

Low-level ^{14}C measurements and Accelerator Mass Spectrometry

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Abstract

Accelerator Mass Spectrometry (AMS) and isotope enrichment were used in 1991 to estimate that the ^{14}C content of methane in natural gas was $\leq 1.6 \times 10^{-18}$ of the total carbon. The low content of ^{14}C in underground hydrocarbons was verified later in the remarkable results from the Borexino test scintillation counter for solar neutrino studies. Since then studies of the background problem have demonstrated that much of the background originally observed in the AMS measurements can, in principle, be eliminated. However, many difficulties and other backgrounds are to be faced as the limit for AMS is pushed still further towards possibly a ratio of $< 10^{-21}$. These will be discussed.

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1. Introduction

It is now 55 years since Libby et al [1] reported the first detection of cosmic ray generated radiocarbon, or ^{14}C , by beta ray counting. At about 0.25Bq/g the radioactivity of a contemporary carbon sample was then just measurable. That activity combined with a mean-life of 8033 years gives an atom ratio for $^{14}\text{C}/\text{C}$ of about 1.2×10^{-12} . It is worth noting that prior to the first publication J. Zacharias (unpublished) had already suggested to Libby that mass spectrometry was a more suitable technique than beta ray counting for a long-lived radioisotope like ^{14}C . Arnold [2] reports that the suggestion was considered but the measurement by mass spectrometry of isotope ratios in the range 10^{-12} to 10^{-13} was then far beyond the state of the art and counting methods worked. About 50 years later the group using the Borexino test scintillation detector made the most remarkable beta-ray counting measurement, at the Gran Sasso underground laboratory in Italy, using some 4.8m^3 of high purity liquid scintillation counter [3]. It was reported that a ratio of $^{14}\text{C}/\text{C}$ equal to $(1.94 \pm 0.09) \times 10^{-18}$ had been measured, a far lower ^{14}C abundance than had been measured by beta-ray counting previously. However, by 1990 a similar low ratio for $^{14}\text{C}/\text{C}$ of $< 1.6 \times 10^{-16}$ had already been measured [4,5] by the method first suggested by Zacharias and this measurement was done as a precursor to the construction of the Borexino test detector. This was done by a variant of mass spectrometry known as accelerator mass spectrometry (AMS), which was developed as a result of the widespread use of accelerators for nuclear physics purposes [6] and their obvious mass spectrometric properties.

In this paper the further development of AMS reaching towards the more distant goal of measurements near the $^{14}\text{C}/\text{C} \sim 10^{-21}$ level will be discussed. This goal is chosen because estimates [3] of the level of radiocarbon deep underground indicate that it may

be near the lower limit in rocks with low levels of uranium and thorium. The actual level of the ^{14}C in material that has been isolated for say >190,000 years from that generated by cosmic rays in the atmosphere is, of course, unknown but could in theory have a $^{14}\text{C}/\text{C}$ ratio $< 10^{-21}$. The actual ratio will depend upon the depth of the material below the earth's surface, if the background is generated by cosmic ray muons, and the actinide content if alpha particles or neutrons generate the ^{14}C . Finally contamination by carbon from the biosphere would then be significant at the ppb level.

Three topics will be discussed or summarised briefly in this paper. In section 4 the background counting rate, introduced in the present AMS itself will be discussed. In section 5 the continuing background study of the ^{14}C introduced by contamination of ion source materials is outlined. Finally in section 6 the problem of the introduction of ^{14}C in the source material during sample handling is mentioned.

2. Accelerator Mass Spectrometry (AMS)

The state of the art of the mass spectrometry of ^{14}C has advanced in parallel with that of beta ray counting since 1950. Beta ray counting has reached an accuracy, for recent samples, approaching $\pm 0.2\%$ but with an age limit (with great difficulty) of near 57,000 years or 1.2×10^{-15} for the $^{14}\text{C}/\text{C}$ ratio. Two noteworthy developments in the mass spectrometry of radiocarbon were first; the realisation that the negative ion of nitrogen could not be detected [7] during acceleration of negative ions in the first tandem accelerator at Chalk River. It had been confidently predicted theoretically that N^- , along with the molecular nitrogen negative ion N_2^- , would be unstable and an effort was soon launched [8] to utilise this apparent fact. Unfortunately the negative ion chosen for the effort in low energy mass spectrometry was $^{14}\text{C}^{15}\text{N}^-$, which is relatively easy to make. The method could not be made to work because of the presence of persistent backgrounds. It was later discovered [9,10] that the ion N_2^- has a metastable excited state, which along with other molecular ions interfered with the detection of $^{14}\text{C}^{15}\text{N}^-$. The second essential step was the development of the high-current solid-carbon caesium sputter ion source [11,12]. At Chalk River in 1960 it was noted that, although the N^- ion might be unstable, ion sources gave good C^- ion beams even when no CO_2 was fed into a radio-frequency ion source. This was clearly due to a huge memory of the use of previous gases in the ion source, which was a situation that could make rare isotope measurements with a tandem accelerator, using such ion sources, very difficult indeed [13]. In 1972 the development of the caesium sputter ion source technology, for bombarding solid carbon samples to produce many μA of C^- ions, turned out to be the key to making radiocarbon measurements utilising existing tandems. Measurements of ^{14}C soon followed [14], by what came to be known as AMS, after it had been noted that the accompanying copious molecular isobars were also destroyed during tandem acceleration. A general description of subsequent events in AMS is given in a comprehensive book [6] on the subject.

The essentials of the AMS of radiocarbon and other long-lived radioactive isotopes have been described many times [6,15] but they can be summarised briefly as a method in three essential steps. The first is the complete removal of the ^{14}N isobar atoms by the use of the negative ions of the carbon atom. The second is that the intense molecular

isobars, such as ^{13}CH and $^{12}\text{CH}_2$ (both form negative ions readily), are destroyed during the charge changing involved in tandem acceleration. Finally the unique ^{14}C positive ions are detected at ion energies of several MeV, which besides providing the possibility of ion identification in an ionisation spectrometer also ensures a very low dark current compared with low energy mass spectrometry. Dark currents of less than 1 count per day are possible. In AMS there must also be adequate mass and charge spectrometry, which will be discussed in section 4.

The very first measurements by AMS of the ^{14}C in reactor grade graphite [14,15] demonstrated a surprisingly low value of the ratio for $^{14}\text{C}/\text{C}$ of near $\sim 10^{-16}$. This low level is still not understood well and it is undoubtedly a mixture of graphite contamination, ion source memory of previously analysed samples and artefacts generated by the mass spectrometry. The study of such low levels of radiocarbon was not a priority in the early years of AMS.

3. The First Measurement of ^{14}C in Natural Gas

In 1990 R. S. Raghavan, in preparation for the construction of the Borexino solar neutrino scintillation detector, wanted to know just how much radiocarbon there might be in the source materials for making such a detector. It was hoped that the source materials would have a ratio $^{14}\text{C}/\text{C} < 10^{-18}$, because of the long temporal separation of the underground hydrocarbons from the biosphere. This would then make the detection of some of the lower energy solar neutrinos possible. However, such measurements had not previously been attempted using AMS. Here it is appropriate to introduce the tenth life of radiocarbon instead of the half-life. With a half-life of 5730 years the tenth life becomes close to 19,000 years. Consequently, if a hydrocarbon has been separated from new ^{14}C for about 114,000 years the decay would have lowered the $^{14}\text{C}/\text{C}$ ratio from 1.2×10^{-12} to about 1.2×10^{-18} . Such a ratio was considered to be a good starting point for a scintillation counter for detecting the solar pep, CNO neutrinos and those following the electron capture by ^7Be . The problem was that the lowest ratios for $^{14}\text{C}/\text{C}$, obtained from AMS measurements at that time, were about 5×10^{-16} . The origin of this limit was unknown at that time. It was known to partly due to the influence of residual ^{13}C and ^{12}C ions in the final counter. In addition it was suspected to be partly due to a memory effect, the contamination of the source material, contamination introduced during the preparation of the solid graphite-like carbon used in the ion source or contamination in the materials of construction of the ion source or target supports.

Raghavan then conceived the daring idea that isotope separation might be useful. Here it must be remembered that the enrichment of carbon isotopes is now carried out on an industrial scale. The enrichment is carried out at the Isotec Company [17], which produces, for example, CO gas enriched in ^{13}C with the ratio of $^{13}\text{C}/^{12}\text{C} \sim 100$. The level of ^{14}C in this material was unknown but Isotec estimated that the ratio of $^{14}\text{C}/^{12}\text{C}$ would be enhanced by a factor of near 200. The CO gas was produced from underground methane and liquefied prior to transportation from Louisiana to Ohio, where it was used in the isotope separation by liquid distillation. As one of the reactions creating ^{14}C by secondary cosmic ray neutrons is the $^{17}\text{O}(n,\alpha)^{14}\text{C}$ reaction, some ^{14}C could be created

during the time spent as liquid CO. The dilute gas of neutrons created at the surface of the earth by cosmic rays and nearby actinides together with the residual primary cosmic rays themselves could therefore generate ^{14}C in the liquid CO during and after enrichment. The actual level of ^{14}C in the CO is expected to be low and is still unknown. A rough estimate is a ratio of $\sim 10^{-21}$ but that depends upon many details.

CO gas was submitted to the IsoTrace laboratory and converted into a graphite-like material for analysis in the AMS equipment. The result reported by Beukens to Raghavan in 1991 was that there was an upper limit for the $^{14}\text{C}/\text{C}$ ratio in the CO gas of $\leq 1.6 \times 10^{-18}$. The limit was determined mainly by the need to subtract the contributions from the ^{13}C ions in the final detector. This result was described briefly in 1993 [5] and the implications discussed [18] in 2000. Subsequently it was shown [3] that the level of ^{14}C at the Borexino test facility was consistent with this value although a very different starting material was used. A counter containing some 5Mg of carbon was analysed.

4. The present AMS Background at IsoTrace

A huge number of molecular ions, such as $^{13}\text{CH}^-$ and $^{12}\text{CH}_2^-$, accompany the rare ^{14}C ions into the accelerator of the mass spectrometer. They are each about 3×10^{-4} of the $^{12}\text{C}^-$ atomic ions [19]. These molecular ions are completely destroyed during conversion to positive atomic ions in the tandem accelerator but the molecular fragments must be removed by the subsequent mass spectrometry. Fortunately the high-energy mass spectrometry can accomplish this, as has been discussed in some detail recently [20,21]. A problem for the majority of AMS laboratories with tandem accelerators with terminal voltage less than 3MV is that the final ^{12}C , ^{13}C and ^{14}C positive ions have very similar values of dE/dx . As a result they cannot easily be distinguished in the final ionisation detector, if they have the same energy. This is discussed further below.

The ^{14}C ions, emerging from the accelerator, are accompanied by an energy continuum of the other isotopes due partly to ion interactions in the residual gas of the accelerator [21]. These can be removed by the high-energy mass spectrometry and for convenience the ions can be separated into two groups. The first group is that part of the continuum of emerging ions with the same value of E/Q as the ^{14}C ion, where E/Q is the energy divided by ion charge. These ions penetrate all electric analysers (EA). The second group of ions with mass M has the same ME/Q^2 as the ^{14}C ion. These can penetrate all magnetic analysers (MA). Consequently a sequence of electric and magnetic analysers should be sufficient to remove all such isotopes of the wrong mass. The AMS equipment was designed to remove such ions for radiocarbon dating [21] only and not for studies of very low ratios of $^{14}\text{C}/\text{C}$. Consequently additional analysers must be added. Two electric and magnetic analyser combinations in the series EA, MA, EA MA should suffice to solve this problem [20] provided they have sufficient energy and mass resolution.

The first experiment in 1991 using enriched isotopes [5] encountered a serious ME/Q^2 background due to the fact that the sequence of analysers was EA, MA, MA was designed for radiocarbon dating to about 60,000 years before the present (BP) or a ratio

for $^{14}\text{C}/\text{C}$ of about 10^{-15} . Later versions of radiocarbon dating machines are different and the properties of two versions for low $^{14}\text{C}/\text{C}$ ratios have been discussed in some detail recently [21].

The tail from the ME/Q^2 interference in each case was first subtracted and then by subtracting the results for the unenriched sample from the results from the enriched sample of CO an estimate of the $^{14}\text{C}/\text{C}$ level was obtained [5]. The measured values for the ratios of $^{14}\text{C}/\text{C}$ were $(5.7 \pm 1.4) \times 10^{-16}$ and $(5.6 \pm 0.5) \times 10^{-16}$ respectively, which after subtraction gives the final result, quoted above, of $< 1.6 \times 10^{-18}$, after allowing for the isotope enrichment. The errors on these numbers are mainly due to the tail of the ME/Q^2 peak in the ionisation counter, so the elimination of that interference by improved high-energy mass spectrometry would be an advantage. The background due to pulses of the same energy, the E/Q background, was small due to the two MA following the EA. It was estimated to contribute $< 10^{-19}$ to $^{14}\text{C}/\text{C}$ the ratio. In contrast the peak of the ME/Q^2 interference from $^{13}\text{C}^{+3}$ ions, which have 14/13 times the energy that of the $^{14}\text{C}^{+3}$ ions, was equivalent to a ratio of near 10^{-14} for $^{14}\text{C}/\text{C}$ from an unenriched target. However, the resolution of the final detector lowers this by a factor of 10^3 so that background subtraction was feasible.

The measurements of 1991 also clearly showed that background was made up of two major components. Usually CO_2 gas is used as a starting gas for the creation of graphite-like material for the sputter ion source and at the IsoTrace AMS laboratory the CO_2 is first turned into acetylene by a reaction with hot lithium. The acetylene is then converted into graphite-like material by cracking in an electrical discharge onto the surface of an aluminium cylinder, which is then inserted as a target into the ion source. Such graphite-like material gives a good efficiency for converting atoms into ions in a caesium sputter ion source with an efficiency that is greater than about 10%.

Such targets made from the CO_2 from natural gas routinely showed $^{14}\text{C}/\text{C}$ ratios of $(9.24 \pm 0.60) \times 10^{-16}$. That level, however, dropped to $(5.88 \pm 1.4) \times 10^{-16}$ when CO from natural gas was used and purified by freezing with liquid nitrogen before converting it to acetylene. It was presumed that some contemporary CO_2 is removed by this process leaving the remainder to come from the lithium metal used to make the acetylene or from the stainless steel bomb used in the process. Undoubtedly both sources are involved. The constancy of these numbers with time allows backgrounds to be subtracted for the radiocarbon dating of younger material. A ratio of 1.2×10^{-15} corresponds to about 57,000 years.

When acetylene generated from calcium carbide is used to create graphite-like targets this gives a lower measured $^{14}\text{C}/\text{C}$ ratio of $(1.4 \pm 1.0) \times 10^{-16}$. This indicates that the process used to create the acetylene from CO, and especially CO_2 , at present introduces ^{14}C atoms. The present system therefore is limited by the method for the preparation of the target material for the sputter ion source. This method will therefore have to be developed further. The creation of acetylene directly from methane is possible [22] so that the step using lithium metal is not essential.

5. The Ultimate AMS Background

First of all it is clear from the recent studies that the addition of electric and magnetic analysers can arbitrarily decrease the ^{14}C background due to the inability of the accelerator mass spectrometry to handle the huge fluxes of ^{12}C and ^{13}C ions from the accompanying mass-14 molecular hydrides. The situation for the heavy element analysis line at IsoTrace, where the ME/Q^2 interference is already at the level of 10^{-21} due to the use of two electric analysers, is already nearly adequate for low-level ^{14}C studies. With the addition of pulse-height spectrometry this level could be reduced further by over a factor of 100. This is to be compared with the ME/Q^2 level of $\sim 10^{-14}$, for the radiocarbon dating equipment, with a further factor of 100 reduction possible, due to the pulse height spectrometry in the final detector. The E/Q interference of the heavy element line will, however, require attention and adding a small magnetic analyser to lower the level to well below 10^{-21} easily does that. Adding a small magnet and electric analyser to the radiocarbon dating line would achieve similar properties to the heavy element line. Consequently both the AMS systems at IsoTrace can have a background lower than the level likely to be encountered with the natural $^{14}\text{C}/\text{C}$ ratios encountered in nature.

At a level of $^{14}\text{C}/\text{C}$ lower than about 10^{-18} the negative ion of nitrogen may appear as the predicted metastable ^9S state of N^- [23]. This is analogous to the He^- ion in that all the electrons have their spins parallel. If such an ion appeared at the 10^{-18} level then by the time the level of 10^{-21} was approached the ^{14}N ions would be some 10^3 times as intense as the ^{14}C . The measurement of $d\text{E}/dx$ for the ions would allow this exotic ion to be identified and eliminated from the spectrum at 10^{-21} . Below that level it could be a nuisance!

The remaining difficult problems of actually determining the $^{14}\text{C}/\text{C}$ ratios in natural samples must now be discussed. These have so far been assessed only in a preliminary way [5] by, for example, using acetylene generated from calcium carbide, which gives for the $^{14}\text{C}/\text{C}$ ratio $(1.4 \pm 1.0) \times 10^{-16}$. Here the error is determined largely by the need to subtract the tail of the ^{13}C peak and to a lesser extent the ^{12}C peak in the final detector. The ME/Q^2 interference was at the level of near $^{14}\text{C}/\text{C} \sim 10^{-14}$ in the system used for the studies. This measurement of the acetylene created from CaC_2 is consistent with the measurement with the enriched and unenriched CO , but it illustrates that ^{14}C contamination, during aspects of sample preparation, is a formidable foe. However, by eliminating the ME/Q^2 interference the origin of the low levels of ^{14}C will become easier to study and the origins of the contamination more easily determined.

A second useful investigation was the study [5] of the level of carbon and radiocarbon in the standard aluminium support blanks in the ion source. This will provide a measure of the sum of the contamination in the Al, the contamination in Cs^+ sputter ion beam and the hydrocarbons in the residual gas in the ion source. After an initial cleaning period the level of $^{14}\text{C}/\text{C}$ reached a low plateau that seems to correspond to carbon with an age of between 7000 and 13,000 years but with a carbon content that is apparently near 100ppm, a rather high level for aluminium. This carbon gives an equivalent background level of

$^{14}\text{C}/\text{C}$ that is near 3×10^{-17} . However, it is possible that this apparent level of carbon in the aluminium target supports is due entirely to vacuum hydrocarbons. This is because a partial pressure of about 1nTorr of a light hydrocarbon could give this result, as the level seems too high for contamination of the aluminium or the Cs^+ ion beam. Further study will be required because even though the measured pressure in the vacuum is usually less than $1\mu\text{Torr}$ the actual pressure near the target being sputtered must be much lower because of the strong gettering action of the sputtered material. The sputtered material is a mixture of carbon, caesium and aluminium.

Lee [24] observed the effects of a partial pressure of hydrocarbons while studying the counting rate of ^{14}C when acetylene with a $^{14}\text{C}/\text{C}$ ratio near 1.2×10^{-12} was let into the ion source with graphite and aluminium targets. The counting rate of ^{14}C remained at the background level for graphite until a critical partial pressure of 40 nTorr of C_2H_2 was reached. This was as expected from the gettering action of the material sputtered onto the surroundings by the Cs^+ ions, which included Cs and C atoms. The counting rate from a standard aluminium graphite-backing target remained near the background for all acetylene pressures up to a partial pressure of 150 nTorr. Reactive layers of Cs, Al and C will be present near all sputtered targets in a radiocarbon dating ion source and this should reduce the partial pressure of the hydrocarbons by a large amount. Consequently even a hydrocarbon partial pressure near the sputtered region of 1nTorr, which is needed to obtain the observed counting rates, seems large unless re-creation of hydrocarbons in the active layer takes place as a result of the interaction with residual water vapour. This problem will have to be investigated further using an ion source that is not used routinely for dating radiocarbon samples. The caesium-sputtering beam itself is also not above suspicion, as one analysis [25] showed many unexpected elements. However, in this case the C^+/Cs^+ ratio needed would have to $\sim 10^{-4}$. This is considered unlikely but it has yet to be checked.

Finally as pointed out by Raghavan [26] the CO depleted industrially in ^{13}C and ^{14}C could be used for making a lower level neutrino or dark matter scintillation counter. Although the CO made from natural gas is only depleted by about a factor of three, it could be the gas that has the lowest $^{14}\text{C}/\text{C}$ value. However, as was pointed out above, the creation of ^{14}C atoms during the enrichment or depletion process would have to be controlled.

6. Conclusions

Studies of the lowest levels of ^{14}C in carbon have been undertaken during recent years on a radiocarbon dating machine continually carrying out routine analyses. These low level studies have had to be fitted in to a tight schedule of analyses using a single ion source, which could only be cleaned partly of the accumulated sputtered carbon. In spite of this handicap it has been possible to demonstrate that underground methane has a very low level of $^{14}\text{C}/\text{C}$ of less than 1.6×10^{-18} . This required the use of isotope enrichment because of the low-level background of ^{14}C in the natural sample. Recent measurements have demonstrated that the accelerator mass spectrometry can be made essentially free of

interference from the residual ^{12}C and ^{13}C . These are created from the destruction of mass 14 molecules injected into the tandem accelerator along with the ^{14}C . However, the region of an ion source dedicated to the problem of looking at the real ^{14}C background will need more attention. The need to prepare samples of material for analysis without introducing contamination and the role of isotope enrichment will also require study. Finally more attention will have to be paid to increasing the ion current from the ion sources to speed up the low counting rate measurements. Only then will it be possible to study the actual level of ^{14}C in deep underground reservoirs and so assess their potential for lower background measurements with large scintillation counters.

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