

# $^{14}\text{C}$ Research at the Laboratory for the Analysis of Radiocarbon with AMS (LARA), University of Bern

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**Abstract:** The Laboratory for the Analysis of Radiocarbon with AMS (LARA) at the University of Bern measures the radioactive carbon isotope  $^{14}\text{C}$  with accelerator mass spectrometry (AMS) in different applications. Besides radiocarbon dating of environmental and archaeological samples, the LARA focuses on source apportionment of air-borne particulate matter (*i.e.* aerosols) as well as greenhouse gases such as carbon dioxide and methane. This approach allows the identification and quantification of fossil carbon emissions in these air components, which is relevant for measures of air-quality improvement. The LARA furthermore develops instrumental setups for and at the AMS in order to analyze  $^{14}\text{C}$  samples in  $\mu\text{g}$ -amounts with low contamination and high throughput, preferably using online-hyphenated systems.

**Keywords:** Accelerator mass spectrometry · Carbonaceous aerosols · Compound-specific  $^{14}\text{C}$  analysis · Radioanalytical chemistry · Radiocarbon



**Sönke Szidat** studied Chemistry and graduated at the Leibniz University of Hannover. He joined the Laboratory of Radiochemistry and Environmental Chemistry at the University of Bern in 2000. He became independent researcher and lecturer in 2010 and Associated Professor in 2017. Since 2013, Sönke Szidat has been the head of the LARA, the Laboratory for the Analysis of Radiocarbon with AMS at the University

of Bern. He was awarded the Atmospheric Chemistry and Physics (ACP) Award of SCNAT in 2008 and the Fritz-Strassmann-Preis of the Nuclear Chemistry Division of the German Chemical Society (GDCh) in 2009. His research targets the apportionment of sources of atmospheric components such as carbonaceous aerosols,  $\text{CO}_2$  and  $\text{CH}_4$  using  $^{14}\text{C}$  and the development of hyphenated analytical systems for  $^{14}\text{C}$  analysis.

## 1. The Laboratory for the Analysis of Radiocarbon with AMS (LARA) at University of Bern

Radiocarbon ( $^{14}\text{C}$ ) is a long-lived radioisotope (half-life  $T_{1/2} = 5730$  yr) of carbon, which is widely used in archaeological, geological, biomedical, environmental and climate research.<sup>[1]</sup> The University of Bern has a long-lasting history in developing and applying  $^{14}\text{C}$  measurement techniques. Early in his career, the climate and environmental physicist Hans Oeschger set up gas proportional counting systems with a revolutionary background suppression,<sup>[2]</sup> which have provided reliable data for more than 60 years. Their operation unfortunately entails several major drawbacks, *e.g.* the requirement of large quantities of sample material (*i.e.* in gram amounts of carbon), the resulting laborious sample preparation and the limited measurement throughput of a few hundred analyses per year caused by long measurement times. The University of Bern therefore established the Laboratory for the Analysis of Radiocarbon with AMS (LARA) in 2013,<sup>[3]</sup> which is equipped

with an accelerator mass spectrometer (AMS) MICADAS (Mini Carbon Dating System)<sup>[4]</sup> as shown in Fig. 1. The LARA is located in the Department of Chemistry and Biochemistry (DCB) and is jointly affiliated to the DCB and the Oeschger Centre for Climate Change Research (OCCR). AMS systems beneficially require sample material in mg-amounts of carbon under routine conditions and even can handle with  $\mu\text{g}$ -amounts under the special operation of a gas ion source (see below in section 2), produce consequently less efforts of sample preparation and allow several thousand measurements per year. The performance of the MICADAS in Bern was validated after commissioning of the instrument,<sup>[3]</sup> which showed a detection limit of  $\sim 52$  kyr for radiocarbon dating and an average measurement uncertainty under routine conditions of  $\pm 2.5\%$ , which corresponds to an uncertainty of the  $^{14}\text{C}$  age of  $\pm 20$  yr for modern samples. (It should be noted, however, that radiocarbon dating requires an additional data evaluation step called ‘calibration’ for the transformation of the measured  $^{14}\text{C}$  age into a calendar age, which further contributes to the dating uncertainty.<sup>[1]</sup>) The performance of the MICADAS is currently being reevaluated after a major revision and technical upgrade of the instrument, which should provide improved measurement uncertainties under routine conditions of  $< 2\%$ .

$^{14}\text{C}$  research at the LARA focuses on several scopes:

- Internal LARA research. This covers a) the development of hyphenating analytical instruments to the gas ion source of the MICADAS for online measurements (see section 2), b) the application of radiocarbon for source apportionment of carbonaceous aerosols as well as carbon-containing greenhouse gases (see section 3) and c) the improvement of sample preparation techniques for the isolation of special carbon fractions for  $^{14}\text{C}$  analysis (section 4).
- Collaborations with research groups at the University of Bern as well as other research facilities both domestic and abroad.
- Service measurements for non-commercial institutions that pursue research, monitoring and service goals, such as cantonal archaeological services or federal offices.

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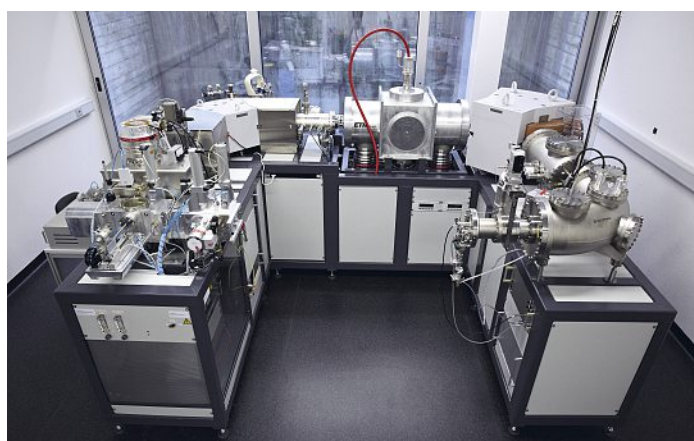


Fig. 1. The MICADAS at the Bern Laboratory for the Analysis of Radiocarbon with AMS (LARA).<sup>[9]</sup> Photo: A. Boutellier. Figure reproduced with permission of Publisher.

## 2. Analysis of Small Radiocarbon Samples, Instrumental Developments and Hyphenations

In many applications of dating, environmental or biomedical studies, the investigation of bulk samples inevitably results in misinterpretations, if the samples are composed of materials from different sources or ages.<sup>[1,5]</sup> Innovative studies have therefore been devoted to investigate specified sub-fractions of samples or even compound-specific radiocarbon analysis (CSRA). The scientific relevance of such specific  $^{14}\text{C}$  determinations is eminent. However, their performance strongly depends on several requirements:

- the establishment of reliable  $^{14}\text{C}$  AMS measurements of very small samples containing a few microgram carbon for minor fractions or trace compounds,
- the development of separation techniques for isolation of pure sub-fractions or compounds and
- hyphenated techniques of separation and AMS analysis aimed at automation to improve the measurement quality and the sample throughput as a consequence of the fact that the number of individual  $^{14}\text{C}$  determinations increase substantially for CSRA.

Until a few years ago, most AMS laboratories focused on the optimization of the production of solid targets for AMS measurement by the reduction of  $\text{CO}_2$  from sample combustion.<sup>[6]</sup> With our contribution, the self-constructed ion source of the MICADAS was modified at the Laboratory of Ion Beam Physics of ETH Zurich in order to insert gases to the focal point of the cesium beam.<sup>[7]</sup> The optimization of the ion source and design of the gas targets resulted in a substantial increase of measurement efficiencies as well as in a reduction of measurement times.<sup>[8]</sup>

Linking separation techniques with AMS for online  $^{14}\text{C}$  analysis is a coherent result of the analysis of small radiocarbon samples with a gas ion source.<sup>[9]</sup> Although the advantage of such an automation for recurrent applications of CSRA is obvious, successful realizations had been rare before the collaborative work of ETH Zurich together with us. We chose the coupling of an elemental analyzer (EA) as the first hyphenated device to the AMS MICADAS.<sup>[10,11]</sup> This combination of instruments is advantageous in several ways: a) it standardizes combustion of bulk material, which is applied in many routine methods; b) once being developed for EA-AMS, coupling interfaces can be adapted with only slight modifications to connect other instruments to AMS. The hyphenation of the EA with the MICADAS was conducted with a multi-purpose gas injection system (GIS, see Fig. 2).<sup>[10,11]</sup>

After commissioning of the LARA facility in Bern, the prolific progress of the gas ion source has been improved even further by our group in order to promote the source apportionment of carbo-

naceous aerosols in the atmosphere (see below in section 3). First, the EA-AMS coupling was investigated for the automated  $^{14}\text{C}$  measurement of the total carbon fraction.<sup>[12]</sup> Second, a commercially available OC/EC analyzer (Sunset Laboratory Inc, USA) was connected to the AMS for time-efficient, semi-automated radiocarbon measurement of organic carbon (OC), elemental carbon (EC), and sub-fractions of those.<sup>[13]</sup> Third, we established a real-time online coupling of the Sunset OC/EC analyzer *via* direct gas injection into the ion source without a gas interface.<sup>[13–15]</sup>

Fig. 2 provides an overview of different of different instruments that have been coupled to the gas ion source of the MICADAS and how this hyphenation has been performed.

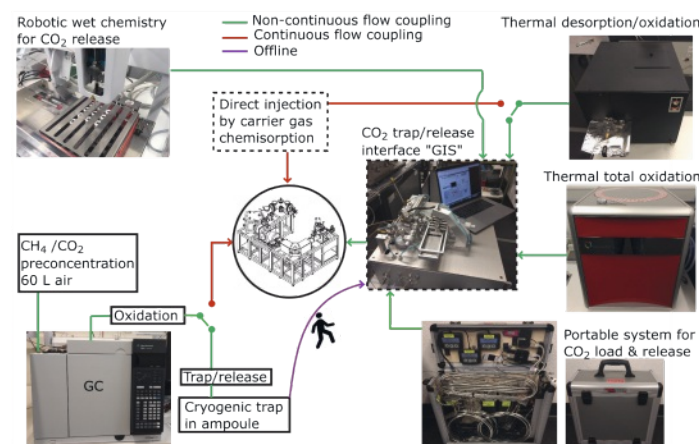


Fig. 2. Overview of hyphenations of analytical separation devices with the gas ion source of the MICADAS at the LARA.

## 3. Source Apportionment of Carbonaceous Aerosols and Carbon-containing Greenhouse Gases

Aside from radiocarbon dating,  $^{14}\text{C}$  may also serve as a qualitative or quantitative tool in environmental sciences for the distinction of carbon-containing material of different origins. This approach especially allows the distinction of fossil from modern material, as  $^{14}\text{C}$  is extinct in the former due to the old age of fossil fuels, whereas the latter shows the well-known modern radiocarbon level.<sup>[1,16,17]</sup> This fact makes the apportionment of emission sources possible for carbonaceous air-borne particulate matter (*i.e.* aerosols) as well as greenhouse gases (*e.g.* carbon dioxide,  $\text{CO}_2$ , and methane,  $\text{CH}_4$ ). In such applications, fossil emissions may be distinguished from biogenic emissions and quantified more precisely and accurately than with other measurement or modeling techniques so that  $^{14}\text{C}$  measurements are conducive to regulatory measures of air-quality improvement or refining atmospheric models of emission inventories.<sup>[9,18–22]</sup>

In an earlier work,<sup>[9]</sup> the general source apportionment approach of carbonaceous aerosols was explained (Fig. 3). Traditionally, the total burden of the carbonaceous aerosol is denoted as total carbon (TC) and subdivided into elemental carbon (EC) and organic carbon (OC).<sup>[23]</sup> Due to their different emission sources, it is necessary to chemically separate OC and EC and to analyze  $^{14}\text{C}$  in both fractions. We developed a method based on combustion of particulate matter filters in pure oxygen using the Sunset OC/EC analyzer and further optimized it to guarantee complete OC removal with high EC yields for radiocarbon analysis of EC by establishing the four-step Swiss\_4S protocol.<sup>[24]</sup> The Sunset OC/EC analyzer was then directly coupled to the MICADAS (see section 2), which allowed  $^{14}\text{C}$  analysis with high sample throughput and low risk of contamination.<sup>[13]</sup> With this technique, we quantified the fossil contribution of OC and EC for different campaigns in collaboration with the Laboratory of Atmospheric Chemistry at the Paul Scherrer Institute (PSI). We investigated,

for instance, aerosol sources of Switzerland under winter-smog conditions<sup>[19]</sup> and triggers of the deterioration of air quality during winter haze episodes in Chinese cities.<sup>[21]</sup> Furthermore, the combination with positive matrix factorization (PMF) using aerosol mass spectrometry, which is a complementary method of aerosol source apportionment,<sup>[25,26]</sup> enabled the elucidation of fossil vs. non-fossil sources of so-called secondary organic aerosols (SOA). These aerosols are formed in the atmosphere by complex photochemical oxidation and condensation reactions of organic vapors, which is currently studied with great interest.<sup>[20,25]</sup> In two studies from the Los Angeles basin and the Swiss Alpine valley of Magadino,<sup>[16,27]</sup> the  $^{14}\text{C}$ -PMF combination uncovered largely differing contributions of fossil sources to different SOA fractions so that these SOA fractions could be classified as mainly of anthropogenic origin.

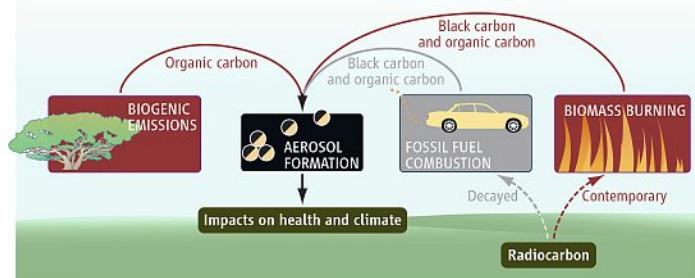


Fig. 3. Source apportionment of carbonaceous aerosols: Radiocarbon analysis allows the quantification of fossil and non-fossil sources of Black Carbon (equivalent to Elemental Carbon) and organic carbon.<sup>[28]</sup> Figure reproduced with permission of Publisher.

$^{14}\text{C}$  is also employed for the identification and quantification of different sources of carbon-containing greenhouse gases. This technique has a long tradition for the detection of fossil  $\text{CO}_2$  emissions on local, regional and global scales.<sup>[1,16,29,30]</sup> In central Europe, long-term  $^{14}\text{CO}_2$  monitoring has been performed in Heidelberg in the upper Rhine valley and at the nearby mountain station Schauinsland (1205 m a.s.l.) in the Black Forest since 1977 as well as at the continental background station Jungfrauoch (3450 m a.s.l.) since 1986.<sup>[29]</sup> From these data, urban and regional fossil  $\text{CO}_2$  was quantified indicating *e.g.* winter peaks of fossil fuel  $\text{CO}_2$  emissions for Heidelberg and Schauinsland compared to Jungfrauoch, which originate from a higher fossil-fuel consumption during winter in combination with a strongly reduced  $\text{CO}_2$  uptake by plants.<sup>[31]</sup> Since 2013, we have measured  $^{14}\text{CO}_2$  at the Beromünster tall tower in collaboration with the Climate and Environmental Physics of the University of Bern. Sporadic samples (*i.e.* one spot sample every second week) were compared with continuous measurements of carbon monoxide ( $\text{CO}$ ) and  $\text{CO}_2$  mixing ratios with high time-resolution in order to link short-term changes of these gases with fossil  $\text{CO}_2$  emissions.<sup>[22]</sup> In combination with stable isotope analysis (*i.e.*  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) of  $\text{CO}_2$ , these data provided an estimation of fossil-fuel and biospheric  $\text{CO}_2$  mixing ratios on short time scales.

Similar to  $\text{CO}_2$ , increasing emissions of  $\text{CH}_4$  induce global warming so that the knowledge of individual contributions of different  $\text{CH}_4$  sources may help to select efficient mitigation measures.<sup>[32]</sup> Even though radiocarbon measurements of atmospheric methane may also provide an identification of  $\text{CH}_4$  sources,  $^{14}\text{CH}_4$  measurements have seldom been used for this purpose, as large air samples are required, a quantitative separation of  $\text{CH}_4$  from  $\text{CO}_2$  and other carbon-containing gases is prerequisite and  $^{14}\text{CH}_4$  emissions of nuclear power plants (NPPs) may interfere with this approach.<sup>[33]</sup> In order to measure  $^{14}\text{CH}_4$ , we developed and validated a setup with which methane is preconcentrated from 50–200 L

of ambient air and purified by several traps and a preparative gas chromatography (GC).<sup>[34]</sup> This process removes  $\text{CO}_2$  and other carbon-containing gases quantitatively, which can be verified for each sample by reinjection of the purified  $\text{CH}_4$  into the GC. Air components are also removed completely except for krypton that co-elutes with  $\text{CH}_4$  from the GC. As Kr has no effect on the  $^{14}\text{CH}_4$  analysis, however, a further optimization of the GC separation was not necessary. After purification and isolation, the methane is oxidized to  $\text{CO}_2$ , which is then sealed in ampoules and transferred into the gas ion source of the MICADAS for  $^{14}\text{C}$  measurement (Fig. 2).<sup>[34]</sup> With this procedure, we have determined  $^{14}\text{CH}_4$  at various sites in Switzerland, including the Beromünster tower.

#### 4. Investigation of the Environment and Irradiated Nuclear Waste Using Compound-specific Radiocarbon Analysis (CSRA)

Methods of extraction and separation for  $^{14}\text{C}$  analysis mainly aim at the isolation of the carbon-containing fraction, which enables dating of a specific event or knowledge of an environmental process, and as well at the removal of contaminating fractions, which may bias this result. Sample preparation methods in routine  $^{14}\text{C}$  analysis are often rather simple (*e.g.* treatment with diluted acids or bases), but still require broad experience for specific sample materials.<sup>[5]</sup> The LARA has carefully verified and optimized widely used methods to prepare samples such as wood, charcoal, terrestrial and marine carbonate, plant macrofossil as well as bone<sup>[3,35–37]</sup> and is continuously improving these procedures. More sophisticated separation techniques aim at the isolation of individual substances for  $^{14}\text{C}$  measurement, which is denoted as compound-specific radiocarbon analysis. In Switzerland, Biogeochemistry groups at ETH and University of Zurich have pioneered this work, *e.g.* for the isolation of individual lignin and pyrolysis degradation products or long-chained fatty acids.<sup>[38,39]</sup> Moreover, biomedical research targets the usage of  $^{14}\text{C}$ -radiolabeled drugs in human ADME (*i.e.* absorption, distribution, metabolism and excretion) microtracer studies.<sup>[40]</sup> The benefit of clearly and specifically interpretable data comes at the cost of laborious and expensive preparation work as well as the requirement of large sample amounts. Besides  $^{14}\text{C}$  measurements of  $\text{CO}_2$  and  $\text{CH}_4$  (see section 3), we have focused in our group on the isolation of small carboxylic acids from air-borne aerosols for source apportionment and the investigation of photochemical reactions in the atmosphere.<sup>[41]</sup>

In collaboration with the Laboratory for Waste Management of PSI,<sup>[42]</sup> we have developed analytical instrumentation and sample preparation methods to investigate chemical speciation of  $^{14}\text{C}$  in low- and intermediate-level (L/ILW) radioactive waste under conditions of a cement-based repository.<sup>[43–45]</sup> The speciation of  $^{14}\text{C}$  affects its relevance in safety assessments, because dissolved and gaseous species may migrate from the repository into the environment and even be incorporated in the food chain. The chemical forms therefore determine migration routes and radioactive dose releases. In Switzerland, the majority of the  $^{14}\text{C}$  inventory in L/ILW is related to irradiated steel.<sup>[43]</sup>  $^{14}\text{C}$  atoms are formed in NPPs from nitrogen impurities in metal components by thermal neutrons and undergo chemical alteration already in the steel or later during slow corrosion of the steel under the alkaline and reducing aqueous conditions of the cement-based L/ILW repository. Consequently, small inorganic and organic  $^{14}\text{C}$ -containing molecules can be formed that may differ from inactive carbon species in the steel due to their diverging origin. In order to identify these species and quantify their contributions, an anoxic corrosion experiment was set up at PSI in May 2016, which has proceeded and continuously been probed since then (Fig. 4). Two pieces of 1 g each of a guide-tube nut that was irradiated at NPP Gösigen for two years were placed in a gas-tight reactor filled with artificial cement pore water (*i.e.* 0.02 M  $\text{Ca}(\text{OH})_2$ , pH ~12.5,

dissolved O<sub>2</sub> ~50 ppb) and an overpressure inert atmosphere of pure nitrogen (5 bar). Through two independent systems, both the gas and the liquid phase have been sampled several times for CSRA of dissolved and gaseous carbon-containing compounds. From the liquid phase, carbonate was isolated by acidification and formate, acetate, oxalate, malonate and further small carboxylates by high performance ion exchange chromatography (HPIEC) after addition of <sup>14</sup>C-free carriers.<sup>[43,44]</sup> The isolated liquid fractions were then transferred from PSI to Bern and the <sup>14</sup>C content of the individual compounds were measured with AMS after wet oxidation of the organic compounds in solution to CO<sub>2</sub>,<sup>[46]</sup> which was injected into the GIS of the MICADAS. From the gas phase, methane, ethane, ethene, ethyne, propane, propene and butane were separated by GC, <sup>14</sup>C-free carrier gases were added, all gases were transformed into <sup>14</sup>CO<sub>2</sub> (mixed with <sup>12,13</sup>CO<sub>2</sub>) using an oxidation oven and stored in separated tubes of a portable gas fraction collector.<sup>[45]</sup> After transfer to Bern, the individual fractions were flushed from the collector tubes into the GIS for <sup>14</sup>C analysis. The first 3.5 years of operation have indicated that the total <sup>14</sup>C activity, which has been released by corrosion, divides into three shares of similar sizes each: small carboxylates (*i.e.* formate, acetate and malonate) in the liquid phase, carbonate in the liquid phase and small alkanes (mainly methane) in the gas phase.<sup>[43–45]</sup>

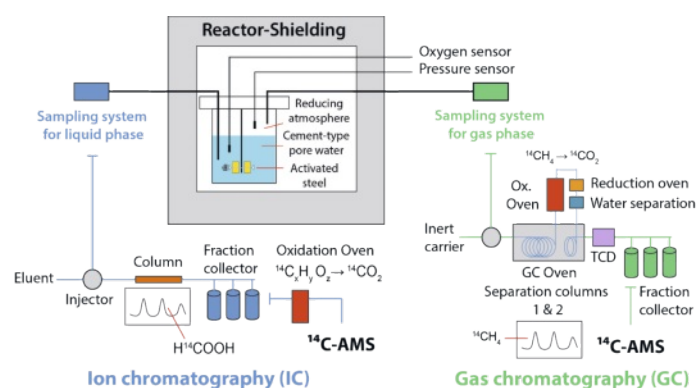


Fig. 4. Corrosion experiment of <sup>14</sup>C speciation under conditions of a nuclear waste repository including compound-specific radiocarbon analysis (CSRA) of the liquid and gas phases sampled from the reactor.

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