

## ON THE PROSPECTS OF AMS $^{14}\text{C}$ WITH REAL-TIME SAMPLE PREPARATION AND SEPARATION

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**ABSTRACT.** The performance of the  $\text{CO}_2$ -accepting SO-110 ion source at Oxford Radiocarbon Accelerator Unit has been investigated in detail. The purpose was to clarify the possibilities of accelerator mass spectrometry (AMS) radiocarbon measurements with real-time separation, e.g. GC AMS or HPLC AMS. The construction of a gas test injector based on the continuous-flow technique made it possible to characterize the response of the ion source to continuous and pulsed input of  $\text{CO}_2$  gas. The source exhibited remarkably good linearity over a wide range of  $\text{CO}_2$ -pulse sizes and fast rise time, but the peak shape varied and memory effects were significant. Appropriate tuning of the gas source proved to be critical.

### INTRODUCTION

In radiocarbon accelerator mass spectrometry (AMS), the ion-source characteristics have a large influence on the overall performance of the entire system. For that reason, a significant effort has been devoted to ion-source developments by the AMS community, as demonstrated by a large number of contributions at the AMS-10 conference recently held at Berkeley (see e.g. Fallon et al. 2007; Roberts et al. 2007; Southon and Santos 2007; Xu et al. 2007). Gas ion sources produce  $\text{C}^-$  ions directly from  $\text{CO}_2$ . Therefore, the samples do not need to be graphitized, and this may result in advantages compared to graphite sources. The sample contamination might be reduced, in particular for extremely small samples. Furthermore,  $^{14}\text{C}$  AMS with real-time sample preparation is in principle feasible. Possible examples include on-line oxidation (using an elemental analyzer or a total carbon [TC] analyzer) and on-line separation (e.g. gas chromatography [GC AMS] or high-performance liquid chromatography [HPLC AMS]). The main drawback of such sources is that output current is low; for example, Shibata et al. (1997) observed about a factor of 10 less  $\text{C}^-$  output with direct  $\text{CO}_2$  injection compared to using graphite cathodes for a dual-mode (graphite/gas) source. On the other hand, in the case of small samples the output of graphite sources is reduced (compared to the output of normal-sized samples) and of the same order of magnitude as that of gas ion sources. In conclusion, gas sources are particularly suited to small samples, and their use may result in an increased sensitivity for extremely small samples ( $\sim 1 \mu\text{g C}$ ). They can also be convenient for measuring a large number of samples utilizing automatic preparation systems.

The HVEE 3MV AMS system (Bronk Ramsey et al. 2004a) at Oxford Radiocarbon Accelerator Unit (commissioned in September 2002) includes 2 recombinators, one for graphite targets using an 846 ion source, the other for gas (or graphite) targets on a SO-110 ion source (Bronk Ramsey et al. 2004b). In this way, the advantages of both types of ion sources can be exploited. The recombinators allow for continuous and simultaneous detection of the 3 carbon isotopes  $^{12}\text{C}$ ,  $^{13}\text{C}$ , and  $^{14}\text{C}$ . This is important when working with  $\text{CO}_2$ -based  $^{14}\text{C}$  measurements, because the response time of the source is short (pulses rise almost vertically).

The purpose of the present project is to characterize and further develop the performance of the SO-110 gas source. Particular emphasis is devoted to study the source's response to short gas pulses in order to clarify the feasibility of  $^{14}\text{C}$  AMS with real-time separation.

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## PRODUCING C<sup>-</sup> IONS FROM CO<sub>2</sub>

The construction of gas ion sources based on Cs sputtering was first reported more than 2 decades ago (Heinemeier and Andersen 1983; Middleton 1984; Bronk and Hedges 1987), and such sources have been installed for routine AMS <sup>14</sup>C dating at Oxford University (Bronk and Hedges 1990; Bronk Ramsey and Humm 2000; Bronk Ramsey et al. 2004b) and other places (see e.g. Shibata et al. 1997; Tanaka et al. 2000; Uhl et al. 2004; Xu et al. 2007). The SO-110 source used in the present project is jointly developed by HVEE (High Voltage Engineering Europe) and Oxford on the basis of the sources previously developed at Oxford University (see Bronk Ramsey and Humm 2000 and references therein). The first tests of the source were reported by Bronk Ramsey et al. (2004b). In brief, the principle of operation is as follows: The CO<sub>2</sub> is led into the source by a stream of helium using a capillary tube (ID = 0.06 mm) and is directed onto a titanium pellet in the center of the cathode. CO<sub>2</sub> may then be converted to C<sup>-</sup> (and O<sup>-</sup>) on the titanium surface and extracted into the accelerator. Typically, we used a sputter (cathode) voltage of 8.5 keV, and the ions are accelerated to a total energy of ~35 keV in the injector (recombinator).

It should be mentioned that alternative approaches based on plasma ion sources producing positive carbon ions from CO<sub>2</sub> are being considered. Since *normal* <sup>14</sup>C AMS relies on negative ions being injected into a tandem accelerator, the positive ions need to be converted to negative ions by a charge exchange in a metal vapor (Schneider et al. 2000, 2004; Roberts et al. 2007). In addition, approaches for isobar suppression based on ion charge exchange mass spectrometry (ICE-MS) have been proposed (Schubank 2000) or are under development (Hotchkis and Wei 2007).

## A GAS INJECTOR FOR ION-SOURCE TESTING

One of the main potential advantages of a gas ion source is that it makes real-time AMS <sup>14</sup>C analysis possible, e.g. gas chromatography (GC AMS) or high-performance liquid chromatography (HPLC AMS), and so it was decided to conduct a feasibility study in order to investigate the properties of the SO-110 source with respect to a pulsed input. For this purpose, the test gas injector shown in Figure 1 was constructed. It works by utilizing the continuous-flow technique as explained in the figure caption. A 4-port valve switches between injecting either pure He, pure CO<sub>2</sub>, or a He/CO<sub>2</sub> mixture to the ion source. It is useful for testing the source response to a constant flow or long pulses (of several seconds) of CO<sub>2</sub>. Each of the two 6-port valves is connected to a sample loop that may either contain pure CO<sub>2</sub> or a He/CO<sub>2</sub> mixture (depending on whether the valve to the left of the 4-port valve is opened or closed). By turning the valves, they switch from the loop-filling mode to the injection mode, and a short ( $\geq 0.01$  sec) pulse of CO<sub>2</sub> is sent into the source. Helium and CO<sub>2</sub> are fed into the injector from pressure bottles through 1-m-long capillary tubes of PEEK; the flow rates can be adjusted using the pressure regulators on the bottles. The inlet into the source takes place through an open split and a 0.7-m-long capillary tube (ID = 0.06 mm). Flow measurements were conducted using a flow meter of the bubble type on the “waste” part of the open split. That is, it was not possible to measure the gas flow to the source directly. Instead, the source flow has been determined by closing the helium and CO<sub>2</sub> inlets and measuring the (negative) flow with the flow meter (see Figure 1). The result was  $7.2 \pm 0.2 \mu\text{L min}^{-1}$ . The actual flow during normal operation will be slightly higher due to the pressure increase within the gas injector; however, the effect is not expected to be significant in this particular case.

## RESULTS AND DISCUSSION

A large number of test measurements have been conducted using the test gas injector described above in order to characterize the response of the source to short and long CO<sub>2</sub> pulses. Figure 2 dis-

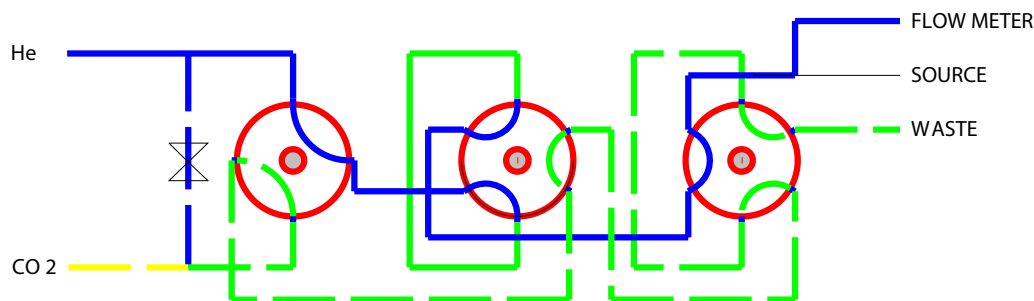


Figure 1 The gas injector built to test the SO-110 sputter ion source. The left 4-port valve allows to switch between injecting either pure He (the position displayed) or a He/CO<sub>2</sub> mixture to the ion source. Each of the two 6-port valves is connected to a sample loop, which may either contain pure CO<sub>2</sub> or a He/CO<sub>2</sub> mixture. The right valve is shown in the loop-filling mode; when it is turned like the valve in the center, a short ( $\geq 0.01$  s) pulse of CO<sub>2</sub> (or a He/CO<sub>2</sub> mixture) is injected into the source. The ion source is connected via an open split. Color code: Blue = He; Yellow = CO<sub>2</sub>; Green = He/CO<sub>2</sub> mixture.

plays the source's response to a continuous flow of  $5.6 \mu\text{L min}^{-1}$  CO<sub>2</sub> ( $1 \mu\text{L CO}_2$  corresponds to  $\sim 0.49 \mu\text{g C}$ ). The rise and decay of the source output both exhibit some kind of exponential behavior with a decay-time constant of about 1–2 s (see below). This fairly rapid response is important because it allows chromatographic resolution to be retained in  $^{14}\text{C}$  measurements. The maximum output observed in the figure corresponds to an ionization efficiency of 2%, which is a typical result with this ion source. A significant background current is visible. It is present because the cathode has been exposed to injected CO<sub>2</sub> previously and is thought to be due to carbon being embedded into the titanium pellet of the cathode. For comparison, stray CO<sub>2</sub> from the rest gas only has a small effect on the ion current. When a cathode is (re-)inserted, a weak current pulse of short duration ( $< 1$  min) is observed. Thus, the magnitude of the background current critically depends on the history of the titanium pellet. As a general rule, the background current increases every time the titanium is exposed to CO<sub>2</sub> and decreases during sputtering. The former effect may be observed in Figure 3 where the background current increases slightly for every pulse of CO<sub>2</sub> injected.

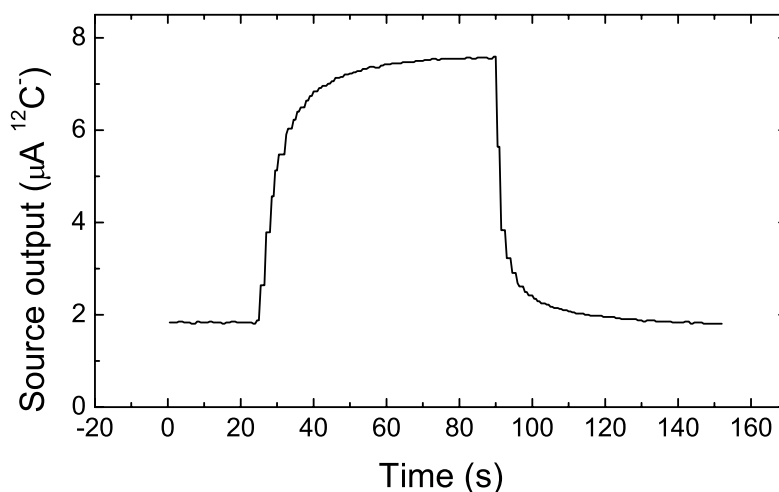


Figure 2 Changes in the source output when a continuous flow of  $5.6 \mu\text{L min}^{-1}$  CO<sub>2</sub> is turned on and off. The maximum source output corresponds to an ionization efficiency of 2%. The background current ( $\sim 2 \mu\text{A }^{12}\text{C}^-$ ) is due to memory effect and is present because the titanium cathode has been exposed to CO<sub>2</sub> previously.

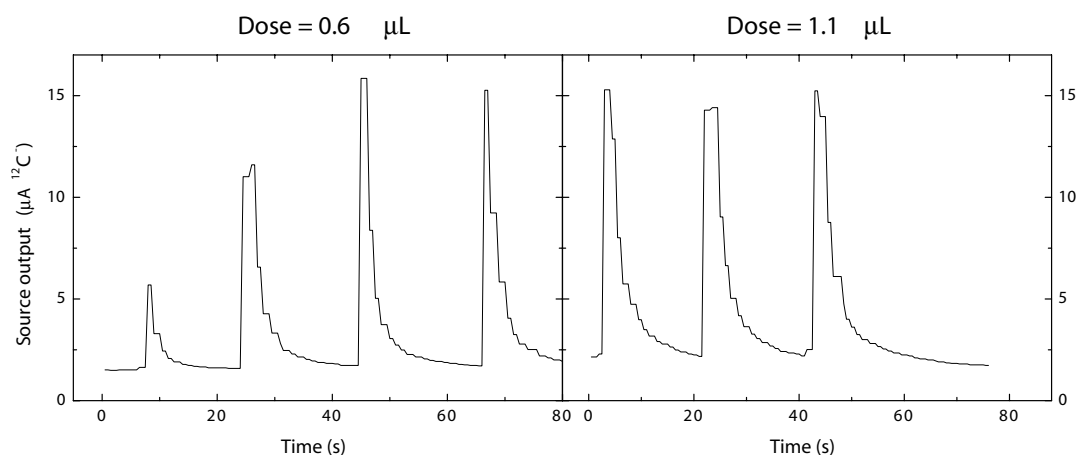


Figure 3 Resulting output of the SO-110 source when exposed to injection of short gas pulses of 0.5- or 1-s duration, corresponding to 0.6 or 1.1  $\mu\text{L}$   $\text{CO}_2$ , respectively. The time resolution is 1 s.

The decay of the background current is very slow and to a good approximation the magnitude of background may often be considered as constant. However, the resulting memory effect needs to be considered in high-precision dating. In general, the effect is insignificant for short pulses because its magnitude is small (limited exposure to target gas) and the statistical uncertainties are very large. On the other hand, if the gas dose is large (“DC” flow, e.g. several minutes of exposure to sample gas), the memory effect is significant, and consequently, individual Ti targets must be used for each gas sample.

Figure 3 shows typical examples of the response of the SO-110 source to fairly large pulses of 0.5- and 1-s duration. The ionization efficiency determined from the peaks is of the order of 1.6–1.8% (except for the case of the first peak, which yields 0.4%—see discussion below). This is slightly smaller than the efficiency observed for continuous  $\text{CO}_2$  injection (cf. 2% in Figure 2), probably because a part of the carbon is sputtered off slowly over an extended period. On the other hand, the maximum peak  $^{12}\text{C}^-$  current is larger in the pulsed mode and can reach about 20  $\mu\text{A}$ . The data in the figure demonstrates an important feature with respect to the performance of the source. Since the maximum current is limited (an experimental fact), it might have been expected that the efficiency would decrease when the injected gas dose increases over a certain limit (see e.g. Ognibene et al. 2007). However, this is generally not the case, and such effects have not been observed in the case of pulsed gas injection, but only for continuous injection. Instead, what happens is that the carbon is accumulated on the titanium pellet and sputtered off over an extended period. Therefore, the peak current and the efficiency do not decrease, but the peaks become broader. In order to understand the behavior, it is important to keep in mind that the source works along a 2-step mechanism (like other similar sources)<sup>3</sup>:  $\text{CO}_2$  is first adsorbed on the surface of a titanium pellet in the cathode and subsequently sputtered off to yield  $\text{C}^-$ .

Two additional series of experiments were conducted in order to investigate the variation of peak shape and efficiency as a function of the injected dose of  $\text{CO}_2$  for short ( $\leq 0.3$  s) and long (10 s)

<sup>3</sup>The corresponding 1-step mechanism where  $\text{C}^-$  is produced directly in the gas phase is also possible but generally much less probable with the present source design. However, in the case when a very high gas load is injected over an extended period, it becomes significant and may even be dominant.

pulses. As shown in Figure 3, the typical response of the ion source to a short gas pulse can be regarded as an almost vertical rise and an exponential decay, possibly with a plateau in between. Consequently, the peak shape can be characterized by the exponential decay time, which may be obtained by peak fitting. Figure 4 summarizes the results of 2 series of measurements; the original measurements are not shown but correspond to those in Figure 3. The efficiency stays almost constant within the range studied in each series, with the exceptions of some scatter observed for very small pulses and the points marked by an arrow (see discussion below). There is a significant difference between the average efficiency of the 2 series, but this is due to different running conditions in the 2 cases. Had there not been such changes, we would have expected the source efficiency to remain approximately constant within the dose range of the experiments. In both series, the decay time remains constant around 1–2 s for small- and medium-size doses. Nevertheless, when the dose size exceeds a certain limit some peak broadening does occur (see Figure 4). This limit corresponds in both series to a maximum flow of about  $10 \mu\text{L min}^{-1} \text{CO}_2$ . The number probably relates to the speed at which carbon (i.e.  $\text{CO}_2$ ) can be transformed or removed in the ion source. For comparison, the flow in Figure 2 was  $5.6 \mu\text{L min}^{-1}$ , and Uhl et al. (2004) observed optimum performance for a dual-mode MC-SNICS source when using a flow of about  $2 \mu\text{L min}^{-1}$ .

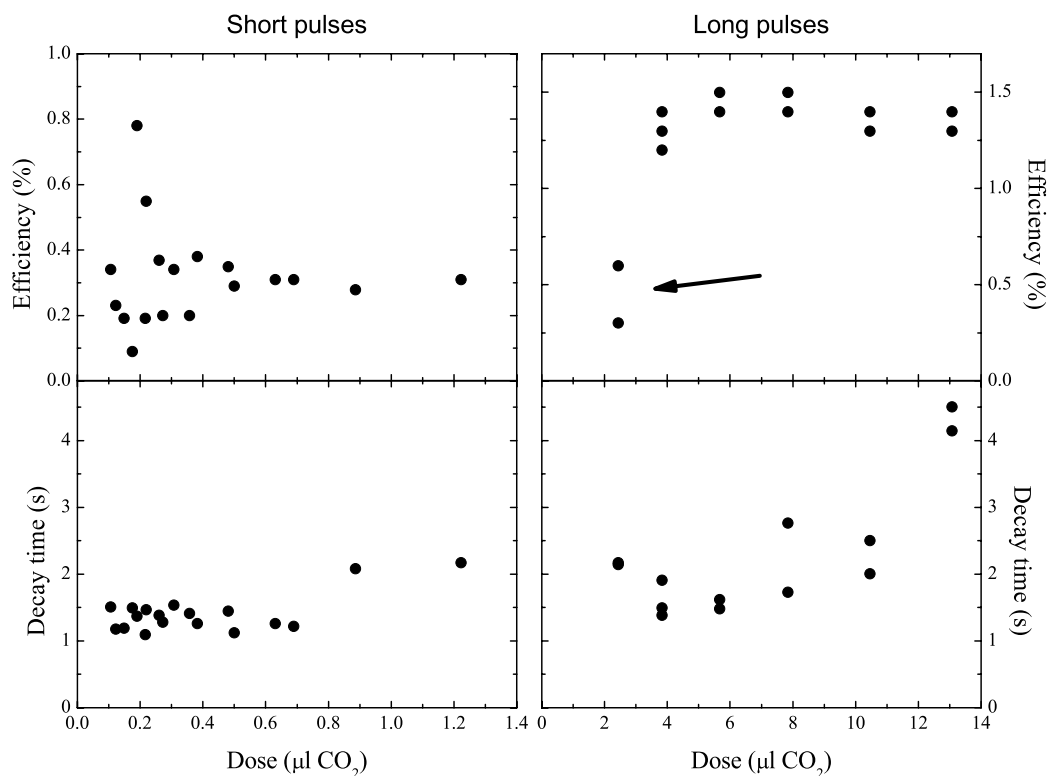


Figure 4 Ionization efficiency (top) and decay time (bottom) of the SO-100 ion source as a function of the injected amount of  $\text{CO}_2$  ( $1 \mu\text{L CO}_2 \sim 0.49 \mu\text{g C}$ ). The left column displays the results for short pulses (0.03–0.3 s), while data for long pulses (10 s) are shown to the right. The change in efficiency between the 2 cases is due to different tunings of the source. The data points marked by the arrow are influenced by a special effect as discussed in the text.

There may be a threshold dose of  $\text{CO}_2$  that has to be injected before the source responds. The effect is observed if the source has not been exposed to gas for some time (tens of minutes) or not at all.

The first peak in Figure 2 and the points indicated by an arrow in Figure 4 have been influenced by this effect. It may possibly be due to adsorption of CO<sub>2</sub> on the sides of the titanium pellets. In order to avoid it in HPLC-AMS measurements, for example, a number of gas pulses (reference gas) should be injected before the chromatographic measurement. Such pulses may also serve for normalization and to monitor the background signal, and similar procedures are standard for GC-IRMS and HPLC-IRMS measurements. We would expect the cross-contamination effects due to the reference-gas pulses to be of little importance.

It is worth considering the impact of the source performance on <sup>14</sup>C AMS with on-line separation. The main problem with such experiments is probably the limited precision that can be obtained. A large, short pulse of CO<sub>2</sub> leads to an integrated <sup>12</sup>C current (i.e. <sup>12</sup>C<sup>-</sup> charge) of about 60 nC (cf. Figure 3). For a modern sample, this corresponds to 450 <sup>14</sup>C atoms, and thus a precision of 7% (540 <sup>14</sup>C yr) may be obtained for the <sup>14</sup>C content of the CO<sub>2</sub> (assuming a detection efficiency of 50%). On the other hand, the corresponding consumption of carbon would only be 0.7 (0.07) μg for an ion-source efficiency of 1% (10%). Consequently, the method would provide the possibility of extracting information on the <sup>14</sup>C content of extremely small samples. Furthermore, higher precision could to some degree be obtained by performing several injections or by injecting larger amounts, but with the result of some peak broadening in the latter case. In conclusion, such a system clearly has potential applications, e.g. for projects in sectors of environmental science and life science.

The tuning of the source is critical, as is evident from comparing the efficiencies in the left and right parts of Figure 4. The SO-110 source requires a higher Cs temperature when running in gas mode than when used for graphite cathodes. This is a problem because the shielding of the insulators in the SO-110 source is marginal, and as a result of the high Cs level, frequent cleaning is required. If there is not enough Cs present, the source cannot produce C<sup>-</sup> from the CO<sub>2</sub> injected. For example, if the supply of Cs is insufficient, a first gas pulse may reduce the amount of Cs available on the surface of the cathode so much that there is not enough for producing a second C<sup>-</sup> peak. Consequently, the effect can be that the second of 2 gas pulses in a row does not show up in the C<sup>-</sup> spectrum. The actual underlying mechanism is probably related to changes in the work function; Cs lowers it and CO<sub>2</sub> raises it. Since the production of negative ions depends critically on the magnitude of the work function, a small increase may reduce the output current to almost zero. The problem is usually avoided by increasing the Cs temperature by 1 or 2 °C. Unfortunately, the adjustment of the Cs level is slow due to the specific design of the SO-110 source.

## STATUS AND OUTLOOK

Progress in separation chemistry and stable isotope ratio mass spectrometry (IRMS) has provided a number of new interesting possibilities. St-Jean (2003) interfaced a total carbon (TC) analyzer to an IRMS system and obtained precise δ<sup>13</sup>C values of total inorganic carbon (TIC) and total organic carbon (TOC); the system may also be considered for automatic oxidation of sample fractions separated by an HPLC. Furthermore, direct coupling of an HPLC to an IRMS system can now be achieved using commercially available wet-oxidation interfaces (LC Isolink from Thermo and Liqueface from GV Instruments, see also Liberman et al. 2004). It is likely that such developments will soon find their way into <sup>14</sup>C AMS.

On-line combustion of samples for <sup>14</sup>C AMS measurements was originally developed by Bronk Ramsey and Humm (2000), and such systems are now available or under construction in a number of AMS labs, see e.g. Bronk Ramsey et al. (2004b) and Uhl et al. (2004, 2007). The method has been used as part of the present project for dating carbonates and for running test samples in connection

with the development of amino-acid specific  $^{14}\text{C}$  dating of bones (Tripp et al. 2006). It would probably be fairly straightforward to replace the elemental analyzer with a TC analyzer in order to perform  $^{14}\text{C}$  dating of water samples or HPLC fractions with automatic sample preparation.

The ion-source tests done here and elsewhere demonstrate that  $^{14}\text{C}$  AMS with real-time sample separation is indeed feasible, although only relatively poor precision may be obtained. The coupling of  $^{14}\text{C}$  AMS with on-line sample preparation was considered in test experiments by Bronk Ramsey and Hedges (1995) and later demonstration for the case of GC AMS (Bronk Ramsey et al. 2004). However, today the vast majority experiments involving HPLC (or GC) are conducted in an off-line mode, i.e. sample fractions are collected and pretreated individually. This may be due to the poor precision obtainable, but also that until recently no appropriate real-time interface for HPLC AMS was readily available. With such interfaces available now and the increased interest in experiments involving ultra-small samples (possibly  $^{14}\text{C}$  enriched), e.g. compound-specific  $^{14}\text{C}$  dating (CSR), it is likely that we will see greater use of gas ion sources in the future.

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