Analysis and determination of secondary organic aerosol (SOA) tracers (markers) in particulate matter standard reference material (SRM 1649b, urban dust)

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Abstract

Secondary organic aerosol (SOA) accounts for a significant fraction of particulate matter (PM) in the atmosphere. Source identification, including the SOA fraction, is critical for the effective management of air pollution. Molecular SOA markers (tracers) are key compounds allowing the source apportionment of SOA using different methodologies. Therefore, accurate SOA marker measurements in ambient air PM are important. This study determined the concentrations of 12 key SOA markers (biogenic and anthropogenic) in the urban dust standard reference material available from the National Institute of Standards and Technology (NIST) (SRM 1649b). Two extraction procedures, sonication and QuEChERS-like (Quick Easy Cheap Effective Rugged and Safe), have been compared. Three research laboratories/institutes using two analytical techniques (gas chromatography/mass spectrometry (GC/MS) and ultra-high-pressure liquid chromatography/tandem mass spectrometry (HPLC/MS-MS)) carried out the analyses. The results obtained were all in good agreement, except for 2-methylerythritol. The analysis of this compound seems still challenging by both, GC/MS (large injection repeatability) and HPLC/MS-MS (separation issues of both 2-methyltetrols: 2-methylthreitol and 2-methylerythritol). Possible inhomogeneity in the SRM for this compound could also explained the large discrepancies observed. Sonication and QuEChERS-like procedures gave comparable results for the extraction of the SOA markers showing that QuEChERS-like extraction is suitable for the analysis of SOA markers in ambient air PM. As this study provides, for the first time, indicative values in a reference material for typical SOA markers, the analysis of SRM 1649b (urban dust) could be used for quality control/assurance purposes.

Keywords: Aerosol; SOA, Tracers, QuEChERS; Analysis

1. Introduction and objectives

Organic matter (OM) accounts for a large fraction of the fine atmospheric particulate matter (PM, aerosol) (about 20 to 90 %) [1]. Carbonaceous species that constitute the organic aerosol fraction (OA) are classified following their origins. Primary organic compounds directly emitted into the atmosphere belongs to the primary OA fraction (POA) while secondary organic particles, formed in the atmosphere by homogenous or heterogenous (photo)-chemical reactions of volatile or semi-volatile organic compounds (COVs) followed by gas-particle conversion processes such as nucleation and/or condensation, are defined as secondary OA (SOA) [2-5]. This latter fraction accounts for up to 80 to 90 % of total OA under certain conditions [1, 6, 7] making its characterization and apportionment essential in terms of air quality or climate impacts.

Different methodologies have been developed and reported in the literature to apportion SOA (or secondary organic carbon, SOC) [7]. Several studies have identified key characteristic molecular compounds of the formation of SOA from specific precursors or sources and commonly defined as molecular SOA markers (or tracers if assuming that they are chemically stable) [7, 8] (Table 1). These compounds are used to apportion SOA in the so-called SOA tracer method [7, 9] or in source-receptor models, such as chemical mass balance (CMB) or positive matrix factorization (PMF) [7, 10-13]. The quantification of these SOA markers is critical because inaccurate values could lead to significant bias in the results obtained [7]. In most cases, no authentic standards are commercially available for these compounds and proxy compounds are generally used for their quantification. In addition, in terms of validation of analytical procedure, quality assurance and control, the analysis of reference material is useful, but no SOA marker concentration values have been reported yet in any particulate matter reference material.

Thus, the objectives of this work were to evaluate the presence and to determine the concentration values of some typical molecular SOA markers in the commonly used National Institute of Standards

and Technology's (NIST) urban dust standard reference material (NIST SRM 1649b). This material has been largely characterized in the past years [28-32] but to our knowledge, no concentration values for such compounds have been reported so far in the literature. Our objectives also included the comparison of the extraction efficiencies, for the analysis of molecular SOA markers in PM, of two different extraction procedures namely, sonication and QuEChERS-like (Quick Easy Cheap Effective Rugged and Safe). Sonication is commonly used for the analysis of SOA marker compounds in aerosol samples [7-9, 16, 27, 33-40] while QuEChERS-like procedure has been developed and successfully applied for the molecular chemical characterization of OA including polycyclic aromatic compounds (PAHs), nitro-PAHs, oxy-PAHs [31, 41-43] and also SOA markers [10, 11, 13, 44]. In addition, this latter technique should minimize the degradation of some fragile SOA marker and preserve the integrity of the sample as it is done at room temperature [31, 44]. Finally, three research laboratories/institutes (INERIS, NIST and LSCE) using two extraction procedures and two analytical techniques (gas chromatography coupled to mass spectrometry (GC-MS) and high-pressure liquid chromatography/tandem mass spectrometry (HPLC/MS-MS)) performed the analysis of 12 key SOA markers in the SRM 1649b (Table 1, except 2-methylthreitol) and their results were compared.

2. Experimental

2.1. Chemical, gases and solvents

Information about the chemicals, gases and solvents used, their degrees of purity, and the supplier data are reported in the Supplementary Information (SI). Pure and authentic SOA marker compounds (liquids or solids) were used in this study. They have been purchased or synthetized on purpose from/by different suppliers (Table S1).

2.2. Standard reference material (SRM) 1649b (urban dust)

During the mid to late 1970s, NIST collected urban PM using a baghouse specially designed for the purpose from the Washington, DC area. PM were collected over a period greater than 12 months and represents an atmospheric particulate matrix to validate analytical methods. SRM 1649b (urban dust) has been prepared from the bulk material (SRM 1649) collected at this time but it has been sieved to a smaller particle size with a mean diameter of 105 µm [29].

For both extraction procedures tested, 5 to 13 (in total 5 for NIST, 10 for LSCE and 23 for INERIS) samples of SRM 1649b of about 50 mg (balance precision = 0.01 mg) were analyzed. Triplicate analyses (3 injections of the sample extracts) were performed, except for 5 samples for each extraction procedure for INERIS, injected only once. Moisture content was determined using a Karl Fischer method (2.94 % moisture, analyzer HR 73, Mettler Toledo). SOA marker concentrations were corrected and are reported here on dry-mass basis.

2.3. Extraction and derivatization procedures

SRM extraction was done by both, sonication and QuEChERS-like procedures using methanol (MeOH) as solvent. SRM 1649b samples were placed in centrifuge glass tubes (Ø = 16 mm, L=100mm, screw cap with PTFE septum face; Duran), spiked with known amounts of 3 to 5 labelled surrogate standards (200 to 800 ng added, depending on the final volume of the extract after evaporation), and 7 mL of solvent was added for the extraction. Sonication was done for 15-20 min while for QuEChERS-like extraction, the tubes were shaken by vortex mixing with a multiposition vortex mixer for 1.5 min (DVX-2500 Multi- Tube Vortexer; VWR). After extraction, samples were centrifuged at room temperature for 5 min at 4500 rpm or 30 min at 3800 rpm, for INERIS/LSCE and NIST, respectively (Sigma 3-16 PK and Beckman GS-6R centrifuge). For GC/MS analyses, supernatant extracts (4.5 or 5.5 ml) were collected and reduced to dryness under a gentle nitrogen stream to remove any trace of water or MeOH and avoid additional consumption of BSTFA or

MSTFA. Extracts were dissolved into 50, 100 or 200 µL of acetonitrile and subjected to derivatization (silylation) for 30 minutes at 60°C after addition of 50 or 100 µl of N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) (INERIS) or 200 µl N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (NIST), both with 1% trimethylchlorosilane (TMCS) (ratio sample extract to derivatizing reagent of 1:1). For LC/MS-MS (LSCE) analyses, the supernatants were directly analyzed without any other sample preparation.

2.4. GC/MS analysis

The analysis of 11 to 12 SOA markers was achieved using GC/MS (Agilent 7890A GC coupled to 5975C MS at INERIS and Agilent 6890 GC coupled to 5973 MS at NIST) in electron ionization mode (EI, 70 eV). 1 or 2 µL of the extracts were injected in the splitless mode at 250 °C using, for INERIS, a programmed temperature vaporizer injector system (CIS-4 Gerstel, with a Restek Sky single baffle liner with wool, 3 × 2 × 71 mm, OD × ID × L) and for NIST, a splitless injector (with a Restek Sky low pressure drop precision inlet liner w/wool, 6.3 × 4 × 78.5 mm). Compounds were separated using capillary columns with equivalent 5% phenyl-methylpolysiloxane phase 60 m × 0.25 mm × 0.25 µm (Agilent J&W DB5-MS with 10 m guard column for INERIS or Restek Rtx-5MS for NIST), using the following temperature programs: INERIS – start at 70 °C for 1 min, then ramped to 260 °C at 5 °C min^{-1}, followed by a ramp to 290 °C at 20 °C min^{-1}, further followed by a ramp to 300 °C at 5 °C min^{-1}, then ramped at 10 °C min^{-1} to 320°C held for 10 min; NIST – start at 70 °C for 1 min, increased at a rate of 5°C min^{-1} to 300 °C held for 1 min. The carrier gas (He) flow was set to 1.2 (NIST) or 1.5 (INERIS) mL min^{-1} throughout the analysis and transfer line heated at 310 °C. The ion source and quadrupole temperatures were 230 and 150 °C, respectively.

Analyses were performed in selected ion monitoring mode (SIM). Autotune parameters were adopted for the electron multiplier conditions with a gain factor of 10. Monitored ions and dwell times are shown in Table 2. The quantification of the SOA markers was based on 8 to 10-points calibration

curves (gravimetrically diluted stock standard solutions (prepared in acetonitrile (ACN) or MeOH) from 5 (or 20) to 5000 pg μl^{-1} in MeOH; $0.99 > r^2 > 0.90$ for all compounds). All SOA marker compounds were quantified using authentic standards and labelled surrogate standards by internal calibration except for both methylnitrocatechols. Preliminary recoveries tests performed on pre-cleaned SRM 1619a powder (twice, with DCM using pressurized liquid extraction and MeOH using sonication) spiked with known amount (500 ng) of SOA marker compounds, showed significant differences in the results between internal and external calibration for the quantification of these compounds highlighting that the initial deuterated surrogate used (4-methylcatechol-d_3) to quantify them was not suitable for the GC/MS analyses (Figure S1). As no labelled methylnitrocatechol standards exists, both compounds were finally quantified by external calibration. In addition, the extraction recoveries obtained for DHOPA and 2-methylerythritol were quite low. The solvent of extraction used (MeOH) was probably not the best for the specific extraction of these compounds. However, it was the best compromise for the analysis of all the SOA markers targeted in this work. The labelled surrogates used (no labelled DHOPA and 2-methylerythritol are commercially available) to quantify these both compounds were not able to fully correct the sample preparation losses but at least, they did not induce any analytical drift like in the case of methylnitrocatechols.

Using these conditions, the instrumental limits of quantification (LOQ), defined as the lowest concentration of the compound than can be determined with a signal to noise ratio of 10 (calculated using the chromatograms obtained from the calibration solution with the lowest concentration level), were within the range 0.6–14.3 pg injected.

The list of all SOA markers quantified, labelled surrogates used, retention times, monitored ions and limits of quantification are given in Table 2 for both, NIST and INERIS GC/MS analytical procedures.

2.5. HPLC/MS-MS analysis

The quantification of SOA markers was achieved by HPLC/MS-MS (HPLC Dionex U3000 coupled to a triple quadrupole MS AB Sciex 3200 QTRAP). Two different columns, Thermo porous graphic carbon (PGC) Hypercarb column (2.1 mm × 150 mm × 3 μm) and Waters Acquity C18 HSST3 column (2.1 mm × 100 mm × 1.8 μm), were employed for the chromatographic separation. For the HSST3 column, the mobile phases consisted of a 0.1% formic acid in Milli-Q water (A) and ACN (B). The following program was applied during the LC analysis: start with eluent B at 5% with a gradient to 60% in 10 min followed by a second one to 100% in 2 min kept at 100% for 4 min, decreased back to 5% in 1 min, and conditioned at 5% for 10 min for the following analysis. For the Hypercarb column, the mobile phases consisted of a 0.1% NH_3 in Milli-Q water (A) and ACN (B). The elution program used was the following: start with eluent B at 4% kept for 2.5 min followed by a with a gradient to 100% in 9.5 min kept at 100% for 4 min, decreased back to 4% in 1 min kept for 5 min for conditioning the following analysis. Samples were injected with an injection volume of 10 μL and the analysis was carried out using a flow rate of 0.2 (Hypercarb) and 0.3 (HSST3) mL min^{-1}, respectively.

The targeted compounds were ionized using electrospray ionization in the negative mode. The mass spectrometer, with unit mass resolution, was operated under the following conditions: source voltage at -4.5 kV; desolvation temperature at 650 °C, desolvation gas pressure (air) of 60 psi, nebulizer gas pressure (air) of 40 psi, collisional activated dissociation (CAD) set on medium with nitrogen used as collision gas, compound-selective scheduled multiple reaction monitoring (MRM) mode with 40 or 140 s detection windows (HSST3 and Hypercarb, respectively), target scan time of 0.5 s, MR pause of 5 ms.

The quantification of the compounds was based on 6-points calibration curves from 1 to 32 pg μl^{-1} in MeOH ($0.99 > r^2 > 0.90$ for all compounds). Again, all SOA marker compounds were quantified by internal calibration, using authentic standards and labelled surrogate standards, except

for 2-methylerythritol which was quantified by external calibration cause, using this method, the labelled meso-erythritol-1,1,2,4,4-d6 surrogate standard was not well detected. Using these parameters, the instrumental LOQ were within the range 20-40 pg injected.

The compounds quantified, labelled surrogates used, retention times, parameters for each MRM transition and limits of quantification are given in Table 3 for the HPLC/MS-MS analytical procedure.

3. Results and discussion

3.1. QuEChERS-like extraction vs sonication and GC/MS vs HPLC/MS-MS

The comparison of the results obtained according to the different extraction procedures and analytical techniques used is shown on Figure 1 (see Table S2 for details). Results are also presented by laboratories/institutes.

Overall, whatever the analytical protocol used, all the results were in quite good agreement, except for 2-methylerythritol, and to a lesser extent MBTCA and 3-hydroxyglutaric acid, which showed large discrepancies. First, this study highlighted that the SRM 1649b contains quantifiable and quite homogeneous amounts of SOA markers. Note that, β-caryophyllinic acid has been reported by NIST as below LOQ (Table S2). This SOA marker is usually observed at low concentration levels in urban atmosphere [7, 10, 11, 36, 45]. Second, these results also showed that the extraction efficiencies of sonication and QuEChERS-like were similar demonstrating the validity of the QuEChERS-like extraction procedure for the analysis of SOA markers in PM. Except 2-methylerythritol, the results obtained showed also a good agreement between both analytical techniques used, GC/MS and HPLC/MS-MS. The differences observed were mainly due the discrepancies obtained between INERIS and NIST, both using GC/MS. In that case, it would difficult to conclude on any influence of the derivatizing agent used (BSTFA and MSTFA). Finally, further tests showed that both 2-methyltetrol isomers, namely 2-methylthreitol and 2-methylerythritol, were not separated with the column and elution program used here for the analyses performed by HPLC/MS-MS (the exact same transitions were also observed). Thus, the concentration values reported on Figure 1 for HPLC/MS-

MS are the sum of both compounds. Based on the literature data about these compounds, 2-methylerythritol accounts generally for about 2/3 of the sum of 2-methyltetrols [9, 35-37, 39, 45-49]. However, this only explained in part the differences observed. In addition, the difference in the results reported by NIST and INERIS were still significant. The analysis of 2-methyltetrols seems still challenging and the results obtained here may also indicate that the homogeneity in the SRM 1649b for this compound is not optimal. Further tests must be done to support our observations.

3.2. SOA marker concentrations in SRM 1649b (urban dust)

The final SOA marker concentration values determined in this study are presented on Table 4. A total of 28 to 38 full replicates (extraction + analysis, triplicate injections), depending on the compound considered, has been considered. Note that, the concentrations of 2-methylerythritol obtained by HPLC/MS-MS have been corrected by a factor 2/3 to consider that the sum of 2-methytetrols was quantified in this case. The value reported here for this compound is given only for information.

Large standard deviations were obtained for some compounds such as DHOPA, pinonic acid, methylnitrocatechols, MBTCA and 2-methylerythritol with coefficients of variation (standard deviation/mean value, CV) larger than 70%. A detailed study of the different analytical steps showed that the injection repeatability (CV ranging from 2 to 15%) accounted for a low part in the variations observed (Table S3). Only DHOPA for LSCE (37%) and 2-methylerythritol (111%) for NIST, showed large injection repeatability variations. This latter result highlighted again the challenge in the analysis of 2-methylerythritol. Finally, the large standard deviations obtained for these SOA markers were due to the different analytical procedures used and the influence of the experimenter/laboratory/institute (variations in terms of reproducibility).

4. Conclusions

The analysis of molecular SOA markers (tracers) is useful to apportion SOA mass in the atmosphere. The different SOA markers studied here were all present in the NIST SRM 1649b (urban dust). Sonication and QuEChERS-like procedures gave comparable results for the extraction of the SOA markers. As this study provides the first indicative values in a reference material for typical SOA markers, the analysis of SRM 1649b (urban dust) should be used for quality control/assurance purposes when such compounds are used to apportion the SOA fraction in ambient air.

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Supplementary information

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/XXXXXXXXX

Conflict of interest

S. Wise and F. Nalin worked at the NIST which also provides the standard reference materials (SRM). The other authors declare that they have no conflict of interest.

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Table 1. Example of SOA markers identified in the literature and their precursors/sources

Organic markers	Predominant origin	Precursors/Sources	References
α-Methylglyceric acid	Biogenic	Isoprene	[14]
2-Methylthreitol 2-Methylerythritol			[14, 15]
3-Methylbutane-1,2,3-tricarboxylic acid (MBTCA)		α-Pinene β-Pinene	[16, 17]
3-Hydroxyglutaric acid			[18]
Pinic acid cis-Pinonic acid			[17, 19-22]
β-Caryophyllinic acid		β-Caryophyllene	[23]
Succinic acid	Anthropogenic	Anthropogenic sources	[24]
Phthalic acid		Naphthalene	[25]
2,3-Dihydroxy-4-oxopentanoic acid (DHOPA)		Toluene	[26]
4-Methyl-5-nitrocatechol 3-Methyl-5-nitrocatechol		Phenolic compounds (biomass burning)	[27]

Table 2. GC/MS conditions used for SOA marker analysis and typical instrumental limits of quantification (LOQ)

Compounds	Monitored ions (m/z)	Retention times[d] (min)	Dwell times (s)	LOQ (pg injected)
Succinic acid-2,3,3,3-d4	147, **251**	19.54	0.06/0.035	-
Succinic acid[a]	**129**, 247	19.61	0.035	1.0-1.3
α-Methylglyceric acid	**219**, 306	19.74	0.06/0.035	1.0 -2.3
2,3-Dihydroxy-4-oxopentanoic acid (DHOPA)	**218**, 189, 350	24.71	0.04/0.05	3.7-11.0
cis-Pinonic acid	**171**, 125	25.27	0.04/0.05	2.2-7.5
3-Hydroxyglutaric acid	185, **349**	26.26	0.08/0.05	1.3-7.0
Pinic acid	**129**, 171	28.50	0.05/0.05	6.3-7.6
Phthalic acid[b]	221, **295**	29.04	0.05/0.05	0.9-8.4
Meso-erythritol-1,1,2,4,4-d6	**208**, 220	24.50	0.04/0.1	-
2-Methylerythritol	116, 117, **219**	25.74	0.05/0.05	1.1-4.2
1,9-Nonanedioic acid-d14	213, **331**	31.10	0.06/0.035	-
3-Methylbutane-1,2,3-tricarboxylic acid (MBTCA)	**204,** 245, **405**	30.34	0.08/0.05	0.6-14.5
β-Caryophyllinic acid	**117, 200**	36.08	0.08/0.05	8.9-14.3
4-Methyl-5-nitrocatechol[c]	296, **313**	31.06	0.06/0.035	1.5-10.3
3-Methyl-5-nitrocatechol[c]	**298**, 313	32.28	0.10/0.10	1.4-6.1

[a] Not analyzed by NIST.
[b] For NIST, quantified using 1,9-nonanedioic acid-d14 as surrogate.
[c] Quantified by external calibration.
[d] For INERIS method.
Underlined: NIST parameters.
Bold: Quantification ions.

Table 3. UPLC/MS-MS conditions used for SOA marker analysis and instrumental limits of quantification (LOQ)

Compounds	Transitions (m/z)	DP[c]	EP[d]	CEP[e]	CE[f]	CXP[g]	Retention time (min)	Column	LOQ (pg injected)
Succinic acid-2,3,3,3-d4	121→77	30	4	10	16	0	1.73	Hypercarb	-
3-Methylbutane-1,2,3-tricarboxylic acid (MBTCA)	203→185	30	5.5	12	16	4	1.61	Hypercarb	40
Succinic acid	117→73	25	8	10	14	0	1.82	Hypercarb	40
α-Methylglyceric acid	119→73	35	2	36	16	0	1.92	Hypercarb	80
2,3-Dihydroxy-4-oxopentanoic acid (DHOPA)	147→73	15	5	10	18	0	2.16	Hypercarb	40
3-Hydroxyglutaric acid[a]	-	-	-	-	-		-	-	-
Phthalic-3,4,5,6-d4 acid	169→125	25	2.5	12	14	0	*1.78*	Hypercarb	
Phthalic acid	165→121	30	5	12	12	0	2.27	Hypercarb	20
1,9-Nonanedioic acid-d14	201→138	35	9.5	30	18	2	2.29	HSS T3	-
Pinic acid	185→141	35	9	12	18	0	5.97	HSS T3	40
cis-Pinonic acid	183→141	30	11.5	12	16	0	7.45	HSS T3	40
β-Caryophyllinic acid	253→209	40	6	10	14	2	10.64	HSS T3	40
4-Methylcatechol-d3	126→108	60	3	10	22	0	6.65	HSS T3	-
4-Methyl-5-nitrocatechol[c]	168→138	35	9	12	14	2	7.83	HSS T3	80
3-Methyl-5-nitrocatechol[c]	168→138	45	5.5	12	22	2	8.66	HSS T3	160
2-Methylerythritol[b]	135→85	30	10.5	12	22	0	2.64	Hypercarb	320

[a] Not analyzed by UPLC/MS-MS
[b] Quantified by external calibration
[c] Declustering potential (V)
[d] Entrance potential (V)
[e] Collision cell entrance potential (V)
[f] Collision energy (eV)
[g] Collision cell exit potential (V)

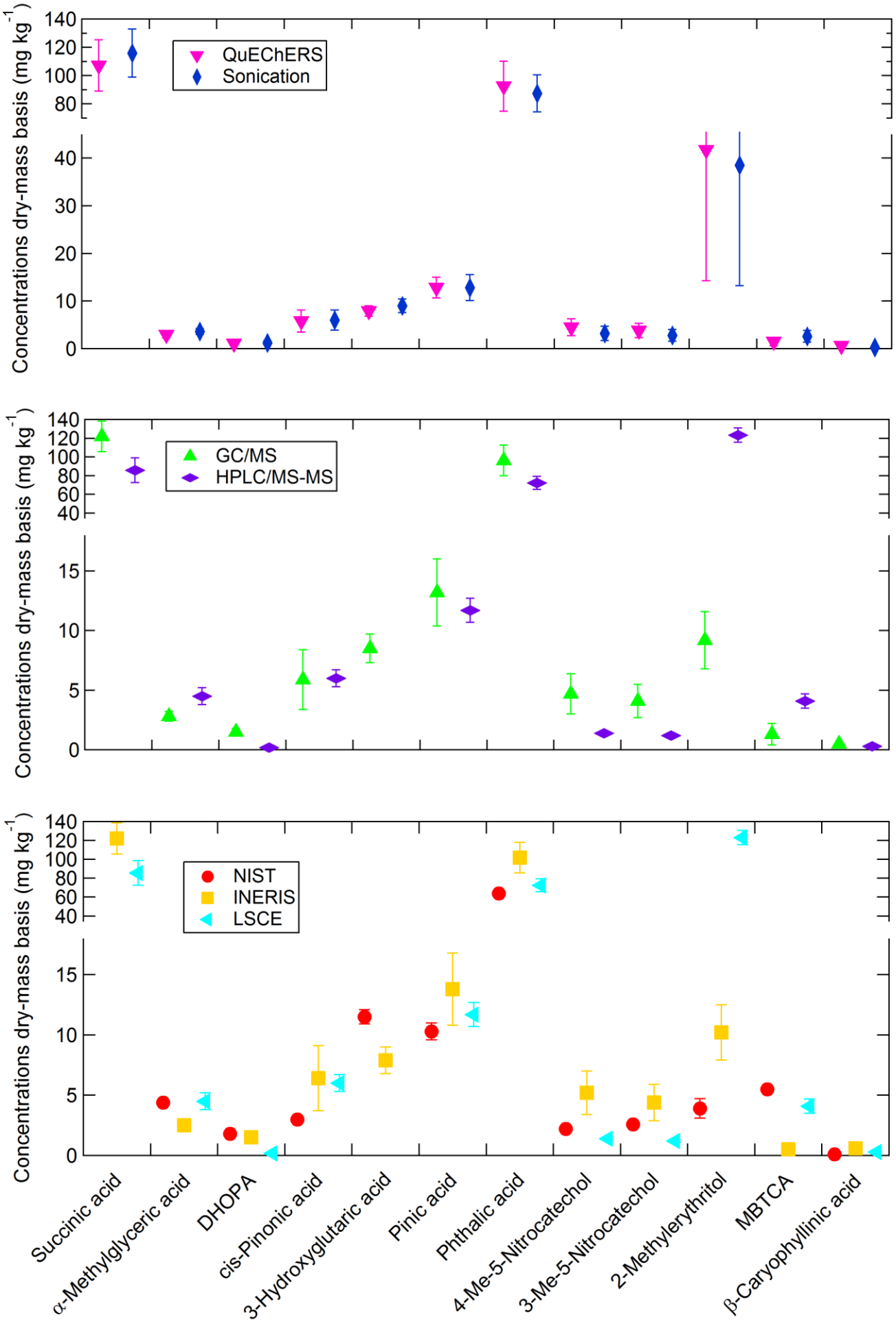
Table 4. SOA marker concentrations (mg kg^{-1}) (dry-mass basis) in SRM 1649b (urban dust)

Compound	Mean[a]	Standard deviation[a]
Succinic acid	104.7	29.6
α-Methylglyceric acid	3.1	1.3
DHOPA	1.1	0.7
cis-Pinonic acid	7.3	5.1
3-Hydroxyglutaric acid	8.2	2.9
Pinic acid	11.1	4.4
Phthalic acid	83.1	25.5
4-Methyl-5-nitrocatechol	2.8	2.7
3-Methyl-5-nitrocatechol	2.5	2.2
2-Methylerythritol[b]	20.6	26.6
MBTCA	2.2	2.1
β-Caryophyllinic acid	0.4	0.3

[a] n=45 to 55

[b] UPLC/MS-MS results were corrected by a factor 2/3 to consider that the sum of 2-methytetrols was quantified in this case

Fig. 1. Comparison of the average SOA marker concentrations (mg kg^{-1}) (dry-mass basis) in the SRM 1649b (urban dust) obtained according to the extraction procedure used (sonication or QuEChERS-like extraction), analytical method (GC/MS or HPLC/MS-MS) and by institution (INERIS, NIST and LSCE). n=18 to 20 for the extraction procedures, 10 to 28 for the analytical methods and 5 to 23 for the laboratories/institutes. Sample extracts were 3 times injected and 50 mg of SRM was used. The error bars correspond to the standard deviation ($\pm 1\ \sigma$) for the total number of analyses performed.


Concentrations dry-mass basis (mg kg-1)
QuEChERS
Sonication
GC/MS
HPLC/MS-MS
NIST
INERIS
LSCE
Succinic acid
α-Methylglyceric acid
DHOPA
cis-Pinonic acid
3-Hydroxyglutaric acid
Pinic acid
Phthalic acid
4-Me-5-Nitrocatechol
3-Me-5-Nitrocatechol
2-Methylerythritol
MBTCA
β-Caryophyllinic acid

Graphical abstract