^{14}C GAS COUNTING: IS THERE STILL A FUTURE?

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ABSTRACT. Reviewed here are developments in low background proportional counters and chambers used for low-level internal gas counting of ^{14}C. I have studied the influence of counter geometry and the nature of the gas filling on counter characteristics and describe in detail operational characteristics of multi-element proportional chambers. I also discuss detector developments for ultra-low-level gas counting based on a time projection chamber. My observations show that proportional and drift chambers, together with multichannel electronics operating on-line with a computer, open new possibilities in ultra-low-level gas counting.

INTRODUCTION

Proportional and liquid scintillation counters are the most reliable counting devices for ^{14}C measurements. They are able to achieve high sensitivity, accuracy and long-term stability. These features are extremely important for high-precision dating, *e.g.*, for establishing the ^{14}C calibration time scale.

Most ^{14}C laboratories engaged in tree-ring dating use gas proportional counting (GPC) techniques. The advantage of GPC is its flexibility in dating either very large samples (several liters, *e.g.*, for high-precision work or very old samples) or very small samples (several milliliters, *e.g.*, for atmospheric studies).

Liquid scintillation counting (LSC) has also become very popular, especially after the introduction of the Quantulus spectrometer, dedicated to low-level environmental isotopes. More efficient passive shielding, anticoincidence shielding, pulse-shape discrimination and the application of a microprocessor multichannel analyzer for recording spectra, rather than for simple counting, have enabled the counters to decrease background considerably and to obtain very good counting parameters (Polach *et al.* 1988). Another great advantage of LSC is fully automated, unattended, measurement for processing many samples per month. Although problems in high-precision dating and counting very small samples (*e.g.*, a large spread of data reported by LSC laboratories or problems with long-term stability) still exist, LSC may replace GPC for conventional ^{14}C counting in the future.

In recent years, accelerator mass spectrometry (AMS) has been the most important innovation for ^{14}C counting. AMS ^{14}C dating, though very expensive, is still developing, especially in improving precision and lowering background. Small tandem machines dedicated to ^{14}C measurements will considerably influence new developments in the ^{14}C field.

It is very healthy that we have, at present, three competing, partly complementary methods of ^{14}C counting. I shall concentrate here on further developments in GPC, which, I believe, are applicable to ^{14}C dating.

NEEDS AND LIMITATIONS

This section elaborates on two ^{14}C dating applications that would benefit from technological improvements in GPC:

1. High-precision ^{14}C counting of single tree rings
2. ^{14}C dating of very old samples (>60 ka) without isotopic enrichment.

At present, analyses of both types of samples are fraught with serious problems. One important contribution of single tree-ring dating is the study of the Earth-Sun relationship in the past, including the history of large solar flares. The present 10-half-life limit of ^{14}C dating may be extended, which will open new investigations for time scales over 60 ka.

What are the present limitations to such investigations? For the first problem, only GPC and LSC can reach a precision required for ^{14}C variations in tree rings (the standard deviation of $\Delta^{14}C$ should be smaller than 0.2 pMC in modern samples). Only long counting periods (more than one week) can achieve such high-precision ^{14}C measurements of single tree rings of limited size.

^{14}C dating of very old samples with both GPC and LSC without enrichment is limited to about 60 ka. We shall see below that certain improvements in GPC can increase the maximum measurable age. Owing to more involved chemical preparation procedures, benzene has higher chemical blanks than CO_2. This, together with limited sample size used in commercial LSC instruments (20 ml), may considerably limit the maximum measurable age by LSC (Long & Kalin 1992). AMS still has serious problems with high blanks and contamination of very old samples.

CRITERIA ON GAS PROPORTIONAL ¹⁴C COUNTERS

Long-Term Stability

When designing a proportional counter, one must consider several conflicting requirements. Limitations are set, *e.g.,* by counter volume, pressure of gas filling, high-voltage insulation, background, detection efficiency and geometry of the counter. The counter should have good counting characteristics, *viz.,* good detection efficiency, long flat plateau, stability of gas gain and good energy resolution. Good counting characteristics may not always be achieved because the electric field per unit pressure at the cathode is not sufficient to ensure saturation of ion collection. The condition for saturation of ion collection is particularly important for proportional counters designed for low-level ^{14}C counting, because the energy of primary electrons is very low and their loss deteriorates counter characteristics.

To achieve saturation of ion collection, the counter's electric field must be sufficient to enable the electrons to drift from their places of origin to the anode. At some distance from the anode, the electrons start to experience inelastic collisions and form electron avalanches. This region, in which the proportional amplification occurs, is of the order of the diameter of the anode wire. Thus, the electrons spend most of their time drifting in the much larger portion of the counter outside the avalanche region. In the case of counting gases with very low electron affinity, few electrons are lost. However, this is not the case in large volume counters with diameters of a few centimeters, where small impurities of electronegative gases are always present. Large diameters of the proportional counters are inimical to primary electrons because they can be captured more easily by electronegative atoms on their path from near the cathode to the anode (Povinec 1979).

The condition for saturation of ion collection can be characterized by the ratio, E_c p^{-1}, where E_c is the intensity of electric field at the cathode and p is the gas pressure in the counter. If E_c p^{-1} is very low, then electrons that originate at the cathode do not drift towards the anode; they are captured by electronegative molecules or they are lost in recombination processes. For a quantitative characterization of the processes in the counter, one must know the transit time of electrons from near the cathode to the anode. I have shown (Povinec 1979) that the electron transit time depends strongly on the type of gas filling and on counter geometry. Gas fillings used for proportional counters can be divided into three groups: 1) "very fast" gas filling, such as methane; 2) "medium fast" fillings (other hydrocarbon gases); 3) "very slow" gases, such as carbon dioxide.

The electron transit time increases or decreases with increasing E_c p^{-1}, caused by typical dependencies of electron drift velocities on E_c p^{-1} (Povinec 1979). The electron transit time depends also on the anode and cathode radii. Short transit times of electrons between the electrodes occur with "small" cathode diameters (~50 mm) and "large" anode diameters (~50 μm). Thus, the length of the counter plateau will increase with increasing diameter of the counter anode.

From the point of view of minimum transit time of electrons in the counter, it would be advantageous to operate the counter at E_c p^{-1} values where the electron drift velocity is at maximum. Table 1 shows E_c p^{-1} values for a few gases.

TABLE 1. $E_c p^{-1}$ Values for Minimum Electron Transit Time

Gas	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_8	CO_2
$E_c p^{-1} (Vcm^{-1}Pa^{-1})$	100	260	130	130	400	>400

Calculations of electron losses due to the attachment of electrons on electronegative impurities present in the gas filling have shown that *ca.* 0.1% of oxygen in carbon dioxide causes *ca.* 10% loss of drifting electrons per centimeter of their trajectories (Povinec 1979). Large-volume counters or counters filled to high pressures have increased sensitivity to electronegative impurities present in the gas. Oxygen admixtures in carbon dioxide filling should be kept below 0.001%, whereas a counter filled with methane has a plateau even with a few percent of oxygen.

Background

Proportional counters attain low backgrounds with passive and active shieldings. The counter is placed within a heavy shield consisting of 10–15 cm of lead or 20–30 cm of iron. A layer of polyethylene (or paraffin) with an admixture of boron blocks part of the neutron component of background. The best shielding conditions are in underground laboratories (Loosli & Oeschger 1982).

Active shielding consists of an anticoincidence system. The inner counter filled with a sample gas is protected against external radiation by a ring counter electronically connected to the inner counter in the anticoincidence. The inner and ring counters can be arranged in several ways. The most popular arrangement is an inner counter in the form of a metal tube surrounded by a ring of Geiger-Mueller counters. The counters with lowest backgrounds consist of a quartz tube coated with a metallic film, inside a copper or steel tube. By careful selection of counter parts to avoid radioactive contamination, one can reach a background of *ca.* 1 cpm liter^{-1} of sensitive volume (Tans *et al.* 1982).

Another possibility is to use inner (sample) and ring (active shield) counters configured as coaxial cylinders. It is advantageous to use a thin foil (Oeschger & Wahlen 1975) for the inner cathode, which is thick enough to allow only a small probability for β-particles from the inner counter to reach the ring counter. This counter became famous because of low background (below 1 cpm liter^{-1} of sensitive volume). Owing to the limited amount of material between the inner and the ring counters, the partial background produced by Compton electrons liberated from the inner cathode is very low. A disadvantage of this design is that it is common to use sample gas filling for both inner and ring counters, and this requires larger samples.

A very important improvement is pulse-rise-time discrimination (Mäntynen *et al.* 1987), which can decrease counter background by a factor of three.

Counter background level, as distinguished from background variability, seriously limits only the maximum measurable age. High-precision ^{14}C measurements require a counter with high-volume efficiency and steady, Gaussian background.

Sensitivity

Detection sensitivity can be improved, first, by increasing the number of radioactive atoms in the sensitive volume. This can be done by increasing the gas pressure in the counter or by using counting gases with more carbon atoms per molecule. However, an increase in gas pressure is rather limited in most proportional counters, because of high-voltage breakdowns and attachment of primary electrons. For large-volume counters, the working voltage may be near 10 kV, which poses serious problems to the electronics (microbreakdowns), if an input sensitivity of *ca.* 1 mV is required. As discussed above, the larger the diameter of the counter, the poorer the counter characteristics. The use of hydrocarbon gases is not recommended for high-precision work because of possible contamination and isotopic fractionation.

Considerable progress has been achieved by using several (7–10) identical counters placed in a common shield (Schoch *et al.* 1980; Tans *et al.* 1982). This system accommodates *ca.* 50-liter STP CO_2 samples to reach a precision below 0.2%. Table 2 compares a few typical counting systems.

TABLE 2. A Comparison of ^{14}C Counting Systems

System	Sample (gC)	B (cpm)	S (cpm)	FOM $S/\sqrt{B}$	Reference
GPC*	20.7	9.4	240	78	Tans *et al.* (1982)
MEPC	3.7	0.3	43	78	This paper
LSC	2.4	0.21	25	55	Polach *et al.* (1988)
AMS	10^{-3}	4	900	450	Damon (personal communication 1990)

*A system consisting of seven counters

NEW DEVELOPMENTS IN ^{14}C GAS COUNTING

Multi-element Proportional Chambers

After a thorough investigation of the characteristics of proportional counters, I have developed (Povinec 1980) a new type of detector for low-level ^{14}C counting, the multi-element proportional chamber (MEPC). The main aim of this detector is to achieve high-precision ^{14}C measurements of atmospheric CO_2 and tree rings with an accuracy of *ca.* 0.2%.

In MEPC, the simple single-wire inner counter has been replaced by a chamber consisting of seven or more element counters of the same dimensions arranged, *e.g.*, hexagonally, separated from each other by cathode wires only (Fig. 1). The counter diameter is considerably decreased, allowing higher gas pressure to be used at the same working voltage. Because the effect of electronegative impurities on the counter characteristics is much weaker, this counter geometry fulfills requirements of long-term stability.

A cylindrical array of wires separates the inner multi-element chamber from the conventional multi-wire ring counter. Thus, the same gas filling is used in both chambers. The design and construction parameters of MEPC should be optimized from several points of view. One should select the number of elements, their structure, dimensions, number and diameter of cathode wires,
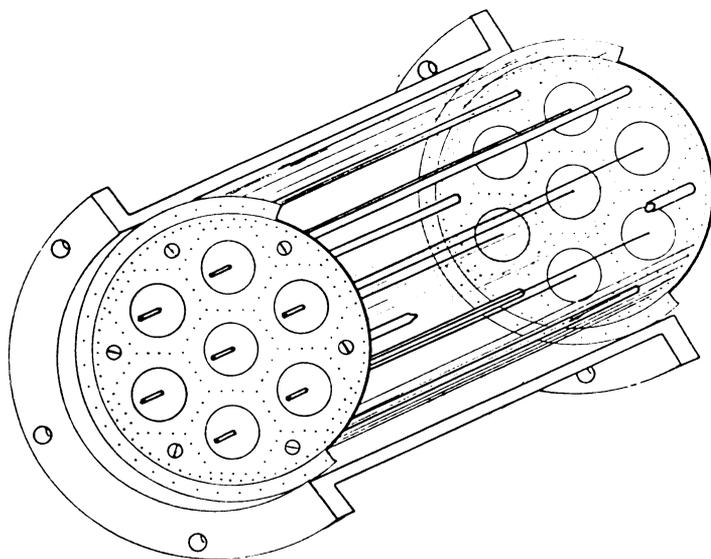
Fig. 1. Multi-element proportional chamber

diameter of anode wires, *etc.* For a properly designed MEPC, one should solve electrostatic problems in the multi-element structures (Szarka & Povinec 1979).

Construction Parameters of MEPC. Several MEPCs were constructed for low-level ^{3}H and ^{14}C counting (Povinec 1972; Povinec, Szarka & Usacev 1979) and for double β-decay experiments with Xe gas filling (Alessandrello *et al.* 1986; Kuzminov *et al.* 1986).

The chamber body of MEPC designed for ^{14}C counting consists of a stainless steel tube that works simultaneously as the outer cathode of the multiwire counter and the vacuum insulation of the chamber. The chamber can be evacuated to 0.1 Pa and filled with a counting gas to 1 MPa. The thickness of the ring counter is 1 cm, which is optimum for high detection efficiency of the ring counter for external radiation and high volume efficiency of MEPC for the internal radiation. The ring counter has 40 anode wires with diameters of 50 μm.

Hexagonal element (cell) counters were chosen as the best compromise between the electrical properties and fitting the element counters into the inner cylinder. The length of the element diagonal is 34 mm for the 7-element chamber and 28 mm for the 19-element chamber. The sensitive volumes of the chambers are 1.4 and 3.4 liters, respectively. The element counters are made of wires with diameters of 100 μm which form the cathodes. The anodes in the centers of the hexagonal element counters have diameters of 50 μm.

Electronics for MEPC. The element counters are supplied by a common high-voltage power supply through a resistance/capacitance high-voltage filter and a load resistor. A charge-sensitive preamplifier picks up the signal and feeds it to a linear amplifier, then to a pulse-height discriminator. Both analog and digital signals are available. Microprocessor-based electronics for signal processing have been developed so that various configurations in the arrangement may be analyzed by suitable software. This makes the electronics cheaper and more universal. A microprocessor-based multichannel analyzer is connected to the analog output for amplitude analysis. The system is controlled by a personal computer. The electronics register every output of the seven-element MEPC. This allows for external anticoincidence (*i.e.,* between the element counters and the ring counter), as well as internal anticoincidence (*i.e.,* between element counters).

The 19 elements are grouped to 3 independent groups, so that no element of a group adjoins any other element of the same group. For further improvements, one should use the electronics developed for double β-decay experiments with the MEPC (Alessandrello *et al.* 1986) for signal processing. The aim of these electronics is to read out the energy deposited in each element of the chamber for every event. After amplification, the charge signal is digitized by a seven-bit flash analog to digital converter (ADC) working at a sampling period of 100 ns. Also, the rise-time of the signal is acquired and all the information is recorded onto magnetic tape for further off-line analysis. The data acquisition system, based on the flash ADC, is a powerful tool for using MEPC as a typical track detector.

Characteristics of MEPC. The differences in the plateau length between element counters are within 50 V, which enables all the elements to perform satisfactorily. This indicates that the non-uniformity in geometry of element counters on the chamber performance is not critical. The background of the 1.4-liter shielded chamber is 170 cpm, when filled with CO_2 to a pressure of 0.5 MPa. With external anticoincidence, the background reduces to 1.9 cpm. Background under these conditions is a positive function of gas pressure. The final background obtained with both internal and external anticoincidence in operation is an almost constant 0.39 cpm and is independent of gas pressure. The final background is still several times higher than that in an underground laboratory (Bellotti *et al.* 1991).

We believe that further decrease in counter background may be obtained by flash-ADC data acquisition, that utilizes both energy and time measurements (Alessandrello *et al.* 1986).

The Time Projection Chamber

Multiwire proportional chambers and drift chambers open new possibilities in ultra-low-level gas counting (Povinec 1980, 1982). These detectors enable perfect track mapping and, if operating in a magnetic field, they also measure the momentum and energy of particles. A time projection chamber (TPC) may be very useful for ultra-low-level ¹⁴C counting. In a TPC, a large drifting space, containing a sample gas, is used for particle registration, and a multiwire proportional chamber is used for particle mapping. The TPC is a powerful detector widely used in high-energy physics experiments. It offers three-dimensional particle track reconstruction with a space resolution of about 0.5 mm, which is much better than needed for low-level counting. Although the electronics are much more complicated in the TPC than in conventional proportional chambers, the TPC can obtain full information about the registered particles. This sophisticated technique not only simply registers particles but also shows what is going on inside the chamber. Several TPCs designed for double β-decay experiments have been constructed (Elliot, Hahn & Moe 1987; Wong *et al.* 1991). However, because of complicated electronics, TPCs still wait for applications in conventional low-level counting.

Figure 2 shows the scheme of the TPC (20-cm diameter × 20-cm height). The proportional chamber is placed at the end of the drifting space. Electrons liberated by the registered particle in the gas drift to anodes. The pulse registration occurs from anodes and from cathode strips. The proportional chamber will furnish the x- and y-coordinates. The z-coordinate derives from the drifting time of electrons from their origins to the anodes. If a larger volume is required, a new drift space can be formed from the side of the proportional chamber, which then works at the center of the TPC. The design follows the construction of the TPC dedicated for double β-decay experiments (Povinec *et al.* 1990).
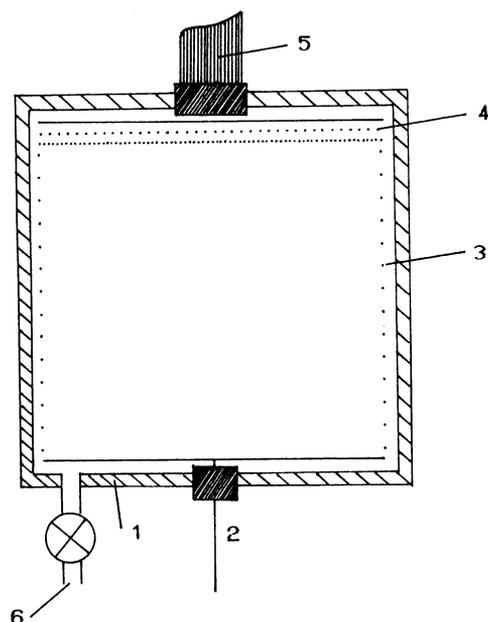
Fig. 2. Time projection chamber. 1. Chamber body; 2. Cathode (-HV); 3. Field-shaping electrodes; 4. Proportional chamber; 5. Signal output; 6. Gas inlet/outlet.

Particle range discrimination eliminates background events. This is especially suitable for short-registered particle ranges, such as ^{14}C βs. Sample gas pressures at several atmospheres ($>10^5$ Pa) are needed to effectively stop βs in the sensitive volume of the TPC. For short drift times, the best gas filling is methane; however, CO_2 can also be used if cleaned of electronegative impurities. The TPC can attain a very low background, perhaps ~1 count per day, if operating in an underground laboratory. The detection efficiency would be almost 100% (Povinec *et al.* 1990), which would enable detection of a few ^{14}C decays per day. This remarkable improvement in detection sensitivity would press back the present counter limitation for maximum determinable age for ^{14}C dating. Thus, if TPC does, in fact, realize expectations for ^{14}C dating, counter background will not be the problem for dating samples >60 ka, and only sample contamination remains. Development will then focus only on elimination of sample contaminants during sampling, pretreatment and gas preparation.

CONCLUSION

After thorough investigation of processes in proportional counters, I have shown that multiwire chambers have several advantages as low-level gas ^{14}C detectors. If they are used in the form of multi-element chambers, they do not require complicated electronics, and with the selection of a suitable dimension of the element counter, they may improve detection sensitivity. Also, with a suitable combination of various discrimination methods, *e.g.*, internal and external anticoincidence, amplitude and pulse-shape discrimination, one can minimize chamber background. Further, new sophisticated detectors for ultra-low-level ^{14}C gas counting may be developed. I believe that new techniques of particle registration developed in high-energy physics will have wide applications in ultra-low-level counting. These techniques will enable us to study very rare decays and processes in fully automated experiments. Time projection chambers, together with multichannel electronics operating on-line with desktop computers, open new possibilities for future ^{14}C investigations.

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