“ALEXANDRU IOAN CUZA” UNIVERSITY OF IASI
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DOCTORAL SCHOOL OF CHEMISTRY

Chemical characterization of secondary organic aerosols in ambient particulate matter from Iasi, north-eastern Romania

SUMMARY OF THE PHD THESIS

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RECENT AIR (My SMIS 127324)

- ATMO-SOS (PCE 74/2022)
- PHONIC-HONO-SOA (444PED/02-11-2020)
- AI-FORECAST (PN-III-P4-ID-PCE-2016-0299)
- IGAC-CYCLO (PN-III-P4-ID-PCE-2016-0807)

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INTRODUCTION

Exploring the composition of the Earth's atmosphere is essential for establishing local, regional, and global regulations aiming the environment and human health protection. In 2019, the World Health Organization (WHO) estimated 4.2 million premature deaths due to exposure to fine particles (particles with an aerodynamic diameter equivalent < 2.5 μm, $PM_{2.5}$), which cause cardiovascular, respiratory and cancer diseases and 89% of the deaths were related to the population from the low-income countries (WHO, 2022). In atmospheric particulate matter, alongside the inorganic fraction, there is an organic fraction, representing from 20 % to 60 % of the aerosols mass (Johnston and Kerecman, 2019). This is extremely complex at the molecular level, comprising up to hundreds of thousands of compounds distributed between the gas phase and the particulate phase. Secondary organic aerosols (SOAs) are formed in the atmosphere by the transformation of the volatile organic compounds (Seinfeld and Pandis, 2006) emitted from various sources. SOAs have a significant impact on the climate(Kanakidou et al., 2005), air quality, and human health (Breysse et al., 2013). Models developed for the characterization of the atmospheric aerosols distribution in Europe (Martinsson et al., 2017; Kanakidou et al., 2005) and not only (Chen et al., 2017), predict underestimations of the organic fraction due to the lack of information associated especially with the SOAs fraction (Tsigaridis et al., 2014).

Regarding the chemical characterization of particulate matter in Romania, there are several studies (Galon-Negru et al., 2018, 2019; Arsene et al., 2011) carried out in urban areas, targeting water-soluble inorganic species and a low number of organic ions. In these studies, ~59% of the gravimetrically determined mass was not identified, suggesting that the organic fraction could present an important contribution that needs to be

investigated. The selection of the research topic aimed increasing the level of knowledge related to the atmospheric organic aerosols, especially of secondary origin in urban areas.

OBJECTIVES OF THE DOCTORAL THESIS

The research topic of the present doctoral thesis is based on the objectives of:

i) development of a method for the identification and quantification of molecular tracers for SOA by High-Performance Liquid Chromatography Electrospray Ionization Time-Of-Flight Mass Spectrometry (HPLC-ESI-ToF-MS);

ii) investigation of the organic fraction of the particulate matter by evaluation of the molecular organic constituents and water-soluble ions in aerosol samples from the Iasi urban area;

iii) investigation of the seasonal distribution of SOA tracers and their size distribution in order to evaluate precursor sources and formation processes counting also the influence of the meteorological factors;

iv) development of a method for the determination of polycyclic aromatic hydrocarbons (PAHs) and aromatic nitro derivatives from aerosol samples by Ultra-High Performance Liquid Chromatography with Diode Array Detector and Fluorescence Detector (UHPLC-DAD-FLD);

v) integration of the aerosol mass spectrometry into online organic aerosol analysis.

The doctoral thesis has the content distributed in 203 pages and includes 71 figures and 24 tables. The presented results are the subject of two scientific articles published as first author in journals with impact factor (10,753 and 4,601), located in the Q1 quartile (red) in the Web of Science database (Amarandei et al., 2023a, 2023b). Some of the results were disseminated in two publications, in journals indexed in databases without impact factor and at conferences organized at national (13) and international (3) levels.

PART II: PERSONAL CONTRIBUTIONS

II.1 EXPERIMENTAL

II.1.1 Presentation of location and atmospheric aerosols sampling

The aerosols sampling was carried out at the Air Quality Monitoring Station (AMOS) within the "Alexandru Ioan Cuza" University of Iasi. The sampling site characteristics are presented in studies conducted by Arsene et al. (2007,2011) and Galon-Negru (2019). AMOS is located north-east of the city center, on the roof of Building C of the "Alexandru Ioan Cuza" University of Iasi at 35 m above the ground level **(Figure II.1.1)**. The sampling point is representative for the urban area and allows assessing the influences of the long-range air masses transport.

Figure II.1.1: Presentation of the sampling location and systems used for aerosols sampling.

The main sampling strategy included a Dekati Low Pressure Impactor (DLPI) that classifies particles by size into 13 fractions distributed in the diameter size range from 0.0276 to 9.94 µm (Galon-Negru et al., 2018, 2019). For the HPLC-ESI-ToF-MS analysis, sampling was performed between July

and December 2018, once per week, with a total of 19 events generating 247 aerosol samples (Amarandei et al. 2023a). The development of the analysis method also included aerosol samples collected on quartz filters (47 mm in diameter, Whatman) with a Stacked Filter Unit (SFU).

Meteorological parameters including atmospheric temperature, relative humidity, wind speed, wind direction and solar radiation were recorded by the Hawk GSM-240 weather station located at the sampling site. Air mass trajectories were generated using the HYSPLIT computational model developed by the Air Resources Laboratory of the National Oceanic and Atmospheric Administration (NOAA) (Rolph et al., 2017; Stein et al., 2015).

II.1.2 Analytical techniques used for aerosol investigation

An HPLC1260 Infinity (Agilent Technologies) coupled with an ESI-ToF-MS 6224 (Agilent Technologies) was used to determine organic tracers. For the experimental investigations, reagents of purity suitable for the analytical determinations were used (purity > 97 %; sources: Sigma-Aldrich, Merck, TCI, Agilent Technologies, Leibniz Institute for Tropospheric Research, Leipzig in Germany). For the analysis of the molecular markers in atmospheric aerosol samples, the extraction method proposed by Amarandei et al. (2023a) was used.

The HPLC-ESI-ToF-MS database obtained for the aerosol samples was processed with MZmine 2.53 (https://github.com/mzmine/mzmine2/releases; Myers et al., 2017; Pluskal et al., 2010), following the specific workflow presented by Amarandei et al. (2023a). Following processing, information such as the exact mass, molecular formula, retention time and chromatographic peak area of the compounds identified in the aerosol samples were obtained. The estimated molecular formulas were grouped considering the constituent elements as follows: CHO, CHON, CHOS, and CHONS. In order to assess the degree of unsaturation,

aromaticity and the oxidation of the constituents with the molecular formula $C_cH_hO_oN_nS_s$, the double bond equivalent (DBE), aromaticity equivalent (X_C) (Yassine et al., 2014), and carbon oxidation state (OS_C) (Kroll et al., 2011) were calculated. The weighted mean for molecular weight (MW_w) and other characteristic parameters such as H/C (H/C_w), O/C (O/C_w), DBE (DBE_w) and X_C (X_{Cw}) were calculated using the method presented by Amarandei et al. (2023a).

In atmospheric aerosol samples, quantification of water-soluble ions was performed using the DIONEX ICS-5000$^+$ DP system (Thermo Scientific, USA) and the procedure presented by Galon-Negru (2019).

For the determination of 18 polycyclic aromatic hydrocarbons (Mix 14, Dr. Ehrenstorfer) and 20 aromatic acids and nitroderivatives (purity > 96 %; source: Sigma Aldrich, TCI, Merck, ACS Dr. Claudiu ROMAN synthesis) was used an UHPLC-DAD-FLD 1290 Infinity (Agilent Technologies).

For the online determination of the mass concentrations and size distributions of the main non-refractory species in indoor aerosols, the High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne) was used. For the calibration of particle size and ionization efficiency were used the following systems: Scanning Mobility Particle Sizer (SMPS, TSI 3936) consisting of an electrostatic classifier (TSI 3080), a Differential Mobility Analyzer (DMA, TSI 3081), and a water-based Condensing Particle Counter (CPC, TSI 3787).

II.2 DEVELOPMENT OF A HPLC-ESI-ToF-MS METHOD FOR THE DETERMINATION OF ORGANIC CONSTITUENTS IN ATMOSPHERIC AEROSOLS

A series of determinations have been conducted to develop an HPLC-ESI-ToF-MS method for SOA molecular markers identification and quantification. The targeted compounds included markers of biogenic SOAs from *α*-/*β*-

pinene (pinic, pinonic, norpinonic, *trans*-norpinic, terpenylic, terebic, 3-methyl-1,2,3-butanetricarboxylic (MBTCA) acids, and diaterpenyl acid acetate(DTAA)) precursor. For anthropogenic sources were considered phenolic derivatives: 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, 2,6-dimethyl-4-nitrophenol, 4-nitrocatechol, 3-methoxycatechol, 4-methylcatechol, catechol, vanillin, and carboxylic acids: vanillic, D-malic, adipic, pimelic, benzoic and phthalic acids. During the method development, the compounds 2-methylresorcinol, 5-methylresorcinol, camphoric acid, camphor-10-sulfonic acid, and octylsulfate were also evaluated. These are suitable to be used as internal standard (camphoric acid), surrogate standards (camphor-10-sulphonic acid and octylsulfate) or allow assessing the performance of the separation method of the isomers (*e.g.,* 2-methylresorcinol, 5-methylresorcinol, and 4-methylcatechol).

The results obtained for the chromatographic separation and detection optimization process are presented below.

II.2.2 Development of the analysis method

II.2.3 Optimization of the chromatographic conditions

Three analytical columns were tested for the separation of the compounds: Zorbax Extend C18 (2.1×50 mm, 1.8 µm), HILIC Luna (4.6×150 mm, 5 µm), and Poroshell 120 EC-C18 (4.6×50 mm, 2.7 µm).

In order to optimize the analytes separation, different gradient elution with methanol (MeOH) or acetonitrile (ACN) and aqueous phase have been tested. The best separation was obtained using the Poroshell column **(Figure II.2.2)**, gradient solution with ACN and aqueous solution with acetic acid modifier (0.1 %), at a flow rate of 0.8 mL min^{-1} (**Figure II.2.2b**). Compared to the use of methanol **(Figure II.2.2a)**, the use of acetonitrile for elution led to a significant improvement in the separation resolution pinc acid (6) and norpinonic acid (7) (from 0.16 to 1.87) while maintaining at a reasonable value

the separation resolution of camphoric acid (9) and pinonic acid (10) compounds (**Figure II.2.2b**).

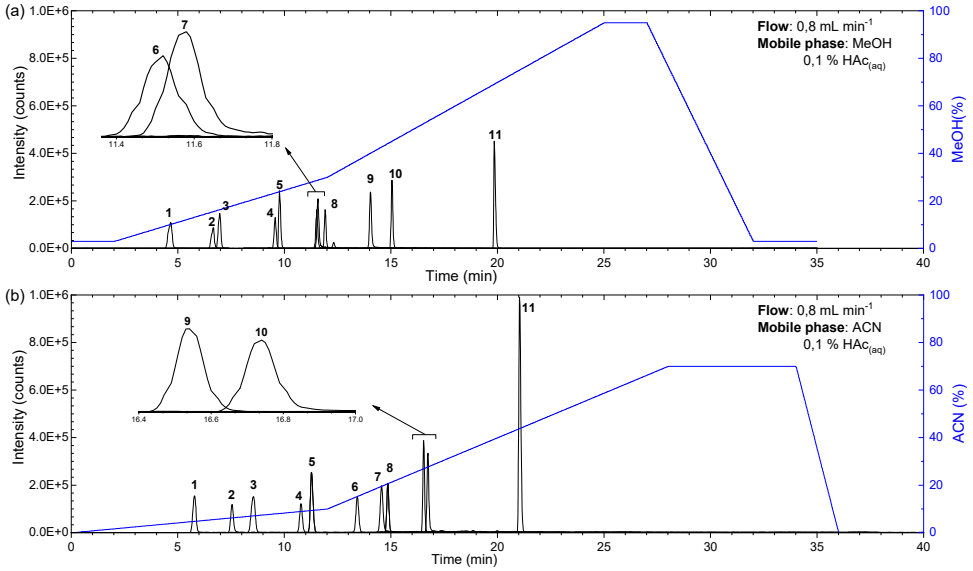

Figure 2.2: Representative chromatograms for separation of 11 compounds using Poroshell column and gradient with methanol **(a)** or ACN **(b)** (terebic acid (1), MBTCA (2), terpenylic acid (3), *trans*-norpinic acid (4), camphor-10-sulfonic acid (5), pinic acid (6), norpinonic acid (7), DTAA (8), camphoric acid (9), acid *cis*-pinonic (10), octylsulfate (11)) (Amarandei et al., 2023b).

Using the Poroshell column, series of tests were conducted to optimize the separation (**Figure II.2.4)** and to improve the sensitivity of the analysis method. As observed in **Figure II.2.4a**, when the aqueous mobile phase is not stained with acetic acid, two isobaric compounds from the standard mixture, *i.e.*, terpenylic acid (3) and *trans*-norpinic acid (4), are not satisfactory separated. For the analysis of complex matrices this aspect is an important analytical issue because the TOF-MS analyzer cannot discriminate between species with identical m/z value (*e.g.*, 171.0657) for associated molecular ions. Tests performed with mobile aqueous phase containing 0.05 or 0.1 % of acetic acid indicated both situations as being favorable for the compounds separation. However, the mobile aqueous phase containing 0.1 % of acetic acid provided an improved peak shape.

The assessment of the influence of column temperature on analyte separation has shown that at ambient temperature (column temperature not controlled) and at 25 °C compounds number 4 (*trans*-norpinic acid) and 5 (camphor-10-sulfonic acid) are not separated (**Figure II.2.4a)**.

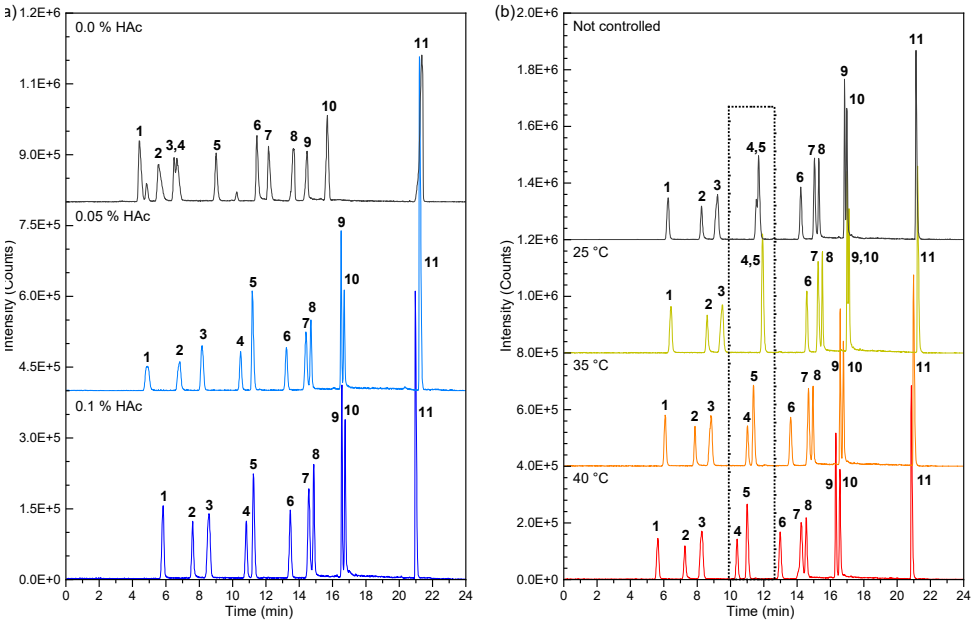

Figure II.2.4: Representative chromatograms for the evaluation of the influence of the acetic acid concentration (**a**) and column temperature **(b)** on analytes separation (terebic acid (1), MBTCA (2), terpenylic acid (3), *trans*-norpinic acid (4), camphor-10-sulfonic acid (5), pinic acid (6), norpinonic acid (7), DTAA (8), camphoric acid (9), *cis*-pinonic acid (10), octylsulfate (11)) (Amarandei et al., 2023b).

The chromatograms presented in **Figure II.2.6a** show the separation on the Poroshell column of 28 compounds included in the further analyses. **Figure II.2.6b** presents six oxidation products of pinene identified in atmospheric aerosol samples collected in Iasi urban area. **Figure II.2.6d** show unknown compounds with the same estimated molecular formula: 6 chromatographic peaks for molecular formula C_7H_7NO4 (168.0302 m/z), 4 peaks for $C_8H_9NO_4$ (182.0872 m/z) and 3 peaks for $C_7H_6NO_3$ (152.0368 m/z).

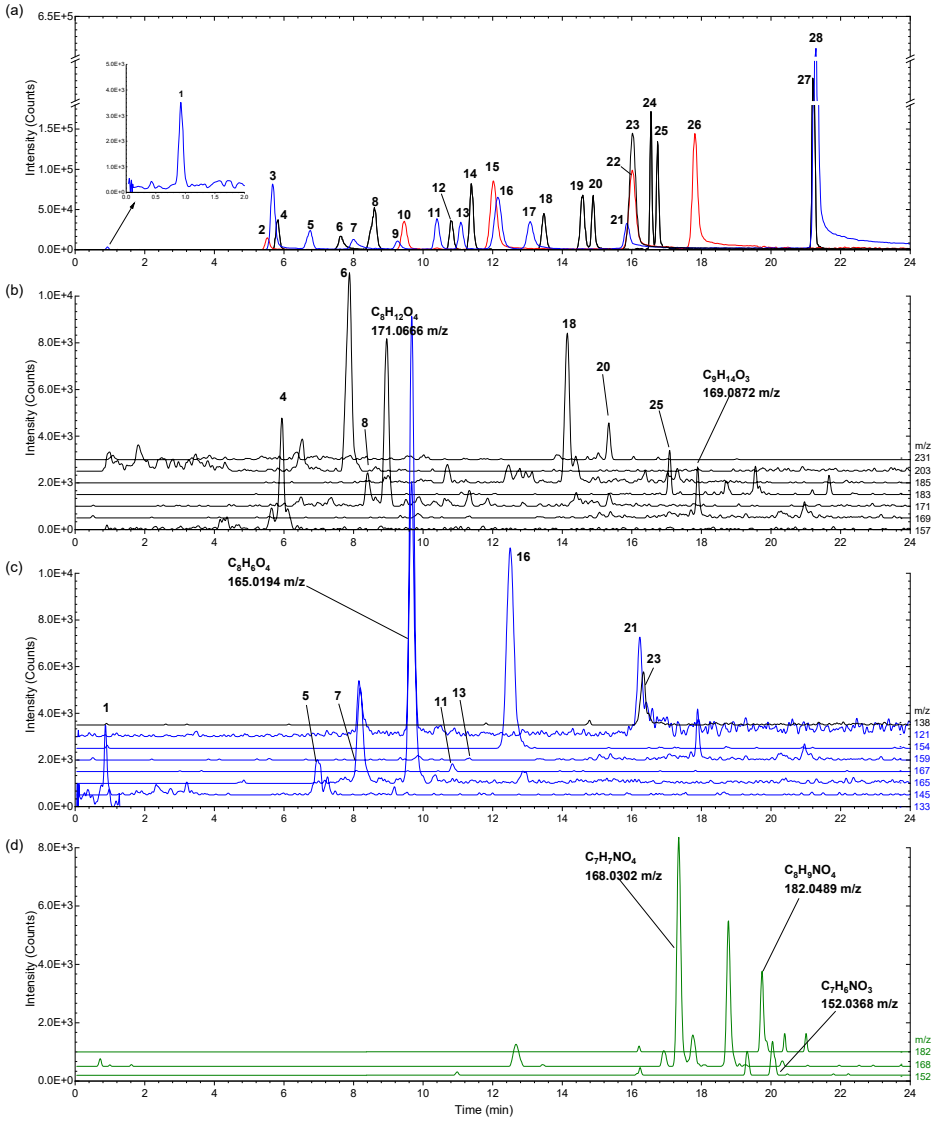

Figure II.2.6: Representative chromatograms obtained for the mixture of standards **(a)** and species identified in an aerosol sample (stage 5) collected from Iasi urban area (3 to 6 September 2018) which are markers of pinene **(b)** and other compounds **(c)** and species with that and molecular weight separated using optimized method **(d)** (D-malic acid (1), 2-methylresorcinol (2), catechol (3), terebic acid (4), adipic acid (5), MBTCA (6), phthalic acid (7), terpenylic acid (8), 3-methoxycatechol (9), 5-methylresorcinol (10), vanillic acid (11), *trans*-norpinic acid(12), pimelic acid (13), camphor-10-sulfonic acid (14), 4-methylcatechol (15), 4-nitrocatechol (16), vanillin (17), pinic acid (18), norpinonic acid (19), DTAA (20), benzoic acid (21), 2,6-dinitrophenol (22), 4-nitrophenol (23), camphoric acid (24), pinonic acid (25), 2,4-dinitrophenol (26), octylsulfate (27), 2,6-dimethyl-4-nitrophenol (28)) (Amarandei et al., 2023b).

II.2.3.1 Optimization of the ionization source operating conditions

The acetonitrile elution method, by comparison with the methanol method, provided a higher sensitivity for the species of interest. Thus, for further tests the acetonitrile elution method was selected, considering also the better separation achievement. For the ionization source, the parameters such as drying gas (temperature and flow), nebulizer pressure and capillary voltage have been optimized (**Figure II.2.7**). The assessment of the skimmer's potential effect on the sensitivity of the method is presented in **Figure II.2.8**.

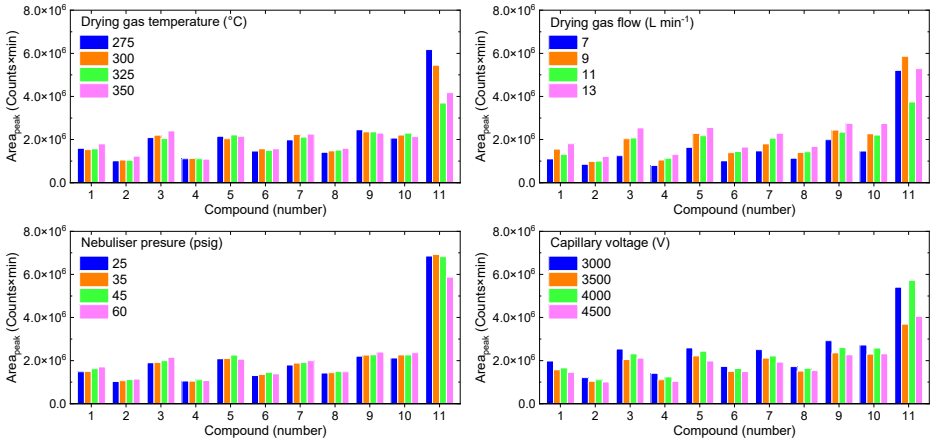

Figure II.2.7:Variation of the peak area at different values of the temperature and flow rate of drying gas, nebuliser pressure and capillary voltage for the selected analytes used to optimize the method (terebic acid (1), MBTCA (2), terpenylic acid (3), *trans*-norpinic acid (4), camphor-10-sulfonic acid (5), pinic acid (6), norpinonic acid (7), DTAA (8), camphoric acid (9), *cis*-pinonic acid (10), octylsulfate (11)).

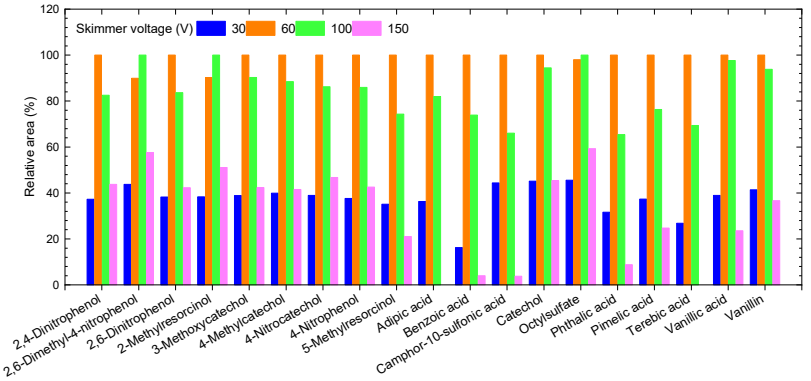

Figure II.2.8: Dependence of the relative area of the chromatographic peak on the skimmer voltage for 19 compounds (Amarandei et al., 2021b).

The variation of peak area has been expressed as a percentage from the maximum value corresponding to each compound under the conditions assessed. The results suggest that the optimal value for the skimmer's potential is 60 V.

II.2.3.2 Evaluation of the fragmentation process of the analytes

Regarding the analytes fragmentation, the potential of the fragmentor was assessed in the present work. It has been observed that when the fragmentor voltage increases above 125 V there is a general decrease in the intensity of the signal (**Figure II.2.9a**), accompanied by a simultaneous increase in the signal intensity of fragments associated with CO_2 and H_2O neutral loss processes for carboxylic acids (**Figure II.2.9b**). The results show that the application of the 150 V potential reduces the formation of clusters with the mobile phase constituents (*e.g.*, with acetic acid).

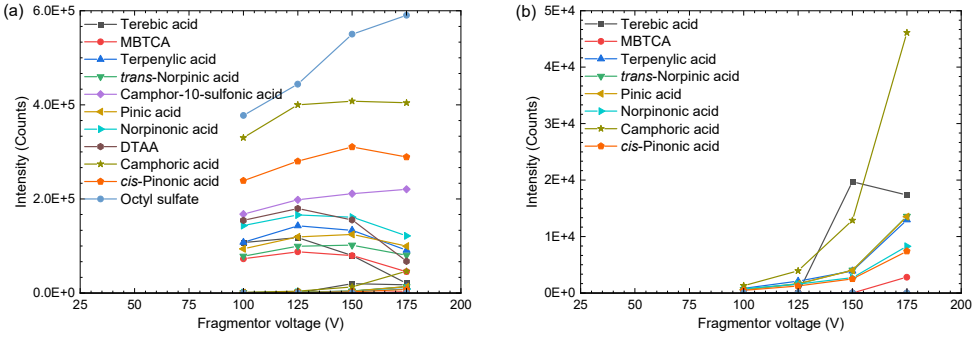

Figure II.2.9: Effect of fragmentor voltage on molecular ion abundance $[M\text{-}H]^-$ **(a)** and fragments associated with the loss of CO_2 from the carboxylic acids $[M\text{-}H\text{-}CO_2]^-$ **(b)** (Amarandei et al., 2023b).

II.2.3.3 Evaluation of the influence of secondary nebulizer pressure on the accuracy of molecular mass determination

In the present work, the effect of the secondary nebulizer pressure, connected to the reference mixture used for continuous correction of m/z values provided by the mass spectrometer, on the accuracy of the m/z ratio measurement and on sensitivity was evaluated. Determinations were made using the acquisition

range from 122 to 500 m/z without introducing the reference mixture. Also, determinations were involved for different pressure values of the reference nebulizer: 0 psig, 1 psig and 5 psig (**Figure II.2.11**).

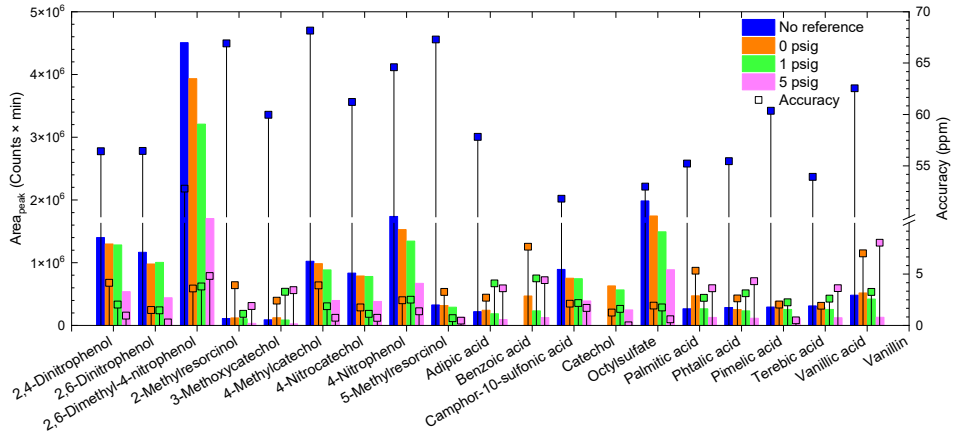

Figure II.2.11: Effect of the reference nebulizer pressure on signal intensity and accuracy of molecular weight determination (ppm). Conditions assessed: no reference (and acquisition in the range of 122-500 m/z) and reference pressure of 0 psig, 1 psig, and 5 psig (and acquisition in the range of 80-1100 m/z) (Amarandei et al., 2023b).

Considering the precision of the molecular mass determination, the values were clearly unsatisfactory when the reference mixture was not used, with values greater than 50 ppm (**Figure II.2.11**). Taking into account the variation in accuracy (< 5 ppm) and method sensitivity under the assessed conditions, a value of 1 psig for reference nebulizer pressure was selected in the final method.

II.2.4 Characterization of the analysis method

II.2.4.1 General characteristics of the method

Using the optimized conditions for HPLC-ESI-ToF-MS analysis, method parameters such as accuracy in the molecular mass determination, the linearity of the analytical signal dependence on analyte concentration, detection and quantification limits were evaluated and presented in **Table II.2.5**.

Table II.2.5:Analytical performance of the developed HPLC-ESI-TOF-MS method (Amarandei et al., 2023b).

No.	Compound	MF	Molecular mass		Calibration curve				LOD[(1)]	LOQ[(1)]
			Theoretic (Da)	Accuracy (ppm)	Range (µg L^{-1})	Slope	Intercept	R^2	(µg L^{-1})/(pg m^{-3})	(µg L^{-1})/(pg m^{-3})
1	D-Malic acid	$C_4H_6O_5$	134.0215	3.84	10-1000	31.2	-2655.1	0.994	1.35 / 5.63	4.5 / 18.76
2	2-Methylresorcinol	$C_7H_8O_2$	124.0524	1.01	25-2500	107.5	-1596.3	0.999	29 / 120.83	96.66 / 402.75
3	Catechol	$C_6H_6O_2$	110.0368	-0.05	10-1000	1189.3	-9487.2	0.999	13.31 / 55.46	44.37 / 184.88
4	Terebic acid	$C_7H_{10}O_4$	158.0579	-0.93	10-1000	612.0	-791.5	0.999	0.68 / 0	2.26 / 0.01
5	Adipic acid	$C_6H_{10}O_4$	146.0579	4.54	10-1000	430.6	-80.9	0.999	7.54 / 31.43	25.15 / 104.78
6	MBTCA	$C_8H_{12}O_6$	204.0634	-0.55	8-500	406.0	-5955.9	0.999	0.91 / 3.8	3.04 / 12.65
7	Phthalic acid	$C_8H_6O_4$	166.0266	2.93	15-1500	462.2	-7888.6	0.997	8.9 / 37.09	29.67 / 123.62
8	Terpenylic acid	$C_8H_{12}O_4$	172.0736	-0.24	8-500	1145.4	-2274.3	0.999	0.49 / 2.05	1.64 / 6.85
9	3-Methoxycatechol	$C_7H_8O_3$	140.0473	2.34	8-800	261.8	-1400.9	0.997	8.92 / 37.16	29.73 / 123.87
10	5-Methylresorcinol	$C_7H_8O_2$	124.0524	-0.18	25-2500	327.5	-1478.5	0.999	0.57 / 2.37	1.89 / 7.89
11	Vanillic acid	$C_8H_8O_4$	168.0423	4.03	20-2000	423.8	-443.7	0.999	2.29 / 9.54	7.63 / 31.81
12	*trans*-Norpinic acid	$C_8H_{12}O_4$	172.0736	0.46	8-500	571.1	-747.4	0.999	1.48 / 6.16	4.93 / 20.53
13	Pimelic acid	$C_7H_{12}O_4$	160.0736	4.37	10-1000	650.8	4196.0	0.999	13.53 / 56.36	45.09 / 187.88
14	Camphor-10-sulfonic acid	$C_{10}H_{16}O_4S$	232.0769	-1.73	15-1500	1289.6	-1264.3	0.999	1.93 / 6.49	6.43 / 21.63
15	4-Methylcatechol	$C_7H_8O_2$	124.0524	-1.18	20-2000	1329.3	-23148.7	0.999	1.48 / 6.16	4.93 / 20.52
16	4-Nitrocatechol	$C_6H_5NO_4$	155.0219	-0.47	10-1000	2197.9	-16922.2	0.999	1.12 / 4.69	3.75 / 15.62
17	Vanillin	$C_8H_8O_3$	152.0473	4.81	15-1500	657.9	-2400.2	0.999	2.64 / 10.99	8.79 / 36.64
18	Pinic acid	$C_9H_{14}O_4$	186.0892	0.69	8-500	741.8	-714.7	0.999	1.04 / 4.34	3.47 / 14.46
19	Norpinonic acid	$C_9H_{14}O_3$	170.0943	-0.75	8-500	1049.2	-284.7	0.999	1.13 / 4.72	3.77 / 15.72
20	DTAA	$C_{10}H_{16}O_6$	232.0947	-1.64	8-500	689.8	-563.9	0.999	1.19 / 4.97	3.98 / 16.58
21	Benzoic acid	$C_7H_6O_2$	122.0368	-4.33	15-1500	546.8	868.9	0.999	7.67 / 31.96	25.57 / 106.54
22	2,6-Dinitrophenol	$C_6H_4N_2O_5$	184.0120	-0.88	10-1000	2415.3	5053.9	0.999	4.73 / 19.72	15.78 / 65.74
23	4-Nitrophenol	$C_6H_5NO_3$	139.0269	-1.35	10-1000	3636.9	-16730.1	0.999	0.26 / 1.1	0.88 / 3.67
24	Camphoric acid	$C_{10}H_{16}O_4$	200.1049	-1.26	8-500	1459.0	-3590.5	0.999	1.56 / 8.03	5.19 / 26.77
25	Pinonic acid	$C_{10}H_{16}O_3$	184.1099	-1.35	8-500	1378.5	-6226.7	0.998	1.18 / 4.93	3.94 / 16.42
26	2,4-Dinitrophenol	$C_6H_4N_2O_5$	184.0120	-1.39	10-1000	3035.2	-11539.2	0.999	13.04 / 54.34	43.47 / 181.13
27	Octylsulfate	$C_8H_{18}O_4S$	210.0926	-0.92	10-1000	4810.3	-35283.1	0.999	4.13 / 17.19	13.75 / 57.29
28	2,6-Dimethyl-4-nitrophenol	$C_8H_9NO_3$	167.0582	4.46	15-1500	7259.5	-1346.3	0.999	14.39 / 59.97	47.98 / 199.9

[(1)]LOD and LOQ values expressed in pg m^{-3} are estimated considering the sampling of 120 m^3 atmospheric air.

II.2.4.2 Matrix effect evaluation

Matrix effect (ME) evaluation is essential for the development of a reliable LC-MS analysis method. **Figure II.2.13** show ME influence on the mass spectrometer response during the analysis of molecular markers in atmospheric aerosols sampled on the aluminum substrate (**Figure II.2.13a**) and quartz filters (**Figure II.2.13b**) spiked with a 19 compounds standard mixture. The mean ME values were in the (84.3 - 120.1)% range. Higher values and greater variability were obtained for 2,6-dimethyl-4-nitrophenol (120.1 ± 27.6)% and benzoic acid (119.3 ± 31.3)% in aerosol samples collected on quartz filters.

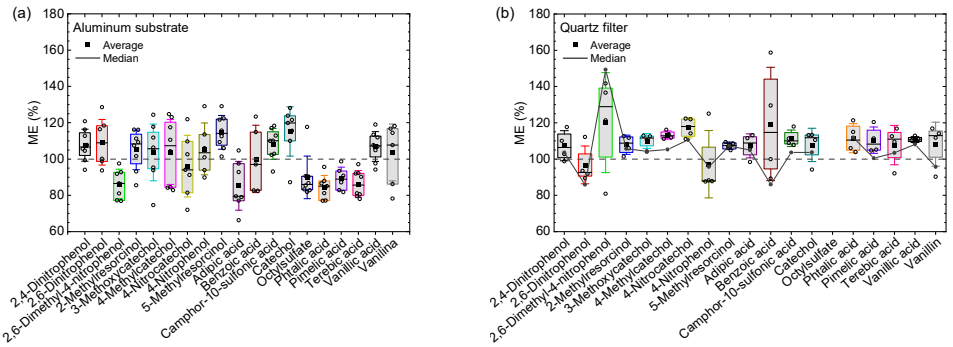

Figure II.2.13: Matrix effect (ME) variation (25th to 75th percentiles) for aerosol samples collected on aluminum substrate (n = 7) **(a)** and quartz filter (n = 4) **(b)**. Solid line represents the values obtained for the ME evaluated by graphical method.

The graphical representation of the dependence between the slopes of the calibration curves for analytes in the presence of the aerosol matrix and in the pure solvent (**Figure II.2.14**), shows a distinct behavior of 2,6-dimethyl-4-nitrophenol.

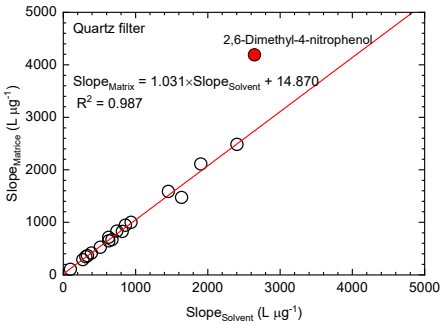

Figure II.2.14: Regression of slopes of the matrix calibration curves (atmospheric aerosols collected on quartz filter) *versus* solvent for the 19 analytes, showing a higher matrix effect for 2,6-dimethyl-4-nitrophenol (excluded from the linear regression of data) compared to other compounds (Amarandei et al., 2020).

II.2.4.3 Evaluation of extraction method and stability of the aerosol samples

The efficiency of the extraction process of the organic molecular markers from the atmospheric aerosol samples was evaluated for both samples collected on aluminum substrate and quartz filters. The recovery factor was determined using atmospheric aerosol samples with standard addition. **Table II.2.6** shows the values obtained for the recovery factors in different extraction conditions.

Table II.2.6: Recovery factors (mean±SD, n=3) for atmospheric aerosols collected on aluminum substrate and quartz filters (Amarandei et al., 2023b).

Compound	Current study				Other studies
	Aluminum substrate		Quartz filter		
	Extraction solvent(acetonitrile: water, v/v)				
	95:5	90:10	95:5	90:10	
2,4-Dinitrophenol	92.5±6.4	88.1±7.5		101.9±1.5	86[a]
2,6-Dinitrophenol	87.4±10.4	75.5±11.3		89.6±4.2	
2,6-Dimethyl-4-nitrophenol	79.4±7.9	85.2±15.7		76.4±14.1	95[a]
2-Methylresorcinol	106.2±8.2	88.4±6.4		92.5±3.5	
3-Methoxy	95.8±14.8	87.2±2.8		87.9±6.8	
4-Methylcatechol	100.5±5.9	91.6±1.3		86.3±2.7	
4-Nitrocatechol	97.8±18.6	88.5±14.6		88.5±3.5	75[a]
4-Nitrophenol	106.7±5.2	87.9±0.2		87.5±3.7	85[a]
5-Methylresorcinol	107.2±11.4	81.2±2.0		83.6±4.9	
Adipic acid	85.2±11.9	89.4±10.4		86±4.2	104[b]; 94±7.5[c], 79±4[d]
Benzoic acid	90.1±14.8	89.9±22.6		94.9±5.7	
Camphor-10-sulfonic acid	92.9±8.1	90.6±1.7	94±10.7	85.7±6.9	74±8[d]
Camphoric acid	82.4±0.6		95.2±11.3		70±11[e]
Catechol	107.8±10.1	86.2±5.8		91.4±3.6	
DTAA	72.2±16.6		76±9.8		36±13[d]
MBTCA	33.7±0.1				55[f]; 11±3[d]
Norpinonic acid	71.8±5.5		87±10.9		105[b]
Octylsulfate	71.4±8.4	97.0±10.2	66.2±12	101±8.1	91[b]
Phthalic acid	114.1±6.5	115.4±14.0		79.5±1.8	88[g]; 105±2.3[c]
Pimelic acid	98±7.0	85.3±3.6		80.9±9.1	100[b]; 96±7.5[c]
Pinic acid	82.4±11		75.5±9.9		78±14[d]; 73±6[e], 66±7[h]
Pinonic acid	73.3±6.4		90.1±15.2		76±3[d]; 72 ±11[e], 77±1[h];
Terebic acid	103±16.6	87.4±8.0	96.8±11.1	89.3±3.8	104[b]
Terpenic acid	59.1±0.8		66.5±9.8		80±8[d]
trans-Norpinic acid	81.4±17.3		94.2±13.1		72±15[e]
Vanillic acid	98±6.0	80.9±7.8		83.9±4.6	94[b]
Vanillin	106.6±5.6	85.1±7.2		85±2.3	89[b]

[a](Hoffmann et al., 2007), [b](Kwiezinski et al., 2021), [c](Kitanovski et al., 2011), [d](Kristensen and Glasius, 2011), [e](Warnke et al., 2006), [f](Emanuelsson et al., 2013), [g](Mirivel et al.,2011), [h](Feltracco et al., 2018)

The stability of the atmospheric aerosol samples was assessed to identify the risks of compound loss or degradation during the filter equilibration step

or during sample storage. The results show an overall loss of 0.5%, 2.8% and 8.9% after filter equilibration **(Figure II.2.16a)**, filter extract storage **(Figure II.2.16b)** and filter storage **(Figure II.2.16c)** at -20 °C, respectively.

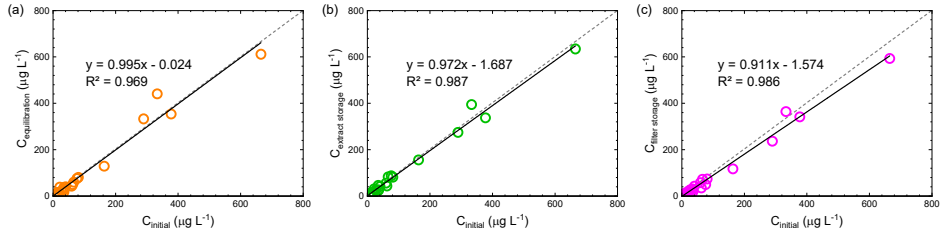

Figure II.2.16: Regression analysis of the dependence between concentrations of the compounds in the extracts after filter equilibration **(a)**, extract storage **(b)**, and filter storage **(c)** *versus* initial extract concentration (Amarandei et al., 2023b).

Based on the presented data, the HPLC-ESI-ToF-MS developed method can be used to identify and quantify the investigated analytes in the atmospheric aerosols.

II.3 INVESTIGATION OF SECONDARY ORGANIC AEROSOLS IN URBAN AREA BY HPLC-ESI-ToF-MS ANALYSIS

In the Eastern Europe, organic constituents of the atmospheric particulate matter are not intensively investigated. The existing studies in the north-eastern Romania have primarily assessed the variation of water-soluble ions or water-soluble elements in atmospheric aerosols taken from urban areas (Galon-Negru et al., 2018, 2019; Arsene et al., 2011).

The current thesis presents, for the first time in Romania, a detailed chemical analysis of the constituents of organic aerosols. Constituents of biogenic origin such as oxidation products of pinene (pinic acid, pinonic acid, norpinonic acid, *trans*-norpinic acid, terpenylic acid, terebic acid, MBTCA, and DTAA) and of anthropogenic origin, such as phenolic nitroderivatives (4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, 2,6-dimethyl-4-nitrophenol, 4-nitrocatechol) or some carboxylic acids (vanillic, D-malic,

adipic, pimelic, benzoic, and phthalic acids) were investigated in aerosol samples from the Iasi urban area.

II.3.2 Contribution of secondary organic aerosols to the fine particulate matter in the urban area of Iasi

The concentrations of the organic constituents were determined in aerosol samples collected from 11 July to 19 December 2018 (19 events, 247 samples) in the Iasi urban area, north-eastern Romania. **Figure II.3.1** shows the relative contributions of water-soluble ions, nitrophenols (4-nitrocatechol, 4NC and 4-nitrophenol, 4NP) and *α-/*β-pinene markers quantified in the $PM_{2.5}$ fraction of the atmospheric aerosol samples in both periods included in the study.

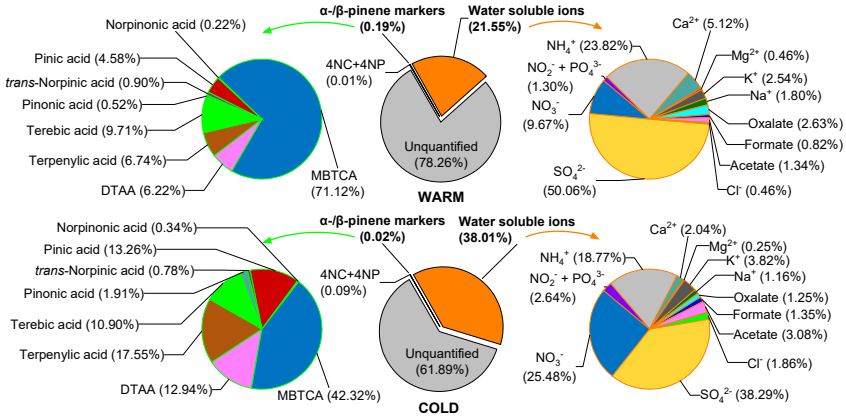

Figure II.3.1: Relative contributions of water-soluble ions, nitrophenols (4-nitrocatechol:4NC and 4-nitrophenol:4NP), and *α-/β*-pinene markers quantified in $PM_{2.5}$ fraction of aerosol samples collected during the warm (July-September) and cold (October-December) periods (Amarandei et al., 2023a).

II.3.3 Time variability of the secondary organic aerosols molecular markers

Variations over time in the mass concentrations of $PM_{2.5}$ as well as mass concentrations of *α-/β*-pinene, nitrophenols, and water-soluble ions in $PM_{2.5}$ fraction are shown in **Figure II.3.2**.

During the warm period, higher mass concentrations for oxidation products of pinene were observed. This may be due to an increase in biogenic

precursor emissions and intensification of the photochemical processes. For compounds with a low vapor pressure (*e.g.*, 4-nitrocatechol, MBTCA, DTAA, and terebic acid), the contribution to the particulate phase is expected to be less affected by variations induced by the atmospheric temperature influencing the gas-particulate partition processes. On the other hand, the distribution of more volatile species, such as 4-nitrophenol, pinic acid, pinonic acid, and terpenic acid, will depend both on the abundance of precursors and on the intensity of photochemical processes and atmospheric temperature.

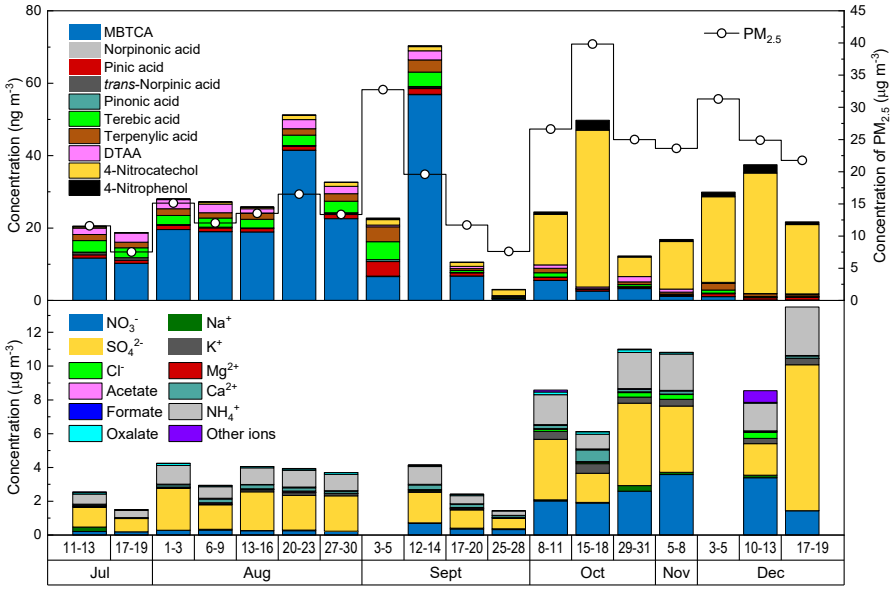

Figure II.3.2: Time variation of $PM_{2.5}$ fraction, *α-/β*-pinene markers, nitrophenols, and water-soluble ions concentrations determined in $PM_{2.5}$ aerosol particles from Iasi, northeastern Romania (Amarandei et al., 2023a).

II.3.4 Size distribution of organic species in atmospheric aerosols

In the present study, the size distributions of the mass concentrations of representative organic species quantified in atmospheric aerosols in Iasi, north-eastern Romania, were investigated.

Figure II.3.4 shows the size distributions of the gravimetrically determined particulate matter mass concentration, mass concentrations of 4-nitrocatechol, 4-nitrophenol, oxidation products of *α-/β*-pinene (pinonic acid,

pinic acid, terpenylic acid, terebic acid, DTAA, and MBTCA), and water-soluble ions (NO_3^- and K^+) in atmospheric aerosols for warm and cold periods.

For most of the investigated compounds, the size distributions of mass concentrations are bimodal, with dominant contributions in the fine mode, with maxima at the diameter values of 260 nm during warm periods and 381 nm during cold period. Among the advanced oxidation products of *α-/β-*pinene, DTAA, and MBTCA presented clear single-mode distributions with maxima in the submicrometer size range. During warm period, the distribution of terebic acid shows a bimodal distribution similar in profile to that of terpenylic acid, with maxima contributions at 260 nm and 2.39 μm.

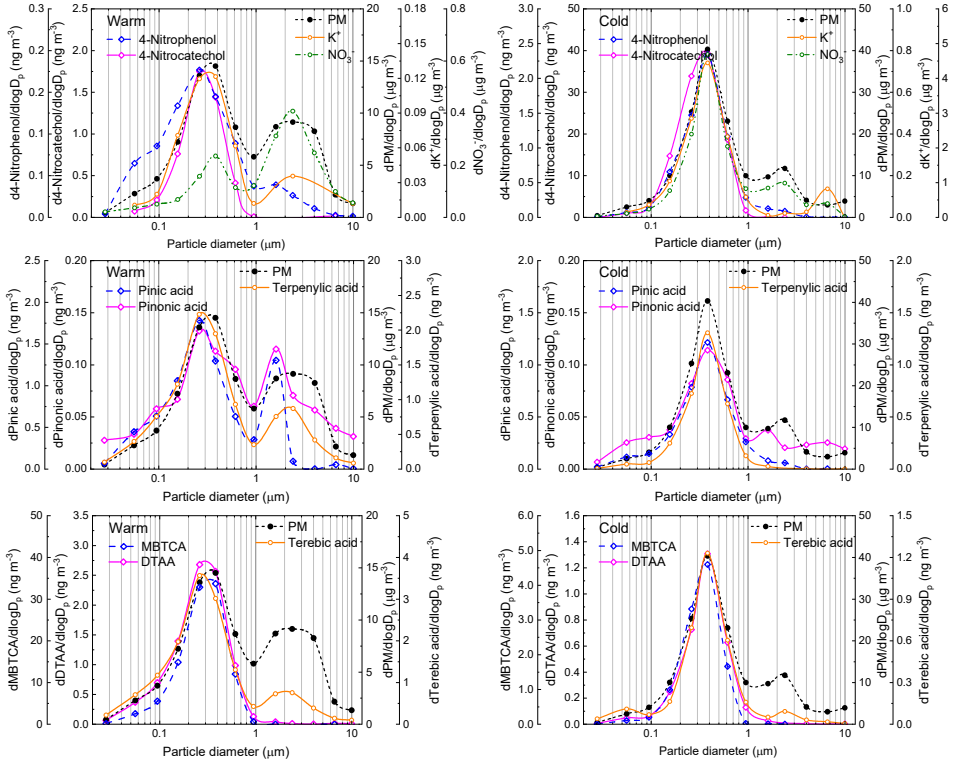

Figure II.3.4: Size distributions of averaged mass concentrations for particulate matter (PM), 4-nitrophenol, 4-nitrocatechol, *α-/β-*pinene oxidation products (pinonic, pinic, terpenylic, terebic acids, DTAA, and MBTCA), and water-soluble NO_3^- and K^+ in atmospheric aerosols collected from the Iasi urban area during the warm and the cold period (Amarandei et al., 2023a).

II.3.5 Characterization of organic aerosols from Iasi urban atmosphere by comprehensive investigation of molecular composition

The molecular formulae identified in aerosol samples analyzed by HPLC-ESI-ToF-MS were classified according to their constituents into the following four groups CHO, CHON, CHONS, and CHOS. The total number of formulas identified have been 424 ± 65 and 847 ± 121 for the warm and cold periods, respectively.

The estimated mean values for DBE and X_C, showing the degree of unsaturation of the identified compounds, were higher during the cold period (5.82 ± 0.13, 1.50 ± 0.06) compared to the warm period (4.73 ±0.33, 1.16 ± 0.08). The normalized abundance of all identified compounds was greater for the cold period compared to the warmer period, with greater differences observed for CHON and CHONS groups. The variation over time in the abundance of the molecular groups showed a similar profile to that of the mass concentration of the $PM_{2.5}$ fraction (**Figure II.3.6**).

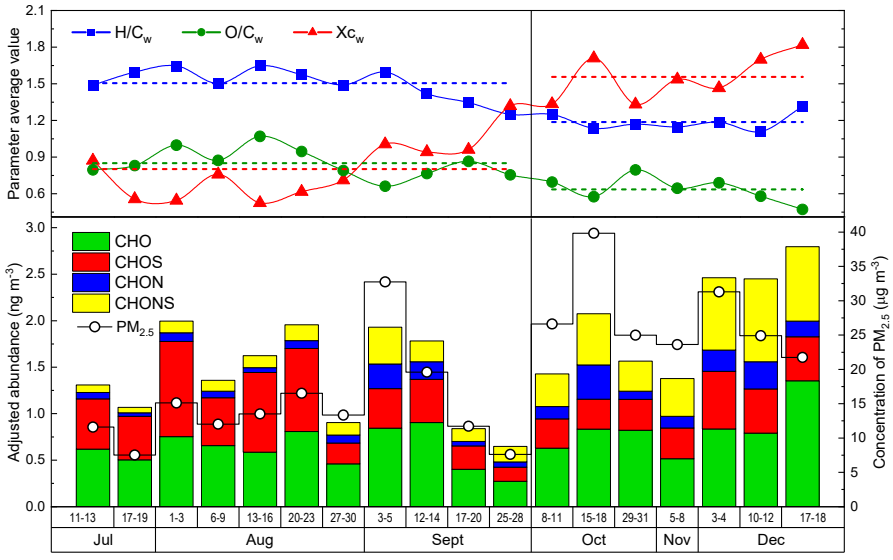

Figure II.3.6: Temporal variation of $PM_{2.5}$, H/C_w, O/C_w, Xc_w, and adjusted abundance of CHON, CHONS, CHO, and CHOS molecular groups. Short dash lines represent the average values of H/C_w, O/C_w, and Xc_w for investigated period (Amarandei et al., 2023a).

Figure II.3.7 shows the size distributions of normalized abundances for the molecular groups during the warm (**FigureII.3.7a**) and cold (**Figure II.3.7b**) periods. The CHO and CHONS groups show bimodal distributions during the warm period, with maxima at 381 nm and 2.39 μm, respectively.

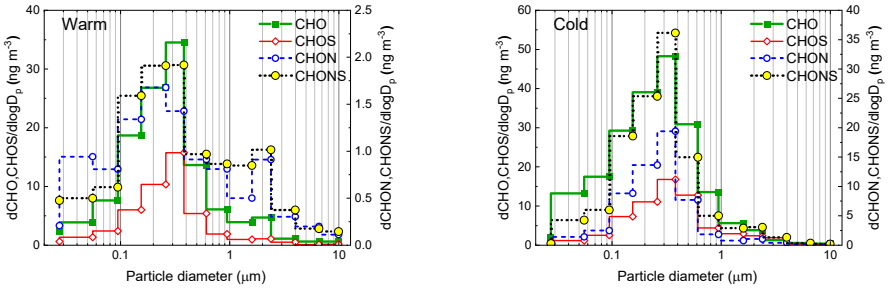

Figure II.3.7: Size distributions of averaged estimated mass concentrations for molecular groups in atmospheric aerosols from Iasi, during the warm period (11 July - 28 September 2018) and the cold period (8 October - 19 December 2018) (Amarandei et al., 2023a).

The CHOS group is characterized by unimodal distributions in both considered periods. The presence of CHO, CHON, and CHONS groups in the coarse particle size range during the warm period is most likely due to the adsorption of semi-volatile compounds on the surface of the pre-existing particles, consisting mostly of mineral dust.

The van Krevelen diagrams presented in **Figure II.3.8** show intense signals of nitrogen-containing compounds distributed within the ratio of the H/C<1 which is associated with aromatic compounds. Most CHO compounds in the van Krevelen diagram are located in the region limited by O/C values from 0.3 to 0.8 and H/C from 1.4 to 1.8 (region d in **Figure II.3.8**) in which compounds can be formed by oxidation processes (ozonolysis, oxidation initiated by the OH radical) of monoterpenes (Kundu et al., 2012). In this region, CHO group constituents are more abundant during the warm period (July, August, and September). For CHO formulas, **Figure II.3.9** shows the variation of carbon oxidation state (OS_C) as a function of carbon atom number and aromaticity equivalent (X_C) values.

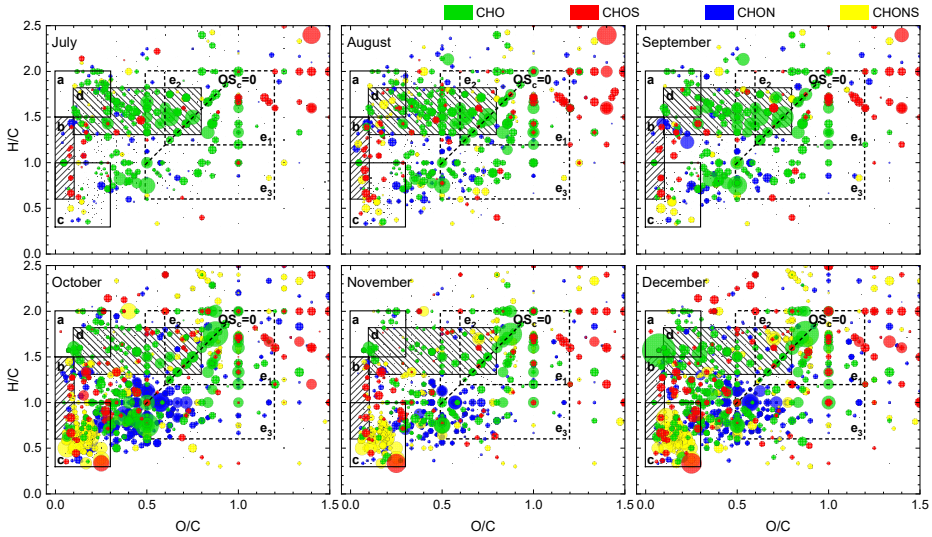

Figure II.3.8: van Krevelen representations of different molecular groups of chemical compounds **(a)** aliphatic, **(b)** unsaturated hydrocarbons, **(c)** aromatics hydrocarbons, **(d)** compounds obtained by ozonolysis (including OH-initiated oxidation), **(e)** highly oxygenated molecules (HOMs): $\mathbf{e_1}$-highly oxygenated and highly oxidized (acids, carbonyls), $\mathbf{e_2}$-very oxygenated and moderately oxidized (alcohols, esters, and peroxides), $\mathbf{e_3}$-moderately oxygenated and highly oxidized molecules formed without O_3/OH radical (Amarandei et al., 2023a).

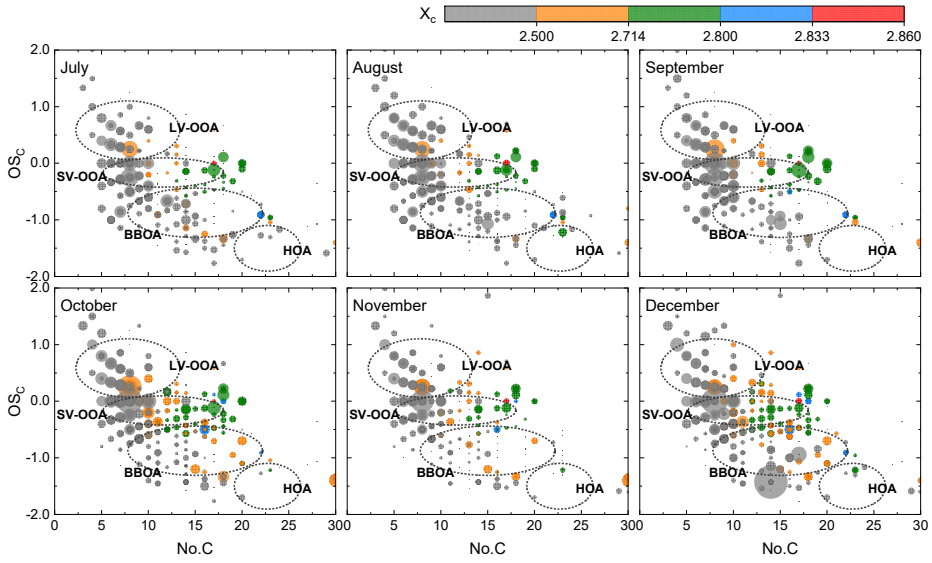

Figure II.3.9:Carbon oxidation state (OS_C) as a function of the carbon atoms number (No. C) for the CHO subgroup of assigned formulas from the $PM_{2.5}$ aerosols samples. The area highlited as HOA, BBOA, SV-OOA, and LV-OOA correspond to the molecules associated with hydrocarbon-like organic aerosol, biomass burning organic aerosol, semivolatile and low-volatility oxidised organic aerosol. The points were colored by X_C value and sized by the adjusted abundance (Amarandei et al., 2023a).

Compounds with $X_C < 2.5$ are considered non-aromatic, the range $2.5 \leq X_C < 2.71$ indicates the presence of mono-aromatics and $X_C \geq 2.71$ indicates the presence of poly-aromatic compounds (Yassine et al., 2014). In the present study the number of the mono- and polyaromatic compounds was higher in October and December. Earlier studies indicate that a molecule with an OS_C between -1 and +1 and with less than 17 carbon atoms can be attributed to semivolatile and/or low-volatility oxidized organic aerosol components (SV-OOA and LV-OOA), which are produced by multistep oxidation reactions (Kourtchev et al., 2016; Kroll et al., 2011).

II.3.6 Influence of the meteorological parameters on the variability of chemical composition of the organic aerosols

The assessment of the influence of atmospheric conditions on the existence of monoterpene (pinene) derived SOAs was carried out by analyzing the molar concentration ratio ($\Sigma C_2/\Sigma C_1$) between advanced oxidation products (MBTCA, DTAA, and terebic acid) and oxidation products from the first oxidation generations (pinonic, pine, *trans*-norpinonic, norpinic, and tepenylic acids) (**Figure II.3.10**). The results were evaluated taking into account the meteorological parameters such as relative humidity, solar radiation, temperature, wind speed and direction measured at the sampling location.

The present study shows the presence of less oxidized SOAs in winter. Lower values ofthe ratio of $\Sigma C_2/\Sigma C_1$ are observed during periods with intense solar radiation (20-23 August and 12-14 September) (**Figure II.3.10**).

During 27-30 August, 25-28 September and 29-31 October, concentrations of $PM_{2,5}$, 4-nitrophenol and 4-nitrocatechol (**Figure II.3.10**) were at a lower level when the atmosphere was characterized by higher levels of wind speed. Therefore, under these conditions, dilution could explain the low concentration of fine particulate matter mass and a lower concentration of nitroaromatic compounds that could be associated with the local sources.

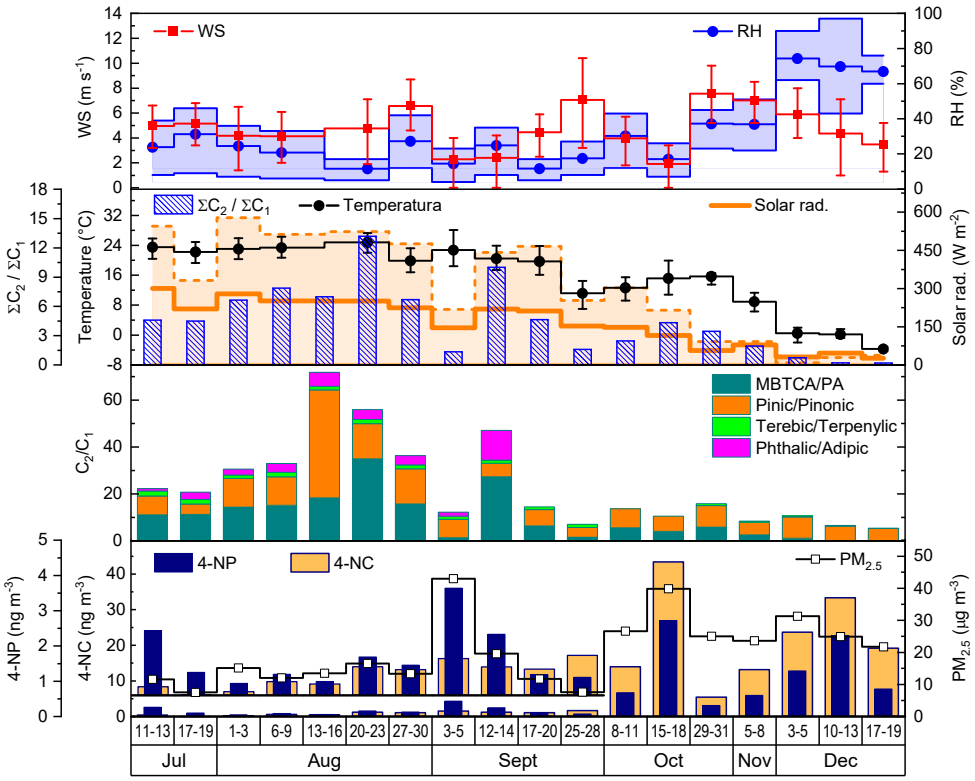

Figure II.3.10: Time variation of the meteorological parameters (wind speed, relative humidity, and temperature), molar concentration ratio ($\Sigma C_{2nd}/\Sigma C_{1st}$) of second-generation oxidation products (MBTCA, DTAA, and terebic acid) to first-generation oxidation products (pinonic, pinic, *trans*-norpinonic, norpinic, and tepenylic acid) and concentration of 4-nitrocatechol (4-NC) and 4-nitrophenol (4-NP) for the $PM_{2.5}$ fraction in Iasi urban area (Amarandei et al., 2023a).

The 48 hours backward air masses trajectories at 500 m altitude, wind direction and speed together with the relative distribution of organic constituents for the 20-23 August, 3-5 September and 15-18 October sampling events are presented in **Figure II.3.11**.

The event of 3-5 September appears to be strongly influenced by the turbulent transport of the air masses, while the 15-18 October event was influenced by a higher incidence of fires in the surrounding areas (Amarandei et al., 2023a) following the direction of the air masses trajectories.

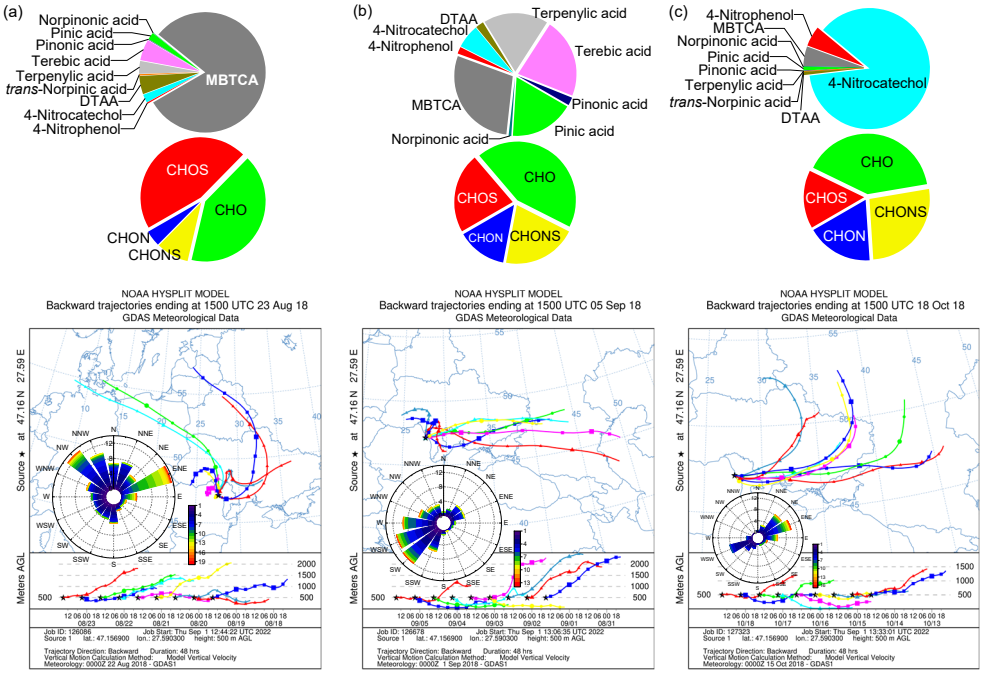

Figure II.3.11: Wind rose and backward air mass trajectories at 500 m altitude and relative distribution of organic constituents highlighting aged biogenic SOAs **(a)**, air mass buoyancy phenomena **(b)**, and biomass-burning contributions **(c)** (Amarandei et al., 2023a).

II.3.7 Identification of associations between constituents of atmospheric aerosols in Iasi urban area

For the evaluation of potential sources of organic aerosols, associations between quantified compounds in aerosol samples have been assessed.

For sources evaluation, the database was investigated by PMF, PCA, correlation matrix, and linear regressions. The database used in the PMF analysis included 12 variables and 51 observables. The species considered "weak" in the applied model were particulate matter mass concentration (PM), 4-nitrophenol and pinic acid concentrations.

The PMF analysis of the database for the period ranging from 11 July to 19 December 2018 highlighted six factors for water-soluble ions and SOA markers determined in the $PM_{2.5}$ fraction collected at AMOS location. Based

on the concentration / contribution of the species considered markers of different sources, the factors discriminated by the PMF analysis have been defined according to the details given in **Table II.3.6**.

Table II.3.6: Attribution of factors discriminated by PMF analysis for constituents in the $PM_{2.5}$ fraction of urban atmospheric aerosols.

Factor	Name	Representative chemical species
Factor 1	▪ biomass burning	▪ K^+
Factor 2	▪ fresh biogenic secondary organic aerosols	▪ pinic acid, terebic acid, and terpenylic acid
Factor 3	▪ aged biogenic secondary organic aerosols	▪ DTAA and MBTCA
Factor 4	▪ anthropogenic organic aerosols	▪ 4-nitrocatechol and 4-nitrophenol
Factor 5	▪ secondary formation from inorganic precursors	▪ SO_4^{2-} and NH_4^+
Factor 6	▪ nitrate	▪ NO_3^-

The profile of all six factors are shown in **Figure II.3.14**.

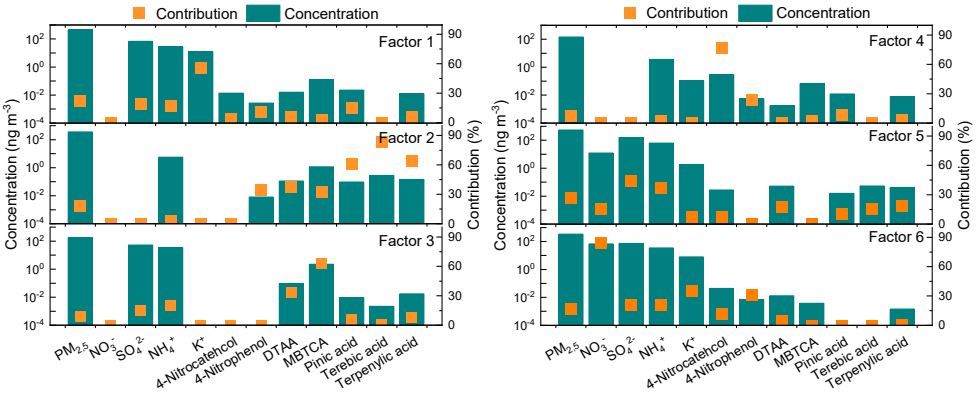

Figure II.3.14: Mass concentrations and relative contributions of the chemical species distributed among six factors discriminated by the PMF analysis for $PM_{2.5}$ fractions in atmospheric aerosols from the urban area of Iasi (Amarandei et al., 2021c).

The PCA analysis, applied on the same database as PMF, discriminated four factors, as shown in **Figure II.3.16** and **Table II.3.7**. The **Figure II.3.16b** showing the distribution of the first three factors, highlights the grouping of the inorganic species, aromatic nitroderivatives, and markers for pinene oxidation. These factors are representative for the contributions from major sources (**Table II.3.8**).

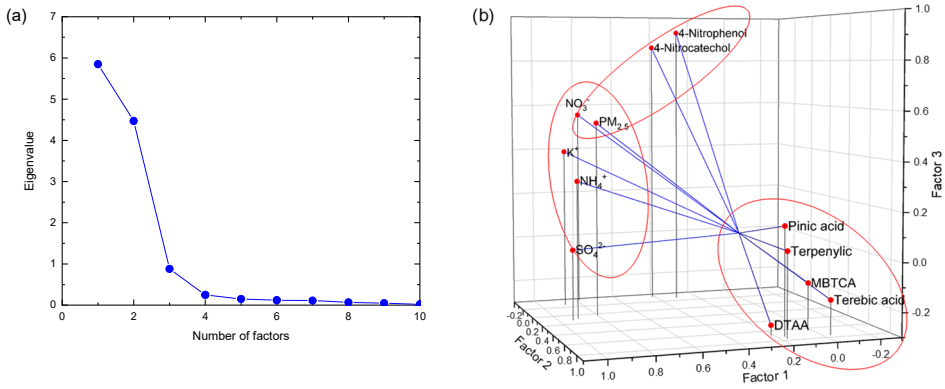

Figure II.3.16: Eigenvalues diagram for establishing the number of factors **(a)** and graphical representation of the first three factors**(b)** (Amarandei et al., 2021c).

TableII.3.7: Contributions of the atmospheric aerosol constituents to the discriminated factors through PCA analysis.

Parameters	**Factor 1**	**Factor 2**	**Factor 3**	***Factor 4*** [(1)]
PM	0.80	0.24	0.53	*-0.04*
NO_3^-	0.78	-0.15	0.55	*0.04*
SO_4^{2-}	0.94	0.32	0.00	*0.01*
NH_4^+	0.91	0.29	0.29	*-0.05*
K^+	0.88	-0.06	0.39	*0.02*
4-Nitrocatechol	0.41	-0.13	0.86	*0.02*
4-Nitrophenol	0.30	-0.07	0.93	*0.03*
DTAA	0.21	0.89	-0.26	*-0.13*
MBTCA	0.02	0.85	-0.10	*-0.51*
Pinic acid	0.17	0.93	0.14	*0.09*
Terebic acid	-0.04	0.96	-0.16	*0.07*
Terpenylic acid	0.17	0.97	0.05	*-0.01*
Cumulative (%)	**49**	**86**	**93**	***96***

[(1)] Factor 4 was taken into account to highlight the separation of the MBTCA compound associated with the advanced oxidation of α-pinene.

Table II.3.8: Attribution of factors obtained by four-factor PCA analysis.

Factor	**Name**	**Representative chemical species**
Factor 1	▪ Biomass burning and secondary formation from inorganic precursors	▪ K^+, SO_4^{2-}, NH_4^+, and NO_3^-
Factor 2	▪ biogenic secondary organic aerosols	▪ DTAA, MBTCA, pinic acid, terebic acid, and terpenylic acid
Factor 3	▪ anthropogenic secondary organic aerosols and nitrate	▪ 4-nitrocatechol, 4-nitrophenol, and NO_3^-
Factor 4	▪ aged biogenic secondary organic aerosols	▪ MBTCA

Figure II.3.18 shows the matrix of Pearson correlation coefficients, including representative variables associated with $PM_{2.5}$ fraction in aerosols collected from the atmosphere of the urban area of Iasi.

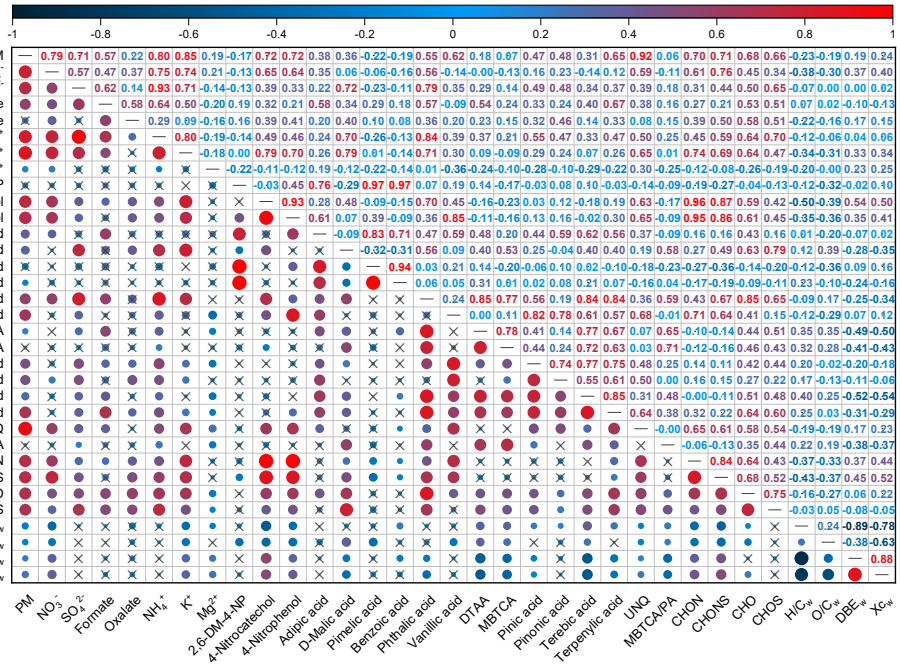

Figure II.3.18: Correlation matrix (Pearson coefficient) including mass concentration of $PM_{2.5}$, quantified analytes in $PM_{2,5}$ fraction and parameters related to the molecular composition (Amarandei et al., 2023a).

II.4 DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS AND MONOAROMATIC DERIVATIVES IN ATMOSPHERIC AEROSOLS BY UHPLC-DAD-FLD

In the UHPLC-DAD-FLD method development study the following 18 PAHs have been included: naphthalene (Nap), 1-methylnaphthalene (1MeNap), 2-methylnaphthalene (2MeNap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene(BaP), dibenzo[*a,h*]anthracene (dBahAnt),

benzo[*g,h,i*]perylene (BghiPer), indeno[1,2,3-cd]pyrene (IndP). A number of 16 PAHs (excluding 1MeNap and 2MeNap) of those presented above are proposed as priority pollutants by the United States Environmental Protection Agency.

II.4.2 Optimization of chromatographic separation and detection conditions of polycyclic aromatic hydrocarbons

In the present study two analytical columns with identical stationary phase composition (C18, Zorbax Eclipse Plus, particle diameter of 1.8 µm and column diameter of 2.1 mm) and different length, 50 mm and 100 mm, respectively, were tested. Different gradient elution programs with acetonitrile and ultrapure water have been tested at different flow rates of the mobile phases and different column temperatures.

Peak purity evaluation and assignment of the chromatographic peaks have been assessed based on the excitation and emission spectra. The BfF and BaPspecies, as well as dBahAnt, BghiPer and IndP species were co-eluted under the initial chromatographic separation conditions (**Figure II.4.1**).

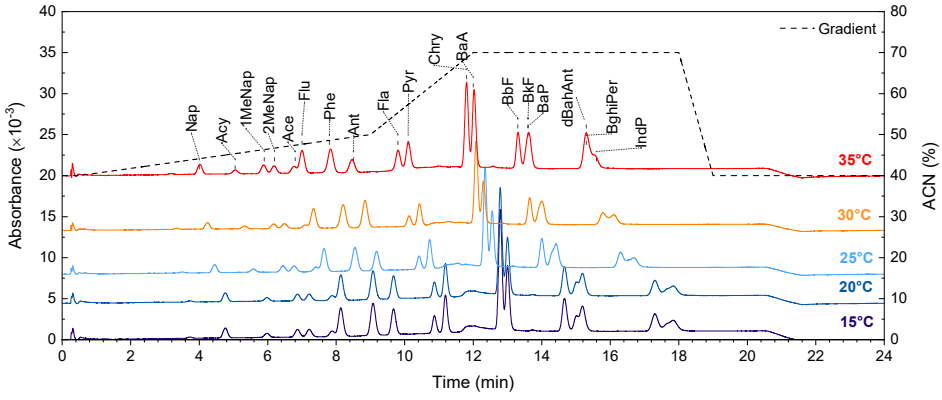

Figure II.4.1: Chromatograms showing the influence of the column temperature (Zorbax Eclipse Plus, 2,1×50 mm, 1,8 µm) on the analytes separation and the elution gradient applied with acetonitrile (ACN) and ultrapure water at a flow rate of 0.4 mL min^{-1} (chromatograms acquired with DAD at the wavelength of 270 nm using standards with the concentrations of 100 ppb).

After the evaluation of the column temperature effect on the separation efficiency, it was found that at low temperature (15 °C) separation is more efficient. As shown in **Figure II.4.2**, the resolution of the separation for BkF and BaP (1.09), dBahAnt and BghiPer (2.00) increased significantly on a Zorbax Eclipse Plus column with a 100 mm in length. However, the resolution of the separation of BghiPer and IndP species has not been improved. However, in this case the interferences contributions have been reduced by measuring emissions at 420 nm and 525 nm for BghiPer and IndP, respectively. The results show a significant higher sensitivity obtained by FLD detection, with signal-to-noise ratios ranging from 45 (Fla) to 24 (IndP, with detection at λ_{em} = 525 nm) and 754 (Ant), compared to the signal-to-noise ratios underDAD acquisition (at 260 nm), for which values were from 4.3 (Nap) to 42 (Chy).

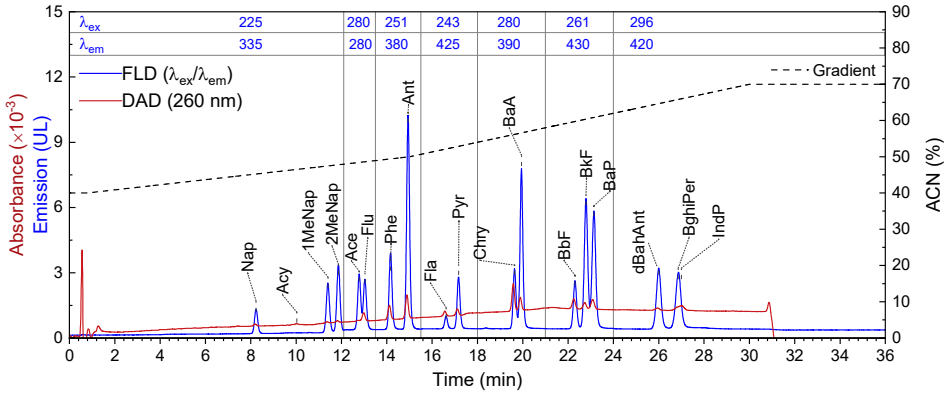

Figure II.4.2:Chromatograms showing the separation of PAHs using the Zorbax Eclipse Plus column (2.1×100 mm, 1.8 µm) with gradient elution at 0.4 mL min-1 flow rate and 15 °C column temperature (8 ppb concentration of individual analytes) (Amarandei et al., 2021a).

In **Figure II.4.4** are presented representative chromatograms for PAHs in atmospheric aerosol samples collected from Iasi urban area and among a standard mixture. The analysis revealed the presence of the following 12 compounds: Phe, Ant, Fla, Pyr, Chry, BaA, BbF, BkF, BaP, dBahAnt, BghiPer, IndP. It is worth mentioning that the identified PAHs included also

benzo[*a*]pyrene (BaP, t_R 23.1 min), the species for which the carcinogenic effect for humans has been confirmed (EEA, 2018).

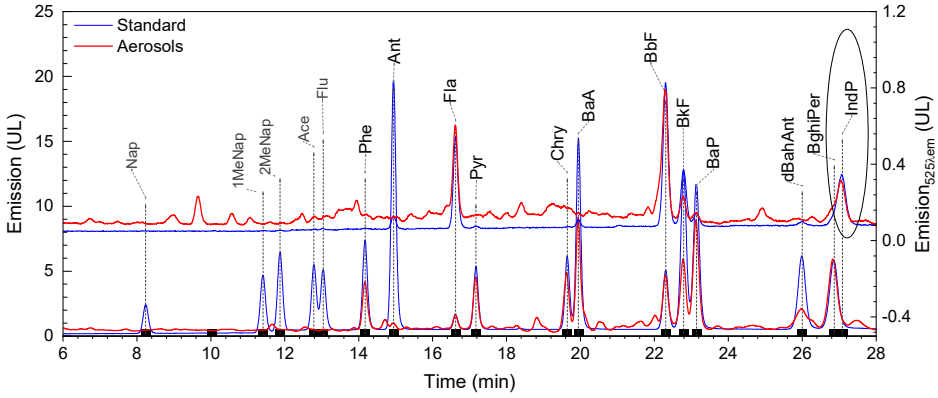

Figure II.4.4: Chromatograms presenting the separation of 18 PAHs for a standard sample and an atmospheric aerosol sample collected in the Iasi urban area (DLPI, stage 5, sampling period from 8 to 11 March 2021) (Amarandei et al., 2021a).

II.4.3 Extraction and determination of polycyclic aromatic hydrocarbons in atmospheric aerosols

In the current study, tests were performed to extract PAHs from atmospheric aerosol samples with acetonitrile and hexane:acetone (1:1) using an orbital vortex (2000 rpm, 60 min). Tests performed using standard samples, without the sample matrix, have shown that the solvent change and pre-concentration step lead to major losses (recovery < 40 %) of compounds with less than 4 rings (Nap, Needles, Flu, Phe and Ant) in the structure of the molecule, due to their higher volatility (**Figure II.4.6**).

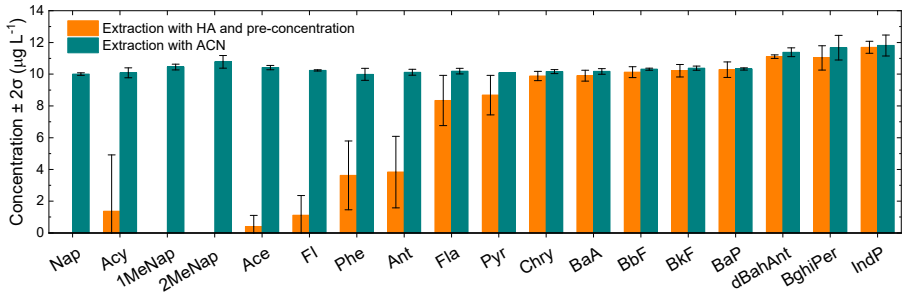

Figure II.4.6: Variation in concentration of PAHs measured for standard samples (without sample matrix) subjected to the extraction with hexane:acetone mixture (1:1, v/v) with the pre-concentration step by evaporation under nitrogen atmosphere

and extraction with acetonitrile without pre-concentration (n = 3) (Amarandei et al.,2021a).

In this study, the quantification of the PAHs was performed on the atmospheric aerosol samples collected with the DLPI system in 8-11 March 2021, at the AMOS station. The results obtained showed that the extraction of PAHs using acetonitrile as the extraction solvent without a pre-concentration step leads to comparative results, even better compared with the case of using hexane:acetone mixture (1:1).

The cumulative concentrations of the three investigated stages (05-07) have been under 0.72 ng m^{-3} (**Figure II.4.8**). The cumulative concentration for benzo[*a*]pyrene (BaP) (0.48 ng m^{-3}) does not exceed the reference value of 1 ng m^{-3} (in PM_{10}) imposed at European level (EEA, 2018). It is quite possible that the concentration for the regulated fraction (in PM_{10}) will exceed the accepted limit because the stages for which determinations have been carried out represent only a part of the PM_{10} fraction and correspond to the particles diameter ($D_{50\%}$) of 0.260 µm (Stage 05), 0.381 µm (Stage 06) and 0.612 µm (Stage 07).

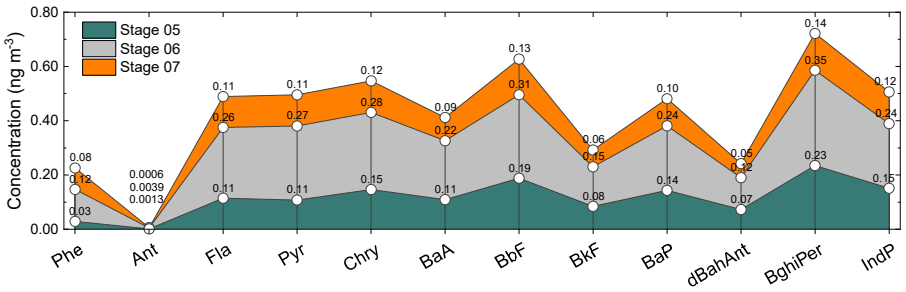

Figure II.4.8: Cumulative concentrations of PAHs determined in aerosol samples collected with the DLPI system (Stages 05, 06, and 07) from 8 to 11 March 2021 at AMOS station using extraction with acetonitrile.

II.4.4 Determination of organic constituents in atmospheric aerosols by UHPLC-DAD

In this section are presented the results obtained for the identification and quantification by UHPLC-DAD analysis of aromatic acids: phthalic acid

(oPA), terephthalic acid (tPA), acid isoftalic acid (iPA), vanillic acid (VA), syringic acid (SiA) and benzoic acid (BA) and aromatic nitroderivatives: 3-nitrosalicylic acid (3NSA), 5-nitrosalicylic acid (5NSA), 4-nitroguaiacol (4NG), 2-nitrophenol (2NP), 4-nitrophenol (4NP), 2,4-dinitrophenol (2,4dNP), 2,6-dinitrophenol (2,6dNP), 2-methyl-4-nitrophenol (2M4NP), 2,6-dimethyl-4-nitrophenol (2,6dMNP), 5-methyl-2-nitrophenol (5M2NP), 3-nitrocatechol (3NC), 4-nitrocatechol (4NC), 3-nitro-5-methylcatechol (3N5MC), and 5-nitro-4-methylcatechol (5N4MC). Among the presented compounds, oPA, VA, and BA acids and nitroderivatives 4NP, 2,4dNP, 2,6dNP and 4NC have been identified and quantified by HPLC-ESI-ToF-MS.

The purpose of the current experimental part was to assess the quantification potential of the UHPLC-DAD technique of the presented analytes in aerosol samples and to compare the results with those obtained by HPLC-ESI-ToF-MS analysis. After testing different gradient elution programs with acetonitrile and acidic acid in water, the chromatographic separation of the 20 compounds was obtained, as presented in **Figure II.4.10**. The chromatograms obtained for constituents in atmospheric aerosol samples show multiple signals for unknown species, while the assessed purity using the acquired absorption spectra showed the presence of the interferences.

In order to make a valid comparisons between UHPLC-DAD and HPLC-ESI-ToF-MS analysis methods for the quantified organic aerosol constituents, the 4NC and 4NPcompounds were considered. 4-Nitrocatechol was determined by UHPLC-DAD measuring the absorbance at 350 nm and 380 nm. It was observed that determination at the wavelength of 380 nm provides results that are in a better agreement (8% difference) with those obtained by HPLC-ESI-ToF-MS (**Figure II.4.13a**), interference contribution from the 5NSA being lower at 380 nm. For 4-nitrophenol, a considerable overestimation of the concentrations determined by UHPLC-DAD (59 %) was

observed (**Figure II.4.13b**) due to the existence of other interfering compounds.

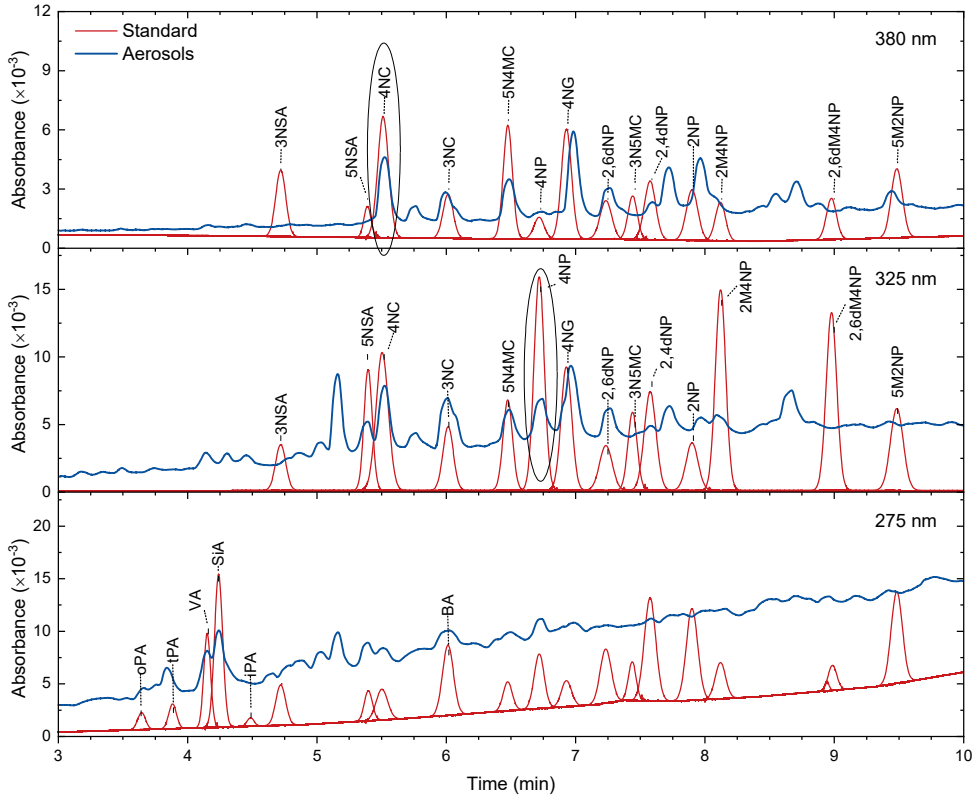

Figure II.4.10: Chromatograms presenting the separation of 20 aromatic compounds, using Zorbax Eclipse Plus column, 2.1×100 mm, 1.8 µm and acquisition with DAD at 3 wavelengths for a standard mixture(concentrations ~ 1.25 mg L^{-1}) and for an atmospheric aerosol sample (December 10-132018, Stage 06).

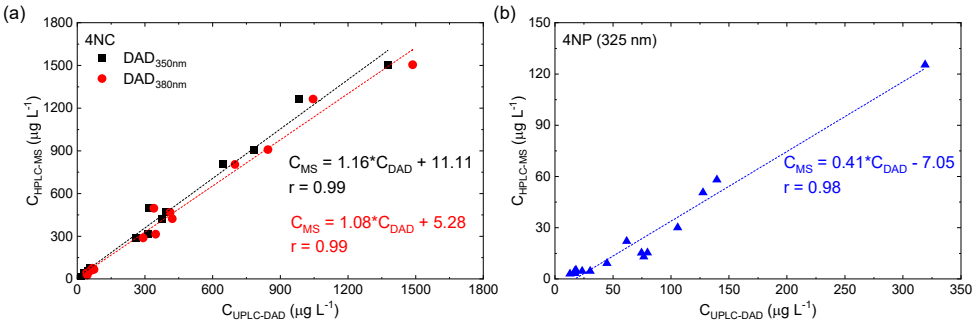

Figure II.4.13: Linear regression analysis of the concentrations determined by analysis of the atmospheric aerosol samples by HPLC-ESI-ToF-MS *versus* UHPLC-DAD for 4NC(**a)** and 4NP **(b)**.

II.5 ONLINE INVESTIGATIONS OF ORGANIC AEROSOLS BY HR-TOF-AMS ANALYSIS

II.5.2 Calibration of the mass spectrometer for aerosol analysis

In order to ensure the operation of the HR-ToF-AMS equipment in optimal conditions, specific calibrations have been performed.

A first calibration was performed for the sampling flow, then for the discrimination of particles according to the size. In order to associate the particle velocity with the aerodynamic diameter in vacuum, a calibration was required using particles with known sizes and velocities. In this study, calibration was performed using ammonium nitrate aerosols, covering a size range from 70 to 400 nm in diameter.

Figures II.5.2ab show the results of the calibration step of the particle velocity as a function of particle diameter at the PToF level**.**

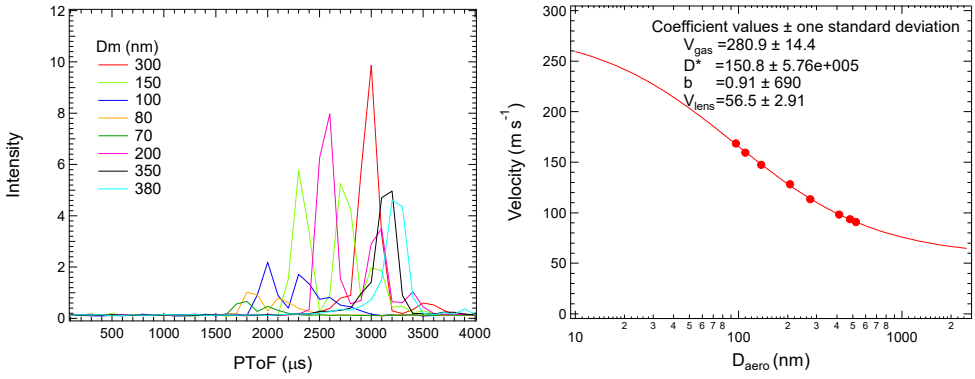

Figure II.5.2: Time distribution of ammonium nitrate particles of different sizes (70 to 380 nm) within PToF **(a)** and aerosol particle velocity function of the aerodynamic diameter of ammonium nitrate particles **(b).**

Particles of NH_4NO_3 with a size in diameter of 300 nm, selected with the DMA (**Figure II.5.3**), were used for the ionization efficiency calibration. The values measured by the HR-ToF-AMS (DAQ) are plotted against the estimations from the CPC measurements (CPC) and the parameters obtained by linear regression are used to process the acquired data (**Figure II.5.3c**).

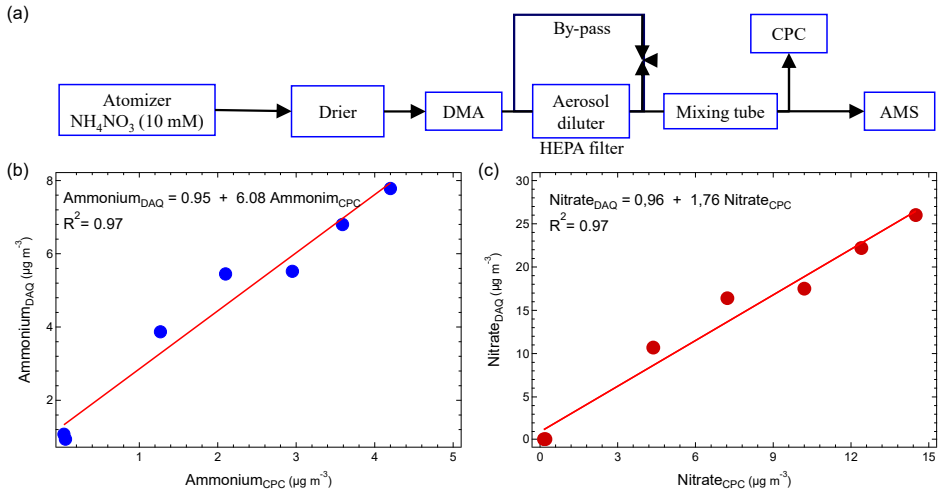

Figure II.5.3: Configuration used for the ionization efficiency calibration **(a)** and mass concentration of ammonium **(b)**and nitrate **(c)** determined by HR-ToF-AMS *versus* concentration estimated from the CPC data (Amarandei et al., 2018).

II.5.3 Investigations performed with the HR-ToF-AMS system for a laboratory-specific environment

The experiments conducted to assess the instrument's response consisted of indoor measurements for approximately 13 hours. The determinations were performed in the area of the Laboratory for investigation of atmospheric physico-chemical processes and testing new environmental gaseous pollutants destruction technologies of the CERNESIM Center.

The experimental data provided by the HR-ToF-AMS analysis were processed using dedicated software packages for such data: SQUIRREL (SeQUential Igor data RetRiEvaL; v1.6W) and PIKA (v1.20W) (https://cires1.colorado.edu/jimenez-group/ToFAMSResources/).

The purpose of signal deconvolution was to minimize the residual signal (< 5 %).

Analysis of the total mass spectrum of aerosols (**Figure II.5.5**) shows the dominance of signals corresponding to hydrocarbon related fragments $C_nH_{2n\pm1}^+$, at m/z values of 41, 43, 44, 55, 57, 69, 71, 83, 85, etc., as well as signals corresponding to ammonium, sulphate, nitrate and chloride ions.

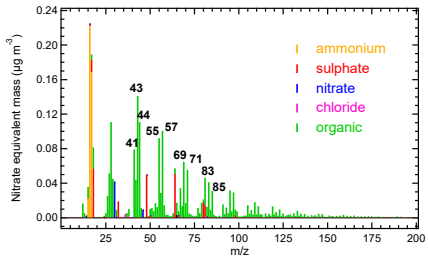

Figure II.5.5: Total mass spectrum of the aerosols collected from the indoor space of the laboratory, highlighting representative signals specific to the organic fraction (Amarandei et al., 2018).

Using the HR-ToF-AMS signals, which are proportional to the mass of the particles, the size distributions of concentrations determined for different fragments ($dM/dlog_{10}d_{va}$) were obtained. **Figure II.5.6a** shows the size distributions of the total organic fraction, nitrate, sulphate, ammonium and chloride. The size distribution of the organic fragments with the m/z of 43, 55 and 57 presented in **Figure II.5.6b** shows monomodal distributions with maxima in the 350-400 nm size range.

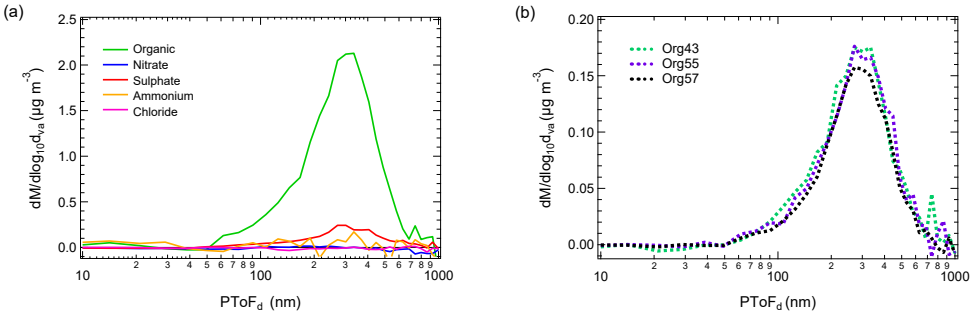

Figure II.5.6: Average size distribution of the total organic fraction, nitrate, sulphate, ammonium, chloride **(a)** and fragments with m/z 43, 55, and 57 **(b)** in submicrometric aerosol particles during the tested period (Amarandei et al., 2018; Galon (Negru) et al., 2018).

The variations of the estimated concentrations in time for sulphate, nitrate, total organic fraction (**Figure II.5.7a**), and selected organic fragments (**Figure II.5.6b**) suggest that most of the organic fragments with m/z values of 43 ($C_3H_7^+$), 55 (C_4H_7+), 57 (C_4H_9+), and 29 ($C_2H_5^+$) are associated with the primary emission sources. The secondary origin of sulphate and its involvement in the formation of new particles is also highlighted (**Figure II.5.7a**).

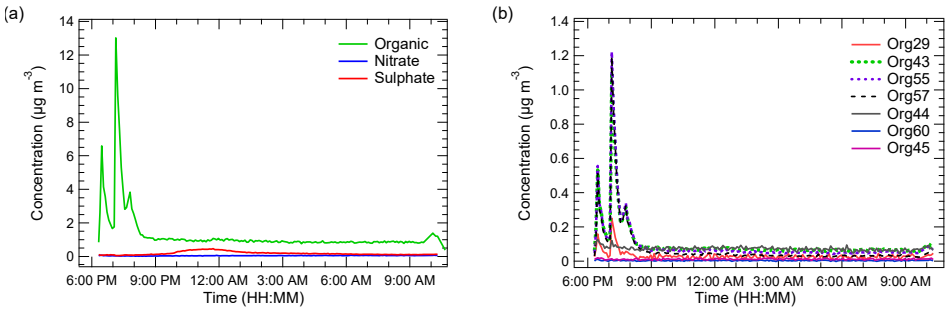

Figure II.5.7: Time distributions of the concentrations of organic fraction, nitrate, sulphate **(a)** and selected organic species (m/z of 29, 43, 44, 45, 55, 57, 60) **(b)** measured in laboratory space during the test period (Amarandei et al., 2018; Galon (Negru) et al., 2018).

Figure II.5.8 presents the fraction of the total organic aerosols signal at 29 m/z value (f29) (**Figure II.5.8a**) and f44 (**Figure II.5.8b**) relative to f43. The variations indicate the existence of a common primary source for fragments of 29 m/z and 44 m/z and the oxidation process of the organic aerosols during the measurements.

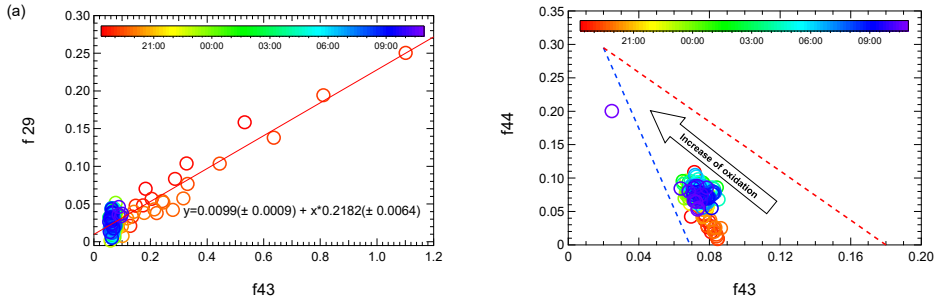

Figure II.5.8: Graphical representation of f29**(a)** and f44 **(b)** *versus* f 43 coloured as a function of aerosol sampling time (Amarandei et al., 2018).

Figure II.5.9 shows the distribution of the signals for families of compounds such as the CHO1 family represented by forms of the formula $C_xH_yO_1$ ($x \geq 1, y \geq 0, z = 1$ $y \geq 0$), CHOgt1 including formulas $C_xH_yO_z$ ($x \geq 1$, $y \geq 0$, $z>1$), CHN including $C_xH_yN_w$ ($x \geq 1$, $y \geq 0$, $w \geq 1$), CHO1N including $C_xH_yO_zN_w$ ($x \geq 1$, $y \geq 0$, $z = 1$, $w \geq 1$), CHOgt1N including formulas $C_xH_yO_zN_w$ ($x \geq 1$, $y \geq 0$, $z>1$, $w \geq 1$), and HO (H_yO_z where $x \geq 1$, $y \geq 0$). Among discriminated species, higher abundances have been observed for CH

and CHO1. The abundance of CH species indicates the dominance of primary sources for the aerosols in the investigated *indoor* environment.

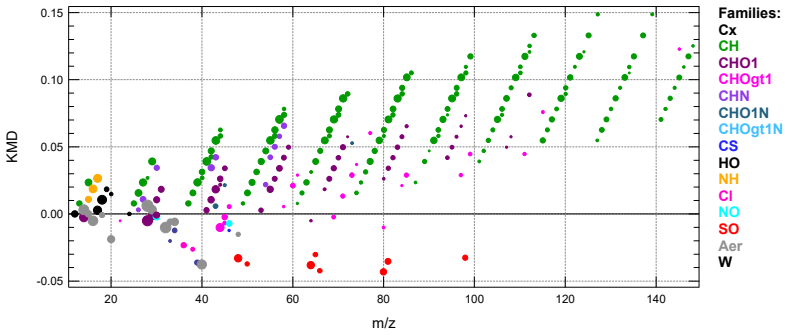

Figure II.5.9: Kendrick mass defect representation (KMD) for families of compounds measured with the HR-ToF-AMS system in the laboratory space.

Figure II.5.10 shows the mass spectra acquired by HR-ToF-AMS for submicrometric aerosols in the ambient air. For the organic fraction, intense signals were observed for fragments associated with alkanes (C_2H_5, C_3H_7, C_4H_9, etc.) and alkenes (C_2H_3, C_3H_5, C_3H_7, etc.).

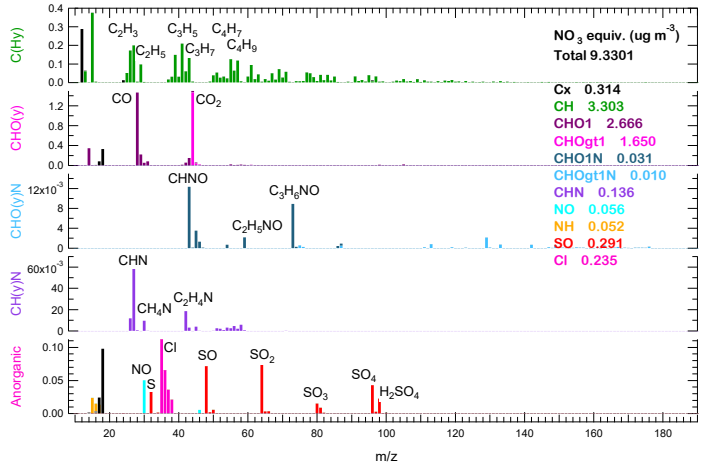

Figure II.5.10: Average mass spectra profile obtained with HR-ToF-AMS for aerosols analyzed in the laboratory space.

The use of the aerosol mass spectrometer brings a significant contribution to the source discrimination studies as well as to the investigation of aerosol ageing processes.

FINAL CONCLUSIONS

In the present study were integrated complementary approaches for chemical characterization of the organic aerosols using different analytical techniques for *offline* (IC, HPLC-ESI-ToF-MS and UHPLC-DAD-FLD) and *online* (HR-ToF-AMS) measurements. Complex processing programs dedicated to high-resolution mass spectrometry data analysis, such as MZmine for HPLC-ESI-ToF-MS data and Igor-integrated SQUIRREL and PIKA programs for HR-ToF have been successfully used. Various statistical processing methods have been used (PMF, PCA, and Pearson correlation coefficient matrix) to investigate the secondary organic aerosol potential sources.

In the present work, an HPLC-ESI-ToF-MS quantification method was developed for determination of 28 organic compounds in atmospheric aerosol particles (*e.g.*, terebica cid, *cis*-pinonic acid, pinic acid, MBTCA, terpenylic acid, 4-nitrocatechol, 4-nitrophenol, 2,6-dinitrophenol, phthalic acid, etc.) for which it is worth highlighting the following results:

- The elution conditions for the chromatographic separation of the analytes, as well as the parameters of the ionization source, have been optimized in order to improve the selectivity and sensitivity of the method.
- The best separation of the interest compounds was obtained using a Poroshell 120 EC-C18 column, at 35 °C column temperature, by gradient elution with 0.1% acetic acid in water and acetonitrile at a flow rate of 0.8 mL min^{-1}.
- The optimal operating conditions identified for ESI-ToF-MS were: drying gas temperature of 350 °C, drying gas flow rate of 13 L min^{-1}, nebuliser pressure of 60 psig, ion transfer capillary voltage of 3000 V, skimmer voltage of 60 V and fragmentor voltage of 150 V.
- The matrix effect on the ionization efficiency and recovery factors of the compounds of interest were evaluated.

- For the first time, evidence has been provided for higher recovery factors for DTAA and MBTCA compounds in the atmospheric aerosols.
- The limits of quantification for the developed method are in the (0.88-48.0) μg L^{-1} concentration range (3.67-200 pg m^{-3}, at 120 m^{-3} of sampled air).
- The mass accuracy of less than 5 ppm and acquisition in full scan mode allowed additional insights to be obtained for investigation of the organic constituents in the atmospheric aerosols.
- Additionally, was highlighted the ability of the method to discriminate an impressive number of compounds (hundreds).

The new HPLC-ESI-ToF-MS developed method was applied for targeted analysis of some organic markers in aerosol samples collected from Iasi urban atmosphere. Molecular composition and data on the SOA molecular tracers in atmospheric aerosol samples were reported for the first time in Romania, as in the following:

- Data on markers of biogenic (pinic acid, terpenylic acid, terebic acid, MBTCA, DTAA, etc.) and anthropogenic (4-nitrocatechol, 4-nitrophenol, benzoic acid, etc.) origin in size segregated atmospheric aerosols have been reported for the first time in Romania.
- The variation in time showed higher mass concentrations of biogenic markers during the warm period, while the aromatic nitro derivatives contributions of were higher during the cold period.
- More than 88% of the mass concentrations of 4-nitrocatechol and 4-nitrophenol have been determined in the submicrometric fraction of atmospheric aerosols, which may be of interest in investigating the toxic potential for human health.
- Aged *α-/β*-pinene SOA markers were abundant in the fine mode (< 1.0 μm), while pinonic, pinic, and terpenylic acids presented an additional maxima in the 1.60 - 2.39 μm size range, corresponding to the coarse mode, which was enhanced in the warm period.

- The sized distributions for species such as terebic acid and terpenylic acid were reported for the first time in the literature.
- The potential sources and the influence of the meteorological parameters in the formation of the secondary organic aerosols were investigated. The formation of aerosols by secondary processes from biogenic organic precursors is strongly dependent by the temperature.
- For the extended molecular composition of the atmospheric aerosols, groups of molecular formulas (CHO, CHON, CHONS, and CHOS) counting a total number of 847 formulas in the warm period and 432 formulas in the cold period were identified.
- Parameters such as X_C, OS_C, H/C, and O/C ratios and the van Krevelen diagram have been used to: i) discriminate aliphatic organic constituents from aromatic ones in aerosol samples, ii) investigate the oxidation state of aerosol samples, and iii) investigate the implications of sources in controlling abundance and the behavior of the organic aerosol constituents.
- For the CHO and CHOS formulas, which were more abundant during the warm period, contributions from increased biogenic emissions and more intense photochemical processes, were attributed.
- Periods of higher levels particulate matter mass concentrations were associated with higher contributions of the CHON molecular group and higher values for the aromaticity equivalent.
- The CHOS formula group presented a higher contribution during the warm period and have been mostly attributed to the secondary formation from biogenic precursors. For the CHONS formula group, a higher abundance was estimated during the cold period, whereas the CHO group did not show a pronounced variation during the investigated period.
- The PMF analysis revealed clear contributions from biomass burning sources, fresh biogenic secondary organic aerosols, aged biogenic secondary

organic aerosols, anthropogenic organic aerosols, secondary formation from inorganic precursors and nitrate.

Using the UPLC-DAD-FLD technique, the following insights were achieved:

- A new UHPLC-FLD method for determination of PAHs in atmospheric aerosols has been developed and tested for aerosol samples collected in Iasi urban area.
- In the atmospheric aerosol samples subjected to analysis, the following PAHs were quantified for the first time in Romania: phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[a]pyrene, benzo[*g,h,i*]perylene, indeno[*1,2,3-cd*]pyrene, dibenzo[*a,h*] anthracene.
- The experimental results obtained for the determination of nitrocatechols and nitrophenols by UHPLC-DAD allowed comparison with the HLPC-ESI-ToF-MS method for 4-nitrocatechol and 4-nitrophenol in the atmospheric aerosol samples.
- The results showed limited applicability of absorbance measurement for atmospheric aerosols organic constituents' discrimination.

Using the HR-ToF-AMS Aerodyne system, the following findings are highlighted:

- The use of HR-ToF-AMS brings significant contributions to source discrimination as well as to the investigation of aerosol formation and transformation processes, among the advantages of this system being the time resolution combined with aerosol size separation, and the high mass resolution measurements of the organic fraction.
- Clear indications have been given for the contribution of sulphate to the formation of the aerosols with equivalent aerodynamic diameters of less than 1 μm.

- The processing of the experimental data using dedicated programs for signal deconvolution and specific processing of data generated from the mass spectra, revealed the grouping of the estimated molecular formulas according to Kendrick mass defect values and elemental composition.
- For the organic fraction and for nitrate and sulphate species in the submicrometric particulate matter, it has been proved that the HR-ToF-AMS measurements provided a single-mode distributions with maxima at particle diameter values of 350-400 nm, confirming the behavior observed using the DLPI system and the offline quantification.
- The results obtained during the activities carried out support the use of the HR-ToF-AMS to the detriment of the DLPI system which allows determinations at a lower time resolution, with a higher effort and with an increased risk of artifacts occurrence.

The doctoral thesis presents for the first-time information on the molecular characteristics of the atmospheric organic aerosols in Romania (Iasi urban area). Also, the HLPC-ESI-ToF-MS developing method section is represented by a comprehensive approach, evaluating a cohort of parameters important for an appropriate operation of the technique. Moreover, quantifying PAHs in the atmospheric aerosols and conducting investigations on the composition of submicrometric aerosols using HR-ToF-AMS are elements of novelty for research in the field of atmospheric chemistry in Romania.

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