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**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 synthesized 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 ($\varnothing = 16$ 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, $3 \times 2 \times 71$ mm, OD $\times$ ID $\times$ L) and for NIST, a splitless injector (with a Restek Sky low pressure drop precision inlet liner w/wool, $6.3 \times 4 \times 78.5$ mm). Compounds were separated using capillary columns with equivalent 5% phenyl-methylpolysiloxane phase $60 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ (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 $20^\circ\text{C min}^{-1}$, further followed by a ramp to 300°C at 5°C min^{-1} , then ramped at $10^\circ\text{C min}^{-1}$ 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 $\times$ 150 mm $\times$ 3 μ m) and Waters Acquity C18 HSST3 column (2.1 mm $\times$ 100 mm $\times$ 1.8 μ m), 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 μ L 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 $^{\circ}\text{C}$, 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 $\text{pg } \mu\text{l}^{-1}$ 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-methyltetrols 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/XXXXXXXXXX>

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.

References

1. Zhang Q, Jimenez JL, Canagaratna MR, Allan JD, Coe H, Ulbrich I, et al. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. *Geophys Res Lett*. 2007;34(13):L13801.

2. Ziemann PJ, Atkinson R. Kinetics, products, and mechanisms of secondary organic aerosol formation. *Chem Soc Rev.* 2013;41(19):6582-605.
3. Carlton AG, Wiedinmyer C, Kroll JH. A review of Secondary Organic Aerosol (SOA) formation from isoprene. *Atmos Chem Phys.* 2009;9(14):4987-5005.
4. Hallquist M, Wenger JC, Baltensperger U, Rudich Y, Simpson D, Claeys M, et al. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos Chem Phys.* 2009;9(14):5155-236.
5. Kroll JH, Seinfeld JH. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos Environ.* 2008;42(16):3593-624.
6. Zhang Q, Jimenez JL, Canagaratna MR, Ulbrich IM, Ng NL, Worsnop DR, et al. Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review. *Anal Bioanal Chem.* 2011;401(10):3045-67.
7. Srivastava D, Favez O, Perraudin E, Villenave E, Albinet A. Comparison of Measurement-Based Methodologies to Apportion Secondary Organic Carbon (SOC) in PM_{2.5}: A Review of Recent Studies. *Atmosphere.* 2018;9(11):452.
8. Nozière B, Kalberer M, Claeys M, Allan J, D'Anna B, Decesari S, et al. The Molecular Identification of Organic Compounds in the Atmosphere: State of the Art and Challenges. *Chem Rev.* 2015;115(10):3919-83.
9. Kleindienst TE, Jaoui M, Lewandowski M, Offenberg JH, Lewis CW, Bhavsar PV, et al. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location. *Atmos Environ.* 2007;41(37):8288-300.
10. Srivastava D, Favez O, Bonnaire N, Lucarelli F, Haeffelin M, Perraudin E, et al. Speciation of organic fractions does matter for aerosol source apportionment. Part 2: Intensive short-term campaign in the Paris area (France). *Sci Total Environ.* 2018;634:267-78.

11. Srivastava D, Tomaz S, Favez O, Lanzafame GM, Golly B, Besombes J-L, et al. Speciation of organic fraction does matter for source apportionment. Part 1: A one-year campaign in Grenoble (France). *Sci Total Environ*. 2018;624:1598-611.
12. Al-Naiema IM, Hettiyadura APS, Wallace HW, Sanchez NP, Madler CJ, Cevik BK, et al. Source apportionment of fine particulate matter in Houston, Texas: insights to secondary organic aerosols. *Atmos Chem Phys*. 2018;18(21):15601-22.
13. Srivastava D, Favez O, Petit J-E, Zhang Y, Sofowote UM, Hopke PK, et al. Speciation of organic fractions does matter for aerosol source apportionment. Part 3: combining off-line and on-line measurements. *Sci Total Environ*. 2019;<https://doi.org/10.1016/j.scitotenv.2019.06.378>.
14. Edney EO, Kleindienst TE, Jaoui M, Lewandowski M, Offenberger JH, Wang W, et al. Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_x/SO₂/air mixtures and their detection in ambient PM_{2.5} samples collected in the eastern United States. *Atmos Environ*. 2005;39(29):5281-9.
15. Claeys M, Graham B, Vas G, Wang W, Vermeylen R, Pashynska V, et al. Formation of Secondary Organic Aerosols Through Photooxidation of Isoprene. *Science*. 2004;303(5661):1173.
16. Szmigielski R, Surratt JD, Gómez-González Y, Van der Veken P, Kourtshev I, Vermeylen R, et al. 3-methyl-1,2,3-butanetricarboxylic acid: An atmospheric tracer for terpene secondary organic aerosol. *Geophys Res Lett*. 2007;34(24):L24811.
17. Mutzel A, Rodigast M, Iinuma Y, Böge O, Herrmann H. Monoterpene SOA – Contribution of first-generation oxidation products to formation and chemical composition. *Atmos Environ*. 2016;130:136-44.
18. Claeys M, Szmigielski R, Kourtshev I, Van der Veken P, Vermeylen R, Maenhaut W, et al. Hydroxydicarboxylic Acids: Markers for Secondary Organic Aerosol from the Photooxidation of α -Pinene. *Environ Sci Technol*. 2007;41(5):1628-34.

19. Yu J, Cocker DR, Griffin RJ, Flagan RC, Seinfeld JH. Gas-Phase Ozone Oxidation of Monoterpenes: Gaseous and Particulate Products. *J Atmos Chem.* 1999;34(2):207-58.
20. Glasius M, Lahaniati M, Calogirou A, Di Bella D, Jensen NR, Hjorth J, et al. Carboxylic Acids in Secondary Aerosols from Oxidation of Cyclic Monoterpenes by Ozone. *Environ Sci Technol.* 2000;34(6):1001-10.
21. Jang M, Kamens RM. Newly characterized products and composition of secondary aerosols from the reaction of α -pinene with ozone. *Atmos Environ.* 1999;33(3):459-74.
22. Christoffersen TS, Hjorth J, Horie O, Jensen NR, Kotzias D, Molander LL, et al. cis-pinic acid, a possible precursor for organic aerosol formation from ozonolysis of α -pinene. *Atmos Environ.* 1998;32(10):1657-61.
23. Jaoui M, Lewandowski M, Kleindienst TE, Offenberg JH, Edney EO. β -caryophyllinic acid: An atmospheric tracer for β -caryophyllene secondary organic aerosol. *Geophys Res Lett.* 2007;34(5):L05816.
24. Kawamura K, Bikkina S. A review of dicarboxylic acids and related compounds in atmospheric aerosols: Molecular distributions, sources and transformation. *Atmos Res.* 2016;170:140-60.
25. Kleindienst TE, Jaoui M, Lewandowski M, Offenberg JH, Docherty KS. The formation of SOA and chemical tracer compounds from the photooxidation of naphthalene and its methyl analogs in the presence and absence of nitrogen oxides. *Atmos Chem Phys.* 2012;12(18):8711-26.
26. Kleindienst TE, Conver TS, McIver CD, Edney EO. Determination of Secondary Organic Aerosol Products from the Photooxidation of Toluene and their Implications in Ambient PM_{2.5}. *J Atmos Chem.* 2004;47(1):79-100.
27. Iinuma Y, Böge O, Gräfe R, Herrmann H. Methyl-nitrocatechols: atmospheric tracer compounds for biomass burning secondary organic aerosols. *Environ Sci Technol.* 2010;44(22):8453-9.

28. Wise S, Poster D, Kucklick J, Keller J, VanderPol S, Sander L, et al. Standard reference materials (SRMs) for determination of organic contaminants in environmental samples. *Anal Bioanal Chem.* 2006;386(4):1153-90.
29. NIST. Standard reference material 1649b, Urban dust. Gaithersburg, MD: National Institute of Standards and Technology; 2015.
30. Albinet A, Leoz-Garziandia E, Budzinski H, Villenave E. Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography-mass spectrometry with negative ion chemical ionisation. *J Chromatogr A.* 2006;1121(1):106-13.
31. Albinet A, Nalin F, Tomaz S, Beaumont J, Lestremau F. A simple QuEChERS-like extraction approach for molecular chemical characterization of organic aerosols: application to nitrated and oxygenated PAH derivatives (NPAH and OPAH) quantified by GC–NICIMS. *Anal Bioanal Chem.* 2014;406(13):3131-48.
32. Larsen RK, Schantz MM, Wise SA. Determination of Levoglucosan in Particulate Matter Reference Materials. *Aerosol Sci Technol.* 2006;40(10):781-7.
33. Kitanovski Z, Grgić I, Vermeulen R, Claeys M, Maenhaut W. Liquid chromatography tandem mass spectrometry method for characterization of monoaromatic nitro-compounds in atmospheric particulate matter. *J Chromatogr A.* 2012;1268(0):35-43.
34. Kitanovski Z, Grgić I, Yasmeeen F, Claeys M, Čusak A. Development of a liquid chromatographic method based on ultraviolet–visible and electrospray ionization mass spectrometric detection for the identification of nitrocatechols and related tracers in biomass burning atmospheric organic aerosol. *Rapid Commun Mass Spectrom.* 2012;26(7):793-804.
35. Clements AL, Seinfeld JH. Detection and quantification of 2-methyltetrols in ambient aerosol in the southeastern United States. *Atmos Environ.* 2007;41(9):1825-30.

36. Fu P, Aggarwal SG, Chen J, Li J, Sun Y, Wang Z, et al. Molecular Markers of Secondary Organic Aerosol in Mumbai, India. *Environ Sci Technol*. 2016;50(9):4659-67.
37. Hu D, Bian Q, Li TWY, Lau AKH, Yu JZ. Contributions of isoprene, monoterpenes, β -caryophyllene, and toluene to secondary organic aerosols in Hong Kong during the summer of 2006. *J Geophys Res, [Atmos]*. 2008;113(D22):D22206.
38. Rutter AP, Snyder DC, Stone EA, Shelton B, DeMinter J, Schauer JJ. Preliminary assessment of the anthropogenic and biogenic contributions to secondary organic aerosols at two industrial cities in the upper Midwest. *Atmos Environ*. 2014;84(0):307-13.
39. Kourtchev I, Ruuskanen TM, Keronen P, Sogacheva L, Dal Maso M, Reissell A, et al. Determination of isoprene and α -/ β -pinene oxidation products in boreal forest aerosols from Hyytiälä, Finland: diel variations and possible link with particle formation events. *Plant Biol*. 2008;10(1):138-49.
40. Gao S, Surratt JD, Knipping EM, Edgerton ES, Shahgholi M, Seinfeld JH. Characterization of polar organic components in fine aerosols in the southeastern United States: Identity, origin, and evolution. *J Geophys Res, [Atmos]*. 2006;111(D14).
41. Albinet A, Tomaz S, Lestremat F. A really quick easy cheap effective rugged and safe (QuEChERS) extraction procedure for the analysis of particle-bound PAHs in ambient air and emission samples. *Sci Total Environ*. 2013;450-451(0):31-8.
42. Tomaz S, Jaffrezo J-L, Favez O, Perraudin E, Villenave E, Albinet A. Sources and atmospheric chemistry of oxy- and nitro-PAHs in the ambient air of Grenoble (France). *Atmos Environ*. 2017;161:144-54.
43. Tomaz S, Shahpoury P, Jaffrezo J-L, Lammel G, Perraudin E, Villenave E, et al. One-year study of polycyclic aromatic compounds at an urban site in Grenoble (France): Seasonal variations, gas/particle partitioning and cancer risk estimation. *Sci Total Environ*. 2016;565:1071-83.

44. Mutzel A, Rodigast M, Iinuma Y, Böge O, Herrmann H. An improved method for the quantification of SOA bound peroxides. *Atmos Environ.* 2013;67:365-9.
45. Kleindienst TE, Lewandowski M, Offenberg JH, Edney EO, Jaoui M, Zheng M, et al. Contribution of primary and secondary sources to organic aerosol and PM_{2.5} at SEARCH network sites. *J Air Waste Manage Assoc.* 2010;60(11):1388-99.
46. Kourtchev I, Ruuskanen T, Maenhaut W, Kulmala M, Claeys M. Observation of 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols from Hyytiälä, Finland. *Atmos Chem Phys.* 2005;5(10):2761-70.
47. Alier M, van Drooge BL, Dall'Osto M, Querol X, Grimalt JO, Tauler R. Source apportionment of submicron organic aerosol at an urban background and a road site in Barcelona (Spain) during SAPUSS. *Atmos Chem Phys.* 2013;13(20):10353-71.
48. Yuan Q, Lai S, Song J, Ding X, Zheng L, Wang X, et al. Seasonal cycles of secondary organic aerosol tracers in rural Guangzhou, Southern China: The importance of atmospheric oxidants. *Environ Pollut.* 2018;240:884-93.
49. Ion AC, Vermeylen R, Kourtchev I, Cafmeyer J, Chi X, Gelencsér A, et al. Polar organic compounds in rural PM_{2.5} aerosols from K-pusztá, Hungary, during a 2003 summer field campaign: Sources and diel variations. *Atmos Chem Phys.* 2005;5(7):1805-14.

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			[14, 15]
2-Methylerythritol			
3-Methylbutane-1,2,3-tricarboxylic acid (MBTCA)		α -Pinene β -Pinene	[16, 17]
3-Hydroxyglutaric acid			[18]
Pinic acid			[17, 19-22]
cis-Pinonic acid			
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		Phenolic compounds (biomass burning)	[27]
3-Methyl-5-nitrocatechol			

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)
<i>Succinic acid-2,3,3,3-d4</i>	147, 251	19.54	<u>0.06</u> /0.035	-
Succinic acid ^a	129 , 247	19.61	0.035	1.0-1.3
α -Methylglyceric acid	219 , 306	19.74	<u>0.06</u> /0.035	1.0 -2.3
2,3-Dihydroxy-4-oxopentanoic acid (DHOPA)	218 , <u>189</u> , 350	24.71	<u>0.04</u> /0.05	3.7-11.0
cis-Pinonic acid	171 , 125	25.27	<u>0.04</u> /0.05	2.2-7.5
3-Hydroxyglutaric acid	185, 349	26.26	<u>0.08</u> /0.05	1.3-7.0
Pinic acid	129 , 171	28.50	<u>0.05</u> /0.05	6.3-7.6
Phthalic acid ^b	221, 295	29.04	<u>0.05</u> /0.05	0.9-8.4
<i>Meso-erythritol-1,1,2,4,4-d6</i>	208 , 220	24.50	<u>0.04</u> /0.1	-
2-Methylerythritol	<u>116</u> , 117, 219	25.74	<u>0.05</u> /0.05	1.1-4.2
<i>1,9-Nonanedioic acid-d14</i>	213, 331	31.10	<u>0.06</u> /0.035	-
3-Methylbutane-1,2,3-tricarboxylic acid (MBTCA)	204 , 245, <u>405</u>	30.34	<u>0.08</u> /0.05	0.6-14.5
β -Caryophyllinic acid	117 , 200	36.08	<u>0.08</u> /0.05	8.9-14.3
4-Methyl-5-nitrocatechol ^c	296, 313	31.06	<u>0.06</u> /0.035	1.5-10.3
3-Methyl-5-nitrocatechol ^c	298 , 313	32.28	<u>0.10</u> /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)
<i>Succinic acid-2,3,3,3-d4</i>	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	-	-	-	-	-	-	-	-	-
<i>Phthalic-3,4,5,6-d4 acid</i>	169→125	25	2.5	12	14	0	1.78	Hypercarb	-
Phthalic acid	165→121	30	5	12	12	0	2.27	Hypercarb	20
<i>1,9-Nonanedioic acid-d14</i>	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
<i>4-Methylcatechol-d3</i>	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.

Graphical abstract