Supplementary information for: Positive Ion Mass Spectrometry Enables Simplified Radiocarbon Analysis

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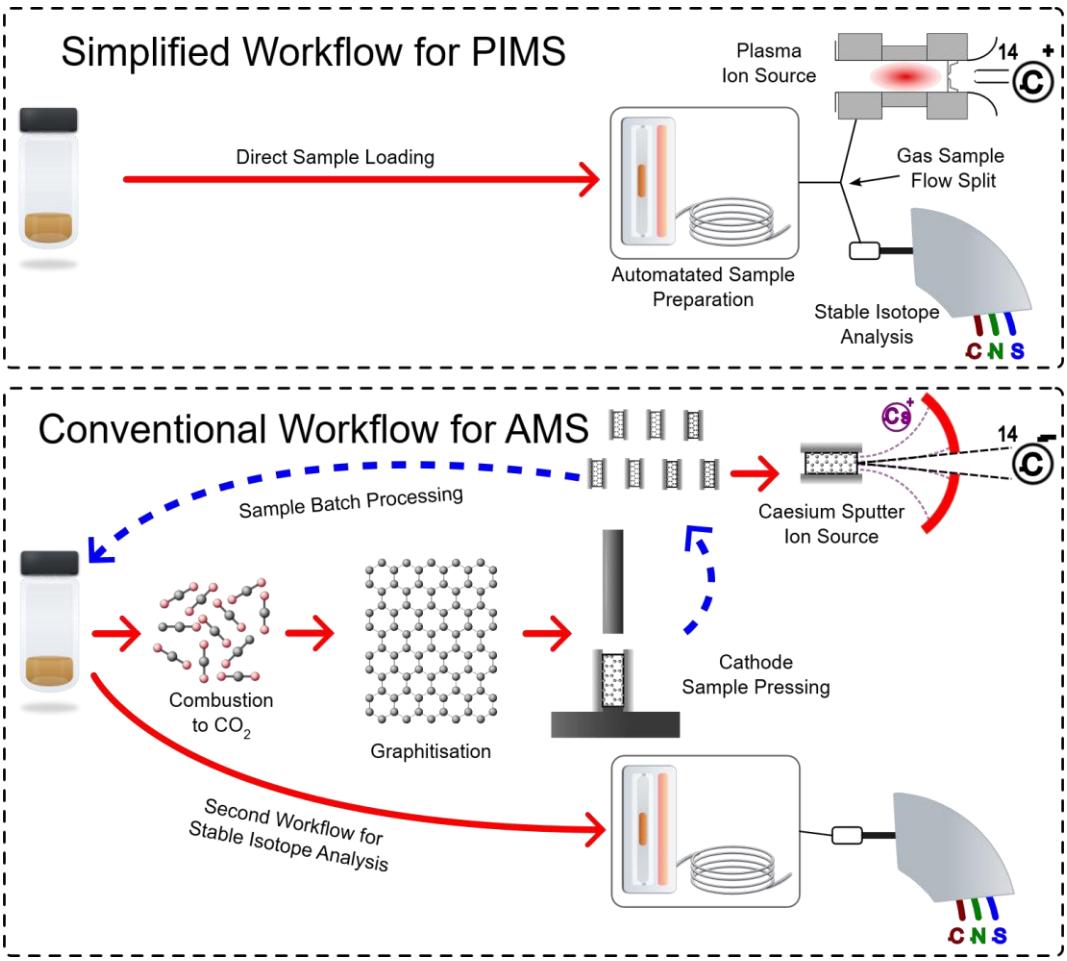
Supplementary Note 1 — Comparison of AMS and PIMS workflows

Supplementary Figure 1 illustrates the key procedural differences between AMS and PIMS sample processing and analysis. The figure highlights how PIMS removes graphite preparation, manual cathode loading, and batch operation, enabling direct integration with automated gas-handling systems.



Supplementary Figure 1. Comparison of AMS and PIMS workflows for radiocarbon analysis.

The workflow for PIMS (top) is similar to commercially available stable isotope analysis, where a sample is loaded directly into an automatic preparation system, such as an elemental analyser, which combusts, separates, and purifies the elements of interest in gaseous form. The gas flow is then split, with one portion sent for stable isotope analysis (e.g., $\delta^{13}C$, $\delta^{15}N$, etc.) and the other directed to the plasma source of the PIMS for radiocarbon analysis.

The typical workflow for conventional AMS (bottom) involves combusting the sample, purifying and trapping the CO_2, then manually transferring it to the graphitisation apparatus, where it is reduced on a catalyst to solid graphite. The graphite is pressed by hand into a sample cathode prior to loading. Samples are commonly loaded in batches, represented by the blue dashed line (up to 200) to minimise delays caused by re-establishing the vacuum in the caesium sputter source of the AMS. Stable isotope analysis requires a second aliquot of the sample to be processed in a separate workflow.

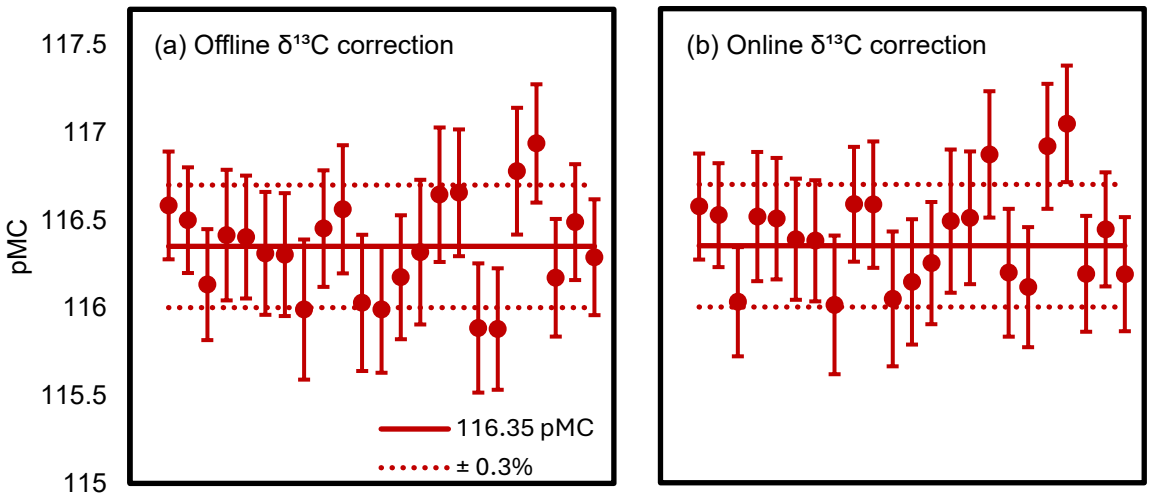
Both processes start with a sample that either requires no pre-treatment or has already undergone pre-treatment, as this step is common to both systems

Supplementary Note 2 — $\delta^{13}C$ Corrections and Comparison of Offline and PIMS-Based Methods

This note evaluates the use of PIMS-derived $\delta^{13}C$ values for radiocarbon correction and compares them directly with the $\delta^{13}C$ values obtained during sample processing, which are used for all results presented in the main text.

Individual samples of TIRI A barley mash were normalised to measurements of NIST SRM 4990C Oxalic Acid II (OXII), following the same $\delta^{13}C$-correction procedure, with off-line generated $\delta^{13}C$ values, used in our AMS workflow. To assess whether $\delta^{13}C$ values generated by the PIMS instrument can also be used for correction, the same datasets were reprocessed using the online $\delta^{13}C$ output from the PIMS system. Supplementary Figure 2 shows the two sets of results side-by-side. The distributions are nearly identical, with no trend or bias introduced using online $\delta^{13}C$ values.

For TIRI A, the offline $\delta^{13}C$ correction yields an average of 116.34 ± 0.06 pMC (SEM), while the PIMS-derived $\delta^{13}C$ correction yields 116.41 ± 0.06 pMC. The two approaches agree within their respective uncertainties, demonstrating that the $\delta^{13}C$ values generated by the PIMS instrument are fully suitable for use in radiocarbon correction.



Supplementary Figure 2. Comparison of offline and PIMS-derived $\delta^{13}C$ corrections for radiocarbon measurements of TIRI A.

Radiocarbon results for 23 ampoules of TIRI A barley normalised to NIST SRM 4990C Oxalic Acid II (OXII) using either (a) $\delta^{13}C$ values measured during sample processing or (b) $\delta^{13}C$ values generated by the PIMS instrument. Consensus values (TIRI A: 116.35 pMC) are indicated by solid lines, with the corresponding 0.3% range shown by dashed lines. The two correction approaches produce statistically indistinguishable results, demonstrating that PIMS-derived $\delta^{13}C$ values are suitable for use in routine radiocarbon correction.

Supplementary Note 3 — Detailed Performance Comparison Between PIMS and AMS

This section provides the quantitative performance comparisons between positive-ion mass spectrometry (PIMS) and accelerator mass spectrometry (AMS) that are summarised in Supplementary Table 1. These values support the system-level distinctions discussed in the main text and illustrate where PIMS matches or exceeds established AMS capabilities.

The ECRIS used in this study produces carbon beam currents up to 700 μA of $^{12}C^{+}$ with an ionisation efficiency of 28%. When coupled with an isobutane charge-exchange target, this is converted to 18–19 μA of $^{12}C^{-}$, corresponding to a total system efficiency of approximately 0.8% of the sample carbon delivered to the detector. For context, gas-accepting AMS systems typically achieve 0.5–3% total efficiency, conventional gas AMS produces 4–10 μA of $^{12}C^{+}$, and graphite-target AMS routinely achieves 20–35 μA of high-energy $^{12}C^{+1}$, [2, 3, 4].

The gas collision cell in the PIMS architecture suppresses molecular and atomic isobars to achieve backgrounds of approximately 0.1 pMC, equivalent to about 50,000 years. This is lower than the ~1 pMC (~40,000 years) background commonly reported for gas-accepting AMS[2, 4] and approaches the chemical-preparation limit of graphite AMS, where backgrounds are typically ~0.1 pMC. Analysis precision of ~0.3% was demonstrated, matching routine graphite AMS performance (0.3–0.4%)[3, 5] and exceeding the precision normally achieved by gas AMS (0.8–1%)[3, 4].

A summary of qualitative and operational differences between PIMS and AMS systems, including instrument architecture, sample-preparation requirements, maintenance considerations, and workflow compatibility, is provided in Supplementary Table 1.

		Graphite AMS	Gas AMS	PIMS
Performance	<0.3% Precision	✓	X	✓
	0.1 pMC Background	✓	X	✓
	> 40 Samples/day (at 0.3%)	✓	X	✓
Sample Preparation	Automation	X	✓	✓
	Sample Range (Tracer to Background)	✓	X	✓
	Cathode Free	X	X	✓
Instrumentation	Cs Free	X	X	✓
	Source Cleaning Free	X	X	✓
	Fast Source Turn-on (< 5min)	X	X	✓
	Continuous Operation	X	X	✓
	Automatic Sample Transfer	X	✓	✓
	Low Memory	✓	✓	✓
	Particle Accelerator Free	X	X	✓

Supplementary Table 1. Comparison of key features of PIMS and conventional AMS systems.

Performance metrics include precision, background, and throughput, while sample preparation and instrumentation requirements highlight differences in automation, consumables, and operational complexity. PIMS eliminates graphite preparation and caesium sources, operates without particle accelerators, and minimises memory effects, offering a simplified and scalable alternative to AMS.

Supplementary References

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