PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Fundamentals of Accelerator Mass Spectrometry [and Discussion]

A. E. Litherland, M. Paul, K. W. Allen and H. E. Gove

Phil. Trans. R. Soc. Lond. A 1987 **323**, 5-21
doi: 10.1098/rsta.1987.0069

Phil. Trans. R. Soc. Lond. A **323**, 5–21 (1987)

Printed in Great Britain

Fundamentals of accelerator mass spectrometry

By A. E. Litherland, F.R.S.

Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7

The extension of high-sensitivity mass spectrometry to isotope ratios in the range 10^{-12}–10^{-15} has been called accelerator mass spectrometry (AMS) because of the use of an additional stage of acceleration that facilitates the removal of molecular interferences and the separation of isobars. In some cases the ultra-high sensitivity is obtained by exploiting the instability of the negative ion of the interfering isobar. It is now possible to measure such isotopes as ^{14}C at natural abundances as low as one atom in 10^{+15} ^{12}C atoms. The ideas behind this significant extension of mass spectrometric techniques will be discussed.

1. Introduction

Accelerator mass spectrometry (AMS) is the term often applied to a collection of techniques, based on the use of an accelerator, that make possible the measurement of isotope ratios below 10^{-12}. Of course, to obtain mass resolution, all mass spectrometers accelerate ions to a few kiloelectronvolts to overwhelm the spread in energy of the ions emitted from an ion source. The second stage of acceleration in an accelerator mass spectrometer ensures the efficient removal of molecular interferences by their complete destruction during charge-changing collisions at energies of a few million electronvolts. In addition, the higher energy generated by the accelerator makes the separation of isobars possible by rate of energy loss, range methods or complete electron stripping. In some cases, such as the measurement of the rare isotopes ^{14}C, ^{26}Al and ^{129}I, very high sensitivity can be obtained without isobar identification at the higher energy because the negative ion of the isobar, such as ^{14}N, is unstable. Consequently, the complete separation of isobars takes place at the ion source. A better term than AMS might be, following Hintenberger (1962), ultra-high-sensitivity mass spectrometry, to include all types of additional filters that make the sensitivity possible. For example, the combination of lasers with mass spectrometers, to be discussed by G. S. Hurst (this symposium), would then be included. Whatever the term used for the application of these new techniques to mass spectrometry, there can be no doubt of the widespread interest in the topic of ultra-high-sensitivity mass spectrometry, as can be seen from the range of applications to be discussed at this meeting.

The second acceleration stage in AMS can increase the ion energy from a few hundred kiloelectronvolts to many gigaelectronvolts depending on the accelerator being used and the ions being analysed. If it is not necessary to separate the isobars by the final ion detector, the lowest energies can be used whereas, when the separation of the isobars must be done by the final ion detector, the highest energies and hence the largest accelerators are favoured. The talk by W. Henning (this symposium) on AMS for heavy elements emphasizes the value of using the highest energies and the largest accelerators. The two areas of AMS can be called low-energy accelerator mass spectrometry and high-energy mass spectrometry respectively, depending upon energy at which the separation of isobars is carried out. High-energy AMS was first employed by Alvarez & Cornog (1939) who used a cyclotron to help in the discovery of ^{3}He in helium. It was reintroduced by Muller (1977) as a result of a search for integrally charged quarks and experiments on long-lived radioisotopes. The emphasis in this latter case was on the use of high energies to facilitate isobar separation. In general, the highest energies available are most suitable for isobar separation by ionization counter measurements.

In parallel with this development was the exploitation of different methods for the separation of isobars. Attempts were made in the 1960s by Schnitzer *et al.* (1974) to exploit the idea that the negative nitrogen molecule ^{14}N ^{15}N is probably unstable whereas the ^{14}C ^{15}N negative ion is strongly bound. This attempt failed partly as a result of the lack of a suitable negative ion source and partly because of interference from the negative ion of ^{29}Si. Ion sources producing microamperes of negative ions were developed in the 1960s for use with tandem accelerators (Bromley 1974), and it was with one of these ion sources and a tandem accelerator that Purser *et al.* (1977) showed that ^{14}N$^-$ was too unstable to interfere with the detection of ^{14}C ions for radiocarbon dating. This development has led to the construction of compact devices for radiocarbon dating by AMS (Purser *et al.* 1980). Tandem accelerators with voltages as low as 1.4 MV have been used for radiocarbon dating (Lee *et al.* 1984) so that this application can properly be called low-energy accelerator mass spectrometry. ^{14}C has also been separated from ^{14}N by Labrie & Reid (1981) by using a laser alone. This method, however, has not yet been developed for dating. Negative ion properties have been summarized recently by Hotop & Lineberger (1985).

During the past nine years, many tandem accelerators originally constructed for nuclear physics purposes have been used with only minor modifications to make a variety of measurements relevant to archaeology and geophysics. We will hear about some of these results later in the meeting. A symposium on AMS has been published recently (Wölfli *et al.* 1984).

2. PRINCIPLES OF ACCELERATOR MASS SPECTROMETRY

The very high sensitivity of AMS is obtained by an appropriate combination of energy, mass and charge spectrometry, as the ions have at all times characteristic ratios of energy divided by charge (E/q) and mass divided by charge (M/q) that may change in a controlled manner during their passage through the spectrometer. The choice of charge can vary from -1, when negative ion stability is used to separate isobars (low energies), to $+Z$, if complete electron stripping is used (very high energies). Often, at some stage during the mass spectrometry, charge state $+3$ ions are formed because molecular interferences are then very rare (Litherland 1980). Molecular ions with charge $+2$ are, however, very common (Galindo-Uribarri *et al.* 1985). The use of negative ions has the added advantage that only singly negative ions of atoms and simple molecules are known. This removes an ambiguity found for multiply charged positive ions due to the fact that magnetic analysers respond to the ratio M/q.

Three analysers, with static electric and magnetic fields, can be employed in mass spectrometry (Litherland 1980). The first two are the electric analyser, which determines (E/q), and the magnetic analyser, which determines $(E/q) \times (M/q)$. In both cases, electric and magnetic fields can be shaped so that the analysers are focusing. The third analyser is the velocity analyser, which determines $(E/q)/(M/q)$. This analyser, however, must use supplementary focusing that depends upon (E/q) or $(E/q) \times (M/q)$. All three types can be used in the suppression of unwanted ions that arise from gas or slit scattering, molecular fragmentation and charge-changing collisions in the residual gas of the spectrometers. In each case, the rejection ratio can be a factor of about 10^{+5} or larger depending upon the design of the analyser. If one of each of these analysers is used in series then, in principle, a rejection ratio of 10^{+15} is possible and this is usually more than sufficient for most work.

A fourth type of analyser that can be used (Muller 1977) is the cyclotron, which determines (M/q) by acceleration of the ions at the cyclotron frequency. This analyser–accelerator is discussed further in § 5.

The resolution requirements for the analysers used in AMS are unusual. For example, the relative intensity of the rare radioactive isotope ^{36}Cl and the neighbouring stable chlorine isotopes can be as low as 10^{-15}. Consequently it is necessary to resolve the isotopes at a much lower level than usual so that the concept of the full width at half maximum height or $W(\frac{1}{2})$ for the resolution of an analyser must be replaced by the width at some much smaller fraction of the height. Let us use the full width at 10^{-N} of the peak height instead. If we assume that the peaks from an analyser are gaussian, then it is easy to show that

$$W(10^{-N}) = 1.82\sqrt{N}W(\tfrac{1}{2}). \tag{1}$$

A magnetic analyser for separating peaks with an intensity ratio of 10^{+5} must therefore have a resolution about four times that of an analyser used to separate peaks of equal intensity. This requirement for increased resolution without the loss of intensity is, of course, the reason for the use of the accelerator as a molecular disintegrator. For example, to resolve $^{12}\mathrm{CH}_2^-$ clearly from $^{14}\mathrm{C}^-$ with an intensity ratio of 10^{+10} and a mass difference ΔM given by $(M/\Delta M) = 1134$, where $M = 14$, would require a very large magnetic analyser with a radius of curvature of about 5 m if the object and image size were about 1 mm. In addition, molecular fragmentation during analysis would make this estimate unreliable because the line shapes would then deviate strongly from the gaussian form. The large object and image size are due to the need to use high-current ion sources and high-ion collection efficiency. The acceleration of the molecules to a few megaelectronvolts to dissociate them into the constituent atoms is therefore a simple alternative that requires only magnetic analysers that can resolve the neighbouring carbon isotopes at large intensity ratios (Purser 1976). The requirements of AMS are quite similar to those of isotope separators (Wollnik & Becker 1985), and clearly the accelerator mass spectrometer is also a high-quality mass separator.

An additional and sometimes crucial advantage of the higher energy provided by the accelerator is that it is possible to use ion detectors that give a variety of output signals well above the detector noise. Signals proportional to the ion energy E and the rate of energy loss $\mathrm{d}E/\mathrm{d}x$ can be obtained. This signals can be used to separate isobars and other interfering ions that penetrate the analysers. The separation of ^{205}Pb and ^{205}Tl (see W. Henning, this symposium) is a good example. Sometimes the very high energy produced by accelerators can be used to strip all electrons from the ions by passing them through thin foils. In this case M/Z, which is unique, can then be specified. Unfortunately this procedure works only when $Z_{\mathrm{rare}} > Z_{\mathrm{common}}$ because there is always a low probability of a nucleus retaining an electron. The separation of ^{59}Ni and ^{59}Co with $Z = 28$ and 29 has been reported by this method (Kutschera 1983).

An accelerator mass spectrometer can be devised for particular problems by combining a suitable ion source with electric and magnetic analysers before and after the accelerator, to remove unwanted ion backgrounds, followed by an ion detector of appropriate complexity. These components will be discussed in the following sections. A schematic diagram of an accelerator mass spectrometer (Kieser *et al.* 1986) with many of the components referred to in this paper is shown in figure 1.

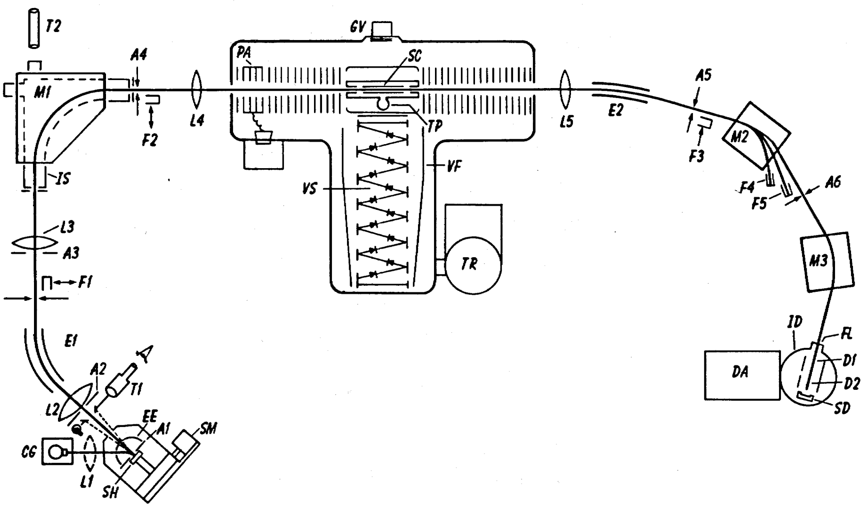

FIGURE 1. Schematic drawing of the accelerator mass spectrometer at Toronto (Kieser *et al.* 1986), showing the elements used for radiocarbon analysis. Labels: A1–A6, apertures: CG, the caesium gun (15 kV); D1 and D2, the ionization detector with ΔE_1 and ΔE_2 collection plates; DA, the data acquisition electronics; E1, a 45° spherical electric analyser; E2, a 15° electric analyser; EE, the sample ion-extraction electrode (0 V); F1–F5, Faraday cups; FL, a mylar foil window; GV, generating voltmeter; ID, gas ionization detector; IS, an insulated magnet box; L1, split einzel lens (focusing and steering); L2 and L4, einzel lenses; L3, gridded lens; L5, the electric quadrupole; M1, 90° magnet; M2 and M3, 45° magnets; PA, pre-acceleration electrode (60 kV); SC, stripping canal; SD, silicon particle detector; SH, sample holder (−20 kV); SM, stepping motor; T1 and T2, viewing and alignment telescopes; TP, stripper gas recycling turbopump; TR, 40 kHz 10:1 step-up transformer; VF, voltage multiplier parallel feed capacitor; VS, voltage multiplier diode stack.

3. ION SOURCES

A number of important isobars such as ^{14}C, ^{14}N; ^{26}Al, ^{26}Mg; etc. can be separated by using negative ions (Litherland 1980). Ion sources that generate intense beams (much greater than 1 μA) of negative ions of the abundant isotope are required to ensure an adequate counting rate of the rare isotope. For example, 1 μA of $^{12}C^-$ from contemporary carbon is accompanied by 7.5 $^{14}C^-$ ions s^{-1}. The ratio $^{14}C:^{12}C$ for contemporary carbon is 1.2×10^{-12}, and this ratio decreases by a factor of ten every 18500 years (the mean life of 8033 years for radiocarbon as used by Libby (1955) is always used in radiocarbon work). After 55500 years, the ratio $^{14}C:^{12}C$ has dropped to 1.2×10^{-15} and the $^{14}C^-$ counting rate to 27 h^{-1}. Ion sources with C^- currents of hundreds of microamperes have been reported by Middleton (1983). The advantage of counting the rare radioactive isotope directly rather than the decay particles is illustrated very well by radiocarbon dating. The number of β-rays emitted per minute per gram of carbon is about 15 whereas counting rates of ^{14}C ions during the radiocarbon dating of milligram-scale samples of carbon can often be 15 s^{-1}. This advantage clearly increases with the half-life of the radioactive isotope.

The ion source most frequently used in accelerator mass spectrometry (Middleton 1983) operates by directing a beam of ions, such as from the caesium gun shown in figure 1, onto a solid sample where neutral atoms are sputtered from the surface. Because of the presence of some caesium on the surface, the work function is lowered. As a result many atoms (several percent in the case of carbon) become negative ions.

An important requirement for an ion source for AMS is a low memory effect. This is because a large range of isotope ratios must be analysed in rapid sequence for radiocarbon dating and for the other applications to be discussed later at this meeting. Sputter-ion sources have a small memory effect, which means that isotope ratios differing by factors of at least a thousand, such as those encountered in radiocarbon dating, can be analysed without mutual interference. A memory effect does, however, exist because of the resputtering of already sputtered material (Wittmaack 1983, 1985) or to the generation of gases, containing the rare isotope being analysed, that ultimately arrive in the region of analysis. These memory effects are mainly a problem for the analysis of materials below atomic concentrations of one in 10^6 (Clegg 1986).

Sputter-ion sources can also be used with gases penetrating, for example, porous titanium, which is in turn sputtered by caesium atoms. The gas molecules are presumably deposited on or near the titanium surface of the ion source being bombarded with the caesium atoms. The use of gases in this way (Middleton 1984) is a potentially important development.

In contrast to the ease of generation of high-electron-affinity negative ions with a caesium sputter source, the generation of intense beams of negative ions with low electron affinity presents a more difficult problem. An alternative procedure involving charge exchange at kiloelectronvolt energies in metal vapours (Heinemeier & Hvelplund 1978) has proved to be useful. In this case, positive ions are first generated by a sputter-ion source such as the I^- source pioneered by Rachidi *et al.* (1976). These ion sources produce many microamperes of positive ions from atoms with low electron-binding energy, such as aluminium, and these can readily be accelerated to many kiloelectronvolts (Aardsma 1983). The energy of conversion to negative ions and the particular metal vapour must be carefully chosen to maximize the negative ion current, and it is usually also necessary to control the ion beam emittance with apertures, in a mass independent way, because of ion beam degradation due to multiple scattering during the charge exchange process (Heinemeier & Hvelplund 1978).

Some of the properties of the ion beams from sputter-ion sources have been studied in recent years and the experiments of Yu & Lang (1983), Vasile (1984) and Shimizu & Hart (1982) tend to support the theories of Thompson & Sigmund (Sigmund 1984), although much work is still needed. The sputtering of the neutral atoms from a flat surface by the ion beam generates an energy spectrum given by

$$P(E/E_b, \phi) = \frac{a(E/E_b)}{(1+E/E_b)^3} \cos\phi, \tag{2}$$

where a is a constant, E_b is the binding energy of the atom to the solid, E is the neutral atom energy, and ϕ is the angle of emission with respect to the normal. This spectrum, which is shown in figure 2*a* for $\phi = 0$, peaks at an energy $\frac{1}{2}E_b$, which is usually a few electronvolts and has a very long tail that extends to the kinematic limit for binary collisions, albeit at very low intensities. For example, in the sputtering of carbon by 30 keV Cs^+ ions, the sputtered ions, which presumably started out as neutrals, extend to at least 6 keV above the energy acquired from the acceleration by the ion-source voltage (Kilius *et al.* 1987).

The neutral atom spectrum is modified above the surface by repeated electron tunnelling

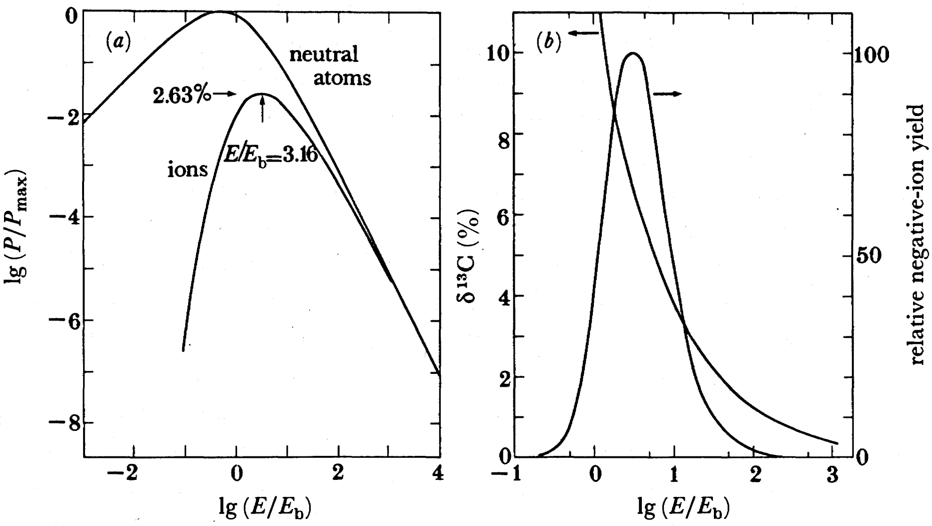

FIGURE 2. (*a*) The logarithm of the intensity of the sputtered neutral atoms is shown as a function of the logarithm of their energy divided by the binding energy of the atoms in the solid. Also shown is the spectrum of the emitted negative ions for a typical value of the constants given in equation (3). (*b*) The spectrum of the negative ions shown in (*a*) is shown together with the fractionation of the ^{13}C and ^{12}C ions $\delta^{13}C$ in percentage deviation from the true value per atomic mass unit.

to and from the low work-function (Φ) surface and the neutral atom (Norskov & Lundqvist 1979). The negative ions that survive this process are then accelerated by the electric field of the ion source. The survival probability is strongly dependent on the normal component of the neutral atom velocity so that the energy spectrum of neutral atoms is multiplied by the survival probability which can be written, following Vasile (1984), as

$$\alpha^{-} = 2/\pi \exp - [\beta(\Phi - A + V_{\mathrm{i}})/v \cos \phi], \tag{3}$$

where A is the electron affinity, $v \cos\phi$ is the atom velocity component perpendicular to the solid surface, V_{i} is an image potential and β is a constant. The product of $P(E/E_{\mathrm{b}}, \phi = 0)$ and α^{-} gives the spectrum of negative ions shown in figure 2*a*, *b*. The survival probability clearly increases as the ion energy increases. In equation (3) it is assumed that all sputtered particles are atoms. However, molecules are also sputtered and, as we shall see later, these are often in excited states (hot molecules) and decay in flight. Consequently, the low-velocity region is undoubtedly a mixture of atoms and fragmented molecules. This possibility is not considered in the discussion of isotope fractionation given below.

The velocity dependent term given in (3) gives the predicted isotope fractionation for the stable carbon isotopes shown in figure 2*b*. The expected fractionation $\delta^{13}C$ is a strong function of the energy due to the velocity dependence of the survival probability given by (3). The negative sign of $\delta^{13}C$ implies that the heavy isotope is depleted relative to the light isotope. Although this theory has not yet been tested thoroughly, it does predict that the mass fractionation is approximately linear in mass. This prediction has been tested over a limited range of velocities, for positive ion emission following sputtering by negative ions, by Shimizu & Hart (1982), for three chromium isotopes, as shown in figure 3. The velocity dependence of the positive and negative ion yield has also been checked in a number of cases (Yu 1978; Vasile 1984) and although there is good agreement in several cases the true situation may be

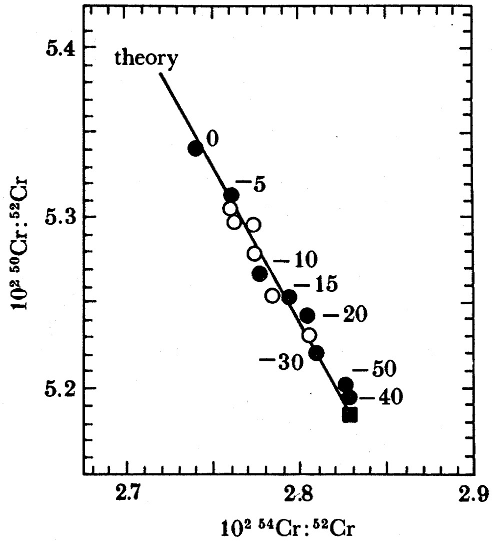

Figure 3. A three-isotope plot for Cr is shown as a function of the excess energy (up to 50 eV) of the sputtered ions. The measured 50/52 and 54/52 ratios (closed circles) are shown to fit a theoretical fractionation line (slope = −1) originating at the absolute values (the square) for these ratios. The open circles show the observed variations in the fractionation of the isotopes as a function of position on the sample (Shimizu & Hart 1982).

more complicated than given by a combination of (2) and (3). Fortunately, in three cases where three stable isotopes have been studied by Shimizu & Hart (1982), the fractionation was linear in mass, suggesting that the fractionation is associated with the ionization process and not the neutral-atom sputtering process. The complex ion spectrum from the sputtering phenomenon may then be used in the measurement of isotope anomalies, such as in radiocarbon dating, as long as care is taken to correct for the fractionation due to the sputtering process by measuring at least two isotopes in addition to the unknown isotope (Beukens *et al.* 1986). However, it is clear also from (3) that variations in Φ the work function, V_1 the image potential, or surface topography can change the isotope ratios. Changes of this sort may be responsible for the 2.5% change in $^{13}C:^{12}C$ isotope ratio observed for the sputtering of different types of carbon (Beukens *et al.* 1986; Litherland *et al.* 1986). If the surface parameters change then again two isotopes must be measured to provide a correction to the measurement of the intensity of an unknown third isotope. This procedure should work provided the parameters do not change between the times of the isotope intensity measurements. In radiocarbon dating, the $^{13}C:^{12}C$ ratio can be used to obtain a corrected $^{14}C:^{12}C$ ratio (Beukens *et al.* 1986) to better than ±1%. It is worth noting that the ratio is also corrected by this method for both Rayleigh fractionation during sample preparation and natural fractionation.

The high-energy tail of the $^{12}C^-$ ions from a sputter-ion source of 20 keV has been observed with the help of a complete accelerator mass spectrometer (Kilius *et al.* 1987), and is shown in figure 4. The prominent peak at 1492 G† is the sputtering peak shown in figure 2*a*, *b* modified by the acceptance geometry of the accelerator mass spectrometer and with an added 20 keV energy due to the electric field of the ion source extraction shown in figure 1. The logarithmic vertical scale should be noted. The tail at magnetic fields greater than 1492 G is mainly from the sputtering process as shown in figure 2*a*. The reduction in intensity near 1750 G is near

† 1 G = 10^{-4} T.

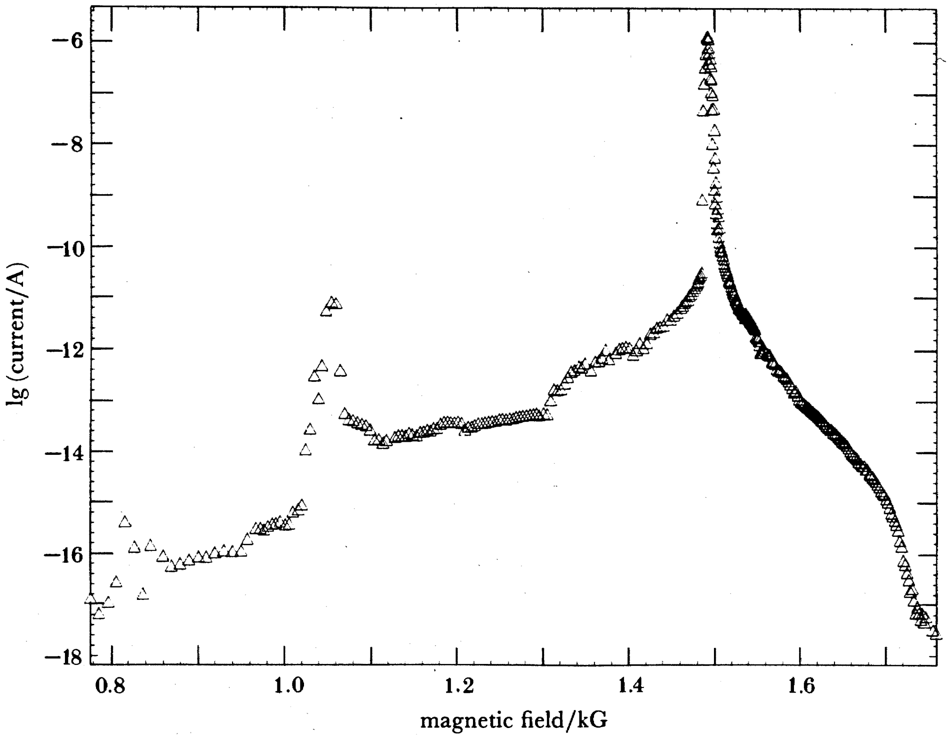

FIGURE 4. The observed logarithm of the ion current of ^{12}C is shown as a function of the magnetic field of the 90° injection magnet. The complete accelerator mass spectrometer was used to obtain these data. The prominent peak at mass 12 is the main peak from the sputtering shown in figures 2*a*, *b*. The tail above mass 12 is mainly that part of the sputtering distribution selected by geometrical constraints. The peak at about mass 6 (1060 G) is the decay in flight of $^{12}C_2^-$ leading to $^{12}C^-$ after the ion source and before the electric analyser.

the kinematic limit for double collisions between Cs and C. The tail at lower magnetic fields is most likely due to the decay of hot molecules during acceleration in the ion source. Peaks from the decay of hot $^{12}C_2^-$ molecules to $^{12}C^-$ immediately after the ion source are also shown. These low-energy tails and high-energy tails have implications for the negative-ion mass spectrometry as discussed in §§4 and 6.

In addition to the complex energy spectrum due to sputtering and other processes in the ion source, the shape of the surface being sputtered changes. Usually a complex crater develops and as a result the electric field is modified near the surface. This in turn increases the angular spread of the sputtered beam because of the variation of yield with angle given by (2). Unless care is taken to limit the phase-space area occupied by the beam in a way independent of mass, that is before magnetic analysis, an additional isotope fractionation variable with time and nonlinear in mass can be introduced (Suter *et al.* 1984; Beukens *et al.* 1986). In (3) the angle with respect to the normal to the surface ϕ also appears. Clearly, isotope fractionation effects should take place during cratering. This fractionation can also be corrected as described earlier.

Positive-ion sources for injection into accelerators other than tandem accelerators can be of a variety of types although low-memory, low-energy spread negative halogen sputter-ion sources are ideal (Rachidi *et al.* 1976; Aardsma 1983).

4. THE PRE-ACCELERATION ANALYSIS SYSTEM

After extraction from the ion source, involving acceleration to tens of kiloelectronvolts, the ions are prepared for injection into the accelerator. For the sake of simplicity we will assume it to be a tandem accelerator, because out of the list of accelerators used world wide (Litherland 1984), 25 of the 28 were tandem accelerators.

The negative ions must be mass analysed to reduce the background from ions of other masses. The tailing mentioned in §3, and illustrated in figure 3, implies that both electric and magnetic analysers should be used, preferably in a non-energy-dispersive combination to minimize the emittance of the ion beam before injection into the accelerator. The sequence of electric and magnetic analysers shown in figure 1 was chosen for convenience during development of the system and is not ideal.

The ions of the isotopes $^{12}C^-$, $^{13}C^-$ and $^{14}C^-$ are usually injected in time sequence into the accelerator by varying the voltage on an insulated magnet vacuum box (Purser *et al.* 1980). The procedure works well (Suter *et al.* 1984; Beukens *et al.* 1986) although it requires a computer control system for handling the two current measurements and the one counting-rate measurement (Nessi *et al.* 1984). In figure 1, the ^{12}C current is measured in Faraday cup F4, the ^{13}C in Faraday cup F5 and the ^{14}C counting rate in the ionization detector ID. The pulsing of the isotopes by this method implies that combinations of magnetic and velocity analysers would require two pulsing systems. However, the addition of an electric analyser (Kilius *et al.* 1987) before the magnetic analyser is straightforward, because the ions of interest all have the same energy. This pre-acceleration analysis system, used at the University of Toronto, is shown in figure 1. The resolution of the magnetic analyser is about 300 ($M/\Delta M$), which although not sufficient to resolve the uranium isotopes completely is more than adequate for the carbon isotopes at ratios of 10^{-15}. The resolution ($M/\Delta M$) needed for high (greater than 10^{-10}) isotope ratio studies of the uranium isotopes would be about a factor of five larger than the magnetic analyser shown in figure 1. However, elastic scattering or molecular fragmentation in the magnet would make such an undertaking difficult.

A decision on the magnitude of the mass, energy or velocity dispersion of the analysers before the accelerator depends upon the problem being studied, but it is clear that it is better, although less convenient, to use two magnets in such a way that their dispersions add (Wilson 1979), rather than a single magnet with the same total dispersion. This is because the elastic scattering of the ions in the gas of the first magnet, from the walls of the magnet box or from the molecular fragmentation in the first magnet, are discriminated against in the second. In other words, it is better to remove the intense isotope beams as early as possible otherwise they will have to be discriminated against after the accelerator where it is more expensive.

5. THE ACCELERATOR

The most widely used accelerator in AMS is the tandem accelerator (Allen 1974), although occasionally cyclotrons (Harvey 1974) and heavy-ion linear accelerators (Bock 1974) are used.

(a) *Tandem accelerators*

The electrostatic tandem accelerator system, such as that shown in figure 1, is particularly suitable for AMS work especially if isobars can be separated with negative ions. After acceleration of the negative ions through the high voltage (V) of the central electrode of the tandem, they acquire an additional energy (eV) above that provided by the ion source. The negative ions readily lose several electrons during passage through an electron-stripping gas such as argon, and are then accelerated again through the same high voltage (V) to acquire a total energy $(q+1)$ eV from the tandem acceleration. q is the charge acquired during electron stripping. If the charge $q > 3$ then the molecular ions are so unstable that they fragment quickly, and as yet no molecular ions with $q = +3$ have been observed to emerge from a tandem accelerator. This feature of tandem accelerators, also discussed in §2, eliminates the need for high mass resolution of the magnetic analysers because only atomic ions are present. Ions with charge 3 can be used for ^{14}C dating, and as the yield of $^{14}\mathrm{C}^{+3}$ ions peaks near 3 MeV (Hofmann *et al.* 1984), this specifies the voltage required for the tandem accelerators designed (Purser *et al.* 1980) for radiocarbon dating. It has also proved to be possible to use tandem accelerators with 1.4 MV central electrodes for radiocarbon dating by using $^{14}\mathrm{C}^{+2}$ ions (Lee *et al.* 1984). Radiocarbon dating with higher charge states and energy is also possible. The charge division after charge changing is responsible for the loss of about 50% of the ions in radiocarbon dating. This is unavoidable.

The negative ions entering a tandem accelerator are focused by the low-energy accelerator tube (Galejs & Rose 1967) to the central high-voltage electrode where a cross over is formed. For the magnification to be near 1, the negative ion must have an energy that is a definite fraction of the energy acquired by the acceleration to the central electrode. Several procedures for achieving the correct focusing of this critical element are discussed by Lawson (1974). The pre-acceleration system PA in figure 1 is for this purpose. The focusing of the ion beam (more correctly, formation of a waist) in the central electrode is a critical procedure because the ion beam must pass through a region of higher gas pressure so that electrons can be stripped from the negative ions to form positive ions. This region is frequently called the charge-changing or stripping canal and is shown as SC in figure 1. The region of higher gas pressure cannot have windows, so some form of differential pumping is necessary (Bromley 1974; Rathmell 1986) to minimize the flow of gas into the acceleration tubes. Alternatively very thin carbon foils can be used, but gas stripping has the advantage that the stripping medium is indestructible and a lower mass of material can be used, thereby reducing the ion energy spread and improving the ion beam quality due to the absence of Coulomb explosions (Gemmell 1980). The multiple scattering of the ions during charge changing is always significant (Sigmund & Winterbon 1974) and should be considered in the design of a gas charge-changing canal. In the tandem shown in figure 1, the areal density of gas within the charge-changing canal, as a result of the differential pumping, is some 5000 times that in both acceleration tubes. Consequently, although a significant continuum of ions is generated, in addition to the ions of interest, this is not a problem because the post-acceleration analysis system is designed to handle the larger flux of ions generated from the fragmentation of the molecules.

The weak focusing of the second stage of acceleration in a tandem accelerator is supplemented by focusing elements, such as L5 in figure 1, outside the tandem (Lawson 1974).

The probability of producing the various multiply charged ions at megaelectronvolt energies has been discussed by Hofmann *et al.* (1984). In general, the cross sections for charge changing are a function of the ion velocity so that as all the ions have the same energy the process of charge changing fractionates the isotopes in a nonlinear way. As a result, comparison with a standard is essential for the measurement of isotope ratios. The procedure for correcting the isotope ratios for the various fractionations encountered has been discussed by Beukens 1983 and Litherland *et al.* 1986.

(*b*) *The cyclotron*

The ions in a cyclotron travel a long distance in a vacuum that is usually far from perfect. However, in this case, the ions, which are scattered or charge changed, are not accelerated further because of the resonant nature of the acceleration and consequently the ion beam does not have the tails that are present after analysis by static or magnetic fields. This is an important advantage of the cyclotron pointed out by Muller (1977). A small 'desk-top' negative-ion cyclotron is being built that accelerates ions to about 40 keV (Welch *et al.* 1984). This cyclotrino, as it is called, is a really high-quality electromagnetic analyser for the rare isotopes. The problems of isotope ratio measurements still have to be solved.

(*c*) *Very-high-energy heavy-ion accelerators*

The ultimate mass spectrometer is a heavy-ion accelerator that produces ions so energetic that all the electrons can be stripped from the atomic nucleus. This requires ion velocities much greater than $(Z/137)\,C$ so that the very heavy ions would be highly relativistic. Such accelerators are being built for nuclear physics research. However, provided $Z_{\text{rare}} > Z_{\text{common}}$, it is possible to separate rare isotopes (Raisbeck *et al.* 1979) with existing machines. If $Z_{\text{common}} > Z_{\text{rare}}$, then there is always the possibility, even at the highest energies, that a fraction of the abundant isobar will retain an electron and therefore have the same M/q as the rare isobar. Attempts to separate the pair ^{205}Tl and ^{205}Pb will be discussed by Dr Henning (this symposium).

6. The post-acceleration analysis system

The post-acceleration analysis system must be able to select the rare isotope from the molecular fragments generated in the central electrode of the tandem and the continuum of ions generated in the residual gas. In addition, even if the vacuum is perfect, there are excited molecular ions and atomic ions, which can decay spontaneously during acceleration, to generate a continuum.

The three types of analyser discussed in §§2 and 4 are all important and widely used. A common arrangement (Wölfli *et al.* 1983) is to start with an electric analyser, which selects all isotopes of the same E/q, followed by a magnetic analyser, which disperses the masses into ion-current measuring Faraday cups or an ionization detector for ion counting (§7). Frequently, a velocity analyser (Andrews *et al.* 1984), or an additional magnetic analyser (Kieser *et al.* 1986), also shown in figure 1, is added for further background reduction.

Each type of analyser can be designed to select ions with the desired M/q and E/q values. However, a new problem arises with AMS because of the higher energy, and that is the charge-changing phenomenon. This re-introduces the neighbouring masses, charges or energies that the analyser was designed to reject. A velocity analyser disperses ions according to their velocity so that ions of all masses and charges with the same velocity are not dispersed. However, as focusing must be used there is a dependency on mass, energy and charge so that charge changing does cause the re-introduction of nearby energies or masses in a velocity analyser also.

Although there seems to have been no systematic study of the quality of analysers for AMS, it is possible to make some general observations based on experience.

(*a*) It is obvious that lowering the gas pressure in the analysers will reduce the intensities of the background ion beams (typically by 10^{+5} of the main beam) due to charge changing or scattering in the gas.

(*b*) In general, for the sake of compactness and hence cost, it is best to combine focusing with dispersion, as simple focusing provides much less background reduction than a focusing analyser with dispersion.

(*c*) Increasing the dispersion of any of the analysers will also reduce the probability of charge-changing collisions in sensitive regions of the analyser. This is because the unwanted ions, which collide with the vacuum enclosure in the larger dispersion analysers, are much less likely to cause interference later because of energy degradation.

(*d*) Cascading the three types of analysers so that adjacent analysers are different is clearly the best strategy for removing the original background or removing any background ions generated by charge changings, vacuum-enclosure interactions or analyser-slit interactions. The number of cascaded analysers will depend upon the problem being solved. For example, if all isotopes are handled simultaneously by the first part of the post-acceleration system, more or higher-dispersion analysers will be needed.

(*e*) In general, as in the case of the injection into the accelerator, two analysers will be better than one because the reduction of the intensity of the background by the first magnet implies that the background generated by the second magnet will often be lowered. However, after the acclerator, the multiplicity of charge states results in backgrounds with same $(M/q) \times (E/q)$ as the rare isotope. Consequently the two magnets should ideally be separated by an electric analyser or velocity analyser.

A problem encountered in AMS is that, because several values of q are present, there can be ambiguities generated by the fact that only M/q and E/q govern the selection of ions by the various analysers. For example, $^{39}K^{+}$ and $^{78}Se^{+2}$ can be simultaneously transmitted and can only be distinguished by their different energies. This can prove to be inconvenient if, for example, $^{78}Se^{+2}$ must be studied in the presence of intense beams of $^{117}Sn^{+3}$ and $^{39}K^{+}$ because an energy-measuring counter cannot handle such a situation. In this sort of work it is usually necessary to avoid analysing isotopes with charges that are divisible into their mass numbers. A good example is $^{36}Cl^{+q}$, which requires at least $q = 5$ before ambiguities are eliminated.

If it is necessary to use ions that have an integral mass-to-charge ratio, then a second charge change to an appropriate charge state can remove the background almost completely (Kilius *et al.* 1984). The use of controlled charge changes between analysers is a powerful technique for reducing backgrounds of unwanted ions and has been used in connection with quark searches (Chang 1984).

Electric analysers scale differently with tandem accelerator voltage than magnetic analysers because for maximum yield, in the negative to positive-ion charge-changing process, the charge q is proportional to the square root of the tandem voltage (Betz 1972). This implies that, for a given radius of curvature of the ions, the magnetic field scales as the fourth root of the tandem voltage, whereas the electric field scales as the tandem voltage. It is therefore worthwhile to minimize the size of the tandem accelerator as high-dispersion electric or velocity analysers are indispensable. In addition, the scale of the apparatus can be reduced significantly by using strong focusing electric or magnetic fields in all cases. The magnets M2 and M3 shown in figure 1 are compact because they consist of strong focusing triplets with $n = 11$ (the field index of $n = \frac{1}{2}$ is more usual (Banford 1966)).

Fortunately, computer programs to assist in the design of analysers with such fields are now available (Matsuo *et al.* 1976). More recently, the interconnection of many of the aberration coefficients has been clarified (Wollnik & Berz 1985) and powerful new techniques are being developed for ion optical calculations (Dragt 1982).

7. ION DETECTORS

The ions, usually with energies in excess of 1 MeV, are detected by gas or solid-state ionization counters of contemporary nuclear physics (Bromley 1979). These sophisticated devices, besides counting the ions of interest, are often used to supplement the inadequate electric and magnetic analysers of many accelerator mass spectrometers and are also used for the essential task of separating isobars when negative-ion separation fails. In contrast to conventional mass spectrometry, there is no dark current or background counting rate, because of the elevated ion energy.

Portions of the pulse-height spectra from an ionization detector are shown in figure 5*a*, *b*. They show the spectra from two carbon samples used in dating. Figure 5*a* shows the spectrum from an oxalic acid contemporary standard (Beukens 1983), and in figure 5*b* the spectrum from an old carbonate sample is shown. The large range of ^{14}C isotope ratios is immediately apparent as are the ^{13}C and ^{12}C peaks, which are molecular fragments that have undergone two charge changes. The first change took place during acceleration and the second took place during transit of the electric analyser. A peak-fitting computer program was used to obtain the solid lines. The low background under the ^{14}C peak from the tails of the ^{13}C and ^{12}C peaks could be eliminated with another electric analyser.

Time-of-flight detectors have also been useful in the separation of rare isotopes such as ^{129}I and background (Litherland 1980) although, unlike velocity analysers, which select only a

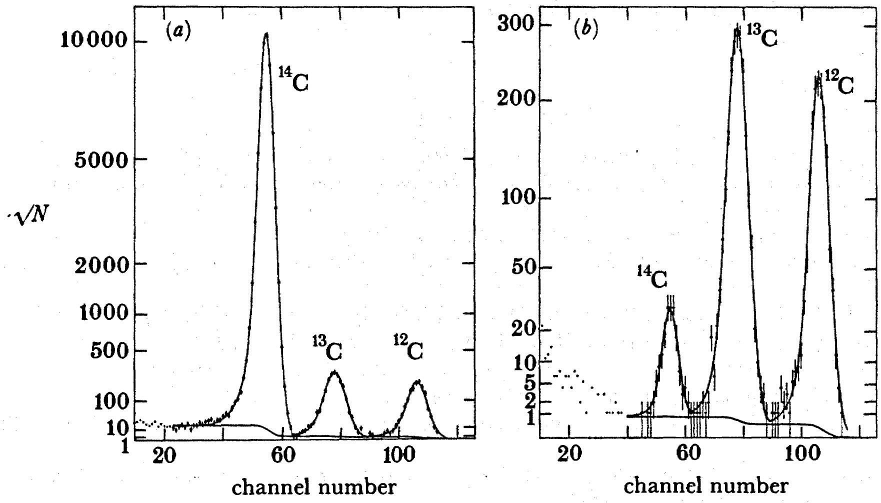

FIGURE 5. (*a*) The pulse-height spectrum from the ionization detector taken during a radiocarbon dating sequence (Beukens 1986). The sample was a contemporary one. (*b*) The pulse-height spectrum taken with an old carbonate sample (47400 years BP). The solid lines for both (*a*) and (*b*) are fitted to the line shapes with the parameters obtained from fit (*a*).

narrow band of velocities, they analyse all ions together. This can create problems if the ions being analysed have a large range of intensities. In this respect a velocity analyser is to be preferred for rare isotope measurements, whereas a time-of-flight analyser is to be preferred if a range of masses of similar intensities are to be analysed, such as from an ion microprobe. The analyser can be isochronous for small energy spreads (Kilius *et al.* 1981, 1987) so that a foil start detector can be used.

A promising new ion counter, the low-temperature bolometer (Anderson 1985), has been described recently. Unlike the silicon crystal counters (Bromley 1979), which (*a*) suffer radiation damage from heavy ions, (*b*) have a thick window and (*c*) have poor resolution, the new detectors promise to be the ideal very-heavy-ion counter provided their cooling to 1 K or lower is not inconvenient.

8. Conclusions

Accelerator mass spectrometry continues to develop steadily with new ideas and applications appearing regularly. We will hear about many of these at this symposium. The combination of lasers and mass spectrometers is particularly promising as a more general solution to the isobar discrimination problem, and it is hoped that the application of very low temperatures to very-heavy-ion detectors will give a resolution in energy comparable to the resolution of the electric and magnetic analysers.

The applications of this new type of mass spectrometry are very wide ranging, as we shall hear, and as the techniques become more widely known among archaeologists and Earth scientists (to name only two areas of endeavour) there will be a growing and fruitful collaboration with the physicists who pioneered the techniques. It is also not too much to hope that the better ion sources and more advanced accelerator systems will provide the nuclear astrophysicist with an instrument for the 1990s.

I thank my colleagues at the Isotrace Laboratory, at University of Toronto and elsewhere, for their encouragement and many valuable discussions. This work was supported in part by the Natural Sciences and Engineering Research Council of Canada.

References

Aardsma, G. E. 1983 Accelerator mass spectrometry of ^{26}Al. Ph.D. thesis, University of Toronto.

Allen, K. W. 1974 Electrostatic analysers. In *Nuclear spectroscopy and reactions, part A* (ed. J. Cerny), pp. 3–34. New York and London: Academic Press.

Alvarez, L. W. & Cornog, R. 1939 ^{3}He in helium. *Phys. Rev.* **56**, 379.

Anderson, H. H. 1985 Energy resolution of a calorimetric charged-particle spectrometer. *Nucl. Instrum. Meth.* B **12**, 437–439.

Andrews, H. R., Ball, G. C., Brown, R. M., Burn, N., Davies, W. G., Imahori, Y., Milton, J. C. D. & Workman, W. 1984 Accelerator mass spectrometry at Chalk River. *Nucl. Instrum. Meth.* **233** (B5), 134–138.

Banford, A. P. 1966 *The transport of charged particle beams*, p. 76. London: E. & F. N. Spon Ltd.

Beukens, R. P. 1983 Radio-isotope dating using tandem accelerators. *PACT* **8**, 177–184.

Beukens, R. P., Gurfinkel, D. M. & Lee, H. W. 1986 Progress at the Isotrace laboratory. *Radiocarbon* **28** (2A), 229–236.

Betz, H.-D. 1972 Charge states and charge-changing cross sections of fast heavy ions penetrating through gaseous and solid media. *Rev. mod. Phys.* **44**, 465–539.

Bock, R. 1974 Heavy ion accelerators. In *Nuclear spectroscopy and reactions, part A* (ed. J. Cerny), pp. 35–77. New York and London: Academic Press.

Bromley, D. A. (ed.) 1974 Large electrostatic accelerators. *Nucl. Instrum. Meth.* **122**, 1–288.

Bromley, D. A. (ed.) 1979 Detectors in nuclear science. *Nucl. Instrum. Meth.* **162**, 1–738.

Chang, K. H. 1984 A charge spectrometer for quark searches. Ph.D. thesis, University of Toronto.

Clegg, J. B. 1986 Memory effects in quadrupole SIMS. In *Secondary ion mass spectrometry SIMS V* (ed. A. Benninghoven, R. J. Colton, D. S. Simons & H. W. Werner), Springer Series in Chemical Physics vol. 44, pp. 112–114. Berlin, Heidelberg, New York and Tokyo: Springer-Verlag.

Dragt, A. J. 1982 Lectures on non-linear orbit dynamics. In *Physics of high energy particle accelerators* (Fermi Lab. Summer School 1981) (Conf. Proc. Am. Inst. Phys. vol. 87) (ed. R. A. Carrigan, F. R. Hudson & M. Month), pp. 147–313. New York: American Institute of Physics.

Galejs, A. & Rose, P. H. 1967 Optics of electrostatic accelerator tubes. In *Ion optics* (ed. A. Septier) vol. 1, pp. 297–327. New York and London: Academic Press.

Galindo-Uribarri, A., Lee, H. W. & Chang, K. H. 1985 Beams of doubly ionized molecules from a tandem accelerator. *J. chem. Phys.* **83**, 3685–3693.

Gemmell, D. S. 1980 Determining the stereochemical structures of molecular ions by 'Coulomb-explosion' techniques with fast (MeV) ion beams. *Chem. Rev.* **80**, 301–311.

Harvey, B. G. 1974 The Cyclotron. In *Nuclear spectroscopy and reactions, part A* (ed. J. Cerny), pp. 79–111. New York and London: Academic Press.

Heinemeier, J. & Hvelplund, P. 1978 Production of 15–90 keV negative heavy ions by charge exchange in Mg vapour. *Nucl. Instrum. Meth.* **148**, 65–75.

Hintenberger, H. 1962 High-sensitivity mass spectroscopy in nuclear studies. *A. Rev. nucl. Sci.* **12**, 435–506.

Hofmann, H., Bonani, G., Morenzoni, E., Nessi, M., Suter, M. & Wölfli, W. 1984 Charge state distributions and resulting isotope fractionation effects of carbon and chlorine in the 1–7 MeV energy range. *Nucl. Instrum. Meth.* **233** (B5), 254–258.

Hotop, H. & Lineberger, W. C. 1985 Binding energies of atomic negative ions II. *J. phys. chem. Ref. Data* **14**, 731–750.

Kieser, W. E., Beukens, R. P., Kilius, L. R., Lee, H. W. & Litherland, A. E. 1986 Isotrace radiocarbon analysis-equipment and procedures. *Nucl. Instrum. Meth.* B **15**, 718–721.

Kilius, L. R. & Litherland, A. E. 1985 High resolution accelerator based mass spectrometry at Isotrace. In *Proceedings of the Workshop on Accelerated Radioactive Beams*, Parksville, B. C., TRIUMF report TRI-85-1 (ed. L. Buchman & J. M. D'Auria), pp. 315–322. Vancouver.

Kilius, L. R., Hallin, E. L., Chang, K. H. & Litherland, A. E. 1981 An all electric mass spectrometer. *Nucl. Instrum. Meth.* **191**, 27–33.

Kilius, L. R., Rucklidge, J. C., Wilson, G. C., Lee, H. W., Chang, K. H., Litherland, A. E., Kieser, W. E., Beukens, R. P. & Gorton, M. P. 1984 Charge ratio mass spectrometry of the heavy elements. *Nucl. Instrum. Meth.* **233** (B5), 185–192.

Kilius, L. R., Rucklidge, J. C. & Litherland, A. E. 1987 Electric and magnetic analysis prior to accelerator mass spectrometry. (In preparation.)

Kutschera, W. 1983 Accelerator mass spectrometry: from nuclear physics to dating. *Radiocarbon* **25**, 677–691.

Labrie, D. & Reid, J. 1981 Radiocarbon dating by infrared laser spectroscopy. *Appl. Phys.* **24**, 381–386.

Lawson, J. D. 1974 New developments in beam transport through tandem accelerators. *Nucl. Instrum. Meth.* **122**, 53–63.

Lee, H. W., Galindo-Uribarri, A., Chang, K. H., Kilius, L. R. & Litherland, A. E. 1984 The $^{12}CH_2^{+2}$ molecule and radiocarbon dating by accelerator mass spectrometry. *Nucl. Instrum. Meth.* **233** (B5), 208–210.

Libby, W. F. 1955 *Radiocarbon dating*, 2nd ed. Chicago: University of Chicago Press.

Litherland, A. E. 1980 Ultrasensitive mass spectrometry with accelerators. *A. Rev. nucl. Part. Sci.* **30**, 437–473.

Litherland, A. E. 1984 Accelerator mass spectrometry. *Nucl. Instrum. Meth.* B **5**, 100–108.

Litherland, A. E., Beukens, R. P., Kieser, W. E., Kilius, L. R. & Lee, H. W. 1986 Carbon-14 dating with small accelerators. *Nucl. Instrum. Meth.* B **13**, 663–666.

Matsuo, T., Matsuda, H., Fujita, Y. & Wollnik, H. 1976 Computer program 'TRIO' for third order calculation of ion trajectory. *Mass Spectrometry* **24**, 19–27. (See also errata in Matsuo, T. *Nucl. Instrum. Meth.* 1975 **126**, 273.)

Middleton, R. 1983 A versatile high intensity negative ion source. *Nucl. Instrum. Meth.* **214**, 139–150.

Middleton, R. 1984 A review of ion sources for accelerator mass spectrometry. *Nucl. Instrum. Meth.* **233** (B5), 193–199.

Muller, R. A. 1977 Radioisotope dating with a cyclotron. *Science, Wash.* **196**, 489–494.

Nessi, M., Morenzoni, E., Suter, M., Bonani, G., Hofmann, H. J., Stoller, C. & Wolfli, W. 1984 Computer controlled accelerator mass spectrometry. *Nucl. Instrum. Meth.* **233** (B5), 238–241.

Norskov, J. K. & Lundqvist, B. I. 1979 Secondary-ion emission probability in sputtering. *Phys. Rev.* B **19**, 5661–5665.

Purser, K. H. 1976 U.S. Patent 4 037 100.

Purser, K. H., Liebert, R. B., Litherland, A. E., Beukens, R. P., Gove, H. E., Bennett, C. L., Clover, M. R. & Sondheim, W. E. 1977 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. *Rev. Phys. appl.* **12**, 1487–1492.

Purser, K. H., Liebert, R. B. & Russo, C. J. 1980 MACS: An accelerator based radioisotope measuring system. *Radiocarbon* **27**, 794–803.

Rachidi, I., Monte, J., Pelletier, J., Pomot, C. & Rinchet, F. 1976 Surface ionization negative ion source. *Appl. Phys. Lett.* **28**, 292–294.
Raisbeck, G. M., Yiou, F. & Stephen, C. 1979 ^{26}Al measurement with a cyclotron. *J. Phys. Lett.* **40**, 241–244.
Rathmell, R. D. 1986 Developments in small electrostatic accelerators. *Rev. scient. Instrum.* **57**, 727–730.
Schnitzer, R., Aberth, W. A., Brown, H. L. & Anbar, M. 1974 *Proc. 22nd Ann. Conf. Mass Spectrosc. and Allied Topics, Philadelphia, Pennsylvania*, pp. 64–69.
Shimizu, N. & Hart, S. R. 1982 Isotope fractionation in secondary ion mass spectrometry. *J. appl. Phys.* **53**, 1303–1311.
Sigmund, P. 1984 Fundamentals of Sputtering. In *Secondary ion mass spectrometry SIMS IV* (ed. A. Benninghoven, J. Okano, R. Shimuzu & H. W. Werner), Springer Series in Chemical Physics vol. 36, pp. 2–7. Berlin, Heidelberg, New York and Tokyo: Springer-Verlag.
Sigmund, P. & Winterbon, K. B. 1974 Small angle multiple scattering of ions in the screened coulomb region. I. Angular distributions. *Nucl. Instrum. Meth.* **119**, 541–557. (See also erratum in 1975 *Nucl. Instrum. Meth.* **125**, 491.)
Suter, M., Balzer, R., Bonani, G. & Wölfli, W. 1984 A fast beam pulsing system for isotope ratio measurements. *Nucl. Instrum. Meth.* **233** (B5), 242–246.
Vasile, M. J. 1984 Velocity dependence of secondary-ion emission. *Phys. Rev.* B **29**, 3785–3794.
Welch, J. J., Bertsche, K. J., Friedman, P. G., Morris, D. E., Muller, R. A. & Tans, P. P. 1984 A 40 keV cyclotron for radioisotope dating. *Nucl. Instrum. Meth.* **233** (B5), 230–232.
Wilson, H. W. 1979 Possibility of measurement of ^{14}C by mass spectrometric techniques. In *Radiocarbon Dating-Proceedings of the Ninth International Conference, Los Angeles and La Jolla 1976* (ed. R. Berger & H. E. Suess), pp. 238–245. Berkeley, Los Angeles and London: University of California Press.
Wittmaack, K. 1983 The effect of work function changes on secondary ion energy spectra. *Physica Scr.* T **6**, 71–75.
Wittmaack, K. 1985 Experimental and theoretical investigations into the origin of cross-contamination effects observed in a quadrupole-based SIMS instrument. *Appl. Phys.* A **38**, 235–252.
Wölfli, W., Bonani, G., Suter, M., Balzer, R., Nessi, M., Stoller, C., Beer, J., Oeschger, H. & Andrée, M. 1983 Radioisotope dating with the ETH-EN tandem accelerator. *Radiocarbon* **25**, 745–753.
Wölfli, W., Polach, H. A. & Anderson, H. H. 1984 Accelerator mass spectrometry. *Nucl. Instrum. Meth.* **233** (B5), 91–488.
Wollnik, H. & Berz, M. 1985 Relations between elements of transfer matrices due to the condition of symplecticity. *Nucl. Instrum. Meth.* A **238**, 127–140.
Wollnik, H. & Becker, K. 1985 Ion optical design for an on-line mass separator with low cross contamination and the capability of good mass resolution. *Nucl. Instrum. Meth.* A **238**, 206–214.
Yu, M. L. 1978 Work-function dependence of negative-ion production during sputtering. *Phys. Rev. Lett.* **40**, 574–577.
Yu, M. L. & Lang, N. D. 1983 Direct evidence of electron tunneling in the ionization of sputtered atoms. *Phys. Rev. Lett.* **50**, 127–130.

Discussion

M. PAUL (*Hebrew University, Jerusalem, Israel*). Would Professor Litherland comment some more on the possible argon-36 negative ions that he mentioned?

A. E. LITHERLAND. I believe that there has been a report on the existence of argon negative ions, which is why I qualified my earlier remark. However, it is worth remembering that there have also been many reports in the past on the observation of nitrogen negative ions, all of which were later disproved.

K. W. ALLEN. There have been some recent developments with carbon dioxide in sputter-ion sources, and of course that does simplify the chemistry of sample preparation. What does Professor Litherland think of the advantages and disadvantages of those sources now?

A. E. LITHERLAND. I expect that one will hear more about those ion sources later in this meeting, but as they are potentially so important it may be appropriate to mention something about them now. A number of groups, including the group at Pennsylvania University, have been pioneering the use of carbon dioxide directly into a sputter-ion source thereby avoiding the preparation of the solid graphitic targets, which are normally used in AMS radiocarbon work. Those tests are very promising. However, the background is reported to be higher than in the solid-sample method.

H. E. Gove. What is the source of the background in ^{14}C AMS measurements? Why is the apparent age limit found to be about 60000 years in most AMS laboratories?

A. E. Litherland. The best way to answer that question is to say that I do not know.