SOURCES OF RANDOM ERROR IN THE DEBRECEN RADIOCARBON LABORATORY

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ABSTRACT. A new high-pressure methane-filled counter system for ^{14}C dating was installed in 1986 when the first stage of the International Collaborative Study (ICS) started. Random errors in the new measuring system and in the process of chemical pretreatment and preparation were checked during the three years of intercomparison. Results show that the most important source of error in our laboratory is gas contamination. This causes variation of the count rate to exceed the statistically expected variability. Other sources of error are also discussed and limits of their contributions are given.

INTRODUCTION

The procedure of assessing errors in radiocarbon measurements using replicate sample analysis is laborious and very time consuming. However, this is the only way to estimate random error. We used our new radiocarbon measuring system to check random errors and various chemical preparation methods during the three years of the International Collaborative Study (ICS).

PREPARATION METHODS, MEASURING SYSTEM

Chemical Pretreatment

Wood. The samples were treated with AAA (acid-alkali-acid) and then fragmented into small pieces (<10mm) and ground. The sieved fraction (0.2mm < grain size < 1mm) was treated with 4% HCl (80°C, 24 hr), then with 4% NaOH (80°C, 24 hr) and finally washed with highly diluted HCl until pH 3 was reached.

Peat. The samples were leached in 4% HCl at 80°C for 24 hr and dried.

Shell. Shell samples were ultrasonically washed several times; then 20-30% of the material was removed with 2% HCl. The remainder material was divided into one outer and one inner fraction.

Preparation of the counting gas. The pretreated organic samples were combusted, the carbonate samples were decomposed by acid evolution or thermal dissociation and the evolved CO_2 was purified and synthesized into methane (Csongor, Szabo & Hertelendi 1982).

Activity measurement. The activity of the methane was measured with proportional counters (Hertelendi et al 1989). The counter system consists of nine electrolytic copper proportional counters of identical diameter with sensitive volumes of 350-700cm^3 and filled with either methane at 0.6MPa or CO_2 at 0.1MPa. The inner counters are surrounded by an anticoincidence shield consisting of five multiwire proportional flat counters filled with propane. Table 1 gives the important parameters of the system.

DISCUSSION OF RESULTS

Errors due to pretreatment were small compared with the errors of the activity measurements. In the case of shell and wood, the various fractions were measured separately and the difference between the fractions was not significant.

TABLE 1
System characteristics

| System parameters | Counters | | |
	Type 1	Type 2	Type 3
Total active volume (cm^3)	350	500	700
Standard counting rate (S) (cpm)	14	19	26.5
Background (B) (cpm)	0.7	1	1.4
Figure of merit (S/√B)	16.7	19	22.4
Max measurable age (2 days) (yr)	40,700	41,700	43,100
Precision for modern sample (7 days) (‰)	4	3.4	2.9

Burning the material and the methane synthesis also did not cause significant errors in the dating process. The yields were nearly 100%. The only exception was the thermal dissociation of carbonate samples, which resulted in low yields and fairly large fractionations compared to the acid evolution method.

Gas purification is a very critical step in the dating process. The simplest and very sensitive test of gas purity is the measurement of the plateau shift of the proportional counter. The disadvantage of this method is that it is not selective and cannot identify the type of electronegative contaminants causing the deterioration of the gas amplification factor. Selective methods such as mass spectrometry, gas chromatography and ion chromatography are expensive, laborious and often not sensitive enough for determining NO_x, SO_2, O_2, H_2O at the required level of a few ppm. The quantitative detection of electronegative trace gases does not allow correction of the count rates. Therefore, the only solution is to use pure gas. In the present system, we use BASF R-3-11 catalyst for gas purification. The reduced form of this catalyst binds the O_2, SO_2 contaminants and reduces the NO_x to nitrogen gas, which can be pumped off after freezing out the CO_2 gas. However, the exhaustion properties of the BASF R-3-11 are not well known and, in some cases, we observed 50-100 V plateau shifts during the last three years. This was probably caused by NO_x contamination. (Other contaminants such as SO_2, O_2 and Cl_2 react with the Ru catalyst during methane synthesis.)

To make the purification process easier, we began using the bomb combustion method instead of an oxygen stream combustion method. At an oxygen pressure of 0.8MPa, the reaction products SO_2 and NO_x are oxidized in the bomb immediately to SO_4^{2-} and NO_3^-. These products precipitate on the wall of the reaction vessel. First experiments show that practically all contaminants are removed in the combustion bomb and only traces of SO_2 and NO_2 must be subsequently trapped in an activated charcoal column for final purification. To measure the amount of SO_2 and NO_x that were removed from the combustion gas inside the combustion bomb, we analyzed by quadrupole mass spectrometry the combustion product gases without further purification. We detected no SO_2 or NO_x contamination after the combustion of peat samples. The sensitivity of the mass spectrometer for the SO_2 and NO_2 is ca 1ppm. The detection of the electronegative trace gases is not possible with a mass spectrometer if the concentration is <1ppm. Therefore, a purity test counter will be used for routine gas purity check in the future.

Counting gases can also be contaminated during storage, filling and measurement. Epoxy sealing of proportional counters, soft-sealed valves and other parts of the measuring system desorb gases practically undetectable by mass spectrometers. This type of contamination caused the decrease of our reference values during the last few years (Fig 1). In this period we used several times the same standard gas produced from NBS oxalic acid. This was an earlier practice in our
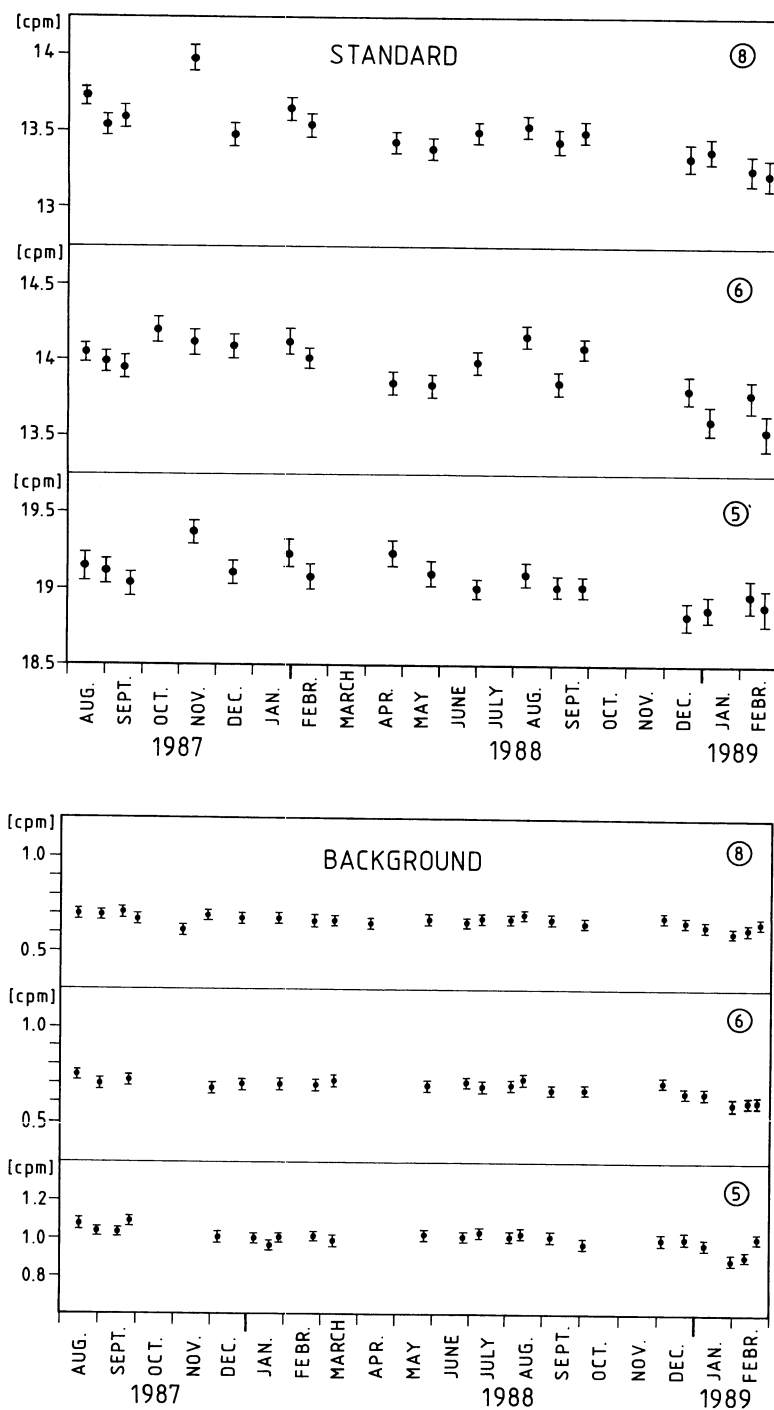
Fig 1. Variation of standard and background values *vs* time counters number 8, 6, 5

laboratory when we filled our previous proportional counters up to 0.1MPa with methane. However, high-pressure CH_4-filled counters are much more sensitive to contaminants and they require the use of high-vacuum valves and an all-metal filling system in order to avoid desorbed gases. The continuous decrease of our standard value due to desorbed gases was the reason we measured significantly higher apparent activity values for samples in the third stage of the ICS. To avoid this type of contamination, the present filling system will use metal seals and NUPRO SS-4BK bellows seal valves and a high-vacuum pump.

The most important source of random error during the activity measurement in our laboratory is gas contamination resulting in variation of the gas amplification factor. We have observed a plateau shift of maximum 100 V in recent years. We do not use an empirical purity correction and we measured the characteristics of the proportional counters with cosmic ray muons. Thus, we did not detect shifts lower than 30 V. Samples of measurable shift were rejected for direct measurement and were to be repurified. A 30 V shift of the characteristic means ca 7‰ in the counting rate if the slope of the plateau is 2%/100 V. This uncertainty exceeds the statistical standard deviation.

Other sources of error are supposed to be smaller than the typical 4‰ statistical standard deviation. These are variation of gas density and background, shift of the working point on the characteristic due to temperature change, inaccurate pressure measurements, memory effect, radon and other radioactive gas contamination, tritium contamination of synthesized methane, remaining excess hydrogen in the methane after the synthesis, spurious counts, shift of the discriminator level and change of the amplification factors in the signal processing system.

We estimated the error contribution caused by the uncorrected gas density variation using the long-term temperature variation of the proportional counters. We typically observed a weekly change of 1°C resulting in a maximum of 3‰ error in the count rate.

The dependence of the background on atmospheric pressure is 2%/kPa. A 2kPa uncorrected atmospheric pressure change results in a 2‰ uncorrected error in the standard counting rate. The long-term decrease of the background shown in Figure 1 is probably caused by gas contamination.

The shift of the working point on the characteristic caused by temperature change is negligible. Our typical 1°C temperature variation causes 3.4‰ pressure change in the counter resulting in a 4-6 V shift of the characteristic and ca 1‰ uncertainty in the count rate.

Regular measurements of ^{14}C stack samples from a nuclear power plant show that the sample-to-background memory is immeasurably small when we date natural samples. Our experiences show that the use of clean active gases in our system is safe as long as the activity is not higher than 100 times the standard activity.

The tritium content of the hydrogen gas used for methane synthesis is <1 TU and the remaining excess hydrogen in the methane gas after the synthesis is <0.3‰. The hydrogen content of the synthesized methane was measured regularly with a Pirani gauge after freezing the methane down to the liquid nitrogen temperature.

The remaining CO_2 after the synthesis is <1‰ checked regularly with a mass spectrometer.

The filling pressure is controlled with a Wallace & Tiernan precision difference pressure gauge Type D-62 A 040. The pressure in the case of the difference gauge is measured with an A 61 A-340 absolute pressure gauge. The technical parameters of these gauges are: accuracy 0.66‰, repeatability 0.3‰, hysteresis 0.5‰, maximum temperature effect 0.1‰/°C of the full scale. Using these parameters, the error in the standard counting rate is <1‰ due to inaccurate pressure measurement.

To avoid radon contamination, the gases are stored for a month after the methane synthesis in stainless-steel containers under high pressure.

The temperature dependence of our electronics is ca 10^{-4}/°C. Thus, the shift of the

discriminator level, the change of the amplification factors and the high voltage cannot cause errors in the counting rate larger than 1‰.

The anticoincidence energy spectrum is continuously monitored by a multichannel analyzer. Spurious pulses due to electrical leakage across the insulators are accumulated in the low-energy region of the spectrum. Observations show that these pulses do not appear in the spectrum if the high voltage of our proportional counters is <5 kV.

The contribution of these sources to the total error cannot be estimated for a specific sample. This is the reason why most of the laboratories calculate only the statistical standard deviation. However, the ICS and some previous studies show a scatter of data 2-3 times larger than the statistical confidence intervals (Scott *et al* 1989; International Study Group 1982, 1983; Otlet *et al* 1980).

CONCLUSION

Some of the results obtained in the frame of the ICS differed consistently from the average values calculated from the data obtained by the participants. The primary reason of the deviation was the use of a contaminated standard. The experiences of the ICS show us that we need pure gases checked routinely by a purity test proportional counter. In order to improve the purity level of gases, further development of the burning, purification and filling system is necessary. The introduction of density and empirical purity correction (Tans & Mook 1978) will also improve our accuracy.

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