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AN ATTEMPT TO DETECT STABLE N^- IONS FROM A SPUTTER ION SOURCE AND SOME IMPLICATIONS OF THE RESULTS FOR THE DESIGN OF TANDEMS FOR ULTRA-SENSITIVE CARBON ANALYSIS

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Résumé. — Dans cette communication on discute d'une expérience où l'on fait une recherche d'ions $^{14}N^-$ en présence d'un faisceau intense de carbone. On utilise une source d'ions Middleton à *sputtering*. Malgré un champ accélérateur de 1,5 MV/m nous n'avons pas trouvé d'ions azote négatifs avec des intensités détectables. La publication indique aussi les conditions que doivent remplir l'accélérateur si on veut bénéficier pleinement de ce résultat négatif afin de faire des mesures avec des faisceaux très faibles de ^{14}C.

Abstract. — The present paper discusses an experiment, using a Middleton sputter ion source, where a sensitive search was made for $^{14}N^-$ ions in the presence of an intense carbon beam. It was found that negative nitrogen ions, capable of withstanding acceleration fields of 1.5 MV/m, were not produced in detectable intensities. The paper also points out some design requirements of tandem facilities that must be satisfied if full advantage is to be taken of this negative result to permit the measurement of very weak ^{14}C beams.

1. **Introduction.** — In the previous talk by Professor Middleton, it was pointed out that useful beams of nitrogen have only been accelerated by tandems using the hydrides of nitrogen, NH^- and NH_2^-. To date, elemental negative nitrogen ions that are sturdy enough to withstand accelerating field gradients of 1.5 MV/m have not been observed. This implies [1] that the electron-binding energy is certainly less than about 20 meV and it has been speculated that the negative nitrogen ion is unstable. An unambiguous determination of the stability of $^{14}N^-$ has not been possible as there are theoretical calculations that show that the electron binding energy of nitrogen is very close to zero [2, 3]. However, the almost zero electro binding energy makes it very likely that metastable N^- ions, built on excited N^0 configurations, can be found that might well be sufficiently stable to allow tandem acceleration. Such an N^- structure would be analogous to the well known [4] metastable He^- ion which has been accelerated successfully.

The absence of stable N^- ions is potentially of great interest to those considering attempting to measure directly the ^{14}C content of materials [5]. Because the ^{14}C atom has the same mass as ^{14}N to within 1 part in 10^5, it will be almost impossible to distinguish ^{14}C atoms from the inevitable contamination of ^{14}N solely on the basis of mass [6]. The problem is particularly troublesome in radiocarbon dating applications as even in recent carbon samples the $^{14}C/^{12}C$ ratio is only 1 part in 10^{12}. The presence of as little as a part per million contamination of nitrogen will make high resolution studies of ^{14}C difficult, if not impossible. If $^{14}N^-$ does not exist or is of very low intensity, the two serious problems of ^{14}C mass spectrometry, nitrogen background and molecular backgrounds, can be eliminated.

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2. **Experimental measurements.** — A preliminary experiment was conducted at the university of Rochester MP tandem facility to look for interfering $^{14}N^-$ ions during carbon $^{14}C^-$ acceleration. The experiment made use of the fact that $^{12}CH_2^-$ injection followed by acceleration and stripping to $^{12}C^{6+}$ ions gives ions of exactly the same magnetic rigidity as $^{14}N^-$ injection followed by acceleration and stripping to $^{14}N^{7+}$ ions. In this case ammonia gas [7] was added to the sputter ion source [7] in an effort to enhance the yield of $^{14}N^-$ ions. No $^{14}N^{7+}$ ions were observed to accompany the $^{12}C^{6+}$ ions and it was estimated that the ratio of carbon negative ions to nitrogen negative ions from the ion source in this case was over 10^6 to 1. This measurement implies strongly, but does not prove, that ^{14}C dating by direct counting is feasible because the ammonia gas must contaminate the carbon with nitrogen more seriously than in a typical dating attempt.

This experiment convinced us that the $^{14}N^-$ yield was indeed very low and that it would be necessary to use very sensitive techniques for detection of any $^{14}N^-$ ions produced. The sputter source [7] was chosen as it is generally believed that the production of excited configurations would be small. For example, $^4He^-$ is not produced readily. The experimental arrangement ultimately adopted is shown in figure 1.

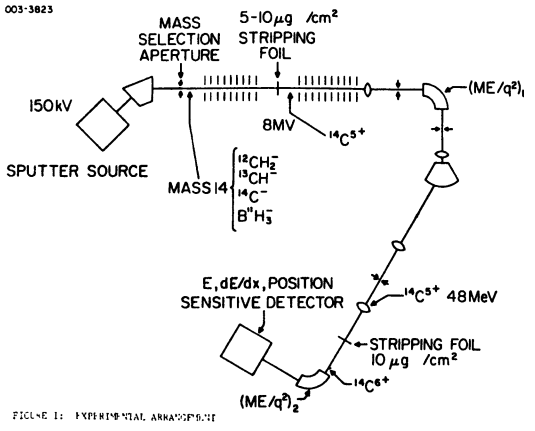

FIG. 1. — Experimental arrangement.

Mass 14 particles, consisting mainly of $^{12}CH_2^-$ and $^{13}CH^-$, were analyzed before acceleration using the $M/\Delta M = 25$ inflection system of the MP tandem. The selected particles were then accelerated to the tandem terminal and stripped by a 10 μg/cm² carbon foil. The terminal potential was maintained constant at 8.000 MV using a generating voltmeter feedback circuit. After further acceleration, the particles were magnetically analyzed by the combination analysis/switcher system set to an ME/q^2 value appropriate to $^{14}C^{5+}$ ions with an energy of 48.170 MeV.

$$(ME/q^2 = 26.981 \text{ MeV-amu})$$

The beams leaving the tandem were studied using a position sensitive $E.dE/dx$ counter in the focal plane of a magnetic spectrometer set at 0° to the incident beam axis. This counter, developed at Rochester [8], is shown in figure 2. It consists of an ion chamber for

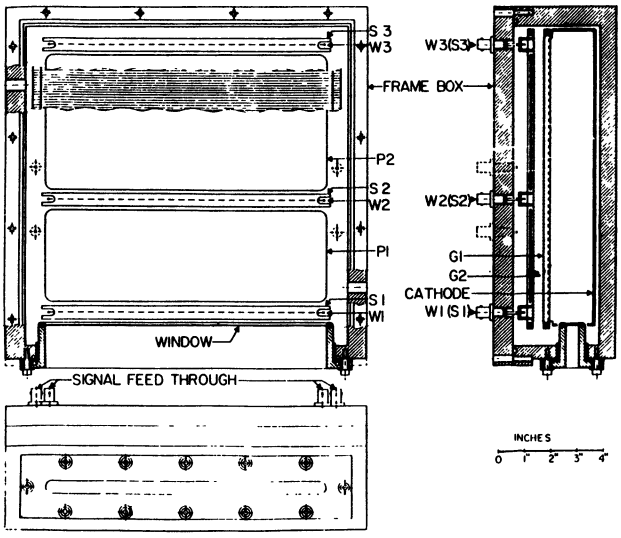

FIG. 2. — The heavy particle detector.

total energy determination, two position sensitive proportional counters which determine the angle and point of intersection of the particles with the focal plane, a dE/dx plate and a final proportional counter at the rear of the chamber for rejecting events which are not stopped within the active volume of the counter. The various counter outputs are digitized and fed to an on-line computer which permits the following quantities to be displayed and used in a variety of gating modes :

1. Momentum/charge distribution across a variable section of the focal plane.
2. Energy spectra for selected particles.
3. dE/dx spectra for selected particles.
4. Atomic-number (Z) spectra for selected $B.\rho$.
5. Mass distribution spectra for selected $B.\rho$.

An on-line analysis program permits individual particles to be uniquely identified at rates up to 1 000/s. An example of some of the outputs from the counter, reproduced from reference [8], is shown in figure 3.

3. **Tandem backgrounds.** — When the 26.981 MeV-amu particles from the tandem were analyzed by the mass sensitive detector, it became clear that significant backgrounds were present. An example is shown in figure 4, where all elements between He and F were present, with the most important contribution, by far, coming from carbon and oxygen. A surprisingly small amount of nitrogen was found notwithstanding the fact that nitrogen is normally used in the terminal for gas stripping.

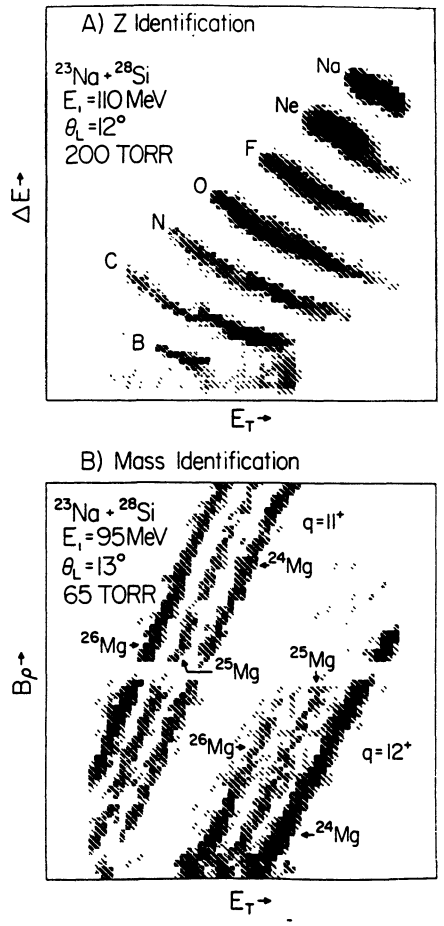

FIG. 3. — Example of Z and mass identification.

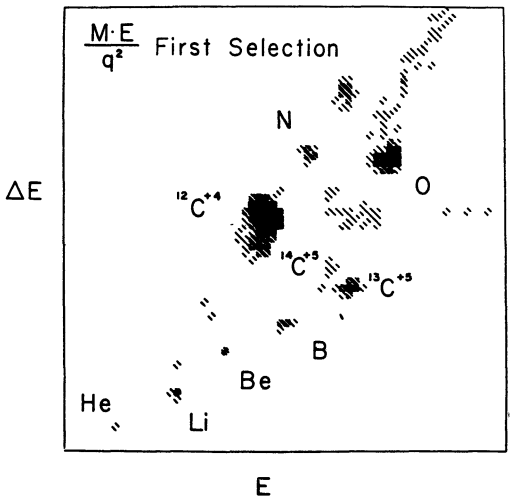

FIG. 4. — Background particles from the accelerator.

The background is of two types :

1. Those particles selected by the magnet system from the white spectrum which originates in the acceleration tubes. Such ions start at unspecified locations by random ionization processes or complicated charge exchange sequences. Such a sequence as

$$^{13}CH^- \rightarrow {}^{13}C^{6+} \rightarrow {}^{13}C^{5+}$$

has a continuous energy spectrum whose shape is not critically dependent upon terminal voltage.

2. Processes such as

$$^{14}NH^- \rightarrow {}^{14}N^{5+}$$

where particles stripped at the terminal can proceed unattenuated through the beam transport system for a critical terminal voltage. The reaction above transmits particles to the final detector if the terminal voltage rises by 1 % to 8.089 MV. The $^{14}NH^-$ ions are injected because of the finite resolution of the inflection magnet or by charge exchange processes in the ion source that give $^{14}NH^-$ ions of 14/15 of the energy of the $^{14}C^-$ ions.

The second type of background is particularly troublesome. When it occurs, the counting rates are intense, causing the gains of the counter to shift; ultimately the intense particle flux can destroy the detector window.

With the terminal at the assigned potential of 8.000 MV, the most serious background was found to be $^{12}C^{4+}$ particles. These particles, which can only pass through the beam transport system if they have an energy of 36.00 MeV, are thought to originate from the continuum of ^{12}C ions due to ionization by residual gas in the high energy tubes of the accelerator. These background particles were often of sufficient intensity that the maximum counting rate of 1 000/second could be significantly exceeded with consequent gain shifts and dead-time losses.

In order to reduce the unwanted beams to manageable levels, a second stripper foil was introduced before the magnetic spectrometer to charge-exchange a large fraction of the selected 5^+ beams to 6^+. Because the additional stripping introduces only a very small change in particle energy, the mass energy product for the spectrometer magnet is reduced by about $(5/6)^2$ from the beam transport value of 26.981 MeV-amu. The intense $^{12}C^{4+}$ background also changes charge, but the available charges of 4^+, 5^+, 6^+ caused the particles to miss the detector.

It was found that the very weak beam of $^{14}C^{6+}$ was contaminated by trace quantities of $^{12}C^{6+}$, $^{13}C^{6+}$, $^{14}N^{6+}$, $^{15}N^{6+}$, $^{16}O^{6+}$, $^{12}C^{4+}$ and $^{16}O^{3+}$ (see Fig. 5). All of these contributions could be uniquely identified by the counter. An example of one mass sensitive spectrum is shown in figure 6. Because all of the particles must satisfy $ME/q^2 = 26.981$ MeV-amu, with q definitely known to be $q = 6^+$, the mass of the particles is inversely proportional to the energy. If the $^{14}N^{6+}$ had come from the ion source, rather than from within the accelerator, the particles would have been transmitted only for terminal voltages of 8.000 MV. This characteristic was not observed and led to the conclusion that there was very little, if any,

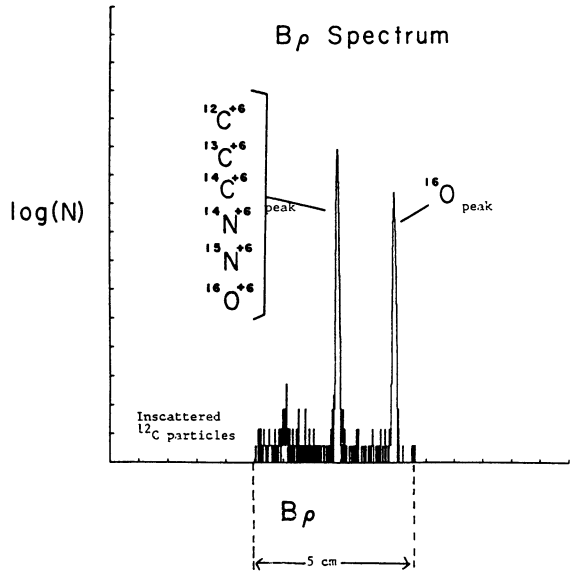

FIG. 5. — B_ρ Spectrum.

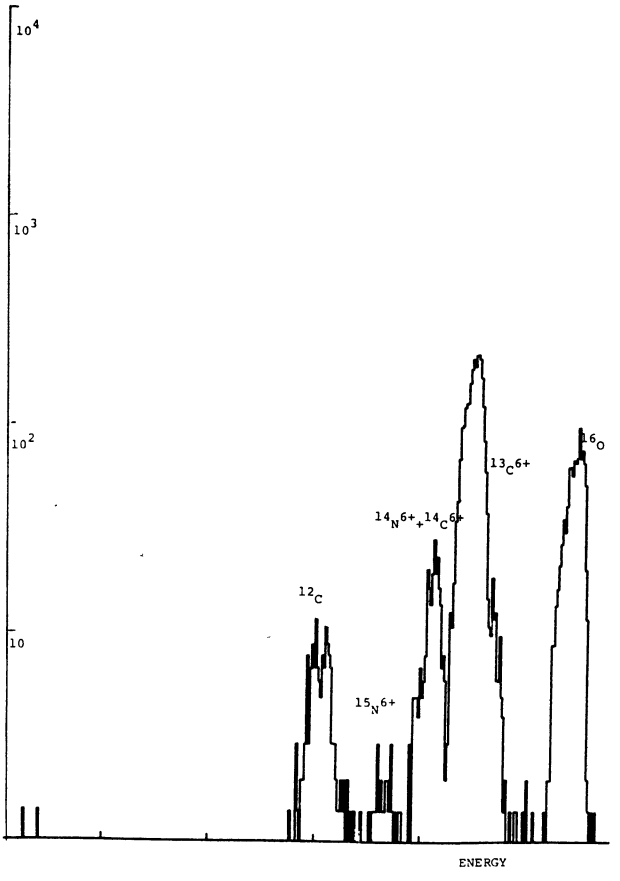

FIG. 6. — Ungated energy spectrum across 7.5 cm section of focal plane.

$^{14}N^-$ produced from a sputter source with a carbon cone.

Figure 7 shows the Z-distribution of particles using a contemporary charcoal cone in the sputter source. The ^{14}C group can be seen completely separated. A comparison is shown in figure 8 between dE/dx

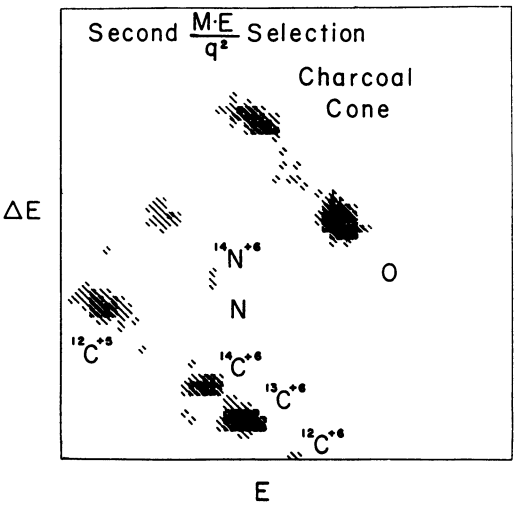

FIG. 7. — Z-Spectrum for recent charcoal cone.

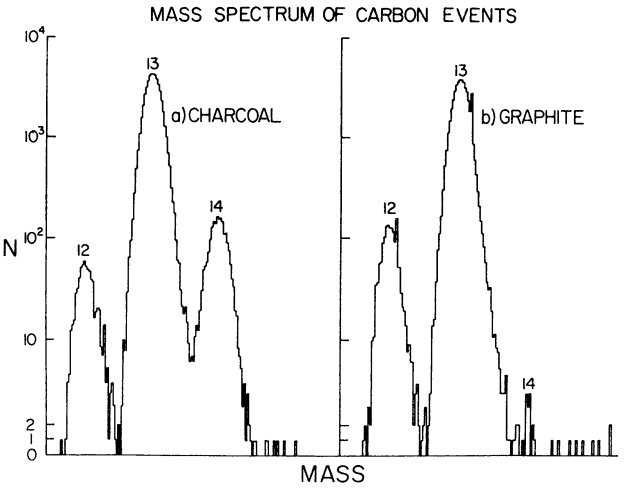

FIG. 8a. — ΔE spectrum from a charcoal cone counting time = 7 minutes.

FIG. 8b. — ΔE spectrum from a graphite cone; counting time = 57 minutes.

spectra, gated for $Z = 6$, for recent charcoal and for a graphite sample derived from petroleum products.

Figure 9 shows one of the tests that were carried out to ensure that the measured ^{14}C atoms originated from the ion source and were not some machine generated artifact. During this test the terminal voltage was changed in 10 kV steps while the ^{14}C counting rate from the antique graphite sample was observed. The *resonant* nature of the curve, which centers around 8 MV, indicated that the particles were indeed from the ion source.

In the final run, data were obtained using a sputter source which produced 5 μA of $^{12}C^-$ by bombarding graphite with ~ 1 mA of caesium. During these runs it was possible to observe, unambiguously, ^{14}C ions at the rate of 0.5/minute. If a comparable contemporary charcoal cone had been available in place of the graphite, a total of 30 $^{14}C^-$ would have been produced per second. The known transmission of the system would have permitted at least 3/second to be detected to give a source-to-background ratio of 360 : 1.

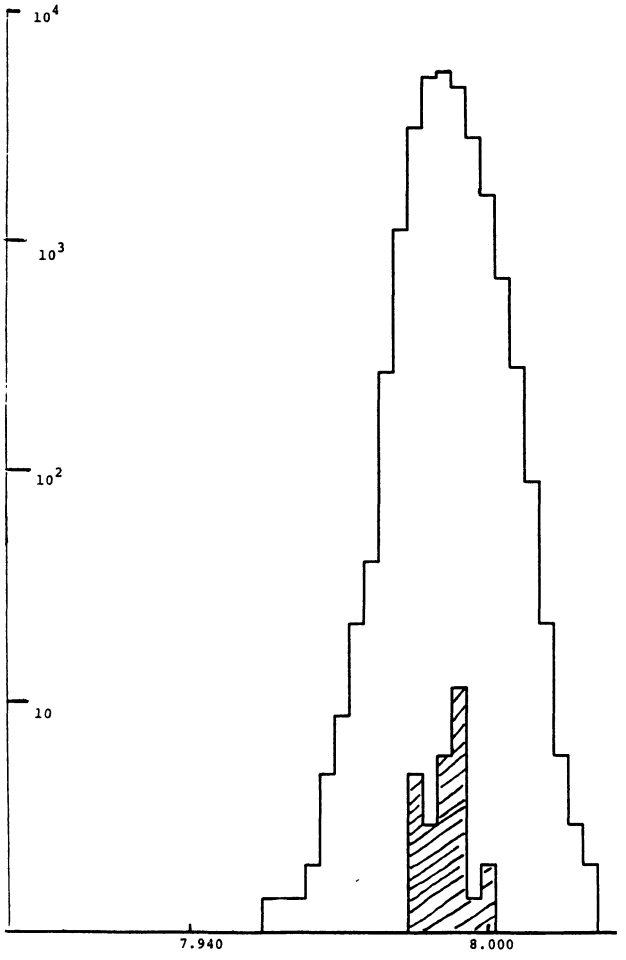

FIG. 9. — Terminal voltage spectrum generated by all detected events and by ^{14}C (shaded) from a graphite source.

4. **Tandem design features.** — It is clear that several features are important in the design of a tandem that is to make spectrometer measurements :

4.1. TERMINAL VOLTAGE CONTROL. — Terminal voltage control should be better than 0.025 % without slit stabilization. This insures that the duty cycle is unity and that unwanted beams from particles such as $^4NH^-$ do no get accidentally accelerated.

4.2. HIGH MASS RESOLUTION AT THE INJECTOR. — The mass resolution of the injector should be at least 50 to minimize the contamination of the mass 14 by the tails from mass 15 ($^{14}NH^-$) and mass 13 ($^{12}CH^-$).

4.3. ADDITIONAL DISPERSION IN VELOCITY OR ENERGY. — Additional dispersions are desirable in a dimension other than magnetic rigidity. Possible types of additional dispersion include :

— Velocity (*Ex B* filter).
— Time-of-Flight (pulsed beam).
— Energy/charge (electrostatic filter).

Elements of this type can be designed to have unity transmission so that the wanted particles are not attenuated but background particles are almost eliminated.

4.4. For high sensitivity ^{14}C measurements, the ion source and the low energy beam transport should be as carbon- or nitrogen-free as possible and deuterium acceleration by the tandem should not be encouraged. ^{14}C production by means of the reactions

$$^{14}N\ (n, p)\ ^{14}C \text{ and } ^{13}C\ (d, p)\ ^{14}C$$

has high cross sections and will reduce the ultimate sensitivity of the instrument.

5. **Additional filter elements.** — A strong case can be made for additional dispersive elements such as velocity or energy filters in the standard beam transport system of heavy ion tandem accelerators. Weak beams are increasingly being used for sophisticated experiments and contaminants can be disastrous. An example of the sort of accidental overlap that can often arise is illustrated by comparing the following acceleration sequences :

1. $^{12}C_4^- \rightarrow {}^{12}C^{3+}$
2. $^{16}O^- \rightarrow {}^{16}O^{4+}$

The negative ions cannot be selected at the injector as they both have almost identical masses. After stripping at the terminal and acceleration, the $^{12}C^{3+}$ and $^{16}O^{4+}$ have almost identical magnetic rigidity so that they are directed simultaneously to the target. The overlaps become more troublesome as additional stripping foils are used.

6. **Conclusion.** — While there are still background questions that must be resolved before any strong claim can be made about the usefulness of the techniques for radiocarbon dating, the absence of $^{14}N^{6+}$ originating from a sputter source at exactly the same energy as the $^{14}C^{6+}$, at the very low levels observed, indicate that the $^{14}N^-$ ions that may be present are not the most serious obstacle to the development of direct ^{14}C measurements. It appears possible to develop a tandem mass-spectrometer [10, 11] for detecting with high precision the ^{14}C present in natural carbon. In a useful instrument high mass resolution at the injector is essential, good terminal voltage control is necessary, additional high energy dispersion elements in velocity or energy space are desirable and deuterium acceleration should be discouraged.

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