type of the beta-decay, in the beta-plus-decay, the case is opposite, the proton converts to neutron.)

$${}^{3}H \rightarrow {}^{3}He + e^{-} + \widetilde{\nu}, \qquad {}^{14}C \rightarrow {}^{14}N + e^{-} + \widetilde{\nu}$$

In the neutron \rightarrow proton conversion according to the conservation of the electric charge there should be a negative charge to be released. This is the electron, and due to the main features of the weak interaction an anti-neutrino will be also created. It is interesting that in this process the energy released in the reaction will be divided into three ways. One part will go to the remaining (daughter) nucleus, one part goes to the electron, and the third goes to the antineutrino. The first is negligible, since the nucleus has large mass compared to the light particles like electron and neutrino. The electron and the anti-neutrino will share almost the total decay energy. The decay energy was determined already in the 20th century by mass spectrometers. The decay energy can be calculated from the masses:

$$Q = m(^{3}H) - m(^{3}He) - m(e^{-}) = 18.6 keV$$

$$Q = m(^{14}C) - m(^{14}N) - m(e^{-}) = 156.5 keV$$

The maximum electron energy (when the neutrino does not get any) is 18.6 keV and 156.5 keV, and both are less than the rest energy of the electron, that is 511 keV. This is another contribution why we call these small energy decays.

1.3 Measurements of tritium in water

1.3.1 The tritium activity

The amount of tritium can be shown according to its radioactivity. For radiocarbon it is also a well-known widely used method, but in that case the isotope separation by mass spectrometers is also an established method. If we determine the radioactivity of a sample and we know the half-life of it, we can calculate the number of radioactive atoms in the sample according to the following formula:

$$A = \lambda N = \frac{\ln 2}{T_{1/2}} N \, .$$

1.3.2 The energy distribution in beta decay

As we mentioned the electron and the anti-neutrino share the energy released in the decay. We assume that this share is a random process (in this study). Every velocity vector of an electron is equally probable and the corresponding direction of the anti-neutrino is also random. Therefore there is a given probability for each kinetic energy of the electron. The bases of this distribution lead to difficult physics, so we do not go into the details now. Instead we will measure this distribution. There are general features of these distributions. When the neutrino gets 0 energy, the electron brings the total. When the electron gets zero all the total decay energy will be carried out by the anti-neutrino. The distribution has its average at about 1/3 of the maximum energy.

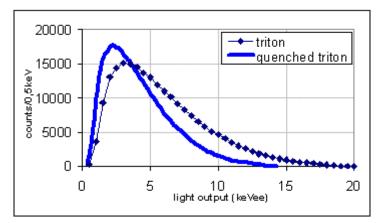


Figure 17.1. The light output distribution of the tritium beta-decay. The squares were used for the case of the unquenched (see details later) tritium standard, and the continuous line is for a real quenched sample.

Figure 17.1 shows the light output distribution in two experimental cases. The light output is a quantity that is proportional to the kinetic energy of the electrons. We will discuss

it later. The shape of this distribution is characteristic for the beta-decaying isotope, and is useful to identify it if we do not know which isotopes cause the radioactivity of the sample.

1.3.3 The detecting intensity

In this laboratory practice and in the general practice, too, the experimental question is the tritium activity concentration of a sample. Generally the required unit is Bq/l. From this we can tell the number of tritium atoms in the sample using the $A=\lambda N$ formula, after determining the activity. We should determine how many atoms decay in a second, and we should identify the element itself. Generally we cannot detect every decay that happens in the sample. Therefore the detected intensity differs from the activity. The loss of event contributes to the detecting efficiency, which is $\eta = I_d/A$, where I_d is the detecting intensity, or in other words CPM, counts per minutes. The efficiency does not depend on the activity but can depend on several factors. For example it depends strongly on which isotope is used, what kind of detector is used, and its parameters are also important. If we give the activity in an unusual unit like DPM, disintegration per minutes (decay per minutes), and the efficiency gets this form:

$CPM = \eta \cdot DPM$

For a tritium measurement our goals are to measure the CPM and the efficiency.

1.4 The liquid scintillation counting techniques (LSC)

The ranges of the released electron in the beta-decays of the radiocarbon and the tritium are so short, that these electrons cannot penetrate even a thin aluminum sheet. But in a general case most of the detectors are covered, they are in a box. The best solution is about the aluminum box, but that is still not enough for the tritium and for the radiocarbon case to let the electrons go through. Therefore the sample cannot be outside the sensitive volume of the detector. It is better to mix up the sample with the detector material. The liquid scintillation technique gives just this possibility. The sample will be mixed up with a scintillator material, in this case it is in liquid phase.

The instrument that will be used is the TriCarb 1000A machine, designed for liquid scintillation analysis of triton and radiocarbon samples. It is also applicable for determination of other isotopes like dissolved radon, or phosphorus in water.

1.4.1 The scintillation detector

The scintillation detectors consist of two parts. One is the scintillator material and the other is the photomultiplier tube (PMT). The scintillator is a material, the molecules of which can emit visible light after excitation. In our case it will be liquid. The scintillation is the process when the scintillator material emits visible or UV photons just after one radioactive decay. The other part, the PMT is used to convert this light to electric pulse. Then an electronic system will analyze the pulses and for example will count them.

The scintillator

The electron that was created in the beta decay will lose its energy quickly in such a way that it will ionize or excite the atoms and molecules of the surrounding medium. The excited atoms or molecules will return to their ground state or lower excited states in some time via emitting the visible or UV photons. The number of excited atoms or molecules can be described with an exponential decay law, if we assume that the excitation process is very fast, and the decay is slower. The characteristic time is called the decay time of the scintillator.

The light output is the number of photons emitted and got out of the scintillator material in one radioactive decay N_{LF} . The number of the created photons can be smaller N_{CR} . But for the first case $N_{LF}=N_{CR}$. We have seen that the light output is an important parameter.

The ionizing particles (e.g. from a radioactive decay) will lose kinetic energy in the scintillator. This is called E_d , and it is proportional to the number of excited atoms or molecules in the scintillator, this will be proportional to the number of scintillation photons, which is the light output itself. Therefore the light output is proportional to the energy deposited in the detector material. Generally in beta decays E_d equals to the kinetic energy of the electron. (If the electron is formed at the very side of the scintillator volume, it might travel out of the volume and in this way some of its energy will not excite the scintillator but the wall of the detector.) If we measure the light output we can determine the maximum kinetic energy of the electrons in the beta-decay, and therefore we can identify the isotope.

If there is an electron that deposited 100keV energy in the scintillator, it cannot be from the decay of the triton, since its maximum energy is 18.6 keV. That event can be a background event or from a different isotope.

The unit of the light output: The light output is measured relatively to the number of the scintillation photons of a special case. The light output is in fact not a number, but a ratio. The special case is the case of 1 keV electrons. The light output tells how many times more photons were emitted in decay than it was emitted in the case of a 1 keV electron.

$L = N_{LF}/N_0$.

Here *L* is the light output, it is a dimensionless quantity, but we use keVee for this, N_0 is the number of scintillation photons from 1 keV electron case. The keVee is called kiloelectronvolt electron equivalent. This unit is material-dependent. But the L itself is not! A 1 keV electron will create different number of photons in one scintillator than in another. In the case of alpha-decays L is proportional to the alpha energy but there is a conversion factor, since we defined the L for electrons. This is called the light emission efficiency. For alphas the ionizing process is different and the excitation mode of the molecules is also different. That is the reason why there will be much less visible photons after exciting the medium by fast alpha particle. As a summary we can write:

$$E_{electron} \sim E_{deposited} \sim N_{excited.mol.} \sim N_{LF} \sim L$$

In a general scintillator $E_d=1$ keV will produce 7 visible photons. The light production is a statistical effect, so it has deviation. Two exactly identical electrons will create slightly different number of photons.

For detection of the soft beta-decays we select liquid scintillator that can be solved in the sample (mainly water). In this case the detector material will cover the whole cone around the decay, and can detect very small energy electrons. The liquid scintillators consist of three components, and therefore they are called cocktail. The largest part of the cocktail is the solvent. This phase will absorb the kinetic energy of the ionizing particle and emit photons of which the wavelength is not optimal. Therefore there are two more components in the cocktail that absorb the photons from the solvent and reemit the energy by longer wavelength photons. We call them wavelength shifters. The first is the primer scintillator and the other is the secunder scintillator that emits already at the optimal wavelength range, which is determined by the photocathode features of the PMT. The primer and secunder scintillators are in the cocktail in a very low concentration.

The scintillation photons will not necessarily go out of the cocktail volume. There is a process that is called quenching, which means the photons will be absorbed in the vial, or on the wall of the vial. So the number of the outgoing photons is $N_{LF} < N_{CR}$. The part that survived the absorption is $e = N_{LF}/N_{CR}$, but the quenched part is q=1-e.

The quench can be resulted in many processes. The liquid can be colorful, it can contain contamination that absorbs the light, there can be contamination on the glass of the vial, there are several ways how a light absorber center can be involved in the detection mechanism.

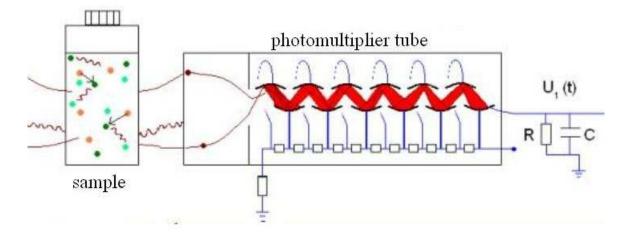


Figure 17.2 The photomultiplier-tube (PMT). On the left side there is vial containing the cocktail and the sample solved in it. The excited atoms are shown and the lines symbolize the emitted scintillation photons. In the left wall of the PMT is the photocathode, where a photon kicked out an electron. That was multiplied by the dynodes. U(t) shows the electric signal.

The photomultiplier tube

The PMT will convert the light output into electric signal. One part of the scintillation photons will enter the photocathode ($N_{FC} \sim N_{LF}$) of the PMT and hit a photoelectron out in a photoelectric process. Every 5th photon will do it generally. The number of photoelectrons taking part in a single decay is N_{PE} . The photocathode is a very thin metal layer that is evaporated on the inside part of the glass of the PMT window. There is vacuum in the PMT, the photoelectrons will be focused into a metal laver, so-called dynode. The dynodes are special metals. If a "fast" electron hits its surface there will be about 3 slower electrons flying out. Then the slower electrons will be accelerated by electric voltage of about 300 V, and the multiplication starts over. In a PMT there are 10-12 dynodes, and those can multiply the number of electrons up to about 3^{12} . The last metal layer is called anode, this will not multiply more the number of electrons, but lead them out of the PMT, the number of electrons that went through the anode is N_A . These electrons will go to a ground potential point across a resistance. There is always scattered capacitance, which also should be taken into account. The short signal is about 1 µs long, or sometimes much shorter. So the average electric current that flowed through the resistance and was caused by 1 photoelectron is $I_I = N_A \cdot e/\Delta t = 3^{12} \cdot e/10^{-6} \text{ s} = 1,5 \cdot 10^{12} \cdot 1,6 \cdot 10^{-19} \text{ Cb/s} = 0,24 \text{ }\mu\text{A}$. If there are more photoelectrons created this current is proportionally higher: $I=N_{FE}\cdot I_I$. Some photoelectrons already give measurable current. While the multiplication factor of the dynodes is constant the amplitude of the electric

signal is proportional to N_{FK} , therefore to *L* as well, and so to the energy of the beta electron. To be able to accelerate the electrons in the vacuum of the PMT we have to apply about 2000-3000 V high voltage on the PMT between the anode part and the photocathode.

The scattered capacitances and the resistance, and also the decay constant of the scintillator determine the time dependence of the electric signal on the resistance. The time shape therefore does not change during the detection. Only the amplitude can be different according to the N_A , or L, which is proportional to it. The constant shape of the signal is a very important feature. This makes the proportionality possible. Taking every step into account the energy of the beta electron is proportional to the amplitude of the electric signal. Digital electronic technologies, very much developed in the last decades, are applied, and an integer number will be determined which is proportional with the electron energy. This number is called the channel number. This can be considered as particle energy but in fact it is proportional to L, the light output.

1.4.2 The measured light output spectrum

In 17.2.2 we described that the energy distribution of the electrons shows a continuous curve, since the electron and the antineutrino share the energy. This is sharply different from the energy distribution of the alpha decays. Where there is no 3^{rd} particle created in the reaction, so the decay energy will determine the kinetic energy of the alpha particle. We get 1 sharp peak at this energy in the alpha decay case.

The light output distribution, in fact the distribution of the channel numbers, that is proportional to the light output, we also can call it amplitude distribution. This distribution will be measured using a multi-channel analyzer (MCA). Above we saw that for every decay the instrument calculates a channel number. If we have a lot of decays, a lot of events, we have a lot of channel numbers. The MCA calculates how many times each channel number happened in the measurement. So it means how many times each electron energies occurred among the beta decays of sample.

The light output distribution should be investigated in every measurement. That will allow us to identify the isotope and/or measure the quenching quantitatively. The effect of the quenching on the energy spectrum can be seen in Figure 17.1. If the quenching reduces every light outputs by a factor of q, the channel numbers will be smaller, and the distribution will be like to which is pressed left along the x-axis in a linear way. The quenching (q) can be measured by a gamma source that should be put aside of the vial. The quenching will modify the known and constant light output distribution of the Compton electrons of this source. The TriCarb machine quantifies a comparison to the standard. This is the tSIE (transformed spectral index) value or quench that we can get for each sample. The value 1000 means the unquenched case and the heavy absorption results in very small tSIE values.

1.4.3 Determination of the efficiency

The investigated samples have different quenching properties. Therefore they have different counting efficiency. The higher the quench the smaller the efficiency is. There is a built-in method, the tSIE parameter, which is useful for determination of the efficiency. There was a calibration measurement when one tritium sample of known activity was mixed with solutions of different quenching properties. The tSIE values (see below) and the efficiencies η =*CPM/DPM* were determined and it resulted in a calibration curve for the efficiency. We should use this curve that is valid on the other hand a given cocktail: ULTIMA GOLD, which

is the most frequently used scintillator for tritium. The background of this method using tSIE parameter is the following. We should measure the known light output distribution in two light output intervals: one at low light outputs and one at higher light outputs. In a measurement the counts in the lower light output range are called N_{low} and in the higher range are N_{high} . For an unquenched sample the ratio of the counts $R=N_{high}/N_{low}$ is a given number. But this ratio will decrease in case of quench. The counts from the higher light output interval will move to the lower light output range. The tSIE value will also be smaller if quench goes high.

The method to determine the efficiency in our case is the following: We have to find a mathematical function to describe the known tSIE – efficiency calibration points. Then tSIE should be measured, and at last efficiency will be calculated using the function and the measured value of tSIE.

1.4.4 Operating the TriCarb machine

Our liquid scintillation machine has two PMT-s in it. We detect the events if there is a coincidence between those PMTs. The vial that holds the liquid sample will be lifted down to the place just between the two PMTs. Lead sheets shadow this area to allow lower background. The machine communicates with the users by a small LCD window. There are command buttons. We need only the button called COUNT that starts the measurements. Before starting the measurement place the vial into the right position and then press COUNT. If this button will be pressed once again the machine cancels the measurement and gives the vial back (lifts it up, out of the inside area).

On the small LCD monitor we can follow how much time elapsed and what the CPM value of the measurement is. After the measurement the machine transfers each channel number to a computer to draw the light output distribution. It also sends the most important values to a printer.

The machine can differentiate 2 regions according to the light outputs. Region A and B can be programmed. The lower and upper light output limits should be given in keVee units. The general setup for tritium is: Region A – lower L=0 keVee, upper L=18.6 keVee, Region B – lower L=2 keVee, upper L=18.6 keVee. The ratio of A and B regions immediately gives information on the quench. For radiocarbon a different setup is necessary. Region A: lower L=0 keVee, upper L=145.6 keVee

1.5 Lab course tasks

- 1. Calculate the tritium and radiocarbon activity of an idealized human body!
- 2. Determine the counting efficiency of an unquenched tritium standard in the A and B regions! Use the initial activity information from the top of the vial.
- 3. Measure the tritium standard *n* times in standard ³H protocol. *n*=10-20. Determine the standard deviation of the CPM values! Compare this with the uncertainty printed by the machine. That is calculated from the \sqrt{N} error estimation!
- 4. Investigate the light output curves of the tritium samples!
- 5. Determine the tritium content of an unknown sample!

6. How can we determine the radioactivity of tritium and radiocarbon in an unquenched sample if both isotopes are present in the sample? (We have ³H and ¹⁴C standards as well.)

1.6 Test questions

- 1. Why do we use liquid scintillator for detecting the decay of triton?
- 2. What process is called scintillation?
- 3. What does a liquid scintillator contain?
- 4. What is the light-output and how does it change in case of quenching?
- 5. How do the radiocarbon and the triton decay?
- 6. How do the radiocarbon and the triton is created in our planet?
- 7. Why is the beta-spectrum continuous?
- 8. What is the spectrum of the amplitude of the electric pulses during a triton measurement?
- 9. How can the scintillation light be quenched?
- 10. How can we determine the efficiency of a triton measurement from the measured value of the quench?
- 11. Why is the amplitude of the electric signal proportional to the energy deposited in the vial?
- 12. What are the operating purposes of the cocktail ingredients?
- 13. How does the photomultiplier work?
- 14. How can we discriminate the triton counts from the radiocarbon counts?