

METHOD DEVELOPMENT FOR THE ^{14}C MEASUREMENT OF ATMOSPHERIC AEROSOLS

**I. Major¹, E. Furu¹, R. Janovics², I. Hajdas³, Zs. Kertész², M.
Molnár²**

¹ University of Debrecen, Debrecen, Hungary, imajor@atomki.hu

² Institute of Nuclear Research of the Hungarian Academy of Sciences
(ATOMKI), Debrecen, Hungary

³ Laboratory of Ion Beam Physics, ETH Zürich, Switzerland

Abstract

Inspired by the results of the fossil atmospheric carbon-dioxide measurements (Molnár et al., 2010), the measurement method was further enhanced by including the investigation of the atmospheric aerosols to gain an even more representative view at the field of research. Parallely with the fossil atmospheric carbon-dioxide monitoring, the ^{14}C concentration of the carbon (0.1 – 1.0 mg C/sample) of the simultaneously collected aerosol samples was measured by a high-precision accelerator mass spectrometer developed specially for environmental samples (MICADAS).

The aim of our research is to investigate the relationship between the results regarding the two atmospheric fossil carbon forms (atmospheric CO_2 and aerosol fraction) to gain a deeper understanding about the extent of the fossil carbon load of the urban air.

I. Introduction

Carbonaceous aerosol particles are of key importance in the atmosphere, as they directly and indirectly influence the change of global climate, as well as, they affect human health (Ramanathan et al., 2001; Venkatamaran et al., 2005).

Aerosol is made up of several simple components and hard-to-identify compounds; therefore, it is extremely hard to determine its exact composition (Chow et al., 2004a). Besides inorganic carbonate, it mostly contains organic carbon (OC) and elemental carbon (EC or BC) making up together at least the 40% of the mass of the urban aerosol. Organic carbon is primarily generated from the direct emission, or secondarily from the condensation of the primarily emitted gases (secondary organic carbon, SOC). Soot is generated by the incomplete combustion of the biomass and the fossil fuels (Castro et al., 1999; Novakov et al., 1997). Although, natural forest fires, the combustion of agricultural and other wastes and the natural emission from plants and soil represent a significant source in the certain periods of the year, the main sources are the public combustion and the vehicle traffic during the autumn and the winter period in Europe (Kupiainen and Klimont 2007).

Previously many tracers were tried to use to identify the different sources of the aerosols, however, their applicability is often restricted by their atmospheric lifetimes depending on their high chemical reactivity, and variable emission factors, and there is another uncertainty arising from the large number of the sources and the chemical compounds. Radiocarbon (^{14}C) as an atmospheric carbon isotope with a long half life, however, is a suitable tracer, since fossil fuels do not contain radiocarbon (0 pMC) due to their old geological age, while fuels of biological and biomass origin have the same radiocarbon content as the atmosphere (13,6 DPM/g carbon). With these assumptions, unambiguous distinction can be made between the non-fossil source (e.g. biomass combustion and the biological source) and the fossil source (Szidat et al., 2006). The method itself was first introduced by Clayton et al. in 1955, and was later successfully used in many studies. For this method, the high-precision measurement of ^{14}C is necessary, however, it would not have been able to be performed without the accelerator mass spectrometry (AMS) technique due to the extremely low amount of the ^{14}C isotope and the low carbon content of the collected aerosol samples (Currie et al., 1983; Bench et al., 2007; Endo et al., 2004).

The aim of this study is to test a sample preparation method that makes the investigation of the total carbon amount of the carbonaceous aerosol possible in Debrecen, Hungary. Up to now, a proper ^{14}C preparation and measurement system to check the quality of the preparation of the low carbon content of the aerosols has not been existed. By the elaboration of the proper preparation and measurement method the ^{14}C data of the carbonaceous aerosols is planned to be used to differentiate the fossil and the biological sources, therefore, it is of

extremely high importance to have a trustworthy and reproducible sample preparation.

In this study, the ^{14}C results of the first three sampling months and the extent of the fossil and modern carbon contributions to the aerosol in Debrecen, the second largest city in Hungary are discussed. By these investigation pieces of information are obtained that can later be important in the preparation of the effective pollution reduction strategies and may serve as input data for the specification of the climate change models.

II. Experimental methods

II.1 Sample collection and pre-treatment

Debrecen with its 200,000 inhabitants is the second largest city in Hungary. As the centre of the North Plain region, it is located at the eastern part of the country surrounded by agricultural lands, in the centre of a huge agricultural area. The location of the sampling was in the territory of the Institute of Nuclear Research, north from the city centre in a residential area surrounded by busy roads. The continuous sampling of the $\text{PM}_{2.5}$ and PM_{10} aerosols for radiocarbon investigation was started in November 2010 in the Institute. The first task was on the basis of the methods successfully applied in Switzerland (ETHZ Zürich) to optimise the sample preparation and treatment methods to our own ^{14}C AMS measurement system that is planned to be further developed.

Sampling was performed by an SKC IMPACT aerosol sampler put onto the roof of one of the buildings of the institute at the height of about 6 m. In this way we tried to avoid the effect of the accidentally chipped soil particles influencing the quality and the quantity of the collected aerosol. The sampler collects the PM_{10} and $\text{PM}_{2.5}$ aerosol samples onto quartz fibre filters (TISSUQUARTZ FILTER with a thickness of 0.4 mm) with diameters of 37 and 47 mm, respectively. Filters were put on the day before use into an oven for 15 hours to remove contamination. On the basis of the experiments of Endo et al. (2004), the heating temperature of 850°C was used.

The sampling period was divided into 1 and 2 week long periods on the one hand to avoid the clogging of the filters, on the other to synchronise with the radiocarbon analyses of the atmospheric CO_2 to compare later the fossil carbon fraction of the two carbonaceous components. Filter replacement occurred biweekly in the first and last months of the seasons, while in the middle months of the seasons (i.e. January, April, July and October) an

additional sampling week was also inserted. Samples collected in the first three months were stored in plastic holders at room temperature until the preparation of the samples. In this work, only the preparation of the PM_{2.5} fraction was performed, however, the collection of the coarse fraction is still going on and they are stored for their later possible investigation.

One tiny part of the sample filters was prepared by the aerosol sample preparation technique of the ETHZ, Switzerland. The filters were sliced, and the pieces of slices containing altogether the required amount of carbon (0.5-1 mg) were put into a preheated quartz combustion tube. Previously, copper oxide to ensure the oxidation of carbon and a silver fibre to purify the gas were placed into the combustion tube. Quartz tubes were then evacuated, sealed and put overnight into an oven with 950°C. Next day, the carbon-dioxide generated was frozen into a clean glass tube that went on for graphitisation (Lawson et al., 2000). The generation of the graphite target was made by an AGE automated graphitisation system working on the basis of hydrogen reduction (Wacker et al., 2000). A day later, the graphite generated was pressed into aluminium holders and its radiocarbon content was determined by the MICADAS AMS equipment of the ETHZ.

After the tests in Switzerland, a piece of the residual samples was subject to experiments in the Hertelendi Laboratory of Environmental Studies, Debrecen, and our self-developed preparation method was applied. As a first step, a slice was cut from the filter containing the fine fraction to get 1 mg of carbon, and the slice was put into a preheated quartz combustion tube (ø7x150 mm). The calculated amount of copper-oxide was weighted into the tubes to provide the sample with oxygen during the conversion into CO₂. However, in our combustion tube, silver fibres were not used, as at a later section of the on-line combustion and purifier system, the purification of the gas occurs with a more developed method. Afterwards, the generated gas was led via a post-combustion furnace of 1000°C and a water trap cooled by isopropyl-alcohol and dry ice (-60°C) into a liquid nitrogen trap (-197°C) where the purified CO₂ froze out. At the known-volume end of the preparation system the amount of the CO₂ was measured and the gas was divided into two parts: one of them went to graphitisation and the other for reservation in a sealed glass tube. To produce a graphite target, the sealed tube graphitisation method was applied. In this method, CO₂ gets reduced by TiH₂ and Zn to graphite on the surface of the high-purity iron catalyst separated in another glass tube. The sealed glass tubes spent 3 hours in an oven of 500°C and 4 hours in 550°C (Vogel et al., 1992; Rinyu et al., 2012). Graphite generated was pressed by a specific pressing tool into aluminium holders and was measured for ¹⁴C by AMS.

II.2 AMS measurement

The AMS facility (EnvironMICADAS) designed and constructed by the ETH institute, Zürich was installed in the summer of 2011 in the Institute of Nuclear Research, Debrecen. Currently, EnvironMICADAS is the least quantity produced AMS facility that was designed specially for ^{14}C measurements. A significant development of the system is the hybrid ion source working on earth potential that is able to accept solid graphite, and CO_2 gas samples introduced with He carrier gas. In the changing cassette with 22 positions there are always at least 3 background and 3 standard samples together with the real aerosol samples. As even the smallest sample contained sufficient amount of carbon to produce graphite, all samples were measured as graphite targets. In case of very small samples ($<100\ \mu\text{g}$) it is suggested to use gas ion source to avoid sample contamination. Another important part of the system is the tandem accelerator unit with a nominal voltage of 195 kV making possible the high-accuracy measurement of ^{14}C . The annihilation of the disturbing molecule ions generated in the course of the ionisation of the graphite occurs by nitrogen stripper gas in the accelerator area. An ionisation chamber filled by iso-butane up to 20 hPa is used for the detection of the ^{14}C ions (Wacker et al., 2010). Stable isotope ratios considered at the evaluation of the ^{14}C results were determined by the EnvironMICADAS equipment.

II.3 Radiocarbon data

The total carbon (TC) of the atmospheric carbonaceous aerosol is made up of components practically of modern (biological and biomass) and fossil origin (Currie et al., 1980). To the investigation of source allocation of the carbonaceous aerosols the radioactive isotope of the carbon provides an appropriate tracer. As the measurement of the small amount of radiocarbon in the samples can only be performed by AMS technique, samples were measured by the EnvironMICADAS AMS of the Hertelendi Laboratory of Environmental Studies. During the ^{14}C measurements, the $^{14}\text{C}/^{12}\text{C}$ ratios of the samples were determined and expressed in the internationally used pMC

(percent Modern Carbon, percent value) or in the modern carbon fraction f_M (fraction of Modern Carbon, $f_M = \text{pMC}/100$). As all of the total ^{14}C content of the fossil fuels have already decayed ($t_{1/2} = 5730$ years) since they were generated millions of years ago, their f_M value is zero relative to the current ^{14}C level. On the contrary, the current aerosols of biological origin have an f_M value identical to the atmosphere (100 pMC, i.e. $f_M \sim 1$). Since part of the firewood was grown during the bomb peak, in the 1-2 decades after the 1960's, according to the internationally accepted assumption, aerosol particles originating from wood combustion have a radiocarbon fraction of 110 pMC on average. This should be accounted for during the calculations. Therefore, to calculate the biogenic carbon fraction (f_C , contemporary carbon) of firewood, the f_M (fraction Modern) result measured as modern carbon content has to be corrected for with a factor of 1.10 due to the nuclear bomb peak preserved in the wood (Szidat et al., 2006, 2009):

$$f_C = f_M / 1.1$$

The f_f value, i.e. the extent of the fossil carbon fraction is determined from the f_C value in a way that the carbon being not of firewood or modern biogenic origin in the aerosol, is considered to be that of fossil origin (Levin and Hesshaimer, 2000):

$$f_f = 1 - f_C = 1 - f_M / 1.1$$

III. Results and discussion

III.1 Comparison of the sample preparation methods

The results of the different preparations of the $\text{PM}_{2.5}$ aerosol fraction collected during the winter of 2010 in Debrecen are depicted in Figure 1. Although there is a year difference between the preparation in Switzerland and that in Debrecen and the steps of the preparation methods are also significantly different, on the basis of the results, the two preparation methods showed identical and correct values. The reproducibility of the Swiss method was tested by the parallel preparation of the samples in 2012 showing the same results within error margin. During the preparation procedure in Debrecen, 2011, aerosol samples were combusted online in a dedicated combustion system where the total duration of the aerosol combustion and the purification

of the produced CO₂ were effectively reduced from 1 day below 1 hour. It was proved that from the graphite produced by the sealed tube graphitisation method is of the same quality as that by the hydrogen reduction method thought to be better and requiring a difficult gas and sample treatment system.

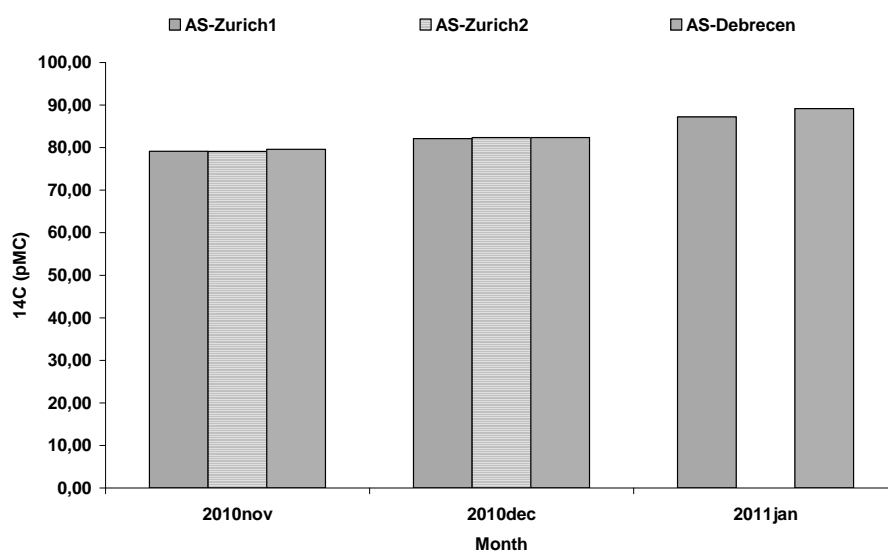


Figure 1. Results of the comparative measurements on the atmospheric carbonaceous aerosols measured by the MICADAS and expressed in pMC.

III.2 Results of the aerosol source apportionment

In this study it was attempted after testing our sample preparation method to differentiate between the monthly carbonaceous aerosols of modern biological and those of fossil origin. The whole amount of the aerosol is made up by components from several different sources, therefore, besides the carbonaceous organic and elemental carbon (OC+EC=TC) many inorganic constituents (ions, salts) contribute to the total aerosol mass, as well. The absolute quantity and their ratios of these components for a given month relative to 1 m³ air are influenced by many factors (enclosure of the sampling location, meteorological conditions etc.), therefore, changes are hard to predict (Figure 2).

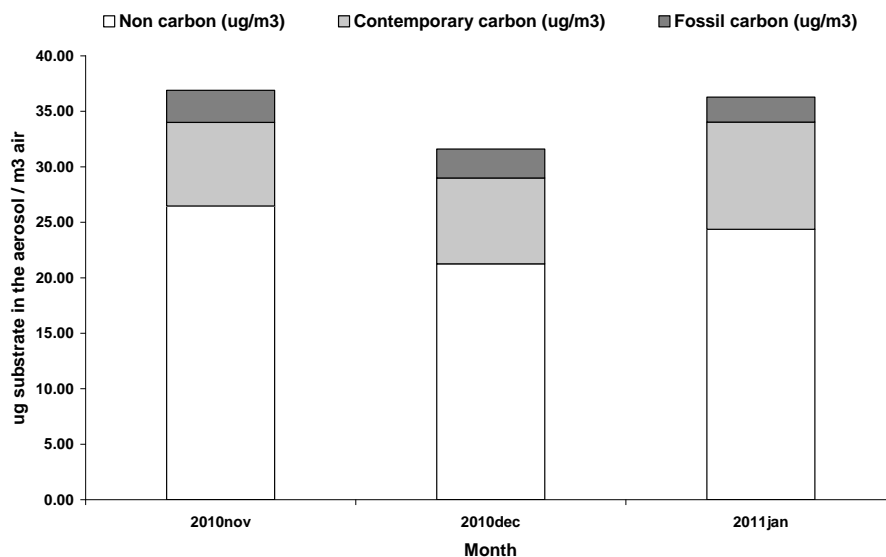


Figure 2. Concentration ratios of the atmospheric carbonaceous aerosols of non-carbon, modern carbon and fossil carbon origin in the sampling period.

After the $\sim 36 \text{ mg/m}^3$ value in November 2010 a slight decrease can be observed in December showing an increase in January again.

Considering the quantity of carbon, no significant change was observed in the first monitoring period, however, in January 2011 a slight increase was seen (Figure 3).

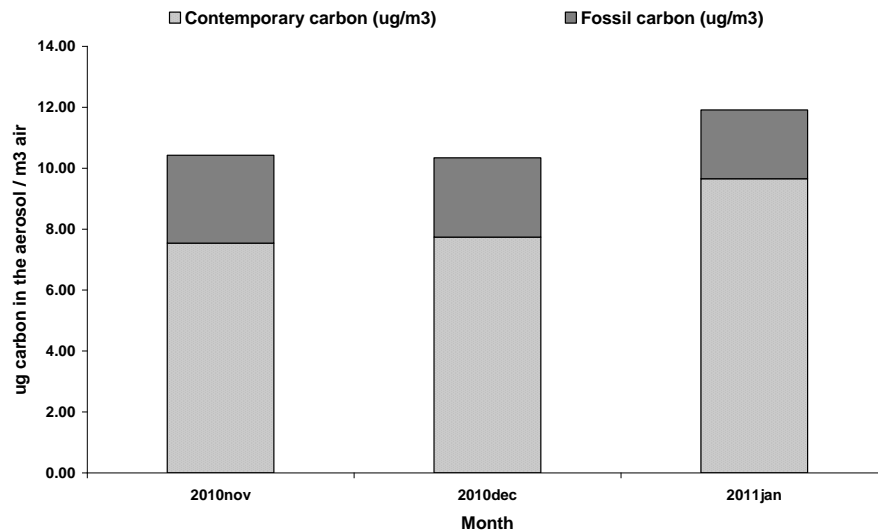


Figure 3. Quantities of the modern and fossil carbon making up the total carbon of the atmospheric aerosol, during the three monitoring months.

Depicting the contemporary (f_C) and the fossil (f_F) fractions, it is clearly seen that the current carbon contribution influencing the f_C value shows a progressively increasing trend towards the end of winter. This means that the contribution of the public wood combustion gets larger and larger compared to the carbon and gas combustion and the emission of the traffic both considered to be fossil sources. This would be right the opposite of the change observed lately in the concentration of the atmospheric CO_2 . While gas heating getting more and more widespread in winters significantly increases the fossil fraction of the atmospheric CO_2 , however it hardly emits aerosols; wood combustion, a very common heating method is accompanied with very intensive aerosol formation significantly increasing the fraction of modern biological origin of the atmospheric aerosol. To understand the changes in the absolute aerosol and carbon concentration, a database covering a whole year is necessary.

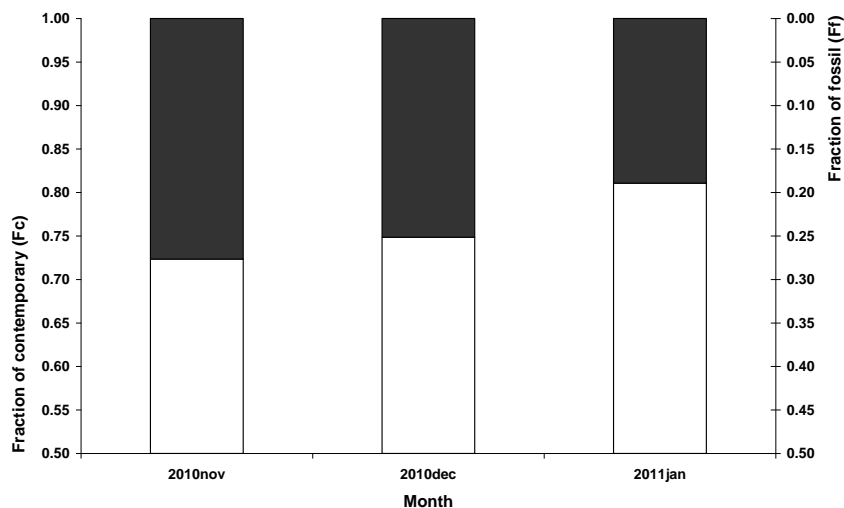


Figure 4. Calculated f_C and f_F values for each month.

IV. Conclusions

Owing to our preparation method based on the routine preparation method applied in Switzerland we decreased the one-day-long preparation below 1 hour. We proved that the sealed tube graphitisation produces graphite of the same quality for target production as the hydrogen reduction method thought to be better and requiring difficult gas and sample treatment system.

We made the first attempts to differentiate between the modern biological and the fossil contribution to the monthly atmospheric carbonaceous aerosol. From the first observations it is obtained that the modern carbon source from the public wood combustion has a larger and larger contribution to the total carbon in aerosols than the fossil source from the emissions of the carbon and gas combustion and the public traffic. To understand the changes in the absolute aerosol and carbon concentration, a database covering a whole year is necessary.

V. Acknowledgments

This work was performed in part of the New Hungary Development Plan under Project No. GOP-2.1.1-09/A-2009-2008 and GOP-1.3.1-09/A-2009-

0032. This publication is supported by OTKA and NDA (NFÜ) contact number MB08-A 81515 and TÁMOP-4.2.2/B-10/1-2010-0024 project. The project is co-financed by the European Union and the European Social Fund.

References

[1] Bench, G., Fallon, S., Schichtel, B., Malm, W., McDade, C. (2007). Relative contributions of fossil and contemporary carbon sources to PM_{2.5} aerosols at nine Interagency Monitoring for Protection of Visual Environments (IMPROVE) network sites. *Journal of Geophysical Research* 112, D10205, 2007. doi:10.1029/2006JD007708.

[2] Castro, L.M., Pio, C.A., Harrison, R.M., Smith, D.J.T. (1999). Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. *Atmospheric Environment* 33, 2771-2781.

[3] Currie, L.A., Klouda, G.A., Cooper, J.A. (1980). Mini-radiocarbon measurements, chemical selectivity, and the impact of man on environmental pollution and climate. *Radiocarbon* 22, 349-362.

[4] Currie, L.A. et al. ((1983). On the origin of carbonaceous particles in American cities: results of radiocarbon "dating" and chemical characterization. *Radiocarbon* 25, 603-614.

[5] Endo, M., Yamamoto, N., Yoshinaga, J., Yanagisawa, Y., Endo, O., Goto, S., Yoneda, M., Shibata, Y., Morita, M. (2004). C-14 measurements for size-fractionated airborne particulate matters. *Atmospheric Environment* 38, 6263-6267.

[6] Lawson, E.M., Elliott, G., Fallon, J., Fink, D., Hotchkis, M.A.C., Hua, Q., Jacobsen, G.E., Lee, P., Smith, A.M., Tuniz, C., Zoppi, U., (2000).

AMS at ANTARES—The first 10 years. *Nuclear Instruments and Methods in Physics Research B* 172, 95–99.

[7] Levin, I., Hesshaimer, V. (2000). Radiocarbon- a unique tracer of global carbon cycle dynamics. *Radiocarbon* 42, 69-80.

[8] Molnár M., Haszpra L., Svingor É., Major I., Svetlik I. (2010). Atmospheric fossil fuel CO₂ measurement using a field unit in a central European city during the winter of 2008/09. *Radiocarbon* 52, Nr. 2-3, p 835-845.

[9] Novakov, T., Hegg, D.A., Hobbs, P.V. (1997). Airborne measurements of carbonaceous aerosols on the East Coast of the United States. *J. Geophys. Res.-Atmos.* 102, 30023-30030.

[10] Rinyu, L., Molnár, M., Major, I., Nagy, T., Veres, M., Kimák, Á., Wacker, L., Synal, H.A.: Optimization of sealed tube graphitization method for environmental C-14 studies using MICADAS. *Nuclear Instruments and Methods in Physics Research Section B*. 2012 in press.

[11] Ramanathan, V., Crutzen, P., Kiehl, J., Rosenfeld D. (2001). Aerosols, climate and the hydrological cycle. *Science* 294, 2119.

[12] Szidat, S., Jenk, T.M., Synal, H.A., Kalberer, M., Wacker, L., Hajdas I., Kasper-Gielb A., Baltensperger U. (2006). Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by ¹⁴C. *Journal of Geophysical Research* 111, D07206. doi:10.1029/2005JD006590.

[13] Szidat, S., Ruff, M., Perron, N., Wacker, L., Synal, H.A. , Hallquist, M., Shannigrahi, A .S., Yttri, K.E., Dye, C., Simpson, D., (2009). Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Goteborg, Sweden. *Atmospheric Chemistry and Physics* 9, 1521 -1535.

[14] Venkataraman, C., Habib, G., Eiguren-Fernandez, A., Miguel, A.H., Friedlander, S.K. (2005). Residential biofuels in south Asia: carbonaceous aerosol emission and climate impacts. *Science* 307, 1454-1456.

[15] Vogel, J.S., Southon, J.R., Nelson, D.E., Brown T.A. (1984). *Nucl. Instrum. Methods* B5289.

[16] Vogel, J.S. (1992). Rapid production of graphite without contamination for biomedical AMS. *Radiocarbon* 34, 344-350.

[17] Wacker, L., Nemeč, M., Bourquin, J. (2010). A revolutionary graphitisation system: Fully automated, compact and simple. *Nucl. Instrum. Meth. B.* 931-944