GAS COUNTING SYSTEM FOR ^{14}C DATING OF SMALL SAMPLES IN THE KRAKÓW LABORATORY

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ABSTRACT. The application of traditional gas or liquid scintillation counting (LSC) is necessary for assessing radionuclide activity in countries without operating accelerator mass spectrometry (AMS) facilities. A simple and relatively inexpensive system of mini gas counters for measurement of radiocarbon in archaeological and environmental samples has been set up recently in the Kraków laboratory (Department of Environmental Physics, University of Mining and Metallurgy). The system is composed of a gas purification and counter filling line, three identical 15-mL copper/quartz counters, active and passive shielding, and an electronic unit with data acquisition. One counter measures 22 mg of carbon as CO_2 with efficiency >95% at a background reduced to 0.044 cpm by a NaJ(Tl) guard counter and lead shield. The detection limit (1 σ) for a two-week measurement of 48 mL of CO_2 is 0.52 pMC. The corresponding counting error of a 100 pMC environmental sample is 1.3 pMC for 22 mgC (one counter) and 0.75 pMC for 66 mgC (three counters filled with the same sample).

INTRODUCTION

Samples containing milligrams of carbon are currently ^{14}C-dated mainly by the accelerator mass spectrometry (AMS) technique. However, in many cases, small gas counters can offer similar measurement parameters at very competitive prices. Traditional techniques, which can assure high sensitivity, accuracy and long-term stability, remain the only choice in countries where access to an appropriate accelerator is limited or impossible. Over the past few years at the Kraków laboratory, we have designed and put into operation a system of small counters. Further extension with counters of higher volumes is possible in order to cover the range from milliliters to *ca.* 0.5 dm^3 of CO_2. Laboratory experience shows that archaeological and numerous environmental samples require a technique for ^{14}C measurements that provides acceptable precision for carbon content <1 g. We present here our construction of a simple and inexpensive system of miniature gas counters consisting of both commercially available parts and self-made electronic elements and mechanical parts.

Gas Counter

The small and miniature gas counters currently operating in ^{14}C laboratories have been developed over last two decades, based on various technologies. The first small quartz-tube counters (Harbottle, Sayre and Stoenner 1979; Otlet *et al.* 1983) initiated further development of metal-tube counters (Jeleń and Geyh 1986) made of low activity copper. The results from gas-counting laboratories point to a high-purity copper (OFHC) as one of the best cathode materials for gas counters. This was confirmed in a review by Mook (1982), showing that when quartz, steel and copper are tested, the best results are obtained with copper counters.

The three miniature proportional counters (PC) studied are made of a modernized version of copper/quartz described elsewhere (Jeleń and Geyh 1986), and produced in cooperation with the ^{14}C Laboratory, Hannover. Isolators, used to close both ends of the counter tube (lids), were made of synthetic quartz (Suprasil, Hereaus, Hanau) and connected to the copper tube using a two-component glue (UHU, hard 300, FRG). The anode wire, made of 25-μm gold-covered stainless steel (Leico Industries Inc, NY) is attached at one end to a small tension spring, and at the other it is soldered to a stainless-steel tube used for high-voltage input (Fig. 1). The effective volume of the counter is 15 mL (*ca.* 94% of total volume), with an active length of 6 cm, diameter 1.8 cm and operating voltage 5200 V at 3 bars of CO_2. All three counters work at the same high voltage. A long plateau of *ca.* 1100 V (Fig. 1) begins at practically the same voltage for all counters and remains constant for at least three months.

The counters have a very stable background, ranging from 0.044 to 0.047 cpm, while 1 σ = 0.001 cpm. Counting efficiency is >95%, providing a counting rate of 0.285 cpm for modern carbon (100 pMC). All three counters have parameters very close to those from a previous version described by Jeleń and Geyh (1986). They are also comparable to the small and mini counters described by Otlet *et al.* (1983) and Kaihola *et al.* (1984).

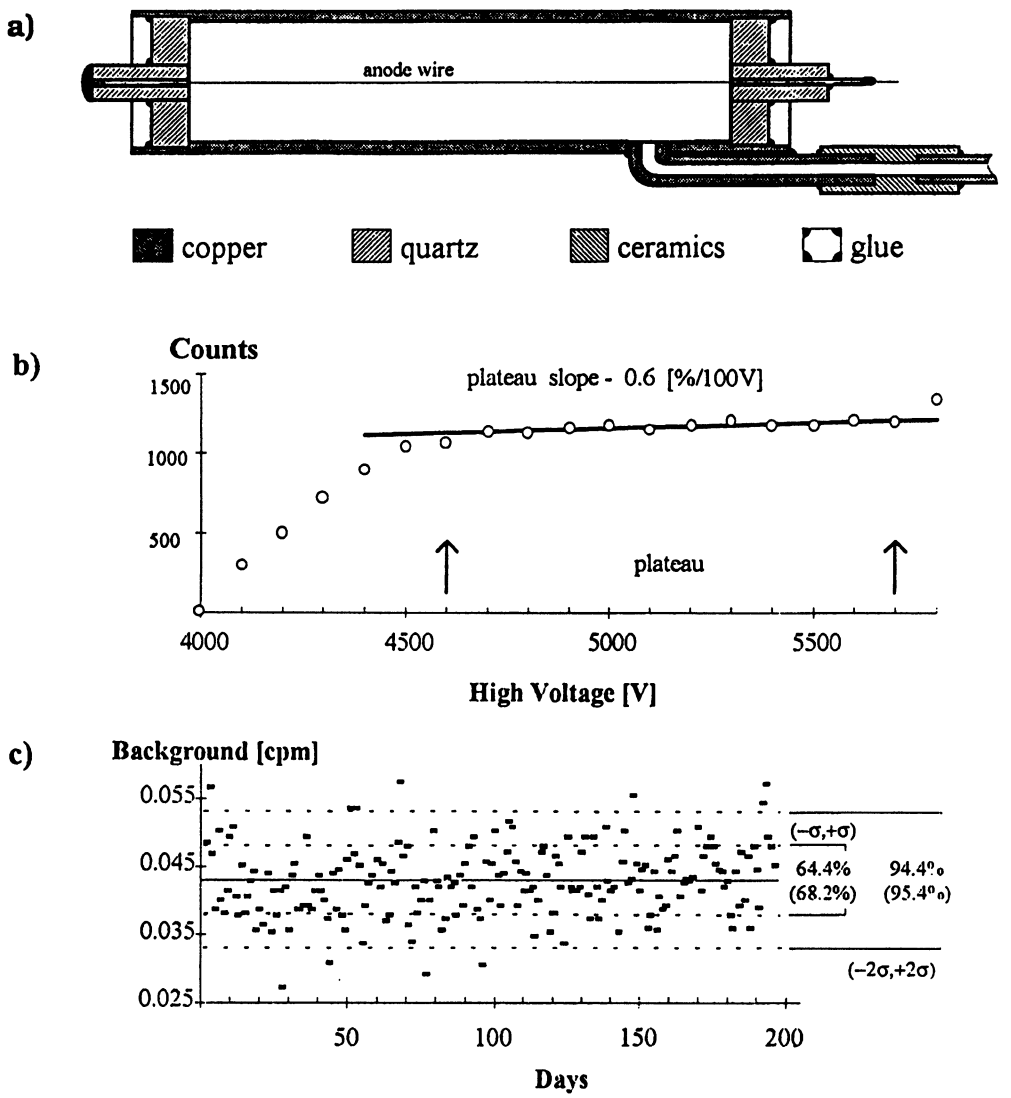


Fig. 1. a) Copper/quartz 15-mL proportional counter. Plateau 1100 V long (CO_2, p = 2300 Tr) was not changed after 190 days of work. b) One day background measurements (N=190) show normal distribution. c) Theoretical frequencies (in brackets) in 1-σ and 2-σ intervals (σ for a single measurement).

Purification System

We decided to use CO_2 as a counting gas because of its simplicity of technical operation and to avoid the complicated chemical procedures necessary for the synthesis of methane or higher hydrocar-

bons. The required high degree of CO_2 purity is obtained either by eliminating contaminants (especially electronegative NO, NO_2, SO_2, O_2, *etc.*) in chemical reactions (Srdoč and Sliepčević 1963; Jeleń and Geyh 1986) or by physical purification on active charcoal (Schoch *et al.* 1980). This is a relatively easy and efficient procedure which can be partially automated. The purification glass line (Fig. 2) was tested with different types of charcoal; temperature, pressure and time for the purification process were optimized. This method turned out to be very efficient for cleaning CO_2, both in the case of wet-oxidized inorganic samples, and for "dirty" organic samples combusted in a stream of O_2. Three types of charcoal were used: Silcarbon SC 40, Silcarbon C 46 (Silcarbon Aktivkohle GmbH, Germany), and Merck 2515 (E. Merck, Germany). In each case, the necessary mass of charcoal was *ca.* 20 g in a column *ca.* 200 cm long for cleaning 6 dm^3 (760 Tr, t = 20°C) of "dirty" CO_2 from organic samples (high content of impurities). For smaller samples the quantity of charcoal can be proportionally reduced. An increase in background when charcoal of unknown origin was used suggests probable radon contamination.

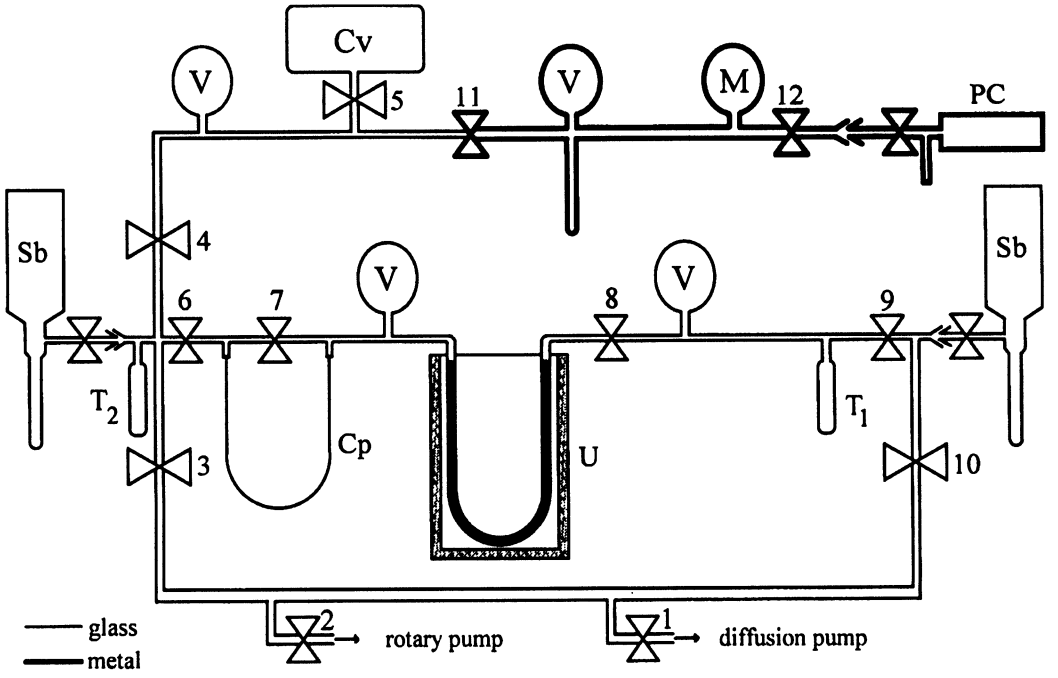


Fig. 2. Purification (glass), and counter filling (metal) system

Carbon dioxide frozen in trap T_1 (Fig. 2) passes after sublimation through a charcoal column (U-tube or spiral shape) kept at 0°C, and a capillary tube before it is again frozen in cold finger T_2. Pressure gauges installed before and after the charcoal column assure permanent control of the pressures which at the inlet to the charcoal is kept at *ca.* 1000 mbars. The Pirani gauge at the outlet indicates when the purification process is completed (p<1 Tr) after *ca.* 45 min. An overall yield >95% is obtained (a small amount of CO_2 is absorbed in the charcoal). Recovery of the charcoal column requires heating

to 430°C with simultaneous pumping for 1 hr, and flushing with pure N_2 in the last 15 min. The metal part of the line (Fig. 2) is equipped with a precise manometer for filling the counter to standard pressure of 2300 Tr, and precise volume calibration of the measured CO_2.

Active and Passive Shielding

For active shielding, we apply a commercially produced well-type NaJ(Tl) scintillation detector (Crismatec, France, model 127YPEA 152) with well depth of 12 cm and diameter of 5 cm. The detector works in a horizontal position, with a type 9791 photomultiplier (high voltage: 760 V, resolution for 662 keV line (^{137}Cs): 9.6%). Background components of low-level gas counters in the last two decades have been thoroughly investigated (Mook 1982; Theodórsson 1992; Theodórsson *et al.* 1992), leading to the conclusion that massive shielding made of selected material (lead or iron) is still an important method for background reduction. Our counting system is located in the cellar (basement) of a four-story building (vertically *ca.* 12.2 m of water equivalent), where we have constructed traditional passive shielding in the form of a cube (130 cm × 120 cm × 105 cm) with four measurement chambers for independent counter systems (Fig. 4). Test experiments of background reduction carried out for different configurations (Table 1) showed that in the case of the best shielding efficiency (chamber A) background was reduced by a factor of 30 compared to that obtained outside the shield.

TABLE 1. Background Reduction for Different Configurations

	Place of measurement			
	Outside the shield (cpm/fraction*)	Chamber C new lead (cpm/fraction*)	Chamber A new lead, borated paraffin, old lead (cpm/fraction*)	Chamber B removed 20% of bottom old lead (cpm/fraction*)
Counter type				
Copper/quartz counter / Backgr., anticoincidence	1.29 ± 0.09/ 1.00	0.068 ± 0.016/ 0.053	0.044 ± 0.001/ 0.034	0.14 ± 0.03/ 0.108
GC (scintill. NaJ(Tl))	48,650 ± 27/ 1.00	1735 ± 7/ 0.036	1185 ± 20/ 0.024	4030 ± 5/ 0.083

*Fraction of count rate outside the shield

A significant contribution is possible from gamma radiation entering from different directions (opened front wall increased background 3.5 times). It has been shown that old lead is the best shielding material since it does not contain primordial radioactivity (Artur, Reevers and Milla 1988; Heusser 1989) in contrast to "young" lead, which may contain 20–500 Bq kg^{-1} of ^{210}Pb and its progenies. In our case, a 5-cm-thick old lead layer inside the shield reduces background 1.6 times (Table 1). A remarkably high contribution of γ radiation from ^{214}Bi content in construction materials (concrete, sand) is observed, *e.g.*, the removal of 20% of the bottom lead layer in chamber B (Fig. 4) increased the background by a factor of 4, mainly due to a very well pronounced broad peak in the energy range 1100–1400 keV, a narrow one at 609 keV, and a higher low-energy continuous spectrum. A small contribution from the 1460 keV line from ^{40}K was possible. Low-level laboratories organized in a basement or underground are potentially subjected to high radon levels. However, the ventilation system in the laboratory rooms and/or flushing the shield by nitrogen or "old" pure air removes this gas. Care should be taken to avoid radon progenies easily sorbed on surfaces.

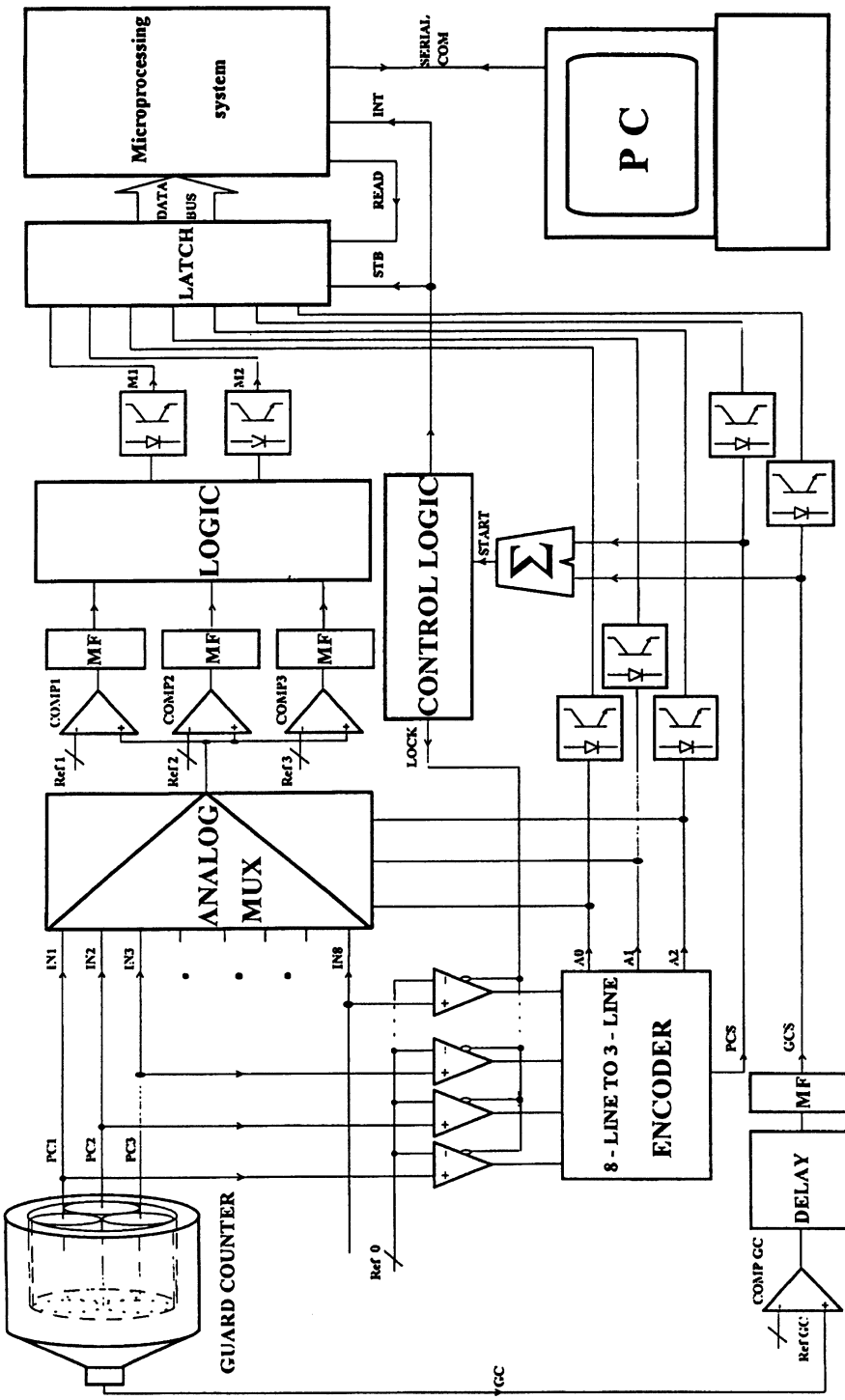


Fig. 3. Block diagram of electronics

HV Supply and Electronics

A long and very stable plateau (Fig. 1) from each of the three counters allows the use of one high-voltage supply for the proportional counters while the second feeds the guard counter. Three counters (PC) are placed inside a well-type scintillation detector NaJ(Tl), which acts as a guard counter (GC).

Each PC specified above is equipped with a two-stage, charge-sensitive preamplifier (gain = 125 V/V) built next to it, in the same metal case. Signals from the preamplifiers feed an analog multiplexer and discriminator circuit, where they are digitized (Fig. 3). Information on amplitude is sent from a logic block to the microprocessing system where it meets signals from PC and GC. Separation of coincidences from anticoincidences is performed with computer software. Input of the microprocessor board is isolated by an opto-coupler in order to avoid backward influences of digital to analog signals. Direct addressing to microprocessor memory (Intel™ 8031) reduces the total resolution time of the detection system to *ca.* 45 μs. A simple personal computer collects data (RS-232 transmission standard) and allows for automatic control of the measurement process.

Our simple electronic unit performs pulse-height analysis; the basic concept is similar to that described by Otlet *et al.* (1983), and also to that used at the ^{14}C Laboratory, Hannover (Jeleń and Geyh 1986). It uses four energy channels with adjustable low-level and upper-level discrimination and 1 channel for GC. Eight independent information channels allow connection to 8 counters. Possible future techniques for more advanced counting evaluation include pulse-shape discrimination with individual analysis of each pulse; the estimated background reduction would be *ca.* 20%.

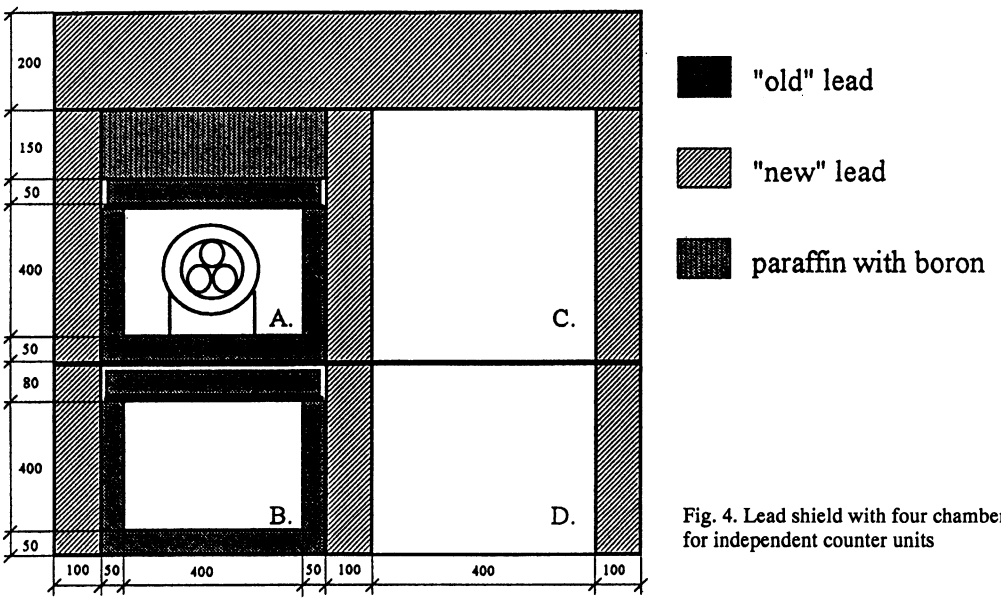


Fig. 4. Lead shield with four chambers for independent counter units

Results and Conclusion

The miniature gas counting system was constructed and set into operation with a relatively small financial effort (total costs *ca.* U.S. $22,000, not including lead shield). The measurement parameters obtained are close or identical to those published by laboratories that have been using this technique for years. A stable background of 0.044 ± 0.0015 cpm (σ calculated for N=200 of 100-min

cycles), and counting efficiency of 95% determines the detection limit (2 σ criterion) in over a two-week counting period to be 37.5 ka (0.93 pMC), and the measurement error (1 σ) for modern samples to be 1.33 pMC for 22 mg (1 counter) and 0.76 pMC for 66 mg (3 counters) of carbon. The dating error (1 σ) for 30 ka and 10 ka samples for standard measurement (1 counter, 2 weeks) is +2.5 ka, −1.9 ka, and +290 a, −280 a, respectively. These figures can be reduced to +1.3 ka, −1.1 ka, and +170 a, −160 a when the sample is counted in three counters.

In many cases, we are interested in the results (dates) at a given precision level that needs counting time adjustment according to sample activity (age). Two percent of the relative error (1 σ) requires 126 counting days for 30 ka samples, and 21 counting days for 10 ka samples. Assuming that we have in a year only three samples of 30 ka, and the others are 10 ka and all dates are with 2% error (1σ), the yearly throughput of our system is 18 samples, except these 30 ka (standard or background is measured for two weeks after each sample).

It was again documented that a massive shield made of materials selected for low radioactivity content plays a dominant role in background reduction, especially when a scintillation counter is used as a guard. The content of uranium and thorium series radioisotopes in constructional materials, especially radon and its progenies, may contribute considerably to the observed background. Purification of CO_2 using the sorption technique seems to be an easy and reliable method for getting counting-grade gas. Further reduction in background by pulse-discrimination analysis for small carbon samples can improve the precision of measurements. However, sophisticated electronics are necessary, and for modern samples, the advantage is negligible.

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