TNA User Report

The completed and signed form below should be returned by email to
eurochamp2020@lisa.u-pec.fr

Project title	First OGTAC CC inter-laboratory (ILC)
Name of the accessed calibration center	LEAK-LACIS OGATC CC
Number of users in the project	10 (+ 3 from Germany)
Project objectives (max 100 words)	The inter-laboratory comparison was focused on biogenic secondary organic aerosol marker compounds. The main goal was to obtain an overview about groups working on BSOA characterization and a comprehensive overview about existing method to extract, detect and quantify BSOA marker compounds.
Description of work (max 100 words):	Each participant received a set of 7 filter extracts composed of 3 filter collected at the research station Melpitz, 3 filter from aerosol chamber experiments in LEAK and 1 Blank filter. The participants were asked to quantify 5 main compounds, namely terbic acid, terpenylic acid, pinic acid, pinonic acid and 3-Methyl-1,2,3-tricarboxylic acid (MBTCA). Aside from this, the participants received a large questionnaire about their method. Each anaylsis had to be repeated three times.

Principal Investigator's and group's information	
First name	Ana
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User status[3]	Postdoctoral researcher
New user	yes

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New user	yes

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User status	Researcher
New user	yes

[1] Physics; Chemistry, Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.
[2] UNI= University and Other Higher Education Organisation;
RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);
SME= Small and Medium Enterprise;
PRV= Other Industrial and/or Profit Private Organisation;
OTH= Other type of organization.
[3] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher EXP= Engineer; ACA= Academic; TEC= Technician.
[4] Reproduce the table for each user who accessed the infrastructure

User 3 Information	
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New user	yes

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New user	yes

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User status	Researcher
New user	no

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New user	no

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User status	Researcher
New user	yes

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User status	Researcher
New user	yes

User 9 Information	
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Institution legal status	Public research Organisation
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Gender	female
User status	Academic
New user	Yes

Trans-National Access (TNA) Scientific Report

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Ana Kroflic
Calibration center's name and location: OGTAC CC, TROPOS Leipzig
Campaign name and period: First OGTAC CC inter-laboratory (ILC)

Text:

Introduction and motivation

Organic compounds makes up a large fraction of aerosol particles and varies in composition depending on the meteorological conditions, the location as well as the stage of processing. Thus aerosol particles contain hundreds of different compounds that affect the chemical and physical properties and with this human health and climate. The organic fraction can be composed of compounds from biogenic as well as from anthropogenic origin. Thus an inter-laboratory comparison (ILC) was performed to compare and validate offline analysis for particle-phase oxidation products of BVOCs. Within Europe many groups are working on the detection and quantification of BSOA marker compounds – from chamber-generated SOA as well as from field samples. The most dominating BSOA marker compounds are terebic acid, terpenylic acid, pinic acid, pinonic acid and 3-methyl-1,2,3-butane-tricarboxylic acid (MBTCA). These compounds can be quantified by various techniques, including LC/MS and GC/MS. Thus far, an ILC on these compounds was never conducted. Therefore, it was important to collect for this first ILC information about all groups working on this area and to figure out which techniques and procedures are present in the participating labs.

Scientific objectives

Even that several groups within Europe are working on detection and quantification of BSOA marker compounds no harmonized protocol exist. Thus, the first ILC is aimed to compile all information about groups working on this fild, their methods, the comparability of the their results and to develop a first draft SOP containing recommendations for storage, extraction etc. Thus, the first ILC will have a great added value as it is the first step in the direction of harmonized procedures for the quantification of BSOA marker compounds in Europe.

Reason for choosing the calibration facility

One of the greatest strength of TROPOS ACD is the development and improvement of analytical methods for the detection and quantification of organic compounds in the gas and particle phase. So far TROPOS ACD published about 20 first-author papers with 380 citations dealing solely with the development of new methods or improvements of existing methods. The large array of state of the art instruments and methods at TROPOS enables them to cover the majority of organics and to serve many groups that usually use only 1-2 instruments.

Method and experimental set-up

Each participant received a set of 7 filter composed of three filter collected in Melpitz, three filter collected at the aerosol chamber LEAK and 1 Blank filter.
Field filter samples were collected with a Digitel PM_{10} impactor at the research station Melpitz for 3 days, each 24 hours sampling time. In total 14 aliquots were punched from one filter, each 7.1 cm2. Each participating laboratory received one aliquot per sampling day. Additionally one aliquot from a blank filter was send.

Chamber-generated filters were produced from the new twin-chamber at TROPOS ACD. The ozonolysis of α-pinene was conducted in the presence of $(NH_4)_2SO_4/H_2SO_4$ (pH=4) at 50% RH. To ensure a high filter loading α-pinene was injected for 4 times over the course of the experiment. The experiment was repeated three times. After the experimental run 4 filter were collected with 1.5 m^3 sampling volume for each filter. The filter were cut in quarters and send to the participants.

The loaded filters were distributed to the participating ILCs partner. At the same time a questionnaire was send to the participants containing information about storage, extraction procedure, type of analysis, column for separation, detector, eluent gradient, type of standards used for quantification (purchased from supplier, surrogate, synthesised standard) and detection limit.

Data description

The deadline for data submission was set to 30th of June. Unfortunately, several groups did not provide data. By the middle of November the data submission was finally closed. Please note, the numbers given to the participating laboratories does not correspond to the User number given in Page 2-5.
The dataset comprises data from 9 participants (6 from Europe and US, 2 from Germany and 1 from TROPOS). 5 Groups did not provide data (4 from Europe + 1 from Germany). Two E2020 partners were within the groups that do not provide data.
From each participating group a full description is of their method is available and the quantification of the majority of compounds with 3 repetitions.

Preliminary results and conclusions

Results from the questionnaire

a) Applied analytical technique

Among the existing techniques 78% of participants used liquid chromatography coupled to mass spectrometry (LC/MS) whereas only 22 % used gas chromatography mass spectrometry (GC/MS). Thus, the analysis of BSOA marker compounds is mainly conducted by LC/MS applications. Within the LC/MS applications, 29% of data were provided from high-resolution mass spectrometry.

b) Extraction procedure

For filter extraction two different proceedings were mainly used within the community, ultrasonic bath and orbital shaker. Even that it has been demonstrated that the ultrasonic bath highly effects the chemical composition due to the artifact formation, 33 % of participants still use ultrasonic agitation for extraction. The remaining groups apply an orbital shaker.

For the extraction different solvents were used. From 9 participants, 4 used pure methanol and 1 used pure acetonitrile. Other extraction solvents were mixtures of acetonitrile/water (1), acetonitrile/water (2), and acetonitrile/methylenechloride (1).

The extraction time varied for ultrasonic agitation between 15-60 min and for the orbital shaker between 20-90 minutes.

c) Use of internal standard

Within the 9 different data sets, 4 groups applied an internal standard (ISTD). ISTD used were: Sebacic acid, 1,2,3,4-cyclobutane-tetra-carboxylic acid, Keto-pinic acid, and toluic acid.

d) type of standard used for quantification

The quantification of marker compounds can be either done using an authentic standard or using a surrogate. The latter method means that compounds were selected for quantification that have a similar structure like the target compound. Assuming a similar ionization efficiency surrogates are used for quantification of those targets without an available standard. In Table 1 an overview is given about the usage of different types of standards used for quantification.

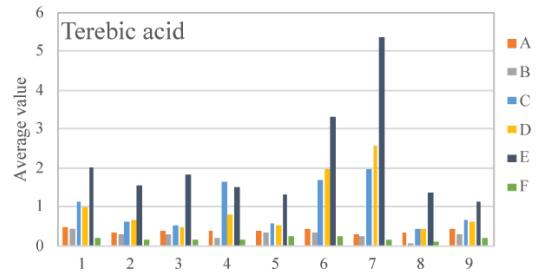
Table 1. Overview about standards used for the quantification of BSOA marker compounds.

	Terebic acid	Terpenylic acid	Pinonic acid	Pinic acid	MBTCA
Numbers of data sets	9/9	6/9	9/9	9/9	9/9
Purchased from supplier	7/9	1/7	6/7	5/7	2/7
Synthesised standard	1/9	2/7	3/7	4/7	5/7
Surrogate	1/9	3/7			

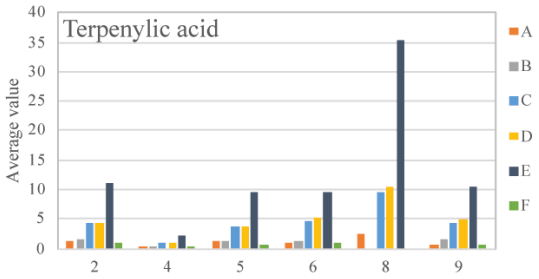
As it can be seen only Terebic and terpenylic acid are quantified by surrogate compounds. These values might differ from the results using authentic standard compounds. Compounds used as surrogate were terebic acid and keto-pinic acid for terpenylic acid and pinonic acid for terebic.

It is worth mentioning that many groups apply synthesized standards for the quantification. This is basically due to the lack of commercially available compounds.

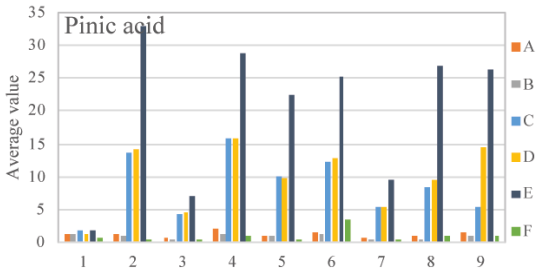
Results from the questionnaire



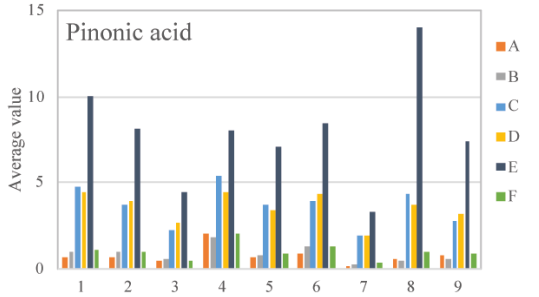
Terebic acid		A	B	C	D	E	E
General mean	m	0.37	0.26	1.02	0.99	2.14	0.16
Repeatability	sr	0.18	0.01	0.07	0.07	0.11	0.02
	sr/m	48.0%	5.6%	7.3%	7.5%	5.1%	14.3%
Reproducibility	sR	0.16	0.10	0.59	0.74	1.37	0.06
	sR/m	42%	39%	58%	75%	64%	40%



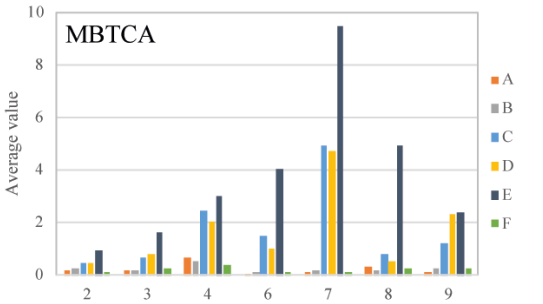
Terpenylic acid		A	B	C	D	E	F
General mean	m	1.20	1.03	4.65	4.9	13.0	0.6
Repeatability	sr	0.33	0.09	0.18	0.2	0.8	0.1
	sr/m	27.3%	8.7%	3.9%	3.7%	6.0%	8.8%
Reproducibility	sR	0.78	0.67	2.76	3.1	11.5	0.4
	sR/m	65%	65%	59%	63%	88%	66%



Pinic acid		A	B	C	D	E	F
General mean	m	1.18	0.84	8.53	9.8	20.1	0.59
Repeatability	sr	0.13	0.04	0.66	0.7	0.8	0.26
	sr/m	10.7%	4.4%	7.8%	6.8%	4.0%	43.0%
Reproducibility	sR	0.46	0.33	4.83	5.1	11.1	0.38
	sR/m	39%	40%	57%	52%	55%	64%

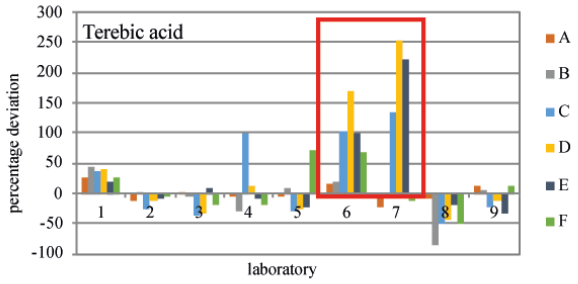


Pinonic acid		A	B	C	D	E	F
General mean	m	0.59	0.81	3.64	3.5	7.9	0.97
Repeatability	sr	0.12	0.10	0.20	0.2	0.4	0.22
	sr/m	20.7%	11.9%	5.5%	5.7%	5.6%	22.9%
Reproducibility	sR	0.24	0.49	1.18	0.9	3.1	0.53
	sR/m	41%	61%	32%	25%	40%	55%

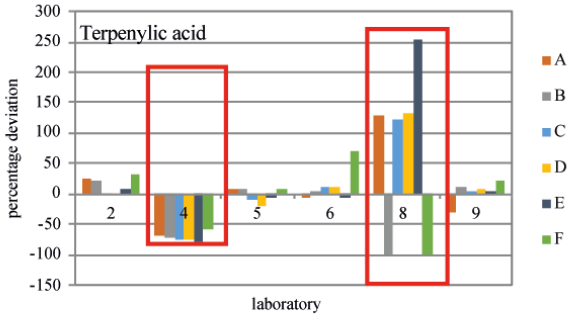


MBTCA		A	B	C	D	E	F
General mean	m	0.26	0.26	1.73	1.7	3.8	0.2
Repeatability	sr	0.06	0.01	0.19	0.2	0.4	0.2
	sr/m	23.5%	4.5%	10.7%	10.8%	9.5%	77.7%
Reproducibility	sR	0.21	0.14	1.57	1.5	2.9	0.2
	sR/m	80%	54%	90%	89%	76%	79%

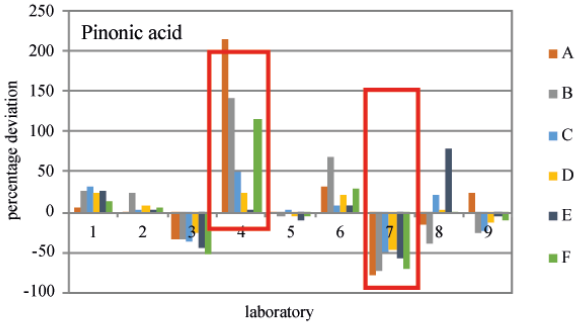
In Figure 1 the average values for all samples from all laboratories. Considering that this is the first time, that an ILC on these compounds was conducted that results are reasonable. Based on the obtained data, the assigned values was calculated and the relative difference of each group determined.



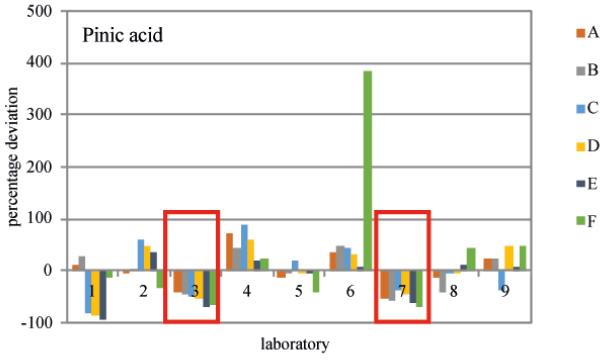
Terebic acid		A	B	C	D	E	F
assigned value	µg	0.37	0.28	0.83	0.72	1.65	0.15
standard deviation	µg	0.06	0.05	0.37	0.27	0.43	0.05
	%	16	18	44	38	26	30
2σ*	%	32	36	89	76	52	61
3σ*	%	48	55	133	114	77	91



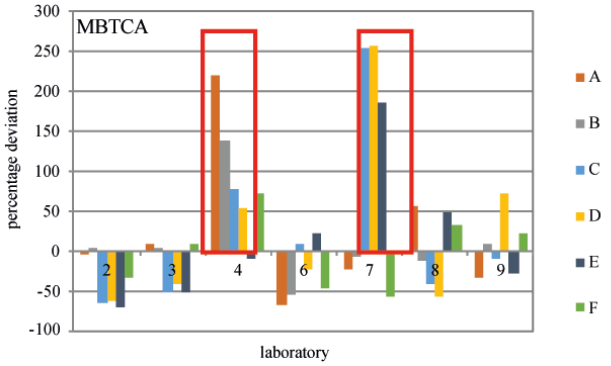
Terpenylic acid		A	B	C	D	E	F
assigned value	µg	1.09	1.32	4.30	4.53	10.07	0.62
standard deviation	µg	0.53	0.25	0.78	1.31	1.30	0.39
	%	49	19	18	29	13	63
2σ*	%	98	38	36	58	26	126
3σ*	%	148	58	55	87	39	189



Pinonic acid		A	B	C	D	E	F
assigned value	µg	0,64	0,74	3,64	3,60	7,91	0,94
standard deviation	µg	0,25	0,40	1,32	0,87	1,65	0,22
	%	38	54	36	24	21	24
2σ*	%	76	108	73	49	42	47
3σ*	%	114	162	109	73	63	71



Pinic acid		A	B	C	D	E	F
assigned value	µg	1.15	0.84	8.53	9.77	24.00	0.68
standard	µg	0.46	0.38	5.44	5.78	6.22	0.45
deviation	%	40	45	64	59	26	66
2σ*	%	79	89	127	118	52	132
3σ*	%	119	134	191	178	78	198



MBTCA		A	B	C	D	E	F
assigned value	µg	0.21	0.23	1.40	1.33	3.32	0.23
standard deviation	µg	0.11	0.03	0.96	0.89	2.10	0.12
	%	54	15	69	67	63	54
2σ*	%	108	30	137	133	126	107
3σ*	%	162	45	206	200	190	161

The majority of the laboratories show deviations from the assigned value below ± 50%. Few groups showed significant over/underestimations of ± 100%. Terebic and Terpenylic acid showed the best results with respect to the deviation of the different groups whereas the results for MBTCA differ significantly.
These first results demonstrate already the need of a harmonization of the quantification of BSOA marker compounds. The deeper analysis of outliers/stragglers pointed already to few problems that might cause problems during quantification including the choice of the supplier.

Choice of the supplier

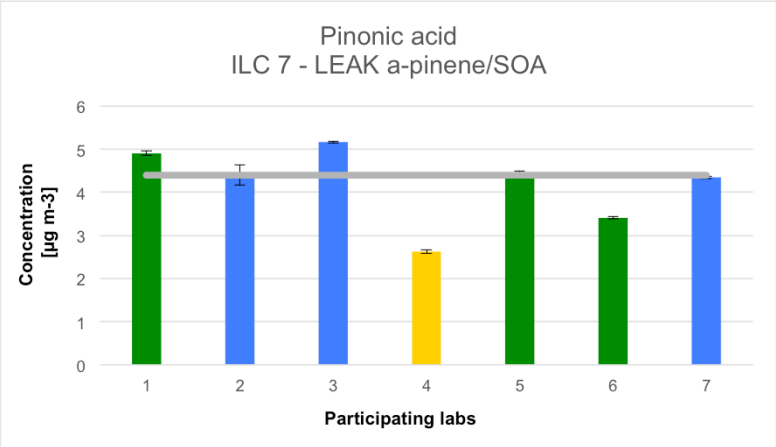


Figure 1. ILC Results for pinonic acid

The results for pinonic acid can be grouped according to the used supplier. The results in blue originate from the quantification with standard purchased from company 1 and yellow refers to company 2. The results given in green correspond to synthesized standards. The data originating from company 1 and synthesized standards are in the same range whereas the results obtained after using the standard from company 2 is much lower than the others. This might be result of the purity and the content of isomers.

Outcome and future studies

Based on the first preliminary data, a huge dataset about existing methods to detect and quantify BSOA marker compounds was obtained. The majority of the groups work with LC/MS and already a great fraction is able to apply HR/MS. Within the existing methods, still a great fraction of users apply ultrasonic agitation to extract their samples. This will be discussed in the future with the respective groups. Also the use of surrogate compounds will be critical discussed with the respective users. Furthermore, it can be stated the special focus has to spend on the choice of commercially suppliers.

Future work

OGTAC CC will work now on the statistical analysis of data. This includes the analysis according to ISO5725-2 applying Grubbs and Cochran Test to identify outliers and stragglers. Secondly, OGTAC CC started to collect information about the suppliers and the purification of their standards. As a parallel acitivity was started Prof. Marianne Glasius (Aarhus University) and Prof. Jian Zhen Yu (Hong Kong University of Science & Technology) a collaboration was started and the respective list is now available under

https://docs.google.com/spreadsheets/d/1ILeAAv12b13f8K456e9uONB-SMgDEYQMRIOze76ZwJA/edit?usp=sharing

The work on this list will be continued within the next months and OGTAC CC will continuously contribute to this. In a second step, based on the statistical analysis, recommendations for storage, extraction and analysis of BSOA marker compounds will developed together with the participants. It is planned to conduct an additional ILC on the same compounds, but applying the new SOP to see if this leads to an improvement of the data quality.