

AN ATTEMPT AT ABSOLUTE ^{14}C DATING

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ABSTRACT. The accepted state-of-the-art ^{14}C dating method relies on calibration curves to determine initial ^{14}C levels in a sample. The paper reconsiders the basis of ^{14}C dating and offers a possible alternative that eliminates the need to employ calibration curves. The idea is to measure the level of radiogenic nitrogen atoms retained in the sample molecules after ^{14}C β -decay. The practicality of this alternative method still has to be proven.

INTRODUCTION

Despite the spectacular achievements of ^{14}C dating in the past and present, it looks like future development of the technique will reach an impasse. The true age of many samples will not be known, even though the most advanced technology and the most rigorous working procedures are employed. The reason lies in the erratic behavior of the calibration curve, which in many cases may transform a narrow ^{14}C age range into a broad one, or even into several different age ranges. This phenomenon is inherent to the accepted, state-of-the-art dating method, and no amount of procedural refinement can eliminate it. This limitation led us to reconsider one of the cornerstones of today's method, the very need to employ a calibration curve.

THEORY OF ^{14}C ABSOLUTE DATING

It is well known that other isotopic dating methods (such as U-Th) have no need to determine the initial radioactive isotope level and therefore do not employ a calibration curve. By using the daughter (D) to parent (P) isotope ratio at the present time, C_D/C_P , the age of a sample is easily determined by the formula

$$\text{Age} = \frac{1}{\lambda} \ln \left[1 + \frac{C_D}{C_P} \right] \quad (1)$$

where the only assumption is that no daughter isotope was present at time zero (Fig. 1).

The use of absolute dating can solve the particular problems encountered in several age ranges, most notably during Iron Age I (Pearson and Stuiver 1993). Notice in Figure 2 the 12% difference between the values of C_D/C_P at the beginning and the end of that problematic period.

There is, however, a "minor" problem that has to be solved before we can give up so easily on the ^{14}C calibration curve. The daughter isotope of ^{14}C is ^{14}N , one of the most abundant isotopes on Earth and also a gas. These facts make it seemingly impossible to determine the level of the radiogenic nitrogen (^{14}N atoms in a particular sample originating from ^{14}C), assuming that they did not leave the sample altogether long ago. However, nature does offer us a glimmer of hope. Due to the relatively low energy involved in the ^{14}C β -decay, there is a good chance that the ^{14}N atom will remain bound to its parent molecule. The recoil energy, E_R , associated with β^- emission is given by

$$E_R = \frac{E_\beta(M_\beta + M_0)}{2M_R} < 6.9 \text{ eV} \quad , \quad (2)$$

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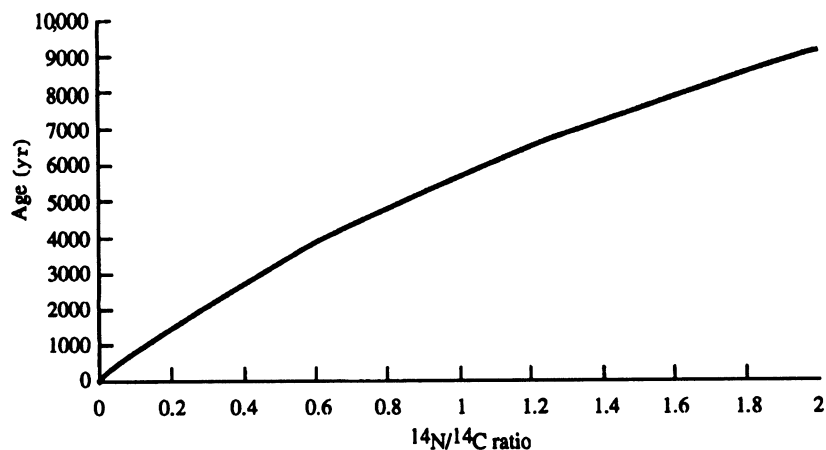


Fig. 1. Age as a function of daughter-to-parent isotope ratio

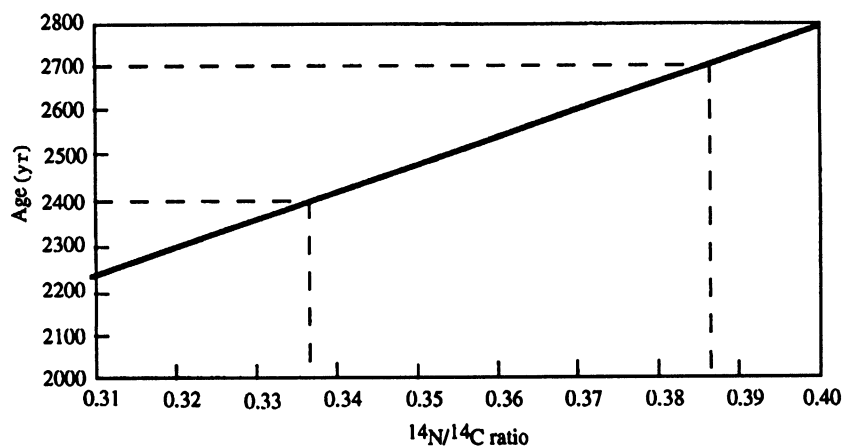


Fig. 2. Absolute dating in the Iron Age-I range

where

E_{β} = the energy of the β particle (up to 155 keV for ^{14}C);

M_{β} = the relativistic mass of the β particle;

M_0 = the rest mass of the β particle;

M_R = the mass of the recoil ^{14}N atom.

To assess whether the kinetic energy of the recoil might be sufficient to cause bond rupture, we compare listed carbon atom bond energies, which are usually higher than 2 eV, to the internal motion recoil kinetic energy E_K , which is inversely proportional to the molecule mass M .

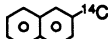

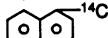

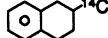

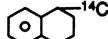

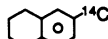

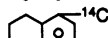

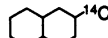

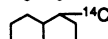

$$E_K = E_R \frac{m(^{14}\text{C})}{M} < 6.9 \frac{14}{M} \quad (3)$$

Wolfsberg (1956) treats the subject rigorously, concluding that the kinetic energy of recoil may be insufficient to cause bond rupture in many compounds. On the other hand, bond rupture may be

caused by disturbances in the arrangement of the orbital electrons. Theoretical calculations of bond rupture probabilities by quantum-mechanics methods become more difficult as the number of atoms in the molecule increases. Raadschelders-Buijze, Roos and Ros (1973) conclude, after some general computer simulations, that the electronic part of the transition probability from parent to daughter molecule is almost independent of the molecular structure and of electronic factors like aromaticity. On the other hand, the direct environment seems to be a significant factor in determining the bond rupture probability. For purposes of the following discussion, we define retention probability (RP) as $(1 - \text{the bond break probability})$.

We found that 19 different molecules have been tested for bond rupture and all of them showed significant RP's (Table 1). The results seem to support the conclusion that RP is independent of molecular structure. Thirteen out of the 19 were measured at the Radionuclidencentrum at the Free University in the Netherlands in the mid-1970s. Since then, this not very well known area of radiation chemistry has been dormant. The experimental method, described in Wolfgang, Anderson and Dodson (1956), includes double labeling of compound molecules by two radioactive atoms, one of them ^{14}C and the second either ^{14}C or tritium. The compound is then placed in storage for several years to allow for significant decay of ^{14}C . The daughter molecules are then separated and quantified by counting their ^{14}C or tritium activity.

TABLE 1. Measurements of 19 Molecules Tested for RP

Parent compound	Retention product	RP (%)	Reference
Ethane	Methyl amine	47	Wolfgang, Anderson and Dodson 1956
Carbon dioxide	$(\text{NO}_2)^+$	81.4	Snell and Pleasonton 1958
Toluene	Aniline	96	Manning and Monk 1962
Ethylbenzene	N-methyl aniline	80	Manning and Monk 1962
Succinic acid	Glycine	65	Nefedov <i>et al.</i> 1963
Benzene	Pyridine	58	Skorobogatov and Nefedov 1966
Benzene	Pyridine	49	Den Hollander, van der Jagt and van Zanten 1975
Propane-1 ^{14}C	Ethylamine	50	Den Hollander, van der Jagt and van Zanten 1975
Propane-2 ^{14}C	Dimethylamine	57	Den Hollander, van der Jagt and van Zanten 1975
Cyclopropane	Ethylene imine	47	Den Hollander, van der Jagt and van Zanten 1975
Cyclohexane	Piperidine	52	Den Hollander, van der Jagt and van Zanten 1975
<i>Two naphthalene molecules</i>			
		95	van der Jagt, Den Hollander and van Zanten 1975
		82	van der Jagt, Den Hollander and van Zanten 1975
<i>Four tetrahydronaphthalene molecules</i>			
		90	van der Jagt, Den Hollander and van Zanten 1975
		59	van der Jagt, Den Hollander and van Zanten 1975
		48	van der Jagt, Den Hollander and van Zanten 1975
		92	van der Jagt, Den Hollander and van Zanten 1975
<i>Two decahydronaphthalene molecules</i>			
		92	van der Jagt, Den Hollander and van Zanten 1975
		67	van der Jagt, Den Hollander and van Zanten 1975

FROM THEORY TO PRACTICE

In theory, then, even though we are dealing with a very difficult to detect daughter isotope, by searching for the daughter molecule instead, we may still be able to quantify it. With the theory quite well established, we attempted to determine its practicality. First, we realized that the amounts of material we are searching for are at the very limit of the latest detection capabilities. Even assuming 100% RP, because the ratio $^{14}\text{C}/^{12}\text{C}$ is on the order of 10^{-12} , the concentration of daughter molecules in the tested material will be on the order of 10^{-13} to 10^{-12} . (The exact value is obviously age-dependent.) Second, at such low levels background control becomes crucial and definitely not trivial. It is this second point that we decided to investigate first. To determine N background levels, we tested two of the most popular sample materials, cellulose and calcite. By standard procedures we prepared two samples of calcite from land snails, one *ca.* 5000 yr old and one modern. The modern snail was *Levantina caesarea*, which is known to have a relatively low organic fraction (canchiolin). Sodium chlorite was used on both, to remove all organic material. The cellulose sample was taken from the TIRI cellulose supplied by the IAEA (Rozanski *et al.* 1992).

The samples were submitted to a gas chromatography (GC) detection system. We used the most advanced nitrogen detection system available in Israel, the model 610 nitrogen analyzer, a product of the Thermo Electron Corporation. In the “nitroso mode” the system can detect all molecules containing NO. As feared, both samples showed levels much higher than 10^{-12} of NO-containing molecules.

Next, we tested the calcite samples in the Weizmann Pelletron[®] accelerator. By focusing on a specific NO_x ion, we were hoping to rid ourselves of the high neutral NO-containing background. We measured the concentration of NO^- and NO_2^- ions, while the test of NO_3^- concentration was set for a future date. Again, the concentration of NO_x^- ions in the calcite was found to be much higher than 10^{-12} . Atmospheric NO_x contamination was the probable cause.

In our last experiment, we analyzed crude petroleum in search of exotic molecules created by the β -decay of ^{14}C in common molecules. The hypothesis is that during the genesis of petroleum, spanning many millions of years, there are β -decays in ^{14}C atoms, but the new structure is stable enough to allow for an unchanged path of genesis. Hence, we may again expect the ratio of molecules containing radiogenic nitrogen to the common molecules in crude oil to be on the order of 10^{-13} to 10^{-12} . A good review of the origin and formation of organic matter in sediments is given in Huc (1980). The general term for N-containing molecules in petroleum is “nitrogen bases” or azaarenes. A thorough process of identifying nitrogen bases was performed in several laboratories, and the result points to an order of magnitude of 10^{-4} for the overall concentration of these molecules in petroleum. This number suggests a direct path for the genesis of nitrogen bases from the N-containing proteins of decaying dead organisms’ bodies.

For our analysis, we chose naphthalene, a common petroleum molecule (2% w/o) and the N-containing parallels, quinoline and isoquinoline. Quinoline is one of the more abundant nitrogen bases, whereas isoquinoline is apparently absent (Schmitter *et al.* 1984). This means that quinoline originates from proteins whereas isoquinoline, if present, is below the detection limit. In that case, any isoquinoline molecules are probably the daughter product of a ^{14}C -containing naphthalene structure. Because isoquinoline is such a rare molecule, we were confident that background would cause no problem.

With the aid of the same GC system, this time in its “nitrogen mode”, which is used for drug detection, we determined the detection limit for quinoline as 5×10^{10} molecules (Figs. 3 and 4). The detection limit for isoquinoline is similar. This means that, by isolating nitrogen bases from an amount of

petroleum containing from 5×10^{22} to 5×10^{23} molecules of naphthalene, we may reach the detection limit for isoquinolines. The respective amounts of petroleum should be from 0.5 to 5 kg.

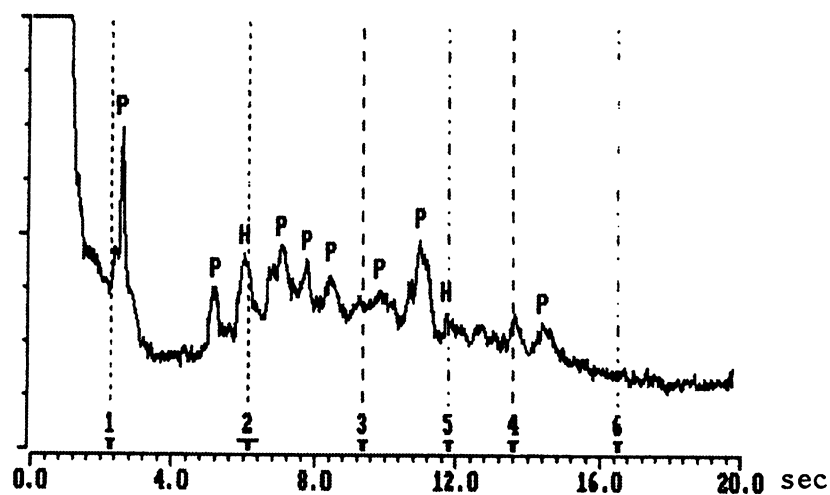


Fig. 3. Chromatogram of pure acetone solvent

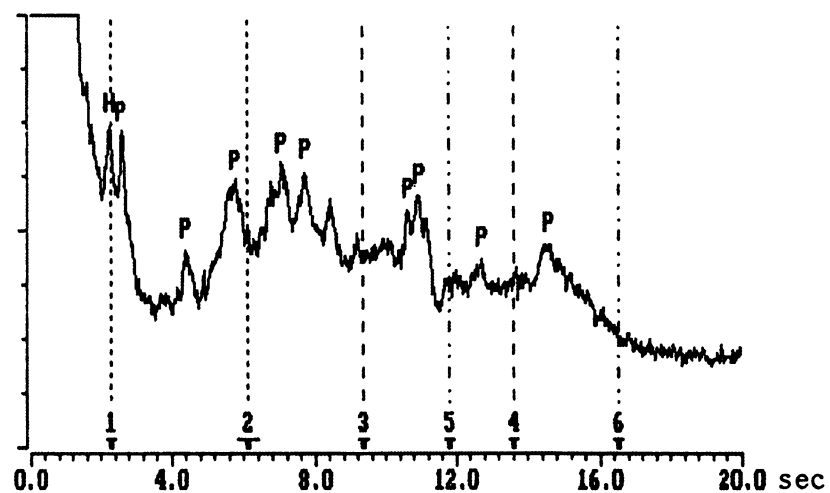


Fig. 4. Quinoline peak shows at dotted line 1 ($t = 2.252$ sec)

For our research, we selectively isolated the nitrogen bases from a 200-g sample of crude oil, by the procedure described in Schmitter *et al.* (1983). The amount processed puts us below the detection limit; however, in this preliminary study we were more interested in proving our ability to isolate nitrogen bases and also in testing the performance of the GC system. As it turns out, the system, with

its fixed settings, does not have the resolution power to discriminate between the abundant quinoline and the scarce isoquinoline. Figures 5 and 6 show the individual peaks of the two molecules; Figure 7 shows one combined peak when they are mixed (90% quinoline and 10% isoquinoline).

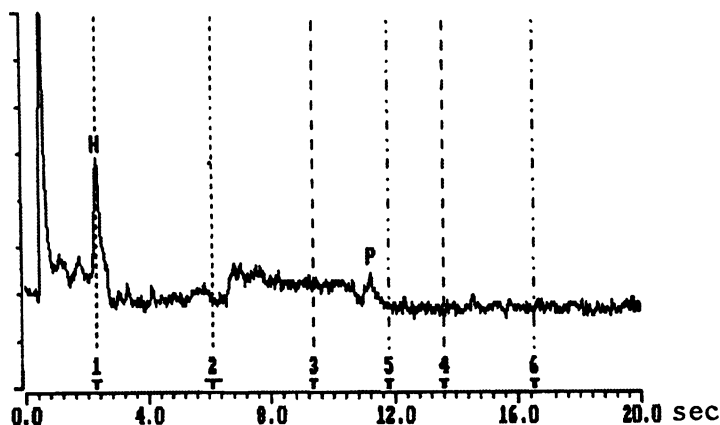


Fig. 5. Quinoline peak at dotted line 1 ($t = 2.276$ sec)

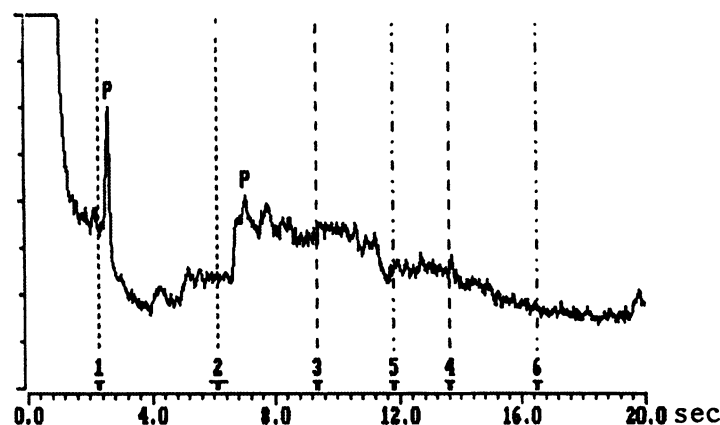


Fig. 6. Isoquinoline peak to the right of dotted line 1 ($t = 2.600$ sec)

CONCLUSION

We believe that the theoretical background for seeking the daughter products of ^{14}C β -decay is firm and that it constitutes an adequate incentive for future research aimed at discovering, for the first time, radiogenic nitrogen at natural concentrations. ^{14}C -labeled cellulose and calcite have to be researched to determine the daughter molecules, and analytical methods in addition to chromatography have to be adapted to detect these molecules at such low levels. An attempt should also be made to detect the radiogenic nitrogen in meteorites. Based on Suess and Wanke (1962), there are meteorites with a ^{14}C activity of 56 dpm kg^{-1} . The activity is a function of level of exposure to cosmic radiation. A meteorite having such a level of exposure for 10^9 yr may have a concentration of radiogenic nitrogen 2 to 3 orders of magnitude higher than samples originating on earth. Rapid

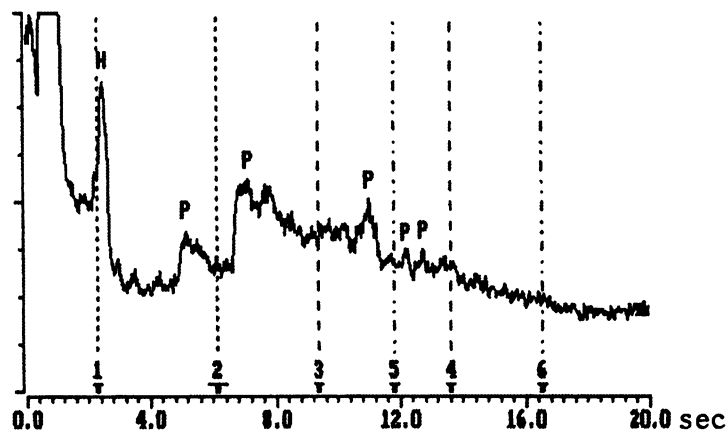


Fig. 7. The combined peaks of quinoline and isoquinoline at dotted line 1 ($t = 2.456$ sec)

advances in ultra-low-level detection techniques will open the way to the detection of the array of organic molecules containing radiogenic nitrogen. Those exotic molecules do exist and are just waiting for the right technology to be counted. Once they are quantified, absolute ^{14}C dating becomes a reality.

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