Nuclear Instruments and Methods in Physics Research B 361 (2015) 288–293

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Online coupling of pure O_2 thermo-optical methods – ^{14}C AMS for source apportionment of carbonaceous aerosols

Konstantinos Agrios[a,b,c], Gary Salazar[a,b], Yan-Lin Zhang[a,b,c,1], Chiara Uglietti[a,b,c], Michael Battaglia[a,b], Marc Luginbühl[a], Viorela Gabriela Ciobanu[c,2], Matthias Vonwiller[a,b,c], Sönke Szidat[a,b,*]

[a] Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland
[b] Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland
[c] Paul Scherrer Institute, Villigen, Switzerland

ARTICLE INFO

Article history:
Received 15 December 2014
Received in revised form 9 June 2015
Accepted 10 June 2015
Available online 19 June 2015

Keywords:
Radiocarbon
Aerosols
Organic carbon
Elemental carbon
Hyphenation

ABSTRACT

This paper reports on novel separation methods developed for the direct determination of ^{14}C in organic carbon (OC) and elemental carbon (EC), two sub-fractions of total carbon (TC) of atmospheric air particulate matter. Until recently, separation of OC and EC has been performed off-line by manual and time-consuming techniques that relied on the collection of massive CO_2 fractions. We present here two on-line hyphenated techniques between a Sunset OC/EC analyzer and a MICADAS (MIni radioCArbon DAting System) accelerator mass spectrometer (AMS) equipped with a gas ion source. The first implementation facilitates the direct measurement in the low sample size range (<10 µg C) with high throughput on a routine basis, while the second explores the potential for a continuous-flow real-time CO_2 gas feed into the ion source. The performance achieved with reference materials and real atmospheric samples will be discussed to draw conclusions on the improvement offered in the field of ^{14}C aerosol source apportionment.

1. Introduction

The carbonaceous aerosol (total carbon, TC) and its sub-fractions organic carbon (OC) and elemental carbon (EC) constitute a significant portion of the atmospheric fine air particulate matter, influencing the global climate and human health [1,2]. The application of radiocarbon (^{14}C) in the field of carbonaceous aerosols is different from radiocarbon dating. Emission sources of OC and EC fractions can be traced back by different radiocarbon levels, as ^{14}C is extinct in emissions from fossil-fuel usage, whereas carbonaceous aerosols from modern material are on the contemporary ^{14}C level. Therefore, ^{14}C characterization provides an unambiguous quantification of fossil and non-fossil aerosols sources. As the partition of these two source types is often quite different for OC and EC, it is necessary to perform radiocarbon measurements on both fractions individually [1,2].

For this type of analysis, we take advantage of the new accelerator mass spectrometer AMS facility MICADAS at University of Bern [3] and its gas-accepting ion source for the direct analysis of CO_2 gas, eliminating the need to graphitize samples. The existing gas introduction system (GIS) [4] has been lending itself very well to the hyphenation with a variety of analytical instruments throughout several joint works between University of Bern and ETH Zurich [3–7]. This allows aerosol analysis with high sample throughput, which substantially improves the source apportionment by ^{14}C. However, sample preparation is still impeded by the use of manual cryogenic CO_2 trapping deriving from the THEODORE setup [8]. This Two-step Heating system for the EC/OC Determination of Radiocarbon in the Environment was used until recently for the production of CO_2 ampoules after being coupled to the combustion instrument. The subsequent use of a semi-automatic ampoule cracking apparatus further made the methodology more complex for environmental routine analysis.

We present here two different methodologies for the direct coupling of an organic carbon/elemental carbon (OC/EC) analyzer using pure O_2 as carrier gas to the AMS gas ion source following the recent installation of a 200 kV MICADAS facility in the University of Bern [3]. By using these methods, we demonstrate that it is feasible to bypass CO_2 cryogenic trapping and ampoule

---

* Corresponding author at: Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland.
E-mail address: szidat@dcb.unibe.ch (S. Szidat).

[1] Present address: Yale-NUIST Center on Atmospheric Environment, Nanjing University of Information Science and Technology, 210044 Nanjing, China.

[2] Present address: Centre for Ice and Climate, Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark.

http://dx.doi.org/10.1016/j.nimb.2015.06.008
0168-583X/© 2015 Elsevier B.V. All rights reserved.

cracking methodology for the measurement of real atmospheric samples as an improvement of an older work [7]. Additionally, for a first series of reference materials analysis, CO_2 gas is directly fed into the ion source without using the GIS. Both methods are best suited to large series of environmental samples $\sim$5–100 μg C.

2. Materials and methods

2.1. The OC/EC analyzer and trapping offline ^{14}C analysis

Our group uses a thermo-optical OC/EC analyzer (Model 4L, Sunset Laboratory Inc., USA) [9]. This instrument produces CO_2 gas as combustion product of atmospheric filters. In this study, we used a temperature program of one step at 760 °C for 170 s for total carbon combustion and an OC/EC thermo-optical separation program of 4 thermal steps (Swiss_4S) developed and characterized previously [1]. For the total carbon combustion program, the carrier gas is pure O_2 (99.9995%). For the Swiss_4S protocol, the carrier gases used are pure O_2 for steps 1, 2 and 4 and He (>99.999%, pre-cleaned with a moisture/O_2/hydrocarbon trap) for step 3. The filter transmittance is monitored by a 660-nm tuned-diode laser. The gas flow parameter of the OC/EC analyzer is set at 60 mL/min. The gaseous carbonaceous species released from the combustion pass through a MnO_2 bed heated to 850 °C and get oxidized to CO_2. The CO_2 fractions are then detected and quantified by a non-dispersive infrared (NDIR) detector before being released to the GIS. The CO_2 can then be trapped cryogenically and, later on, transferred and sealed in glass ampoules. CO_2 samples prepared in this way are introduced in the GIS via means of an ampoule cracker, which utilizes mechanical bellows to crack delicately the glass vessel. We denote this method as trapping offline, which we used in previous studies (e.g., [1,2]).

For the validation of both systems, trapping online and continuous-flow coupling, we prepared aqueous solutions of C7 (oxalic acid), C6 (sucrose) as well as combusted grains of C5 (wood) as such in the sample holder (all reference materials from the International Atomic Energy Agency, IAEA) and aqueous solutions of oxalic acid 2 (HOx2, reference material SRM 4990c, National Institute of Standards and Technology, NIST) and fossil sodium acetate, (NaOAc, p.a., Merck, Germany) in the range of 2–10 g/L. For the aqueous solutions, we then pipetted 5–10 μL on 1.5 cm^2 prebaked quartz-fiber filters before inserting them in the OC/EC analyzer. The filters were then dried for 2 min before initiating a total carbon combustion temperature program by a dedicated drying program of the Sunset OC/EC analyzer. This approach is contrasting the online trapping from [7], where the punches were dried in a flow box, thus exposing the filter to contaminant volatile organic compounds.

For the validation of the trapping online method, we used filters from 2010 to 2011 that were part of a five-years Swiss air pollution study and were collected with high-volume samplers for 24 h on quartz fiber filters [2]. After the sampling, all filters were wrapped in aluminum foil, packed in air-tight polyethylene bags and stored at -18 °C. All filters were heavily loaded with particulate matter (typical loading: 30–100 μg C/cm^2 and 10–30 μg C/cm^2 for OC and EC, respectively). For the analysis, one single 1.5 cm^2 quartz filter punch per sample was used.

2.2. Trapping online CO_2 via GIS

In the trapping online method, the CO_2 is collected in a zeolite trap of the GIS (Fig. 1). The control of the GIS and the communication with the Sunset Analyzer and the MICADAS is performed by a LabView program. The carrier gas flow of the OC/EC analyzer is set to 60 mL/min measured after the CO_2 trap with an electronic flow meter (Restek, USA). When connected to the CO_2 trap, the OC/EC analyzer exhibits a backpressure of 200 hPa. This was in agreement with similar findings of [7], where the operators observed a backpressure of 240 hPa – albeit while using a different Sunset OC/EC analyzer model (i.e., RT 3080, Sunset Laboratory Inc, USA). Due to this, a prime/purge solenoid valve used by the instrument for switching the flow from the combustion tube to the NDIR or to the vent leaked a significant portion of the gas to the vent during our first tests. This resulted in a 50% loss in CO_2 recovery. On account of that, the OC/EC analyzer connection was adjusted in order to bypass the valve and lead the combustion products directly to the NDIR detector without purging option. The internal calibration constant of the instrument requires correction by a factor of 0.8 based on analyzing known amounts of sucrose solutions (multi-point calibration with 3 repetitions of 10, 20 and 40 μg C yielding sucrose solutions, D(+)-Sucrose, Fluka Analytical) under that backpressure. There is another pressure increase of about 20–30 hPa on heating the sample (Fig. 5) due to the thermal expansion of the gas. This is taken into consideration for recalibrating the instrument by commencing trapping of each fraction after the pressure has equilibrated.

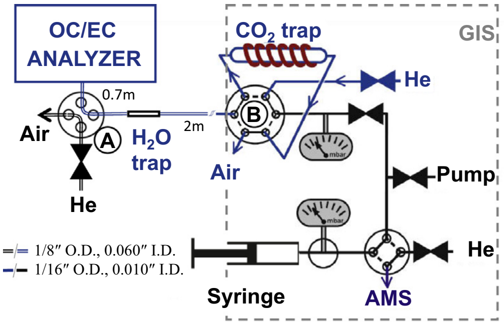

Fig. 1. Schematic of the gas handling system (GIS) for the MICADAS gas ion source at University of Bern. The main elements of the system are two VICI 2-position multi-port valves (labeled A and B) and the CO_2 trap. The valves are shown here in the configuration for collection of CO_2 in the trap.

A 2 m 1/8″ I.D. stainless steel tube directs the CO_2 fractions into the zeolite trap after previously passing through a water trap (Sicapent, Merck, Germany). The connection starts with a 1/8″ O.D. stainless steel tube ending in a 1/8″ × 1/16″ reduction union about 30 cm before the CO_2 trap. The 4-port 2-way valve (VICI, USA) (valve A) positioned after the OC/EC analyzer performs the interchangeable connection between the OC/EC analyzer and the CO_2 trap or the vent. A He stream flushes the line to the GIS whenever the OC/EC analyzer is vented so that air contamination is minimized. By switching valve B, the OC/EC analyzer combustion products pass through the CO_2 trap while analyzing a fraction of interest. The syringe cleaning from remains of the previous sample is conducted in parallel with the trapping. After collection is complete, valve B is switched to the atmosphere and the trap is back-flushed with He at room temperature to minimize contamination from other adsorbed combustion products or O_2 traces from the carrier gas.

We use the trapping online hyphenation for the measurement of ^{14}C from reference materials and water-extracted filters prepared and analyzed by the Swiss_4S method [1]. Alternatively, for standard material measurements, a total carbon combustion program allows for the total carbon load of a filter to be desorbed and quantified as one single peak. 50 s before the commencement of the temperature ramp, the OC/EC analyzer outlet is directed to the packed CO_2 trap by switching valve B. This period is adequate for pressure stabilization before the loading of a CO_2 fraction on the trap. The OC/EC analyzer outlet remains connected to the CO_2 trap