

## **WP3- NA3: In-situ chemical, physical and optical properties of aerosols**

### **Deliverable D3.19: Implementation of organic tracer measurements at European sites**

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Our original objective of Task 3.3b was to establish a set of common European Standard Operating Procedures (SOP) for sampling and subsequent analysis of a selection of organic tracers, and then to implement them at several ACTRIS sites for the purpose of organic aerosol (OA) source apportionment.

As noted already in D3.14 (M24, “Standardization of sampling and analysis of specific organic tracers”) and in the report for the MTR evaluation, it is not likely that this can actually be achieved in full within the ACTRIS time frame. Considerable progress has nevertheless been made towards this goal. Here, we summarize the achievements made until M36, discuss the obstacles that need to be overcome, as well as possible ways forward.

## **1 Background**

The objectives and tasks for WP3 Organic tracers can be summarized as follows:

- To develop standardized protocols (SOP) for sampling and quantification of organic tracers for source identification;
- To implement sampling and analysis of organic tracers for source identification.

The WP3 deliverables related to the work on Organic tracers are:

- Expert workshop on organic tracer measurements (D3.7, public report, M12)
- Standardization of sampling and analysis of specific organic tracers (D3.14, public report, M24)
- Implementation of organic tracer measurements at European sites (D3.19, public report, M36)

This deliverable (D3.19) is thus the final one of this WP3 task.

As for the first step, an “Expert workshop on organic tracer measurements” was held at JRC in Ispra 25-26 October 2011, and the recommendations of this meeting were reported as the first deliverable of this activity (D3.7, M12). These issues were then further discussed during the ACTRIS WP3 Meetings on Organic tracers in Leipzig 18 Oct 2012 (D3.14, M24) and in Athens 10 October 2013, as described in the minutes and presentations of those meetings.

Although SOPs do exist for various research groups within the EU, these differ in their respective details and are not straightforward to harmonize on the European scale. See D3.14 (M24, “Standardization of sampling and analysis of specific organic tracers”) for a more detailed discussion.

Our strategy is instead to suggest “Procedures of best practice” or “Draft SOPs”, and to test and implement them to the extent possible within ACTRIS. These “Draft SOPs” will be openly accessible from the ACTRIS web pages and refer to both sampling and analysis of specific organic tracers within ACTRIS, for a limited number of tracers.

## 2 Intercomparisons

Intercomparison studies are essential elements of ACTRIS, since they are the tool by which to determine the applicability of a certain SOP across the ACTRIS network. Ideally, all suggested SOPs for organic tracers should be subjected to regular intercomparison studies, as is the case already for OC/EC. Such an endeavor for organic tracers would be very time-consuming and costly, and is not the aim of ACTRIS. Nevertheless, two intercomparison studies for organic tracers have been performed within ACTRIS. Both of these (for levoglucosan and  $^{14}\text{C}$ ) were carried out with the intention to prepare for setting up new SOPs, and not to test already established SOPs.

### **Anhydrous sugars as biomass burning tracers**

An intercomparison exercise for the anhydrous sugars (levoglucosan, mannosan, galactosan) was carried out among the ACTRIS partners involved, organized by INERIS, FR (Stephane Verlhac and Alexandre Albinet). This intercomparison was overall very successful. Considering also the previous (EU FP6 I3 project) EUSAAR study for the same biomass burning tracers with largely the same partners participating (organized by: Karl Espen Yttri, NILU, NO), this means that we now have a solid basis to suggest SOPs for these compounds for various analytical techniques (GC, LC, HPAEC). None of these techniques was shown to be superior to the others. The results of both these intercomparisons will be further disseminated in peer-reviewed papers.

There will be no other intercomparison study for these compounds with ACTRIS. Instead, this should be the task of the follow-up of ACTRIS.

### ***ACTRIS conclusion from intercomparison studies of anhydrous sugars***

There is adequate information regarding the interlaboratory applicability and suitability of anhydrous sugars (levoglucosan, mannosan, galactosan) as tracers for biomass burning for ACTRIS to suggest Draft SOPs for these compounds using GC, LC and HPAEC analytical techniques.

### **Radiocarbon as tracer for modern versus fossil carbon**

A radiocarbon intercomparison study was organized by Sönke Szidat at the University of Bern, CH, and is now published (Szidat et al, Radiocarbon, 2013). The outcome is quite satisfactory for  $^{14}\text{C}$  in TC, but less encouraging for EC due to the difficulties in avoiding contamination of the EC fraction. Several methods for OC/EC separation prior to  $^{14}\text{C}$  analysis have been suggested. Due to time constraints, there will be no additional radiocarbon intercomparison within EU FP7 ACTRIS. Nor were there any such plans within Task 3.3b.

There are only two groups in ACTRIS that are capable of actually performing  $^{14}\text{C}$  analysis on aerosol samples themselves (ULUND and PSI through University of Bern). These two groups employ different SOPs (graphitization versus gas ion source; analysis on TC only versus separation of OC/EC prior to analysis). As a consequence, ACTRIS is recommending two different SOPs, one for sample graphitization for use in a normal ion source followed by  $^{14}\text{C}$  analysis mainly on TC, and the other for a gas ion source and  $^{14}\text{C}$  analysis on both TC and on OC/EC separately.

### ***ACTRIS conclusion from intercomparison studies of radiocarbon***

There is adequate information from the radiocarbon intercomparison study for ACTRIS to suggest Draft SOPs for analysis of  $^{14}\text{C}$  as tracer for the fraction of modern versus fossil carbon in the organic aerosol. SOPs are given for the analytical procedures for graphitization (normal ion source followed by  $^{14}\text{C}$  analysis on TC) and for a gas ion source and  $^{14}\text{C}$  analysis of OC/EC separately.

### **Other organic tracers**

No intercomparison exercise was carried out for the other organic tracers that were discussed within ACTRIS, nor was it the intention to do so. There is definitely a need to perform such intercomparisons in the future, beyond the EU FP7 ACTRIS project timeframe.

### 3 SOPs for sampling of organic tracers

Low-volume sampling is often preferred simply because ACTRIS sites already collect aerosols on quartz filters for OC/EC analysis using low volume flow rates. However, the analysis of some organic tracers require that fairly large quantities of OA mass is sampled. For these reasons, ACTRIS need to recommend sampling SOPs for both these types of sampling.

#### Low-volume OA sampling

##### ***ACTRIS recommendation for low-volume sampling prior to OA tracer analysis***

For all OA analytic methods for which a low-volume sampler is adequate, ACTRIS recommends that the EUSAAR OC/EC sampling train and sampling protocol is used, as described in Cavalli et al (2010), and available at

<http://www.actris.net/language/en-GB/ProjectResults/QualityStandards.aspx>

under “In-situ aerosol measurements” and “OC/EC and organic tracers”.

#### Motivation

There is no need to develop a new sampling SOP for this purpose. The main reasons are:

- The EUSAAR OC/EC sampling train has been tested repeatedly for artefacts within ACTRIS;
- Several organic analyses can be performed on the same quartz fibre filter.

The 47 mm quartz fibre filter will then have to be shared between the analytical techniques. Within ACTRIS, this has been implemented and shown to work for a combination of OA tracers, for instance for OC/EC, levoglucosan, <sup>14</sup>C, and selected SOA products (Genberg et al ,2011; Hyder et al 2012).

#### High-volume OA sampling

##### ***ACTRIS recommendation for high-volume sampling prior to OA tracer analysis***

For the OA analytic methods for which a high-volume sampler is required, ACTRIS concludes that a denuder is not needed during the cold season.

ACTRIS is recommending an SOP for high-volume sampling of organic compounds for the purpose of OA source apportionment, providing details on sample handling and storage.

#### Motivation

A prototype High-Flow Atmospheric Denuder (HFAD) system for high-volume sampling was tested within ACTRIS (LGGE and LCME, France). Parallel sampling with Hi-Vol samplers with and without activated carbon denuders were performed during the winter 2012-2013, and the samples were analyzed for a range of chemical species, including several tracers under consideration within ACTRIS.

The field tests show that no, or very little, denuder effect was observed. If anything, the results imply that there seems to be lower artefacts for high-volume sampling than for low-volume sampling!

On the basis of this study, our judgement is that ACTRIS is not recommending the use of a denuder for high-volume sampling of organic compounds for the purpose of OA source apportionment. There is, however, a need to follow up on this study, especially with more denuder tests in summer conditions.

### 4 SOPs on organic tracers suggested by ACTRIS

For a more detailed discussion on the selection of OA tracers for apportionment to various sources, see D3.14 (M24, “Standardization of sampling and analysis of specific organic tracers”).

All ACTRIS partner (including associated partners) were requested to send their SOPs to the WP3 Organic Tracer Task Leader Erik Swietlicki (ULUND), in whatever form they may exist. SOPs for both sampling and analytical procedures are of interest. Comments regarding the experience gained on the usage of the SOPs were also collected. As noted, there will typically be several SOPs for each organic tracer. This compilation of SOPs was discussed at the 3rd ACTRIS WP3 Technical Meeting in Athens 10 October 2013, and serves as a basis for the Draft SOPs suggested within ACTRIS.

SOPs for (i) high-volume sampling, analysis of (ii) anhydrous sugars, (iii) arabitol, mannitol and trehalose, (iv) PAHs, (v) hopanes and steranes, (vi) organic acids, (vii) organosulfates and (viii) radiocarbon were received. For many of these OA tracers, several SOPs were collected using different analytical techniques.

A template for the Draft SOPs on OA tracers was prepared, using the received SOPs as inspiration. The various SOPs were modified to adhere to the format of this template. An example of this template is given as an appendix to this Deliverable.

The SOPs that are recommended by EU FP7 ACTRIS Task 3.3b are available on the ACTRIS public web site, under "Quality Standards", and further under "In-situ aerosol measurements" and "OC/EC and organic tracers".

<http://www.actris.net/language/en-GB/ProjectResults/QualityStandards.aspx>

This public web location is **openly accessible to all potential users**, not only ACTRIS partners and associates.

Draft SOPs will be added to this location up until the end of the EU FP7 ACTRIS project. Decisions will be made by the Task 3.3b community and Task Leader for each OA tracer and analytical technique on how best to condense the various submitted partner SOPs into succinct Draft SOPs adhering to the template.

In some cases, a single analytical protocol can be used for the analysis of several OA tracers, as for GC-MS analysis of both PAHs and hopanes. This will be made evident to the potential users.

## 5 Implementation at European field sites

During ACTRIS, sampling and analysis of OA tracers for the purpose of OA source apportionment was performed at a large number of sites in Europe in connection to several field campaigns and projects.

ACTRIS could provide only very limited funding for the active participation in these studies. Instead, these studies were made possible only by support from other EU FP7 projects or national funding sources. ACTRIS Task 3.3b actively encouraged all ACTRIS partners and associates to take part. We further collaborated with the various institutes that were coordinating the study in question, for maximum efficiency and mutual benefit. We also recommended that suggested ACTRIS SOPs should be used whenever possible.

Note that the decision whether to take part or not in the OA source apportionment studies was up to the individual ACTRIS partner or associate, and that neither the ACTRIS WP3 Leader nor the Task 3.3b Leader had any means of forcing active participation. Fortunately, the compilation below clearly shows that ACTRIS partners and associates have been very active in this respect.

### **ACTRIS participation in the EMEP intensive measurement periods (EIMPS 2012/2013)**

One important outcome of the work on OA tracers for source apportionment would be that the ACTRIS SOPs are implemented within the EMEP station network. Obvious candidates for implementation are those sites that are both active as EMEP and ACTRIS sites, and therefore operate on a more advanced and extensive measurement schedule.

Several ACTRIS partners and associates took part in either or both of the EMEP intensive measurement periods (EIMPS) in June – July 2012 and January – February 2013. These represent a major effort to conduct European-scale coordinated aerosol measurements and to perform OA source apportionment.

Coordination was made with NILU (Wenche Aas) for the overall EIMPS operation and André Prevot (PSI) specifically for the AMS measurements during these campaigns.

The following sites were operated by ACTRIS partners and associates during the two EIMPS:

Summer 2012 (14 sites)

- Birkenes (NO), Houdelaincourt (FR), Hyytiälä (FIN), JRC-Ispra (IT), Melpitz (DE), Monseny (ES), Monte Cimone (IT), Montelibretti (IT), NEO (GR), Puy de Dôme (FR), Revin (FR), San Pietro Capofiume (IT), SIRTA (FR), Vavihill (SE).

Winter 2013 (16 sites)

- Birkenes (NO), Cabauw (NL), Houdelaincourt (FR), Hyytiälä (FIN), JRC-Ispra (IT), K-puszta (HU), Melpitz (DE), Monseny (ES), Monte Cimone (IT), Montelibretti (IT), NEO (GR), Puy de Dôme (FR), Revin (FR), San Pietro Capofiume (IT), SIRTA (FR), Vavihill (SE).

A more complete list of participating sites including also the specifics of each sampling can be obtained from Wenche Aas at NILU ([Wenche.Aas@nilu.no](mailto:Wenche.Aas@nilu.no)).

In addition, a number of sites operated an ACSM or AMS during the two EMEP intensive measurements campaigns as part of ACTRIS. A comprehensive overview (compiled by Roman Fröhlich at PSI) is given at:

<http://www.psi.ch/acsm-stations/overview-full-period>

These ACSM and AMS data will be analyzed using the PMF (ME-2) source receptor model, according to the methodology described by Crippa et al. (2014).

For more details on the Aerosol Mass Spectrometers (ACSM and AMS), we refer to ACTRIS JRA2 (WP21, Task 21.1 Aerosol Chemistry; Lead: PSI). SOPs for ACSM/AMS measurements are being developed within ACTRIS JRA2.

The Aerosol Mass Spectrometers employed in ACTRIS are capable of quantifying the impact of several important primary OA sources (Hydrocarbon-like OA, biomass burning, cooking OA), as well as the contribution of aged secondary OA (low-volatile and semi-volatile oxygenated OA, marine secondary OA). These measurements therefore constitute a significant contribution to European OA source apportionment studies, highly complementary to the work on OA tracers within Task 3.3b.

### **ACTRIS participation in other intensive measurement periods (EU or national projects)**

ACTRIS partners and associates were also taking part in EU FP7 projects or national projects, performing OA sampling and source apportionment. Funding from these sources actually made it possible for ACTRIS partners to participate in the EIMPS.

OA source apportionment was performed within:

- EU FP7 **PEGASOS** (Pan-European gas-aerosols-climate interaction study)
- EU FP7 **MEGAPOLI** (Megacities: Emissions, urban, regional, global atmospheric pollution and climate effects, and integrated tools for assessment and mitigation)

The French ACTRIS community working with OA tracers and source apportionment is very active, and several French projects were supporting ACTRIS in this respect. These include:

- **ChArMEx** (Chemistry-Aerosol Mediterranean Experiment)
- **FORMES** (ORganic Fraction of urban aerosols: Source apportionment MEthod)
- **Particul'Air** (Inter-Regional study of the particulate pollution in rural air, in collaboration with air quality networks)
- **CAMERA** and **ANDRA** (Long-term monitoring programs French in rural background, > 3 years, 1 filter/week)

- **APICE** (Marine site ; Common Mediterranean strategy and local practical Actions for the mitigation of Port, Industries and Cities Emissions)
- **Part'Aera** (Intereg program Rhône-Alpes ; PACA ; Lombardia ; Liguria) 1 year sampling 1d / 3
- **Research studies in collaboration with French Air Quality Networks** and LCSQA (Laboratoire Central de Surveillance de la Qualité de l'Air) (at 3 French Alpine valley sites, in Lens, Lyon, Bordeaux, Nice, Marseille (Waked et al., 2014)

During these French campaigns, the same SOPs for filter sampling and subsequent tracer analyses that form the basis for the SOPs suggested by ACTRIS were implemented, which means that their suitability for field studies at a wide range of concentrations has been tested extensively.

Studies with Nordic funding (**SORGA, SONORA, BCNOR**) have also been conducted, and some of the results are already published (Genberg et al ACP(2011), Yttri et al, ACP(2011a,b). These studies also tested the suggested ACTRIS SOPs, and at fairly low OA concentrations.

These examples show that

- ACTRIS partners and associates are dedicated to the task of OA source apportionment;
- Considerable funding resources outside ACTRIS were utilized in full to support ACTRIS Task 3.3b;
- Coordination of efforts across Europe is essential to ensure geographical coverage and intercomparability;
- EMEP relies on the support of ACTRIS scientists regarding OA source apportionment.

The vast amount of data and experience on OA tracer sampling, analysis and applicability for source apportionment purposes that has been gained with the ACTRIS timeframe needs to be digested further. It is obvious that this will not be possible within the EU FP7 ACTRIS project, but requires follow-up work. Nevertheless, the experience gained will be used to the largest extent possible to add credibility to the suggested ACTRIS SOPs on OA tracers.

## 6 Possible ways forward

### Remaining issues beyond EU FP7 ACTRIS

Our original objectives of Task 3.3b are not likely to be met in full. In retrospect, our level of ambition was somewhat too high given the timeframe and resources available in EU FP7 ACTRIS. Considerable progress has nevertheless been made, as described in the Task 3.3b Deliverables D3.7, D3.14 and D3.19.

There are still issues that need to be resolved, and that have hampered firm decisions in ACTRIS:

- There is a large number of optional organic tracers that need to be considered;
- There is a lack of suitable reference material for several of the optional organic tracers;
- There are a multitude of suitable analytical techniques available for each organic tracer;
- There exists separate SOPs for each analytical technique and each organic tracer in use in Europe today;
- There is a lack of intercomparison studies ensuring the credibility of organic tracer analyses;
- Organic analytical techniques are rapidly evolving to become more sensitive, accurate and reliable, and at the same time less time-consuming.

Future work also need to consider the general criteria for suitable organic tracer compounds in that they should:

- be unique to a specific source and emitted in sufficient quantities from this source;
- be possible to sample and analyze with reasonable accuracy, precision and cost;
- have low vapour pressures (so that they partition preferentially to the particle phase);

- be stable during atmospheric transport (at least a lifetime of a few days in the particle phase), or alternatively that the degradation can be estimated in a straightforward and reliable manner.

Further considerations for selecting the SOP basically deal with ease-of-use and affordability and include:

- Minimum sample preparation required;
- Low consumption of consumables (chemicals etc.);
- Equipment available in most laboratories involved, alternatively;
- Moderate cost of purchase of the required analytical equipment (multiple manufacturers);
- Cost-effective analysis;
- Simple-to-use analytical protocol;
- Simple calibration and quantification methods available;
- Fast and automatic analysis (low labour intensity);
- Versatility (possible to use the method to analyze also other OA tracers simultaneously).

This work is time-consuming and will most likely be iterative, in the sense that SOPs will be updated at irregular time intervals as new knowledge and analytical techniques appear.

#### **Suggestion for further work on intercomparisons beyond EU FP7 ACTRIS**

As already noted, regular intercomparison studies are needed in order to ensure intercomparability between laboratories and to gain credibility for the organic tracer data to be used as basis for OA source apportionment in Europe. Future work, beyond the EU FP7 ACTRIS timeframe, should therefore have the ambition to perform such intercomparison exercises for all tracer compounds for which SOPs are suggested. Only after such efforts will the OA tracer data be fully applicable on the European scale, and the SOPs likely to be extensively implemented throughout a wide-ranging station network. The case of OC/EC can serve as a good example of how it can be done (although not directly comparable to organic tracers that are well-defined compounds and not operationally defined as OC/EC).

One suggested way forward would be to organize a selection of laboratories, each of which committed to performing intercomparisons for a specific OA tracer. These laboratories could for instance each be focusing on (i) OC/EC, (ii) anhydrous sugars (levoglucosan, mannosan, galactosan), (iii) carbon isotopes ( $^{14}\text{C}$  and  $^{13}\text{C}$ ), and (iv) other OA tracers (need to be defined which). Resources would have to be allocated to this effort, which is both time-consuming and costly.

As is the case for the **anhydrous sugars**, none of the analytical techniques could be shown to be outperforming the others. For this reason, and since we also strive to include as many laboratories in Europe as possible, we suggest several Draft SOPs. To qualify, all of these must have participated in at least one of the intercomparison studies with satisfactory results. Future work needs to re-examine whether it would indeed be more beneficial to recommend only one technique for a specific set of OA tracers, such as for the anhydrous sugars. Novel analytical approaches should be considered as well.

As for the **radiocarbon**, there is definitely more work to be done on EC/OC separation prior to  $^{14}\text{C}$  analysis. This has proven to be an exceedingly tricky task, and has not been fully solved despite year-long efforts. Future intercomparisons would then need to focus on  $^{14}\text{C}$  analysis of the separate OC and EC fractions in order to closely examine our ability to deliver credible data on the mass fractions of modern versus fossil carbon in each of the separate fractions. An exact definition of what the OC/EC fractions actually incorporate is also pending, but should closely resemble the OC/EC split resulting from the EUSAAR-2 protocol for thermo-optical OC/EC analysis, since these OC and EC concentrations are what we aim to apportion to their various sources. Novel separation approaches also need to be developed, which is a research task in itself.

Much work remains on the **other OA tracers** that are under consideration. Once the tracer selection has been made, intercomparisons need to be carried also for these. The EU FP7 ACTRIS is only recommending Draft SOPs for a few additional tracers, but we lack data on the inter-laboratory comparability.

## References

- Cavalli et al. Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. *Atmos. Meas. Tech.*, 3, 79-89, 2010, doi:10.5194/amt-3-79-2010.
- Crippa, M., F. Canonaco, V. A. Lanz, M. Äijälä, J. D. Allan, S. Carbone, G. Capes, M. Dall'Osto, D. A. Day, P. F. DeCarlo, C. F. Di Marco, M. Ehn, A. Eriksson, E. Freney, L. Hildebrandt Ruiz, R. Hillamo, J.-L. Jimenez, H. Junninen, A. Kiendler-Scharr, A.-M. Kortelainen, M. Kulmala, A. A. Mensah, C. Mohr, E. Nemitz, C. O'Dowd, J. Ovadnevaite, S. N. Pandis, T. Petäjä, L. Poulain, S. Saarikoski, K. Sellegri, E. Swietlicki, P. Tiitta, D. R. Worsnop, U. Baltensperger, and A. S. H. Prévôt. Organic aerosol components derived from 25 AMS datasets across Europe using a newly developed ME-2 based source apportionment strategy. *Atmos. Chem. Phys. Discuss.*, 13, 23325-23371, 2013 (Accepted in ACP)
- Genberg, J., M. Hyder, K. Stenström, R. Bergström, D. Simpson, E. Fors, J. Å. Jönsson, and E. Swietlicki. Source apportionment of carbonaceous aerosol in southern Sweden. *Atmos. Chem. Phys.*, 11, 11387-11400, 2011.
- Hyder, M; Genberg, J; Sandahl, M; Swietlicki, E; Jönsson, J.Å. Yearly trend of dicarboxylic acids in organic aerosols from south of Sweden and source attribution. *Atmospheric Environment* 57(2012) 197-204.
- Szidat S, Bench G, Bernardoni V, Calzolari G, Czimczik C I, Derendorp L, Dusek U, Elder K, Fedi M E, Genberg J, Gustafsson Ö, Kirillova E, Kondo M., McNichol A P, Perron N, Santos G M, Stenström K, Swietlicki E, Uchida M, Vecchi R, Wacker L, Zhang Y L, Prévôt A.S.H. Intercomparison of <sup>14</sup>C analysis of carbonaceous aerosols: Exercise 2009. *Radiocarbon* 55(2013)1496-1509
- Waked A, Favez O, Alleman LY, Piot C, Petit JE, Delaunay T, Golly B, Besombes JL, Jaffrezo JL, and Leoz-Garziandia E (2014) Source apportionment of PM<sub>10</sub> in an urban site using a PMF model applied on inorganic and organic chemical species. *Atmos. Chem. Phys.*, 14, 3325-3346.
- Yttri, K.E., Simpson, D., Stenström, K., Puxbaum, H., Svendby, T. (2011) Source apportionment of the carbonaceous aerosol in Norway - quantitative estimates based on <sup>14</sup>C, thermal-optical and organic tracer analysis. *Atmos. Chem. Phys.*, 11, 9375-9394. doi:10.5194/acp-11-9375-2011.
- Yttri, K.E., D. Simpson, J. K. Nøjgaard, K. Kristensen, J. Genberg, K. Stenström, E. Swietlicki, R. Hillamo, M. Aurela, H. Bauer, J. H. Offenberg, M. Jaoui, C. Dye, S. Eckhardt, J. F. Burkhardt, A. Stohl, and M. Glasius. Source apportionment of the summer time carbonaceous aerosol at Nordic rural background sites. *Atmos. Chem. Phys.*, 11, 13339-13357, 2011



## Appendix D3.19-A

An example of a Draft ACTRIS SOP using the format of the suggested template. The example is for HPLC-PAD analysis of anhydrous sugars and is currently used by LGGE, Grenoble, FR.

### Protocol for HPLC-PAD analysis of levoglucosan & its isomers.

#### Objective

In aerosol studies, source appointment of different pollutants has always been an area of interest. Levoglucosan is a well-known organic tracer in the context of biomass burning. Its quantification can help estimate the role of biomass burning in depleting the air quality.

#### Application

HPLC-PAD is an ultra-sensitive technique. It can be used to separate and quantify levoglucosan & its isomers present in atmospheric samples. Steps involving extraction and sample preparation are relatively easy since no derivatization is required. The technique is also more green & environment friendly as it employs little use of organic solvents. The efficiency of this method has also been reported as good.

#### Extraction protocol for aerosol filter samples

A punch of filter is cut in slices using a clean surgical knife and soaked in a specific volume of ultrapure water for 20 min in polypropylene centrifuge tube placed in a vortex shaker. The tubes are rinsed in ultrapure water before use and are close with their polyethylene sealing caps during extraction. The extract is then filtered using disposable Acrodisc filters (Millipore Millex-EIMF) with a porosity of 0.22 $\mu$ m. The Acrodisc are rinsed with 80 ml of ultrapure water before use. These extractions are stored at low temperature (6°C or below) until analysis. Extraction efficiencies were close to 100 % in these conditions.

Standard conditions for the extractions of background rural atmospheric samples are of a punch of 38 mm in diameter (11.34 cm<sup>2</sup>) extracted in 8 ml of ultrapure water.

#### Instrumental description

The equipment used for analysis is composed of:

- Pump: DX500 from Dionex
- Detector: Pulse amperometric detector (PAD), ED 40 with a gold measure electrode and an Ag/AgCl reference electrode from Dionex
- Column oven: LC 30 oven with Rheodyne valve
- Injection loop: 250  $\mu$ L
- Autosampler: autosampler "AS-950" from Jasco
- Control software: Chroméléon

Analyses are performed with a set of separation columns from Metrohm:

- Guard column: Metrosep Carb 1-Guard/4.0
- 1<sup>st</sup> separation column: Metrosep A Supp 15-150/4.0 (150 mm)
- 2<sup>nd</sup> separation column: Metrosep Carb 1-Guard/4.0 (150 mm)

- 3<sup>rd</sup> separation column: Metrosep Carb 1-Guard/4.0 (150 mm)

Eluents :

- Eluents are prepared from NaOH 50% (Prolabo) and degassed ultrapure water.
- Solution of NaOH (70mM) for the analysis
- Solution of NaOH (120 mM) for a gradient cleaning step.

#### Analytical conditions and program

- Flow: 0.52 ml.min<sup>-1</sup>
- Pressure: ≈ 1850 psi
- pH: 12.6
- Temperature of the columns : 30 °C

The analysis is composed in three stages:

- An analysis step: to 0 from 39 min with 100% of NaOH 70 mM
- A cleaning step: to 40 from 48 min with an eluent gradient until 120 mM
- A reconditioning step: to 49 from 60 min with 100% of NaOH 70 mM.

#### Carbohydrates in the standards

This technique allows the quantification (without known interferences from usual compounds in atmospheric samples) of 10 important carbohydrates interesting for atmospheric studies. The following table lists these 10 compounds, with their CAS number and the high and low concentrations for the standard mixes used for calibration, and their corresponding atmospheric concentration calculated according to the conditions described above. The chromatogram of a standard solution from the middle of this range (STD 3 ; 1250 ppb in levoglucosan) is presented in figure 1.

	Reference	Low range [ppb]	Atmospheric concentration [ng.m <sup>-3</sup> ]	High range [ppb]	Atmospheric concentration [ng.m <sup>-3</sup> ]
<b>Xylitol</b>	"Xylitol >99% (CAS 87-99-0, Fluka Biochemica)"	5	0.66	1000	131.96
<b>Arabitol</b>	"Arabitol (L-(-)-Arabitol) 98% (CAS 7643-75-6, Sigma-Aldrich, Steinheim, Germany)"	5	0.66	1000	131.96
<b>Sorbitol</b>	"D-Sorbitol >99,5% (CAS 50-70-4, Fluka Biochemica)"	2	0.26	400	52.79
<b>Mannitol</b>	"D-Mannitol >99,5% (CAS 69-65-8, Fluka Biochemica)"	5	0.66	1000	131.96
<b>Levoglucosan</b>	"1,6-Anhydro-b-D galactose 99% (CAS 498-07-7, Sigma-Aldrich, Steinheim, Germany)"	25	3.30	5000	659.82
<b>Mannosan</b>	"1,6-Anhydro-b-D mannopyranose (CAS 14168-65-1, abcr,Karlsruhe,	5	0.66	1000	131.96

	Germany)"				
<b>Galactosan</b>	"1,6-Anhydro-b-D galactose (CAS 644-76-8, Carbosynth, Compton, U.K.)"	2	0.26	400	52.79
<b>Glucose</b>	"D-(+)-Glucose anhydrous >99% (CAS 50-99-7, Fluka Biochemica)"	5	0.66	1000	131.96
<b>Fructose</b>	"D-Fructose >99% (CAS 57-48-7, Fluka Biochemica)"	20	2.64	4000	527.85
<b>Sucrose</b>	"D-(+)-Sucrose >99% (CAS 57-50-1, Fluka Biochemica)"	1.5	0.20	300	39.59

Table 1: Standard solutions with their CAS number and the high and low ranges of calibration

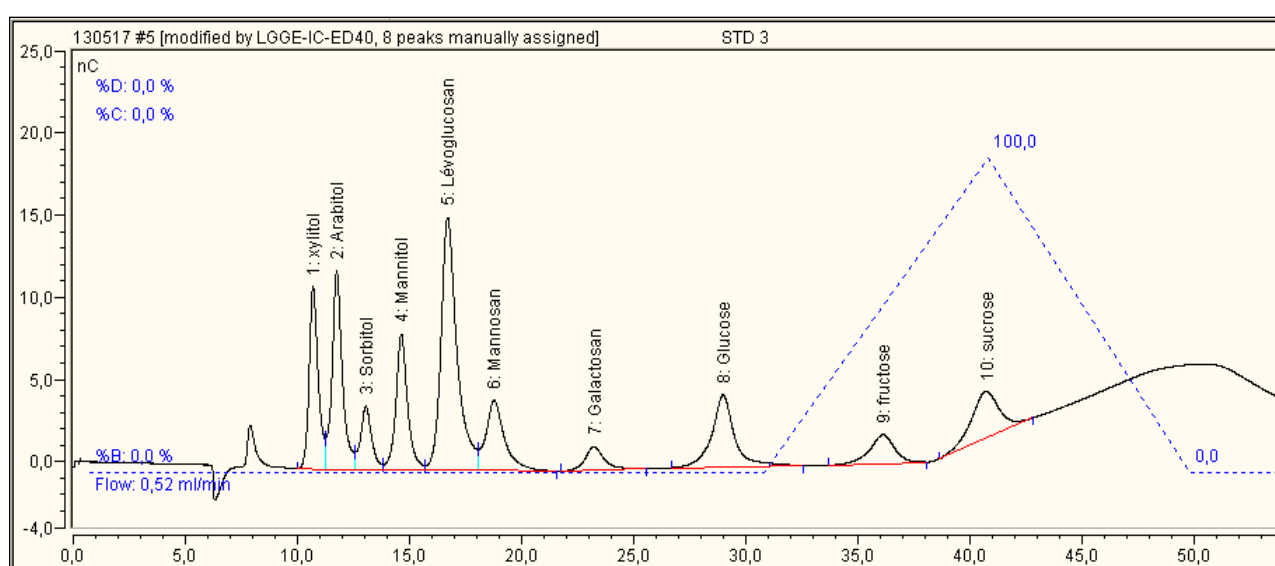


Figure 1: Chromatogram of a STD 3

### Data acquisition and processing

A typical analytical batch of 48 hours includes a couple of blank runs to stabilize the base line, followed by a series of 6 standards for calibration; 3 series of 10 samples plus 3 standards are subsequently analyzed. The chromatograms are integrated in Chromeleon using the height of the peaks and systematic manual check.

Samples with concentration of any compounds above the highest concentration of the calibration range are systematically diluted and reanalyzed because of potential interferences. Concentrations are not corrected for extraction efficiency. Procedures for a follow up of the quality of the overall analysis, including analysis of SRM, evaluation of the efficiency of the extraction, repeatability of injection, are performed on a regular basis (on average every two months).

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