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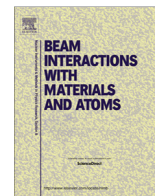
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Radiocarbon positive-ion mass spectrometry

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ABSTRACT

Proof-of-principle of a new mass spectrometric technique for radiocarbon measurement is demonstrated. Interfering nitrogen and hydrocarbon molecules are largely eliminated in a charge-exchange cell operating on non-metallic gas. The positive-to-negative ion conversion is the reverse of that conventionally used in accelerator mass spectrometry (AMS) and is compatible with plasma ion sources that may be significantly more efficient and capable of greater output than are AMS sputter ion sources. The Nanogan electron cyclotron resonance (ECR) ion source employed exhibited no sample memory and the >50 kyrs age range of AMS was reproduced. A bespoke prototype new instrument is now required to optimise the plasma and cell physics and to realise hypothetical performance gains over AMS.

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1. Introduction

The diverse scientific applications of radiocarbon detection might benefit from a revision to the metrology [1]. The established technique of accelerator mass spectrometry (AMS) is powerful, routinely measuring ¹⁴C to one part in 10¹⁵ of sample carbon, but requires considerable expertise and other resources, and is inherently inefficient [2]. Largely these are consequences of the use of sputter negative ion sources. Importantly sample atom negative ionisation overcomes any measurement interference from the ¹⁴N isobar as the nitrogen anion is unstable. However, of the sample carbon atoms only of the order of a per cent are ionised and usefully extracted from such an ion source. This determines the minimum sample size sufficient for desirable ¹⁴C detection statistics and the sputter source ion beam current sets the measurement rate, and therefore the analysis cost. More than an hour of measurement time is required to achieve 3% Poisson statistics with a Contemporary carbon sample introduced into the ion source as CO₂ and producing typically 10 μA C⁻.

Additionally converting sample gas to denser graphite for sputtering results in 100 μA C⁻ representative output and measurements in minutes. However, ion beam emittance change may be severe as the sputtered surface evolves and irrespective of sample form it is usual to alternate repeat measurements of samples with analyses of standards requiring the complexity of ion source sample recovery and storage. This is also to compensate for ion source and spectrometer instability; achieving dependable ion source

performance is challenging because of the difficulties of Cs metal vapour manipulation for consistent sputtering and the changing source environment caused by the deposition of sample atoms not extracted from the ion source. Samples must be especially prepared for the sputter source conditions in any case, but AMS is slow compared with the possible rate of sample production automation and is barely compatible with sample speciation tools such as continuous flow gas chromatography.

AMS further energises ions from a sputter source with an electrostatic particle accelerator. ¹⁴C atoms of sufficient energy can be separated from remaining ¹³CH and ¹²CH₂ molecular isobars by passing the selected mass 14 beam through a solid or gas ‘stripper’ target to invert ion charge and analysing the results: in the originally-practiced method the ion-stripper interaction removes some ion electrons resulting in some sample atoms in a charge state of 3+ or more that cannot be sustained by interfering molecules and so molecular interference to radiocarbon ion detection is reduced by selecting for such a charge state with a following mass spectrometer; a modern method applicable at lower ion energies is to destroy molecules directly in thicker stripper gas by repeated ion-gas molecule collision. Consequently accelerator mass spectrometers are usually deployed in specialised centres with the resources to procure and the expertise to operate these large, expensive and complicated mass spectrometers. The scientists commissioning the analyses and their sample-defining laboratories may be quite remote.

The deficiencies of AMS have long been apparent and mass spectrometric alternatives pursued. Since 1978 it is appreciated that the usual AMS negative-to-positive atom charging arrangement might be reversed and molecular isobars removed before the atomic

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interference. The 3+ positive-to-negative alternative proposed by Roy Middleton promises reduced or even absent necessary particle accelerator (beyond energisation in the ion source) but the scheme first required positive ion source development [3]. In lapsed Canadian patent 2131942 Ronald Schubank specified the use of an inductively coupled plasma ion source as the primary molecular dissociator at the part-per-trillion level followed by a foil or gas electron-‘adder’ that also was a secondary molecular dissociator, and in a paper he proposed transmitting C^{3+} from an electron cyclotron resonance (ECR) ion source into a metal foil/vapour charge-exchange cell [4]. This was subsequently realised in practice by Michael Hotchkis and Tao Wei who managed measurement of radiocarbon-enriched materials [5]. Fred Meyer et al. achieved similar results by grazing ion-scatter charge-exchange [6]. In contrast AMS measurement background is a million-fold lower. The SUERC group has previously also only achieved measurement background insufficient for natural carbon analysis, by using a thin SiN membrane instead metal negative ionisation [7,8]. (The use of a microwave ion source in [9] whereby positive ions are immediately charge-exchanged negative and then subsequently stripped positive again is actually an example of the conventional AMS scheme, but indicates the elaboration pursued to compensate for the problems of sputter ion sources.)

2. Experiment

In a novel approach we simultaneously suppress the two kinds of interference by combining atom negative ionisation and molecule dissociation in the same non-metallic thick gas separate from the ion source. This is shown schematically in Fig. 1 and is called positive-ion mass spectrometry (PIMS) to distinguish it from AMS, as only positive ions are energised and the use of a separate particle accelerator is optional.

We have performed proof-of-principle radiocarbon PIMS on our adapted uniquely-bipolar single-stage accelerator mass spectrometer (SSAMS) [10,11]. The SSAMS was first rebuilt to accommodate a new source of positive ions in addition to the conventional sputter negative ion source [12]. Plasma positive ion sources nearly perfectly efficient and capable of milliamp carbon beams of a particular charge state are available, but we mounted a Pantechnik S.A. Nanogan 10 GHz ECR ion source capable of significant carbon beams in many charge states for experimentation with. CO_2 samples and optional He carrier were introduced by the gas-sample handling system from our gas-ready sputter ion source capable

of rapid sample switching [13]. No attempt was made to match the ions source and SSAMS ion optics beyond reshaping the spectrometer injector ion source extract electrode whilst retaining the beam collimators within. This limited the extracted beam to ~ 1 mA He^+ and ~ 30 μA C^+ , etc., so as to not overload the SSAMS. The spectrometer stripper canal served as the PIMS charge-exchange cell and the mass flow controller regulating the gas flow was calibrated for the gases used. The existing pre- and post-cell Faraday cups and PIPS particle detector were employed and fast-switching isotope ratio measurement was possible. $^{14}C^-$ identification was secure; the histogram of the detector signal showed only a single peak that scaled with ion energy and matched the AMS radiocarbon signal at the same ion energy, and the measured $^{14}C/^{13}C$ ratios were similar to those generated by AMS of the same sample materials with the same instrument. Measured sample carbon isotope ratios were subsequently normalised to those of standards in the usual manner.

In the case of an efficient positive ion source PIMS minimum sample size will be determined by the charge-exchange cell efficiency, which depends on ion energy and gas medium employed. The negative ion yield is difficult to study directly because of scattering losses, but the C^-/C^+ ratio of the beams exiting the cell is independent of such scattering. Therefore the measured ratio is a convenient proxy for negative ionisation that, furthermore, is previously studied enabling comparisons. Fig. 2 shows that some negative ions can be formed in N_2 gas such as is employed when the cell functions conventionally as a stripper, but that more-electronegative isobutane is more efficient and even capable of producing as many negative ions as positive ones. The data was generated by adjusting the cell gas flow and following spectrometer for maximum C^- before switching the analysis magnet and Faraday cup log-amp polarities for C^+ determination, except for the 20 and 140 keV isobutane results when the C^-/C^+ ratio was also derived at multiple flow rates. This is plotted in Fig. 3. It shows that negative ionisation is constant once there is gas flow sufficient for charge-state equilibrium, presumably. Correlating detector dark-count corrected measurements of our organic-blank CO_2 (but without additional ion source optimisation for low background as is considered below) were individually normalised to measurements of a Contemporary standard at the different isobutane flow rates, except for the points above 0.1 Modern where the blank isotope ratio measurements were normalised to the average of the measurements of the standard employed in the derivation of the data <0.01 Modern because of significant molecular interference even to the standard measurement. Background was smallest with a

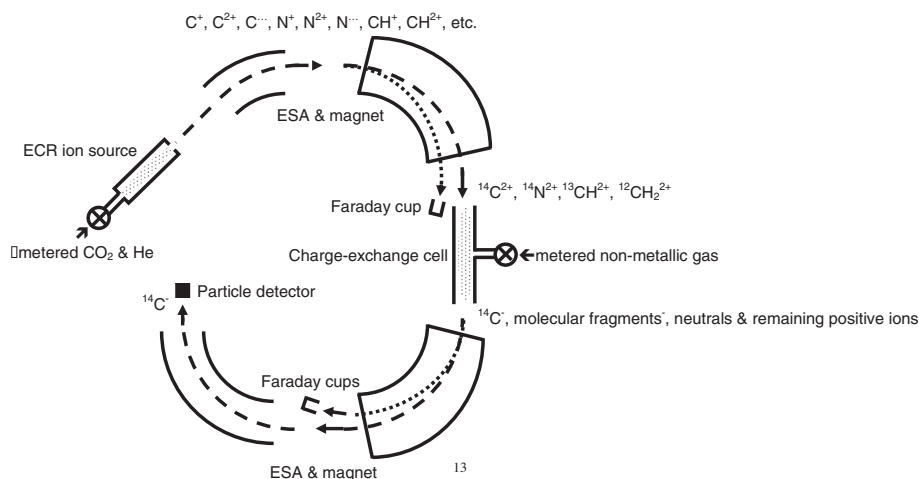


Fig. 1. A schematic of radiocarbon measurement by the new method. The proof-of-principle demonstration improvised a charge-exchange cell on the SUERC SSAMS high-voltage deck but in future implementations only the ion source need be biased.

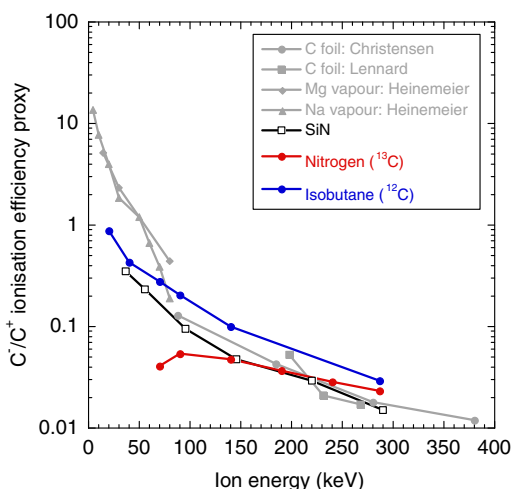


Fig. 2. The ratio of C^- to C^+ ions exiting the charge-exchange cell with non-metallic gases using incident C^{2+} ions of the stable isotope noted. The black data from [8] and the grey from the references cited therein are for comparison.

gas flow sufficient to substantially destroy molecules without significantly scattering ions into the detector.

At lowest ion energy metal vapour charge-exchange is most efficient but metallic and non-metallic charge-exchange media can be similarly efficient at the 10s keV ion energy necessary to traverse a gas sufficiently thick to significantly destroy molecules and be analysed with a mass spectrometer. Moreover non-metallic gas flow is readily controlled and will not compromise electrical insulators. The metal vapour absolute negative ion yields corresponding to the plotted proxy values are known permitting a calibration of our results, assuming that the negative ionisation process is consistent [8]. Accordingly we derive a measured isobutane maximum negative ionisation yield of 10%. Corresponding measured ion transmission through the charge-exchange cell and preceding accelerator tube was significantly lower, however, as is to be expected when operating an accelerator far below its intended accelerating field gradient.

Sufficient interference rejection is crucial and molecule dissociation in the charge-exchange cell was augmented by positive-ion

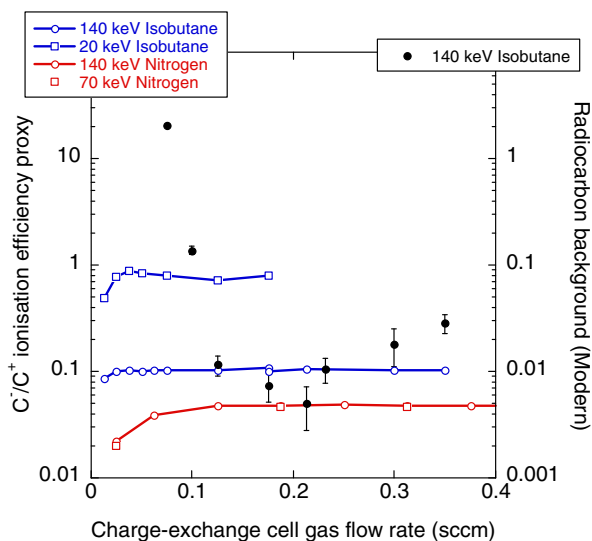


Fig. 3. $^{12}C^-/^{12}C^+$ negative ionisation proxy dependence on charge-exchange cell gas flow rate with isobutane and nitrogen gas using incident C^{2+} of the ion energies noted, and correlating radiocarbon measurement background with isobutane only. The background signal is due to incomplete molecule destruction and ion scattering.

charge state selection and ion source operation; an ion source producing an atomic particle beam from molecular samples destroys molecules to some extent. Fig. 4 shows that hydrocarbons are increasingly discriminated against as the ion source gas intake is increased, whether this is by ion source conditioning or plasma change, so that the natural carbon isotope ratio can be observed in extracted beams. By adjusting the ion source we duly achieved 2‰ Modern with 280 keV C^{2+} from our usual organic carbon background CO_2 with He admixture, when matching our SSAMS normal AMS operating conditions and correcting for PIPS detector dark count, and a slightly elevated result at half this 140 keV ion energy. In like-for-like conditions nitrogen and isobutane similarly removed molecules but the background was raised by three orders at equivalent ion energy when selecting the 1+ charge-state. No ion source retention of ^{14}C was observed when switching between Contemporary materials and background samples but continuous-flow sample variation was not attempted. The selection of less-copious 3+ or more ions proved unnecessary.

3. Discussion

We have reproduced the >50 kyrs age range of AMS with a new mass spectrometric technique that combines rather than fundamentally separating suppression of the different measurement interferences. PIMS may prove superior. The constant-emittance ECR ion source is inherently more compatible with established sample speciation and preparation techniques as gas samples need not be recovered and stored for repeat measurement. For instance, automated sample combustion may therefore become integrated. Certainly sample graphitisation is avoided. Hypothetically the new technique may be combined orders-of-magnitude more efficient and faster than AMS with high-precision analyses in seconds, or even in real time as samples are produced. However, investigation of this requires a bespoke new instrument capable of accommodating very large ion beams and of particularly high emittance post the charge-exchange cell. Subsequently the optimum ion source may be specified once it is established whether the prohibition on successful 1+ measurement is fundamental or simply a consequence of SSAMS engineering [12].

Cell processes and ion source physics need optimisation. Molecules will be destroyed and created in the plasma and it

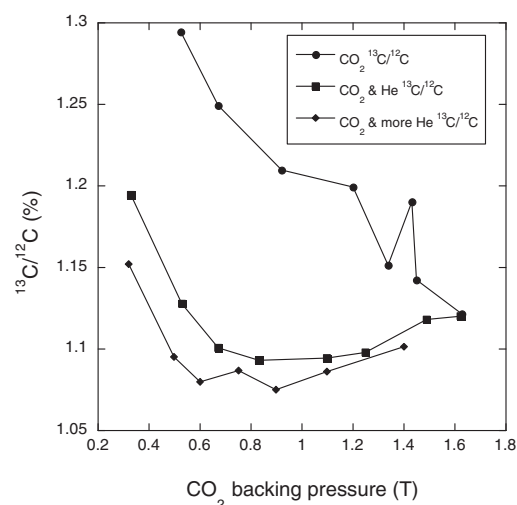


Fig. 4. The carbon 1+ stable isotope ratio measured before the charge-exchange cell. The ratio declines towards the natural (fractionated) ratio with increasing plasma source CO_2 sample gas or He carrier as hydrocarbon molecular ions are suppressed.

may be possible to beneficially scavenge released hydrogen atoms with a different admixture, although we conjecture that the helium we employed was responsible for the excellent ion source memory. Charge-exchange cell negative ionisation, ion transmission without excessive scattering and molecule destruction may not be maximised simultaneously and any compromise needs study. However, no additional particle acceleration is envisaged. Ultimately the cost and relative simplicity of plasma ion source operation and of a spectrometer without particle accelerator may promote technique adoption and analysis accessibility.

Moreover, radionuclide positive-ion mass spectrometry may not be confined to radiocarbon measurement. Separately we have demonstrated with a sputter ion source that environmental-level ^{26}Al measurement is also possible at very low ion energy [14] and we are modifying the Nanogan ion source to accept such solid samples too. Currently terrestrial sample Be-AMS is typically preferred to Al-AMS because of the greater possible negative ion beams, but much larger aluminium positive ion beams may be produced with a plasma ion source and Al-PIMS be competitive with Be-AMS.

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