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SOME POSSIBILITIES FOR THE DEVELOPMENT OF ^{14}C MEASUREMENTS BY LIQUID SCINTILLATION COUNTING

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ABSTRACT. The possibilities of widening the ranges of usage of scintillation counters are studied. As a result of the introduction of the active guard, the background in ^{14}C channel reduces 30 to 75 percent and the stability of background increases. The application of quartz vials and a plastic scintillator as an active guard establishes ^{14}C activity in small amounts of scintillation cocktail (up to 0.1g C) and dates samples with older ages (up to 57,000 years). The parameters of devices are given in case of different amounts of scintillation cocktail.

INTRODUCTION

For wide and successful application of the ^{14}C dating method in geologic and archaeologic institutions, research techniques should meet the following requirements: devices must be compact and easy to handle. At the same time, they must be able to measure both very low ^{14}C activities (old samples) and ^{14}C activities in small samples. Thus, it seems reasonable to connect, in measuring devices, the positive technical characteristics of gas and scintillation counters. The problem raised is how to attain high counting efficiency of a liquid scintillation counter at the lowest background level and stable counting regime.

Counter design

Single and two-channel devices were constructed in the laboratory to date samples and carry out methodical studies. Benzene served as the natural ^{14}C carrier and 4.0g/l of PPO and 0.1g/l of POPOP were added. Aluminum, steel, teflon, and quartz counting vials were in direct optical connection with the photomultipliers ФЭУ-93, ФЭУ-97, and EMI-S/A. Detectors were surrounded by active and passive guards. In a one-channel device the passive guard consists of 25mmHg and 50mmPb; in a two-channel device, it is comprised of 100mmPb, only. An increase in Pb thickness is not expedient as its contribution to the background reduction is insignificant (Alessio and others, 1976). In the two-channel device, the detector was directly surrounded by the active guard of 15 Geiger-Mueller gamma-counters or of plastic scintillator (polystyrole, p–terfenyle + POPOP). The energy spectrum of beta-rays was investigated with a multidimensional impulse analyzer. Scintillation efficiency of the measuring device was checked with the help of outer gamma-source, ^{137}Cs. The devices were thermostated with the accuracy of ±0.5°C.

Background observations

The aim of the studies was to achieve the background reduction and high stability during long counting periods. The background of the liquid scintillation device is due to the following components: 1) derangements due to devices, 2) component due to the work of photomultipliers, 3) cosmic radiation, 4) radioactive impurities in construction materials of the detector and its surroundings.

The first component could be relatively easily eliminated by thermostating the device, stabilization of supply voltage, and filtration of derangements. Occasional derangements are detectable and should not be considered while performing statistical analyses of measuring results.

The component of background due to the work of photomultipliers is conditioned by their own noises and by optical feedback. The aim of our studies (Punning and Rajamäe, 1977) was to investigate photomultipliers and set up criteria for the selection of suitable types. We learned that the ratio, signal/noise, dependence of noise on temperature, stability of work in long-term operations, and the amplification of spectral characteristics of the photocathode serve as the main criteria.

The selection of photomultipliers is of special importance in single-channel devices, where the amplitude of noise is decisive. The noises of photomultiplier considerably affect total background. In the case of two-channel device the stability of work and the content of radioactive impurities in construction materials of the photomultiplier play an important role. For example, in the case of ФЭУ-97, ФЭУ-93 and EMI-S/A the mean content of ^{40}K in the windows of photomultipliers amounts to 10 percent from the total background (Punning and Rajamäe, 1977). Also, the impurities contained in the construction materials of the vial should be regarded as an important background source. The authors have compared counting vials from different materials. For this purpose vials of similar shape and the same volume made from aluminum, stainless steel, and teflon were used. The energy spectrum of the background in the output of anticoincidence block was similar for all counting vials, indicating relative radioactive purity of construction materials. The low-energy component of cosmic radiation is entirely absorbed by Pb and Hg used as shielding materials. The contribution of the penetrating high-energy component to the background was studied with the help of active guards comprised of Geiger-Mueller gamma-counters and plastic scintillator. In both cases, the ^{14}C detector was surrounded by the active guard in the 2π geometry. In the first case the active guard consisted of 17 counting tubes, each 20mm in diameter and 200mm long. The signal in the output of active guard, placed into the lead chamber walls, 10cm thick, was 600 imp/min. Due to these impulses the dead time of the measuring device increased to 0.2 percent. Since our Geiger-Mueller tubes are not very sensitive to particles with low ionization ability, especially to gamma-quanta, the active guard was constructed on the basis of a plastic scintillator. This surrounded the measuring vial in a hollow semicylinder, 200mm long, walls, 50mm thick. Light impulses were recorded with a photomultiplier ФЭУ-97 (cathode diameter 40mm). The signal in the output of the active guard consisting of the plastic scintillator was 550imp/min and the dead time of the device increased only 0.005 percent.

The efficiency of several active guards in dependence of the volume of scintillator in the vial is shown in figure 1. As illustrated, the effect of the active guard increases in smaller samples. This regularity is due to the fact that in samples of small volume the paths of ionizing particles in the scintillator are relatively shorter and light impulses occur mainly in the radiocarbon channel. High-energy impulses induced in larger samples were eliminated with the help of a discriminator. The introduction of Geiger-Mueller gamma-counters in active guard brought about the reduction of background 40 to 10 percent with the volume of scintillation cocktail 2 to 25ml, whereas with the plastic scintillator the background decreased 60 to 20 percent. In small samples 0.5 to 1.0ml the background reduced about 75 percent. This enabled us to start dating samples that contained very little carbon.

Figure 2 presents energy spectra of background and radiocarbon for aluminum and quartz vials. The upper curves show the distribution of background when the active guard is switched off, the lower ones, when the active guard is working. The plastic scintillator is used here as an active guard. As is seen from figure 2, the active guard is very effective with low-energy particles. The minimal value of the background of aluminum vials with the active guard switched off refers to the shielding effect of the material of the vial (upper curves). The highest background of aluminum vial with the active guard switched on shows the presence of radioactive impurities in aluminum (lower curves).

Dependence of the values of the figure of merit $N_O/\sqrt{N_B}$ upon the amount of carbon in the scintillation cocktail is shown in figure 3. In each case, the radiocarbon channel was selected according to maximal value of the figure of merit. ^{14}C counting efficiency ranged from 47 to 54 percent. Higher efficiency of the plastic scintillator in reducing background resulting from the cosmic component, determines that the parameters of the active guard with the above scintillator are the best and the device can be used for a wide range of samples sizes. Figure 3 presents also the data on the proportional counter of the Radiocarbon Dating Laboratory of the Geological Survey of Canada (Dyck, 1967). As shown, the parameters of our device are correlative throughout the range of

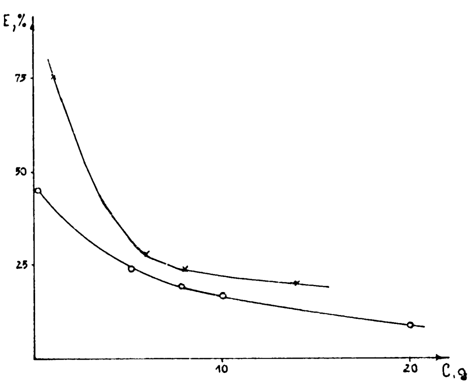

Fig 1. Active guard efficiency in reducing background with different amounts of scintillation cocktail. × — plastic scintillator, ○ — Geiger-Mueller counters.

carbon amounts used in proportional counters. The advantages of the scintillation counter are evident for greater sample sizes (up to 100g C). It should be mentioned that in our quartz vials, the value of the figure of merit is even higher. The figure of merit in a single-channel device is lower and this counting variant is used for standard serial measurements with the samples containing 3 to 20g C. Table 1 lists some standard systems used in our laboratory.

TABLE 1
Data for different scintillation counters

Type of counter	Amount of C (g)	Background (cpm)	Recent standard (cpm)	Efficiency (%)	Figure of merit $N_O/\sqrt{N_B}$
1-channel	9.7	4.3	63.6	48	30.7
2-channel					
shield from Geiger-Muller counters	9.7	4.2	69.6	53	34.0
"	20.2	6.9	141.6	52	53.9
shield from plastic scintillator	15.8	3.2	111.7	52	62.5
"	0.77	0.44	4.6	41	6.5

The scintillation method used for the measurements of ^{14}C in small carbon amounts

For ^{14}C measurements by the traditional liquid scintillation variant, 2 to 20g of carbon are needed for the scintillation cocktail. The application of the radiocarbon method has shown that quite often scintillation

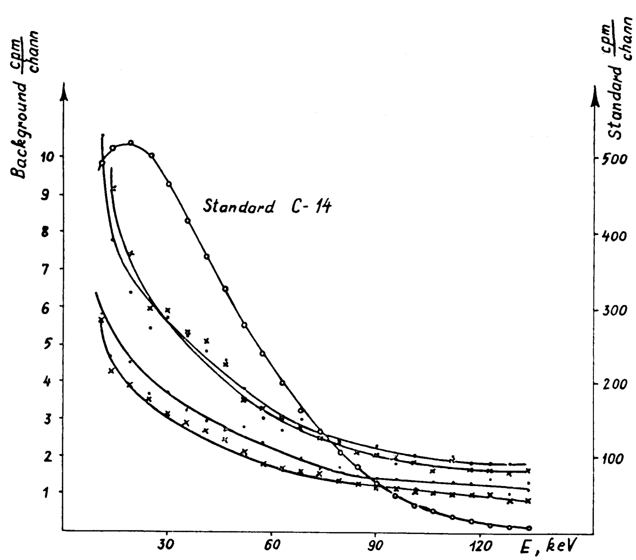

Fig 2. Energy spectra of ^{14}C and background with the active guard switched on (lower curves) and switched off (upper curves). ○ — ^{14}C, × — background with quartz vial, ● — background with aluminum vial.

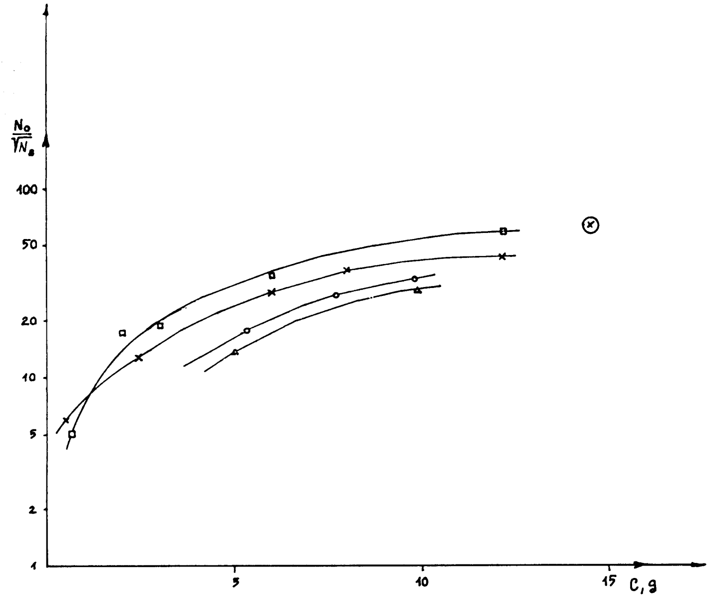

Fig 3. Dependence of the figure of merit on the amount of scintillation cocktail.
× — two-channel device with active guard from plastic scintillator
○ — two-channel device surrounded by Geiger-Mueller counters
△ — one-channel device
□ — proportional counter (Dyck, 1967)
⊗ — two-channel device with active guard from plastic scintillator, scintillation coctail in quartz vial.

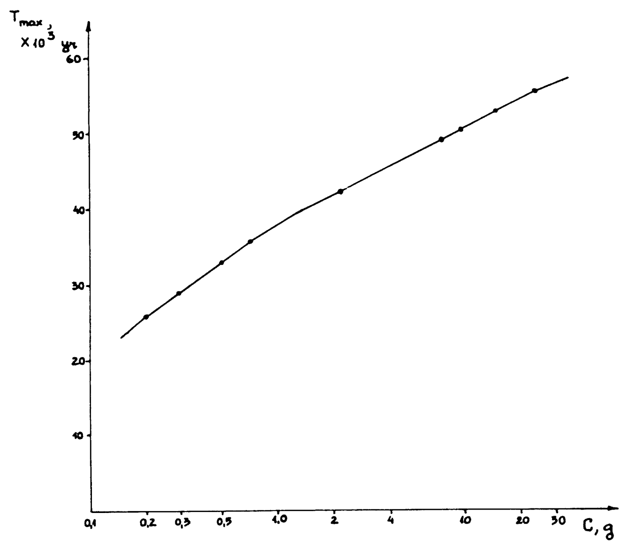

Fig 4. Maximum ages determinable with different amounts of scintillation cocktail (48hr, 3σ).

cocktails in which the carbon content is tens of times lower have to be used. In this case, proportional counters are usually used in which the traditional effective volume of counters varies from 0.5 to 5.0L of CO_2, C_2H_2, or other carbon containing gas and the amount of carbon subjected to measurements from 0.5 to 5.0g. Thus, the liquid scintillation and proportional variants supply each other. It is not always expedient to introduce both variants for serial measurements, especially when the problem may be solved by a single method.

Our studies were aimed at applying the scintillation variant to ^{14}C measurements of small samples. In order to synthesize the scintillation cocktail, benzene, from small carbon amounts or from samples poor in carbon, a special device was constructed. All the stages of the synthesis of the scintillation cocktail

$$(C \xrightarrow{O_2} CO_2 \xrightarrow{Li} Li_2C_2 \xrightarrow{H_2O} H_2C_2 \xrightarrow{cat} C_6H_6$$

were performed in the same system. Solid and liquid absorbers were avoided. The purification and transport of gases and C_6H_6 is performed with the help of freezing mixtures at different temperatures. C_6H_6 is frozen directly in the vial. Constantly high yield at all the stages of synthesis, small volume of the system and the lack of absorbers reduce the losses and eliminate the contamination or isotope fractionation during the synthesis. A quartz vial, 0.88ml in volume was made and was filled with the scintillation cocktail, containing 0.77g ^{14}C. ^{14}C activity was recorded on the counter of the two-channel active guard using photomultipliers, EMI-9524 and ФЭУ-85. The effect of the active guard was 73 percent and the background of the anticoincidence output was 0.44 ± 0.017cpm. Figure 4 presents maximum ages obtainable during a 48-hour measuring cycle with 3σ criteria dependence of the amount of carbon subjected to the studies. Although the statistical error increases (fig 5) with the decrease of carbon, it is quite possible to measure 0.1g of carbon (equivalent to 0.18L CO_2) and date samples up to 10,000 to 15,000 years old.

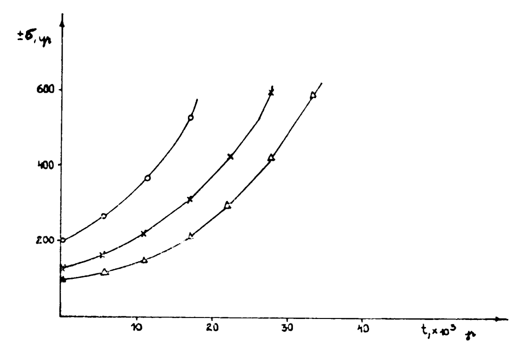

Fig 5. Statistical error with different amounts of scintillation cocktails (24hr measuring cycle). ● — 0.1g C, × — 0.3gC, ▲ — 0.6g C.

CONCLUSION

With the introduction of the plastic scintillator in active guard, the background of the liquid scintillation device in the ^{14}C channel decreased 30 to 75 percent. The efficiency of the active guard increases with the decrease of scintillation cocktail. The application of the active guard increases the stability of the device. Results obtained in studies of selection criteria for photomultipliers and reflecting properties of vials from different materials as well as thermostating the device, enabled us to date carbon of samples as old as 57,000 years.

Due to the low background of the two-channel device and stable working system, the ranges of the scintillation method increased. Improved sample synthesis technique, special vials, and photomultipliers enabled us to date samples with very low carbon content (up to 0.1g) and use the scintillation variant for solving some specific problems.

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DISCUSSION

Evin: How do you reduce sample evaporation?

Punning: To exclude evaporation we use stop-corks with special stoppings. For aluminium or steel vials we use aluminium stop corks. In the case of teflon or quartz, the stop corks are made from teflon.

Rauert: What is the maximum volume of benzene you can produce and measure?

Punning: For serial measurements, we use vials with volumes of 30ml, for solving special problems, 60 to 70ml.

Willkomm: What is efficiency of your plastic scintillation active guard?

Punning: It depends on the scintillation volume. The highest efficiency (75%) is obtained for small samples (0.5ml).

Eichinger: What is the total ^{14}C and ^{3}H counting efficiency?

Punning: I estimate total ^{14}C counting efficiency at about 80 to 85 percent. We have not used our devices for ^{3}H measurements.