# WP3- NA3: In-situ chemical, physical and optical properties of aerosols
# Deliverable D3.14: Standardization of the sampling and analysis of specific organic tracers

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Our original objective of this Deliverable was to establish a set of common European Standard Operating Procedures (SOP) for sampling and subsequent analysis of organic tracers. This has been shown to be premature for M24, for several reasons deliberated upon below. Instead, we summarize the achievements made until M24, and discuss 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)

These deliverables also outline the strategy of this WP3 task. First, information regarding the needs and current use of organic tracers in Europe is gathered. Secondly, this information serves as a basis for determining Standard Operating Procedures (SOP) for sampling and analysis of organic tracers. Thirdly, these SOPs are implemented at a number of ACTRIS sites across Europe.

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 Meeting on Organic tracers in Leipzig 18 Oct 2012, as described in the minutes of that meeting.

While this original three-step plan appears straightforward and clearly defined, there are several obstacles that became apparent during the initial phase of ACTRIS, and in particular during the two dedicated meetings in October 2011 and 2012. These obstacles can be summarized as follows:

- 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;
- Organic analytical techniques are rapidly evolving to become more sensitive, accurate and reliable, and at the same time less time-consuming.

Although SOPs do exist for various EU nations, these differ in their respective details and are not straightforward to harmonize on the European scale. Furthermore, both meetings dealing with organic tracers (October 2011 and 2012) debated whether SOPs should indeed be settled within the time frame of ACTRIS, since the field of analytical chemistry and organic aerosol analysis is rapidly developing. Fixing

operation procedures within Europe may actually hinder this development, which might then be detrimental for future studies on organic aerosols and their apportionment beyond the ACTRIS time frame.

These difficult issues are further discussed below.

Nevertheless, there is agreement within the ACTRIS community regarding several organic tracers that need to be further considered for development of SOPs and implementation at selected ACTRIS sites. These organic aerosol (OA) tracers are:

- **OC, EC**
  Method → Thermal-optical Analysis - EUSAAR-2 protocol
- **Biomass burning**: Levoglucosan (mannosan, galactosan)
  Methods → GC, LC and HPAEC
- **Modern/fossil carbon**: $^{14}C$ on TC (if possible on OC and EC separately)
  Method → AMS (Accelerator Mass Spectrometry)
- **Traffic (gasoline, diesel)**: PAH, hopanes, steranes
  Method → GC
- **Mass spectrometric group analysis, several sources**: (OC only)
  Method → ACSM, HR-TOF-AMS (Aerodyne)

In brief, the motivation for selecting these OA tracers can be summarized:

- OC and EC are the two basic OA components that each needs to be apportioned to their various sources;
- Biomass burning and traffic are the two dominating sources of primary anthropogenic OA in Europe;
- Radiocarbon ($^{14}C$) is unique as a tracer for the relative contribution of modern versus fossil carbon;
- The Aerosol Mass Spectrometer (AMS) is capable of quantifying the impact of, not only several important primary OA sources, but also the contribution of aged secondary OA.

The selected tracers naturally adhere to 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).

It should be noted that it is the aim of this WP3 activity to apportion only the carbonaceous aerosol material (expressed as OA, TC, OC, EC) and not PM (Particulate Matter given as PM10, PM2.5 or PM1).

## 2 Organic tracers for which SOPs will be developed

**Biomass burning tracers**

Biomass burning and wood combustion are the major sources of primary anthropogenic modern OA in Europe. As such, the selection of suitable organic tracers for this source category is essential for European OA source apportionment. The organic tracers for these sources may also serve to illustrate the complexity that ACTRIS WP3 is facing regarding the establishment of common European SOPs for organic tracers.

The anhydrous sugars (levoglucosan, mannosan, galactosan) are cellulose pyrolysis products and have been shown to be suitable as tracers for primary OA originating from biomass burning and wood combustion. Although well established as OA tracers, and accepted as such by the ACTRIS WP3 community, there are still remaining issues that hinder the development of a common European SOP for these compounds.

Levoglucosan, mannosan and galactosan, and several other primary OA tracers of biogenic origin, can all be analysed using a variety of methods, including:

- Derivatization followed by GC-MS
- LC-MS or other LC techniques
- HPAEC-PAD (High performance Anion Exchange Chromatography with Pulsed Amperometric Detection)

The advantages and disadvantages of the commonly used techniques are summarized in the table below (adopted from Y. Iinuma, TROPOS).

| | **HPAEC-PAD** | **Derivatization GC/MS** | **HPLC/ESI-MS** | **HPLC-Universal Detector (e.g. Corona CAD)** |
|---|---|---|---|---|
| Sample preparation | Easy and simple | Time-consuming and cumbersome | Pre-concentration necessary | Pre-concentration necessary |
| Ease of use | Easy | Steep learning curve | Easy | Easy |
| Sensitivity | Very high | High | Moderate | Low |
| Reproducibility | Good | Operator dependent | Reasonable | Reasonable |
| Monosaccharide selectivity | Universal | Universal | Selective | Universal |
| Running cost | Low | High | High | High |

Although this compilation of pros and cons appears to favour the use of HPAEC-PAD for these tracers, other laboratories in Europe employ GC or LC in various analytical protocols that also deliver reliable and accurate results. This became apparent when examining the outcome of the first ACTRIS levoglucosan intercomparison exercise, that was initiated during EU FP6 EUSAAR and evaluated within ACTRIS (Yttri et al, 2013; Manuscript in preparation; Lead partner NILU).

The main conclusions of this levoglucosan intercomparison exercise are:

- All major methods used for analysis of levoglucosan, mannosan and galactosan in ambient aerosol filter samples, and which have been reported in the scientific literature so far, are represented in the present intercomparison.

- Each of the (13) laboratories used a method that can be considered as a separate analytical operating procedure, since there were significant differences between laboratories when considering the entire protocol used in terms of sample preparation (extraction and derivatization), chromatographic technique and detection system.

- This great diversity prevents us from drawing conclusions regarding the relative performance of different sub-classes of analytical methods, e.g. GC versus LC based methods.

- None of the laboratories/methods could be shown to underperform in a way that would warrant this method to be ruled out from further discussions regarding a common European SOP for these compounds.

As in the case of levoglucosan, when none of the candidate analytical protocols appears to outperform the others, other criteria will have to be given more weight when deciding on the final SOP. All SOPs should of course fulfill the basic analytical requirements:

- High accuracy and precision;
- Adequate sensitivity for operation at European remote background sites with reasonable time resolution (days);
- Reproducibility.

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);
- Selectivity (possible to use the method to analyze also other OA tracers simultaneously).

For the anhydrous sugars, these additional criteria would seem to favour HPAEC-PAD (see table above). However, there is currently no consensus within the ACTRIS WP3 community for recommending this or any other analytical method for levoglucosan.

To further elucidate the situation for the anhydrous sugars (levoglucosan, mannosan, galactosan), it was decided at the ACTRIS WP3 Meeting on Organic tracers in Leipzig 18 Oct 2012 that yet another levoglucosan intercomparison exercise should be carried out among the ACTRIS partners involved. INERIS volunteered to lead this work, and have prepared the samples that were sent around. The final deadline for submitting results was set to 7 June 2013.

The follow-up intercomparison includes the same participants using the same analytical methods as during the previous intercomparison. It therefore has the potential to confirm the results from the previous intercomparison. In addition, it extends the number of variables to be tested; for instance by including a standard reference material, and aerosol filter samples collected during different seasons that are likely to reflect levoglucosan emitted from various sources (emissions from wild/agricultural fires and residential wood burning).

**Radiocarbon determination for fossil and modern aerosol carbon apportionment**

There is consensus within the ACTRIS WP3 community for recommending the use of radiocarbon ($^{14}C$), since it is a unique tracer for the relative contribution of modern versus fossil carbon in the atmospheric carbonaceous aerosol. It is thus one of the cornerstones of OA source apportionment.

Despite this, there is as yet no decision within ACTRIS regarding a recommended SOP for radiocarbon ($^{14}C$) analysis in aerosol samples. There is a present only two groups in ACTRIS that are capable of actually performing $^{14}C$ 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). The probable outcome is that ACTRIS will recommend two different SOPs, one for sample graphitization for use in a normal ion source followed by $^{14}C$ analysis on TC, and the other for a gas ion source and $^{14}C$ analysis of OC/EC separately.

An intercomparison for $^{14}C$ in TC, OC and EC was performed as part of ACTRIS WP3, although the exercise was initiated already during EU FP6 I3 EUSAAR and EU FP6 IP EUCAARI. The study was coordinated by Sönke Szidat (University of Bern). The results are presented in the peer-reviewed publication: Szidat et al, Intercomparison of $^{14}C$ analysis of carbonaceous aerosols: Exercise 2009. Radiocarbon, 2013, in press.

Nine laboratories participated, of which two are involved in ACTRIS. Each laboratory received two ambient samples collected on quartz fibre filters, in addition to a field blank and a reference material. It was observed that the NIST standard RM 8785 is not suitable for $^{14}C$ analysis, partly because the TC concentrations are too low. This standard also has an inhomogeneous filter loading, and even the EC/TC ratio was not constant.

For $^{14}C$ in TC, the results were considered acceptable for all participating groups. This means that for TC, the fraction modern carbon, $F^{14}C$, is within 0.015–0.025 for the ambient filters, and within 0.041 for RM 8785.

Only a few laboratories attempted to separate OC from EC prior to for $^{14}C$ analysis. There is currently no generally accepted method for this OC/EC separation, despite considerable efforts at several $^{14}C$ laboratories. In the intercomparison exercise, $^{14}C$ analysis of EC revealed a large deviation between the laboratories of 28-79% as a consequence of different OC/EC separation techniques. These results clearly points to the need for further discussion and work on optimal methods of EC isolation for $^{14}C$ analysis.

It should be noted that the EUSAAR-2 OC/EC thermo-optical separation protocol is unsuitable for this purpose, mainly since EC is typically a minor fraction of TC, and any contamination of OC (as pyrolized OC) into the EC fraction will severely distort the value of $F^{14}C$ in EC.

Since the actual $^{14}C$ measurements in this intercomparison were performed already in 2009, another exercise should be considered within ACTRIS. However, only two groups in ACTRIS are capable of actually performing $^{14}C$ analysis on aerosol samples, as already noted. Therefore, more $^{14}C$ laboratories outside ACTRIS need to be involved in such an intercomparison effort. European $^{14}C$ laboratories can also be encouraged to join ACTRIS as associated partners. The new intercomparison exercise should ideally include more groups that are able to perform $^{14}C$ analysis on EC and OC separately, which would be a major achievement for OA source apportionment. The Swiss Swis_4S method was suggested as an improved method for the OC/EC separation, and other methods have also been suggested and tested. As already mentioned, the separation of OC/EC prior to $^{14}C$ analysis has proven to be a very difficult analytical task.

No decision was taken by the ACTRIS community regarding the issue of yet another intercomparison, but it will be pursued further.

The $^{14}C$ analysis is now sensitive enough to allow the use of the SOP for (low-volume) sampling prior to thermo-optical analysis of OC/EC (EUSAAR-2) to be used also for the sampling for $^{14}C$ analysis with minimal adjustments. This significantly simplifies the sampling procedures, since this sampling train has already been tested for artefacts. Furthermore, several analyses can be performed on the same quartz fibre filter (OC/EC, $^{14}C$ and several organic tracers including levoglucosan).

The problems with supermodern samples (fraction of modern carbon $F^{14}C$ >100%) are still to be solved. Nuclear power plants can be a problem, but if these are 50 km away from the sampling location it should not pose a problem. The pharmaceutical industry has been shown to be a source of $^{14}C$, which might affect radiocarbon measurements in urban environments, but should have a minor effect on $F^{14}C$ at ACTRIS sites.

**ACSM and AMS in ACTRIS**

For work on Aerosol Mass Spectrometers (ACSM and AMS), we refer to ACTRIS JRA2 (WP21, Task 21.1 Aerosol Chemistry; Lead: PSI).

In short, 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, and considerable progress has been made in this respect. Both long-term ACSM measurements as well as several intensive AMS measurement campaigns have been performed within ACTRIS or in close coordination with ACTRIS.

The excellent time resolution of ACSM/AMS measurements will enable the community to study source impact variability in great detail, and provide valuable data for model validation.

SOPs for ACSM/AMS measurements are being developed within ACTRIS JRA2, and the progress will be closely followed by the ACTRIS WP3 community dealing with organic tracers.

**Traffic (gasoline, diesel)**

Traffic sources are often clearly identified and apportioned based on PAHs, hopanes and steranes. GC is the preferred method of analysis. Rural sites can have very low concentrations of these compounds, often below their detection limit. In addition to dilution and dispersion, atmospheric degradation may be one reason for the low concentration at the rural sites, in particular in summer.

When analyzing for PAHs as part of routine GC/MS measurements, it is also possible to analyze for hopanes, so the extra effort is minor. High quality standards are available for the hopanes which yields reliable quantification.

A compilation of existing long time series data on the concentrations of hopanes and steranes at rural sites is being prepared based on previous studies (LGGE, ULUND). A literature search for these compounds is also included for rural European sites. In France, two sites (Revin, Peyrussa), which are EMEP sites, are measuring hopanes systematically as part of the national MERA program. In Germany, there are data on hopanes for 2 years (2 days per week approximately) for about 8 sites in Germany.

All these data will help us assess the usefulness of these traffic OA tracers for source apportionment at European background sites, and the possibilities for setting up a SOP for hopane and sterane sampling and analysis within ACTRIS.

# 3 SOPs for sampling of organic tracers

**Low-volume OA sampling**
For all OA analytic methods for which a low-volume sampler is adequate, we recommend that the EUSAAR OC/EC sampling train and sampling protocol is used. There is no need to develop a new sampling SOP for this purpose. The main reasons are that:

- The EUSAAR OC/EC sampling train has already been tested for artefacts, and will continue to be tested within ACTRIS;
- Several organic analyses are performed on the same quartz fibre filter.

The 47 mm quartz fibre filter will then have to be shared between the analytical techniques.

**High-volume OA sampling**
For the OA analytic methods for which a high-volume sampler is required, there is still a need for a separate OA sampling SOP. Work is ongoing within ACTRIS WP3 to prepare for such a SOP. Issues that need to be resolved and are currently being tested include:

- High-volume denuder to minimize positive artefacts;
- Handling and conservation of high volume samples.

Regarding the development of a suitable protocol for handling and conservation of high volume samples, there are several propositions under evaluation. These are not being implemented and tested by ACTRIS partners.

A denuder system for high-volume sampling is currently being 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 (sampling under progress during spring / summer 2013) and the samples are analyzed for a range of chemical species, including several tracers under consideration within ACTRIS. The outcome of these tests will be discussed at the 3rd ACTRIS WP3 Technical Meeting in Athens 7-11 October 2013. A decision regarding an SOP for OA high-volume sampling is expected then.

Another issue that needs attention is the potential reactivity of the organic tracers under consideration. Work on this issue is in progress by French partners, and will also be presented at the 3rd ACTRIS WP3 Technical Meeting.

# 4 Other possible organic tracers under consideration within ACTRIS

During the first two years of ACTRIS, the WP3 community focusing on organic tracers have discussed a wide range of potential tracer compounds than might qualify for recommendation by ACTRIS. These are briefly discussed below.

**Primary biogenic OA, fungal spores**

The fungal spore tracers mannitol, arabitol and trehalose can all be determined with LC and HPAEC. It is very likely that these tracers for primary biogenic organic aerosol will be included in the final ACTRIS recommendations. No decision has been taken yet, pending the final decision regarding the SOP for levoglucosan.

**Primary biogenic OA, cellulose**

Another important primary biogenic source of OA is plant debris, which can be determined using cellulose as tracer. As far as we are aware, only one group in Europe performs analysis of cellulose in aerosol samples on a regular basis (TU Vienna; enzymatic method). ACTRIS will gain experience on the

usefulness of cellulose as tracer from the Nordic groups, who will report on the outcome of the EIMP winter campaign 2013. It is not likely that ACTRIS will recommend this tracer for wider use.

**Biomass burning SOA**

Methyl-nitrocatechols are formed by atmospheric oxidation of cresols that are emitted during biomass burning. They are therefore potential tracers for SOA originating from biomass burning. The formation pathways are only partly understood, but they have been identified in both smog chamber experiments (at TROPOS) and in the atmosphere. So far, TROPOS is the only laboratory that analyzes for methyl-nitrocatechols (using LC/ESI-MS). No decision has been taken yet regarding the use of this tracer.

**Biogenic SOA formed from BVOC**

Biogenic SOA are oxidation products of biogenic VOC (BVOC) that are emitted from vegetation. These secondary components may also act as tracers, but the quantitative apportionment to the source in question will then depend on an estimate of the yield of this secondary compound relative to all other SOA components from the same source. An example is the compound 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA), which has been shown to be a unique tracer compound for terpene BSOA. In order to determine the amount of terpene BSOA in the total OA, the mass fraction of MBTCA in terpene BSOA will then have to be known over a range of atmospheric conditions. This requires estimates of the yields – through chemical and physical processes – of the tracer as well as all SOA produced from VOCs emitted from that source. Such knowledge is in most cases lacking today.

The most studied BVOC in terms of their BSOA formation potential are the monoterpenes, including $\alpha$-pinene, β-pinene, limonene, Δ3-carene, camphene and sabinene. Several issues remain to be resolved before the oxidation products that have been identified in chamber studies can be used for OA source apportionment. Until then, quantification and source apportionment of BSOA remains a challenge. In short, the issues are as follows:

- The relative yields of BSOA components are not adequately known or constrained;
- There is a lack of authentic standard compounds;
- There is as yet no standardized analytical procedure;
- Smog chamber BSOA may differ significantly from ambient BSOA;
- Many BSOA peaks are not identified;
- Structural elucidation is an extremely daunting task;
- BVOCs that are significant contributors to ambient BSOA may have been overlooked.

Further work needs to be performed by the wider organic aerosol community before firm decisions on BSOA tracers can be made. Most likely, this lies beyond the EU FP7 ACTRIS project timeframe.

**Functional group analysis using HNMR**

HNMR can be used as analytical method for WSOC functional groups. These can then be used for source apportionment by applying multivariate statistical methods, for instance PMF, to the NMR spectra. In Europe today, only one group performs HNMR analysis on aerosol samples on a regular basis; ACTRIS partner (CNR-ISAC, contact person Stefano Decesari).

Although the HNMR method is appealing in the sense that it offers a novel view of the water-soluble OA fraction, the lack of wider experience among European aerosol scientists and the remaining ambiguities as to the interpretation of the apportionment results means that it is not likely that ACTRIS will recommend the use of HNMR for European OA source apportionment. Nevertheless, it would be advantageous if ACTRIS could contribute to develop an SOP for sampling and HNMR analysis.

**Additional tracers to be considered further**

There are also a number of other interesting candidates for OA tracers that need to be examined further. The following tracers that have been discussed within ACTRIS WP3:

- Cholesterol (meat cooking)
- Methoxyphenols (tracer for combustion of lignin in wood)
- Glucose (biomass burning, fungi, soil biota)
- Ergosterol (fungi)
- Erythritol (lichens)
- Fructose (lichens)
- Mannose and galactose (soil biota)
- Organosulphates (anthropogenic/biogenic source mixing)
- Methane sulfonic acid (MSA, marine SOA)
- Methyltetrols, terpenoic acids (BSOA)

These are by no means excluded and will be discussed further during the WP3 meetings.

## 5 SOPs currently in use by ACTRIS partners

A request was sent to all ACTRIS partner (including associated partners) to send their SOPs to the WP3 Organic Tracer Task Leader Erik Swietlicki (ULUND), in whatever form they may exist. SOPs should preferably cover both sampling and analytical procedures. 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 will be discussed at the 3rd ACTRIS WP3 Technical Meeting in Athens 7-11 October 2013, and serve as a basis for future SOP decisions within ACTRIS.