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FAST ^{14}C SAMPLE PREPARATION OF ORGANIC MATERIAL

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ABSTRACT. A fast ^{14}C sample preparation technique for organic material in conventional ^{14}C counting is described. The basic difference from conventional preparation is oxidation of the organic substances in a closed system under an oxygen pressure of ca 10 bars. After the explosion-like combustion, the reaction products SO_2 and NO_2 are oxidized immediately to SO_4^{2-} and NO_3^- and precipitated on the wall of the reaction vessel. The residual gas mixture is passed first through a cold trap at −78°C to remove water vapor and then through an activated charcoal column at 0°C for purification. CO_2 is removed from the remaining O_2–CO_2 gas mixture in a LN_2 trap at a pressure of ≃ 100mbar. With this method sample preparation time is reduced from ca 10 hr to ca 1 hr. The efficiency and reproducibility of the procedure is shown with ^{14}C and ^{13}C measurements of a sugar-carbon standard. The results obtained by the new technique agree well with conventionally prepared wood and bone samples.

INTRODUCTION

In conventional ^{14}C counting, the established ^{14}C sample preparation technique for organic material (wood, bone, coal, soil and plant material) is burning the sample in an O_2 stream, cleaning the evolved CO_2 by chemical absorption or precipitation in alkaline solution and recovering the CO_2 by acidification in a vacuum extraction system (Münnich, 1957). Using CO_2 as a counting gas requires a highly efficient purification of the sample from NO, NO_2, SO_2 and other electronegative impurities. The nitrogen and sulfur content of organic material is in the order of percent, while the concentration of electronegative impurities in the counting gas should be less than some ppm (Brenninkmeijer & Mook, 1979). During purification, however, a considerable loss of CO_2 should be avoided to prevent isotope fractionation. These requirements lead to an extensive preparation procedure and a preparation time of at least 10 hours.

An alternative technique (bomb combustion) of ^{14}C sample preparation in CO_2 proportional and liquid scintillation counting (LSC) was described by Switsur *et al* (1970), Burleigh (1972), Switsur (1972) and Switsur *et al* (1974).

We describe a fast ^{14}C sample preparation technique for organic material in conventional CO_2 proportional counting. The basic difference from conventional preparation (burning of the sample in an O_2 stream) is oxidation of organic substances in a closed system and preparation time is reduced to ca 1 hour.

MATERIALS AND METHODS

Figure 1 shows the experimental setup for ^{14}C sample preparation of organic material. The combustion bomb (Parr Oxygen Combustion Bomb 1121, H Kürner, Rosenheim, FRG) is made of specially selected stainless

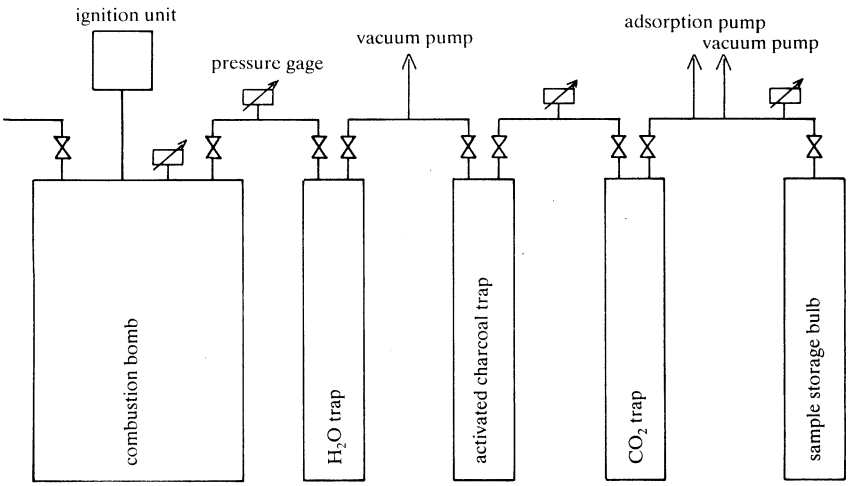

Fig 1. Schematic diagram of the experimental setup

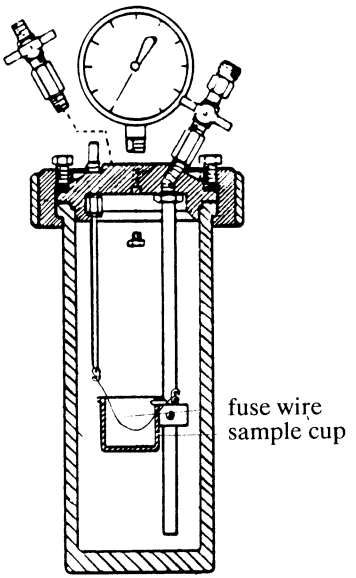

Fig 2. Schematic diagram of the oxygen combustion bomb (Parr Operating Instructions No210M)

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steel; all other parts of the preparation system are made of standard borosilicate glass. The organic sample is oxidized in a combustion bomb of 1850ml volume at an oxygen pressure of ca 10 bars. The sample is compressed, together with a fuse wire in a stainless steel sample cup (Fig 2). Maximum sample size is ca 10g of organic material. The sample cup has a volume of 46ml. The bomb is fired by an external ignition unit providing the proper electrical current to burn the sample. Pressure rises rapidly during the first seconds after firing due to the increasing temperature of the gases. In most instances, combustion is complete after the first minute.

SO_2, NO, NO_2 and H_2O are generated during the combustion. In excess of oxygen and water vapor (ca 5ml of distilled water are added before ignition), these contaminants precipitate immediately on the wall of the reaction vessel. The residual gas mixture is passed through a cold trap at −78°C (acetone-dry-ice mixture) to remove water vapor. The flow rate is 0.8 – 1L/min at a pressure of 0.8 – 1 bar. The line pressure is controlled by the outlet valve of the combustion bomb. The cold trap has a total length of 130cm and an inner diameter of 1cm. The gas is then passed through an activated charcoal column at 0°C (ice-water mixture) for further purification (Bruns, 1976). Gas purification with activated charcoal is routinely used in the Heidelberg ^{14}C laboratory since several years. The charcoal trap has a total length of 220cm and an inner diameter of 0.9cm. It is filled with 45g of Degusorb F12/470 (Degussa AG, Frankfurt, FRG). This activated carbon has a specific surface of $1.1 m^2/g$, a grain size of ca 1mm and a bulk density of $0.46 g/cm^3$. The pressure at the outlet of the charcoal trap is set to be 50–100mbars.

Finally, CO_2 is removed from the residual CO_2–O_2 gas mixture in a LN_2 trap at a pressure of 50–100mbars. The dimensions of this trap are comparable with the dimensions of the H_2O trap. During the whole process, O_2 is being removed continuously with a vacuum pump. At a final pressure of 20mbars (water vapor partial pressure), the combustion bomb is closed at the outlet valve. This pressure is reached after a processing time of ca 20 min. The final pressure of ca 1mbar at the outlet of the activated charcoal column is reached after an additional 10 min. The CO_2 trap with the frozen sample is evacuated to a pressure of 10^{-3}mbars using a liquid N_2 cooled adsorption pump.

The CO_2 sample is expanded in a pre-evacuated storage bulb. The amount of CO_2 is estimated from pressure, temperature and volume of the storage bulb ($\simeq$ 5L). The complete sample is again frozen to remove traces of trapped O_2. The collected CO_2 can then be used as a counting gas in a conventional CO_2 proportional counter system without any further purification.

For regeneration, the activated charcoal column is heated at 400°C and flushed with N_2 during cooling to room temperature to remove trapped contaminants. The total time for sample preparation is ca 1 hr; the time for regeneration of the activated charcoal trap is ca 30 min.

RESULTS

To design the length and inner diameter of the water vapor and CO_2 trap, the efficiency is estimated from the diffusion relaxation time, $\tau \simeq r^2/(6D)$, where r is the radius of the trap and D is the molecular diffusion coefficient of water vapor or CO_2, and the diffusion relaxation length $l \simeq v\tau$, where v is the gas velocity. The relaxation length, 1, is the distance along which the concentration of water vapor or CO_2 decreases to 1/e of the initial content. The relaxation length of the H_2O trap is ca 4cm and of the CO_2 trap ca 6cm. At a total length of 130cm the CO_2 and H_2O concentration at the outlet of the trap is negligible. This was confirmed by separate experiments: water vapor saturated N_2 or pure CO_2 was passed through two traps in series and the amount of H_2O and CO_2 in the traps was measured. At flow rates of 0.5 – 1 L/min, H_2O or CO_2 could not be detected in the second trap.

To measure the amount of SO_2 and NO_2 removed from the combustion gas inside the combustion bomb, 50ml of distilled water were added to the combustion vessel and mixed with the precipitated SO_4^{2-} and NO_3^-. SO_2 and NO_2 removed by the activated charcoal trap were sampled by heating the trap and collecting the desorbed gases in a flask filled with 5ml of distilled water. The flask was shaken for 24 hr to enable complete oxidation of SO_2 and NO_2 to SO_4^{2-} and NO_3^-. The same technique was used to determine the SO_2 and NO_2 content in the CO_2 sample. The SO_4^{2-} and NO_3^- concentration of the liquid samples were measured by ion chromatography.

The total amount of nitrogen and sulfur desorbed from the charcoal trap was <1‰ of the amount precipitated at the walls of the combustion vessel. The SO_2 and NO_2 concentration in the CO_2 sample was <0.1 ppm.

The results obtained from samples with a sulphur and nitrogen content of ca 1% show that practically all contaminants are already removed in the combustion bomb and that only traces of SO_2 and NO_2 must be trapped in the activated charcoal column. The sample loss in the activated charcoal trap was determined by measuring the amount of CO_2 desorbed during regeneration of the charcoal column. Ca 2% of the sample is lost when all gases are drawn through the charcoal until a final pressure of 1mbar is reached at the outlet of the charcoal trap. The sample loss increases to ca 8% at a final pressure of 5mbars. These values are considered an upper limit, because we cannot completely exclude the possibility that traces of charcoal are being oxidized to CO_2 when the trap is heated to 400°C. $\delta^{13}C$ measurements show that the trapped CO_2 is enriched in ^{13}C by 1.1 ± 0.1‰. The difference in $\delta^{13}C$ between the sample and the trapped CO_2 was independent of the percentage loss of CO_2 in the charcoal column. This supports the assumption that excess CO_2 is produced by heating the charcoal trap. The observed difference in $\delta^{13}C$ will shift the ^{13}C content of the sample by <0.1‰. To prevent memory effects, the charcoal trap is flushed with N2 before each sample preparation.

^{14}C and ^{13}C measurements of a sugar carbon substandard obtained by this technique agree well with published data and show that isotope fractionation and contamination are negligible (Table 1). ^{14}C and ^{13}C measurements of wood and bone samples obtained with this technique agreed, within a statistical counting error of ca 4‰, with conventionally prepared ^{14}C samples and within ± 0.15‰ of $\delta^{13}C$ samples.

TABLE 1

Comparison of ^{14}C and ^{13}C measurements of a sugar carbon standard with published data

	Standard	This method
$\Delta^{14}C$ [‰]	362±3	364±5
$\delta^{13}C$ [‰]	−19.47±.54	−19.56±.03

CONCLUSIONS

The described method proves to be a convenient and accurate ^{14}C sample preparation technique for organic samples in conventional ^{14}C counting. The method is successfully tested with wood and bone (collagen) samples, fresh plant material (beech leaves and spruce needles) and soil organic material. The organic carbon content in soil samples, however, should not be < 1.5% to prevent incomplete combustion. By minimizing the volume of the combustion bomb and traps, this technique may also be used to combust low volume samples for ^{14}C dating with accelerator mass spectrometry (AMS) (Grabitz, 1988).

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