



Research Article

Classification and Characterization of Organic Aerosols in the Atmosphere over Seoul Using Two Dimensional Gas Chromatography-time of Flight Mass Spectrometry (GC × GC/TOF-MS) Data

So Hyeon Jeon, Hyung Bae Lim¹⁾, Na Rae Choi²⁾, Ji Yi Lee²⁾, Yun Kyong Ahn³⁾, Yong Pyo Kim^{4),*}

Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, Missouri, United State

¹⁾Air Quality Research Division, National Institute of Environmental Research, Seoul, Republic of Korea

²⁾Department of Environmental Science and Engineering, Ewha Womans University, Seoul, Republic of Korea

³⁾Western Seoul Center, Korea Basic Science Institute, Seoul, Republic of Korea

⁴⁾Department of Chemical Engineering & Materials Science, Ewha Womans University, Seoul, Republic of Korea

*Corresponding author.

Tel: +82-2-3277-2832

E-mail: yong@ewha.ac.kr

Received: 14 November 2018

Revised: 19 February 2019

Accepted: 1 April 2019

ABSTRACT Two approaches were applied for characterization of organic compounds in the atmospheric aerosols. These were chemical and statistical grouping analysis. We applied chemical group analysis as a new approach using the GC × GC data. Based on the principle of GC × GC, analytes in two dimensional data were divided into 6 chemical group depending on their volatility and polarity. Using this classification standards, all analytes were classified as one of 6 chemical groups, HP-VOC, LP-VOC, HP-SVOC, LP-SVOC, HP-NVOC and LP-NVOC. The relationship between the sum of the peak areas of each chemical group with other variables such as the concentrations of OC, EC, OC_{POC}, OC/EC and OC_{SOC} were studied. However, no apparent relationship was observed. The principle component analysis (PCA) was carried out to find out the relationship among the analytes based on their sources. The OVOCs were dominant compounds in 3 out of 4 factors in summer. In winter, factor 1 was related to secondary organic aerosol and factor 3 was related to primary emission sources. The proposed approach looks promising in characterization of chemical groups but have limitations at current stage which are discussed.

KEY WORDS GC × GC/TOF-MS, Chemical grouping, PCA analysis, Organic aerosols

1. INTRODUCTION

Organic compounds in the atmospheric aerosols occupy a large fraction (20–80%) of the mass of the fine particulate matter (Kanakidou *et al.*, 2005). Organic compounds are emitted from variety of sources such as combustion of organic matter and vegetation and also formed by atmospheric photo-oxidation reactions. Exposure to organic aerosols may cause several health effects such as respiratory, cardiovascular and neural effects. According to the U.S. EPA, out of the 177 hazardous air pollutants (HAPs) selected for the U.S. EPA 1999 National-Scale Air Toxics Assessment, 167 are either organic compounds or mixtures (Mauderly and Chow, 2008). Organic aerosols influence radiative forcing arising from the aerosol scattering and absorption of radiation directly or perturb the albedo of the Earth's clouds through their important role as cloud condensation indirectly

(Kanakidou *et al.*, 2005; Ramanathan *et al.*, 2001).

Only 10–40% of organic compounds were identified and quantified with unidentified compounds called ‘unknowns’, since organic aerosols are usually mixed with complex matrix and consist of extreme range of species (Goldstein and Galbally, 2007; Kanakidou *et al.*, 2005; Zheng *et al.*, 2002). Therefore organic compounds in aerosol has been studied incompletely such as classifying into two groups (organic carbon, OC and elemental carbon, EC) or selecting and analyzing target compounds such as n-alkanes, carboxylic acid, and polycyclic aromatic hydrocarbons (PAHs) (see, for example, Choi *et al.*, 2016).

Thus, it is essential to identify organic compounds in the ambient aerosols to assess their effects reliably. Therefore, finding unknowns exhibiting their own characteristics according to season or chemical characteristics and identifying these unknowns are important.

To analyze carbonaceous compounds in the atmospheric aerosols, several technique have been used such as gas chromatography/mass spectrometer (GC/MS), liquid chromatography/MS (LC/MS), nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy (Hallquist *et al.*, 2009). Although GC is common technique to analyze organic compounds in the atmospheric aerosols, separation efficiency of a single chromatographic technique is still unsatisfactory.

Comprehensive two-dimensional gas chromatography (GC × GC), one of the multidimensional techniques, has been recently used in analysis of organic compounds in atmospheric aerosols (Dallüge *et al.*, 2002). In GC × GC, two different columns are connected through a modulator. Since GC × GC separates organic compounds in an aerosol sample based on different chemical mechanisms in two columns, it has high resolving power and provide enormous number of peaks than conventional GC. Commonly used columns in GC × GC are non-polar column in first column and polar column in second column. Separation takes place according to vapor pressure of analytes in the first column and polarity in the second column. Modulator improve sensitivity by cutting and refocusing narrow adjacent fractions of the first column eluate, focusing and releasing these rapidly into the second column (Dallüge *et al.*, 2002). Xu *et al.* (2003) identified 235 volatile organic compounds (VOCs) in situ measurements using GC × GC coupled with a time-of-flight mass spectrometer (TOF-MS). Kallio *et al.* (2003) identified and quantified

23 PAHs and oxygenated PAHs (oxy-PAHs) in urban aerosols collected in Helsinki, Finland using GC × GC coupled with flame ionization detector (FID) and quadrupole mass spectrometer (QMS). Kallio *et al.* (2006) identified 50 organic compounds in atmospheric aerosols from coniferous forest using GC × GC-TOF-MS. Lee *et al.* (2009) identified about 300 organic compounds in PM_{2.5} collected in Seoul using thermal-desorption (TD) GC × GC-TOF-MS. GC × GC has been also applied to analyze organic aerosols from emission sources such as cigarette smoke, particulate matter from wood combustion and industrial chemicals (Weggler *et al.*, 2016; Alam *et al.*, 2013; Dallüge *et al.*, 2002).

Application of GC × GC-TOFMS for analysis of organic aerosols in the atmosphere contributed to provide much more and specific information of organic aerosols. Still, researchers have had difficulty in data processing methods dealing with huge information.

Welthagen *et al.* (2003) identified 697 organic compounds (out of 1,060) in atmospheric aerosols and characterized unidentified chemical compounds depending on their volatility and polarity. According to their volatility, 1st dimension retention time was divided into half. Then chemical compounds detected in the front retention time were considered as ‘volatile’ compounds and those detected in the rear retention time were considered as ‘semi-volatile’ compounds. In the same way, 2nd dimension retention time reflecting their polarity divided the compounds into two parts, ‘polar’ for the compounds detected in the front retention time and ‘non-polar’ compounds detected in the rear retention time, respectively. As a result, unidentified chemical compounds were classified 4 group; (i) polar volatile, (ii) non-polar volatile, (iii) polar semi-volatile and (iv) non-polar semi-volatile. Based on this classification, their study tried to suggest detailed criterion for dividing 1st and 2nd retention time (Welthagen *et al.*, 2003).

In this study, we used two kinds of grouping methods for characterization of unknowns, since it is needed to extract unknowns exhibiting their own characteristics through group analysis before identification of unknowns. First, chemical grouping was carried out with volatility and polarity following the approach of Welthagen *et al.* (2003). We investigated seasonal and diurnal variation of each chemical group. Second method was statistical analysis by using the principle component analysis (PCA) method to group the compounds with similar sources or transformation characteristics.

2. DATA

The total suspended particle (TSP) samples were collected at Asan engineering building, Ewha Womans University, Seoul, Korea (37.56°N, 126.94°E, 20 m above ground level). The sampling site is located in the mixed resident area, commercial area, forest area and nearby roadside. A total of 67 samples were obtained during summer (August 12–30, 2013, $n = 32$) and winter (January 27–February 16, 2014, $n = 35$) and day (9 a.m.–6 p.m., $n = 16$ in summer, $n = 17$ in winter) and night (8 p.m.–6 a.m., $n = 16$ in summer, $n = 18$ in winter) with a PUF sampler (Tisch, TE-1000) on quartz fiber filter (Quartz fiber filter, QFF, Ø10.16 cm, Whatman, UK). Prior to sampling, quartz fiber filters were baked for 8 hours in an electric oven at 550°C to remove possible organic contaminants. The sampled filters were wrapped in aluminium foils and stored in a freezer at -20°C until analysis.

Sampled filters were extracted twice using accelerated solvent extractor (ASE) (Dionex ASE-200) with a mixture of dichloromethane and methanol (3 : 1, v/v) at 40°C and 1,700 psi for 5 minutes. Prior to extraction 4 internal standards (naphthalene- d_8 , acnaphthene- d_{10} , phenanthrene- d_{10} , and fluoranthene- d_{10}) were spiked in the sampled filters to estimate recovery of the extraction procedure. Extracts were blown down to 1 mL using a nitrogen evaporator (Turbo Vap II, caliper Life Sciences). Concentrated samples were transferred to 2 mL vial and blown down again to 0.5 mL using a nitrogen evaporator.

GC × GC-TOF-MS analysis was carried out using a cryo-jet Pegasus 4D (LECO, St. Joseph, MI, USA) equipped with an Agilent 7890B gas chromatography and a Pegasus time-of-flight mass spectrometer (TOF-MS). A 1 µL sample was injected on the splitless mode at 300°C. The chromatographic separation was executed by volatility in first dimension column and by polarity in second dimension column. The first dimension column was DB-5MS (30 m × 0.25 mm I.D; 0.25-µm film thickness) from J&W Scientific capillary column (Santa Clara, CA, USA). The second dimension column was DB-17MS (1.17 m × 0.18 mm I.D; 0.18-µm film thickness) from J&W Scientific capillary column. The GC was held at 60°C for 1 minute and then raised at 6°C/min to 300°C for 15 minutes. The carrier gas was helium (99.999%) flowed at 1.3 mL/min. The secondary oven temperature was 5°C higher than GC oven temperature.

The modulator was operated at 15°C higher than second oven temperature. The transfer line temperature was 250°C and the ion source temperature was 230°C. The TOF-MS was operated in electron impact (EI) mode at 70 eV electron energy. The TOF-MS mass range was set at 40–550 amu. ChromaTOF software was used for all acquisition control and data processing. To align analytes of each daily samples, “statistical compare” in ChromaTOF software was used.

Generally, the average concentrations of primary air pollutants in the winter sampling period were higher than the summer sampling period (Choi *et al.*, 2018). For example, the average concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in winter and summer were 17.23 and 39.94 ng/m³, respectively. Also the average concentrations of sulfur dioxide, nitrogen dioxide and carbon monoxide in winter were higher than summer by the factors of 1.4, 1.9 and 4.0, respectively.

3. RESULTS AND DISCUSSION

3.1 Chemical Group Separation

While Welthagen *et al.* (2003) classified all analytes in the ambient aerosols sample to 4 chemical groups, we divided them to 6 according to volatility and polarity. In 2-dimensional (2D) chromatogram, 1st dimension retention time reflected volatility (vapor pressure) of analytes and 2nd dimension retention time reflected polarity of analytes. We established a clear criterion to separate analytes on the basis of retention time of specific analytes.

To separate analytes according to their volatility, retention time of naphthalene ($P_v = 11.332$ Pa at 25°C) and benzo[a]pyrene ($P_v = 7.319 \times 10^{-9}$ Pa at 25°C) were used as bases. Because naphthalene is typically observed in the gas phase, analytes detected in less than retention time of naphthalene were considered as a VOC. Meanwhile, benzo[a]pyrene has been typically observed in the particle phase and analytes detected in more than retention time of benzo[a]pyrene were considered non-volatile organic compounds (NVOC). The other analytes detected between retention time of naphthalene and benzo[a]pyrene were grouped as semi-volatile organic compounds (SVOC).

For polarity, retention time of hentriacontane was used as a basis. Polarity of organic compounds are decided by the electronegativity difference between atoms

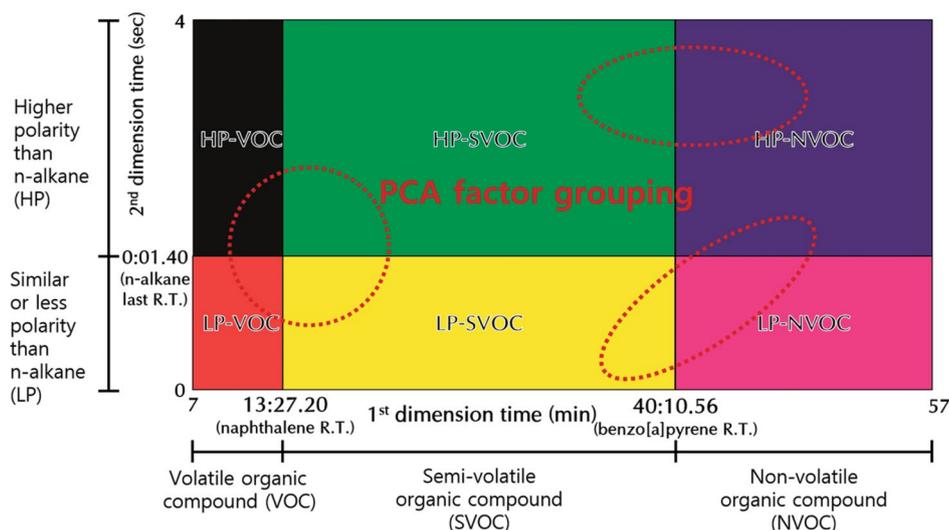


Fig. 1. Schematic diagram of chemical group separation by volatility and polarity in 2D chromatogram. Red letters and circles are correlation between partial analytes in chemical separation group with the PCA result.

in a bond. Since the functional group primarily affects the polarity of the chemical compounds, the polarity of chemical compounds can be ranked by a functional group. Amide is the most polar, followed by acid, alcohol, ketone, aldehyde, amine, ester, ether and alkane. Alkanes are generally considered as non-polar compounds, therefore, alkane was chosen as an indicator of polarity in this study. Among n-alkanes, hentriacontane was used as a separating compound because it is the last observed compounds in n-alkanes group on second dimension time. The analytes detected in less than retention time of hentriacontane were considered as similar or less polar than n-alkane (LP), the other as higher polar than n-alkanes (HP). Fig. 1 shows the scheme of chemical group separation by volatility and polarity in 2D chromatogram. Each group was named as HP-VOC, LP-VOC, HP-SVOC, LP-SVOC, HP-NVOC and LP-NVOC, respectively.

There are two variables one can use to interpret the result, peak area and peak number. Ideally, both variables should be used but it is hard to use both since there is too much information to start with. The main aim of this study is to characterize major compounds in organic aerosols and if peak number is used as a variable, there would be too many compounds the concentrations of which are very low. Thus, we judged that peak number be not appropriate for the current study and used peak area as the main variable. To use both peak area and peak number, further studies are warranted.

3.2 Seasonal and Diurnal Variation

To understand the behavior of each group by season and day, we summed the peak area of all analytes detected in each chemical group including unidentified compounds. Fig. 2 shows the seasonal variation and contribution of each group. The sum of the peak areas in summer was larger than winter by a factor of ~ 2 . The VOC group contributed less than 5% of the summed area irrespective of their polarity. Meanwhile, the SVOC group showed difference between summer and winter in contribution according to their polarity. The HP-SVOC contributed 43.6% in summer, while in winter it contributed less than half in summer, 18.9%. The LP-SVOC consisted of more than 50% of the whole organic part in both season. In winter, the LP-SVOC was 3 times larger than the HP-SVOC, but the variation of the LP-SVOC and the HP-SVOC group in summer was less than 10%. The HP-VOC group contributed the least fraction among the chemical groups, 1.22% in summer and 0.11% in winter, respectively. The NVOC group had a small fraction in whole peaks regardless of their polarity in summer. However, in winter, the LP-NVOC contributed 16.4% which was almost 14 times higher than the HP-NVOC.

Fig. 3 shows the diurnal variation and contribution of each group in summer and winter. In summer, the sum of the peak areas showed clear difference between day and night. The summed areas at nighttime was almost 2 times larger than daytime. While in winter, it showed

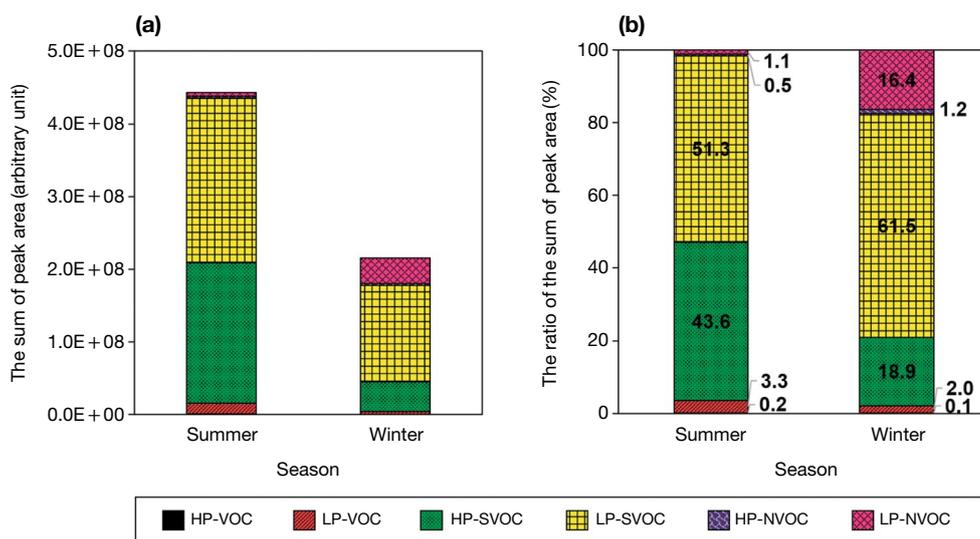


Fig. 2. The average seasonal variation (a) and ratio of contribution (b) of each chemical group using the sum of the peak areas.

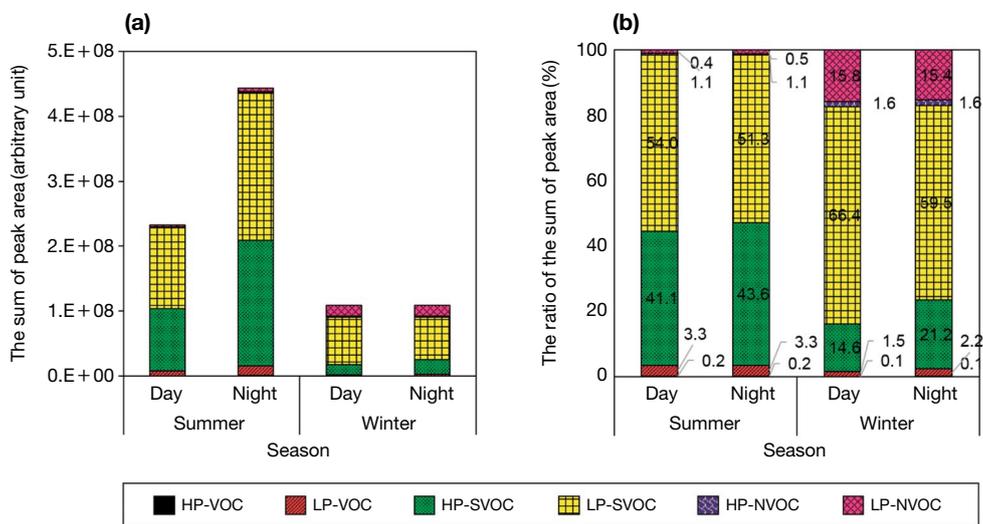


Fig. 3. Diurnal variation (a) and ratio of contribution (b) of each chemical group using the sum of the peak areas.

almost same total peak area whose variation between day and night is less than 1%. The composition of each group showed similar patterns at both day and night. In summer, the VOC and NVOC group contributed less than 5%, while the SVOC group accounted for about 40% in HP and 50% in LP. However, in winter, the NVOC group, particularly LP-NVOC, grew by 17%. In the SVOC group, the fraction of the HP-SVOC declined from summer to winter, from 41.1% to 14.0% during daytime and from 43.6% to 21.2% at nighttime, respectively. On the contrary, the fraction of the LP-SVOC in-

creased from summer to winter, from 54.0% to 66.4% during daytime and from 52.3% to 59.5% at nighttime, respectively. As a result, the contribution of low polar group increased in winter.

To find out relationship between each chemical group and emissions of atmospheric aerosols, correlation analysis was carried out between the sum of peak area of each chemical group and the concentrations of OC, elemental carbon (EC), primary organic carbon (OC_{POC}) which was a marker of primary organic aerosols, the OC/EC ratio and secondary organic carbon (OC_{SOC}) which

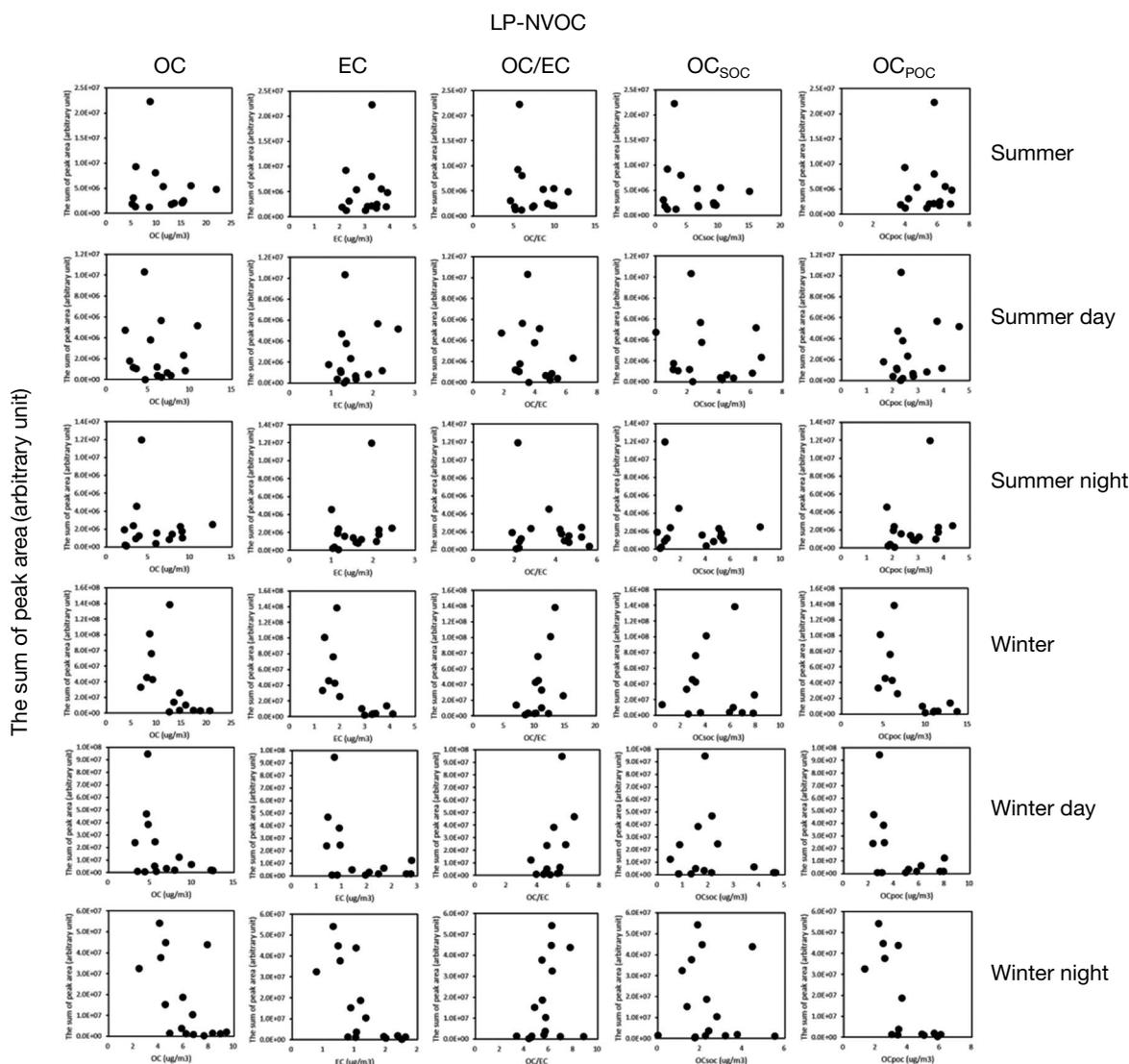


Fig. 4. Scattering plot between the daily sum of peak area in LP-NVOC group, organic carbon and elemental carbon.

was a marker of secondary organic aerosols. OC_{POC} and OC_{SOC} were calculated following the method in Lim and Turpin (2002). However, most chemical groups had no apparent correlation with OC, EC, OC_{POC} , OC/EC and OC_{SOC} . One example of the relationship between the summed area and other variables is shown in Fig. 4.

3.3 Principle Component Analysis (PCA)

To carry out a statistical analysis, the PCA was performed with the SPSS statistical package (version 20). To compare the data in summer and winter, only the peak appeared at least more than 50% the samples in each season was counted. The factor having more than

10% of variance and individual analytes having more than 0.6 of factor loadings in each factor was analyzed. Each analytes with their peak area were used as variables for PCA with the varimax rotation method. Factor loading is correlation coefficient between each variables and the factor. Then, individual analyte was classified for determining factor characteristics such as oxygenated volatile organic compounds (OVOCs), volatile organic compounds (VOCs), PAHs, organic nitrogen compounds (ON), organophosphates, organosulphates and phthalate as used in Alam *et al.* (2013). OVOCs and VOCs were further divided into linear and branched compounds, substituted aromatic compounds and cyclic

Table 1. Chemical information of analytes in factor 1 in summer.

Compound	CAS no	Molecular formula	Class	1st RT	2nd RT	Chemical group separation
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	C ₁₇ H ₂₄ O ₃	Cyclic OVOCs	27:49.3	00:01.6	HP-SVOC
cis-9,10-Epoxyoctadecanamide	172995-07-2	C ₁₈ H ₃₅ NO ₂	Linear and branched ON	37:09.0	00:02.0	
9,12,15-Octadecatrienal	26537-71-3	C ₁₈ H ₃₀ O	Linear and branched OVOC	35:48.2	00:01.8	
9,12-Octadecadienal	26537-70-2	C ₁₈ H ₃₂ O	Linear and branched OVOC	35:33.6	00:01.8	
9,12-Octadecadienoic acid, methyl ester, (E,E)-	2566-97-4	C ₁₉ H ₃₄ O ₂	Linear and branched OVOC	36:14.1	00:01.8	
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	719-22-2	C ₁₄ H ₂₀ O ₂	Cyclic OVOCs	19:33.9	00:01.2	
Furan, 2-[(2-ethoxy-3,4-dimethyl-2-cyclohexen-1-ylidene)methyl]-	55162-49-7	C ₁₅ H ₂₀ O ₂	Cyclic OVOCs	22:45.4	00:01.3	LP-SVOC
2-Undecenal	2463-77-6	C ₁₁ H ₂₀ O	Linear and branched OVOC	17:24.0	00:01.2	
2-Decenal, (E)-	3913-81-3	C ₁₀ H ₁₈ O	Linear and branched OVOC	15:04.2	00:01.1	
Nonanoic acid, methyl ester	1731-84-6	C ₁₀ H ₂₀ O ₂	Linear and branched OVOC	14:04.8	00:01.1	
Decanal	112-31-2	C ₁₀ H ₂₀ O	Linear and branched OVOC	13:43.2	00:01.1	
Eicosanoic acid, 2-hydroxyethyl ester	-	C ₂₂ H ₄₄ O ₃	Linear and branched OVOC	35:43.7	00:01.4	
Nonadecane, 2-methyl-	1560-86-7	C ₂₀ H ₄₂	Linear and branched VOCs	24:38.5	00:00.9	
Eicosane	112-95-8	C ₂₀ H ₄₂	Linear and branched VOCs	26:45.0	00:00.9	
Decane, 2,3,5,8-tetramethyl-	192823-15-7	C ₁₄ H ₃₀	Linear and branched VOCs	17:28.9	00:00.9	
Hexadecane	544-76-3	C ₁₆ H ₃₄	Linear and branched VOCs	21:37.2	00:00.9	
Hordenine	539-15-1	C ₁₀ H ₁₅ NO	Substituted aromatic ON	20:50.4	00:01.0	
1-Octanone, 1-phenyl-	1674-37-9	C ₁₄ H ₂₀ O	Substituted aromatic OVOC	23:43.2	00:01.4	
Phenol, 2,4-bis(1,1-dimethylethyl)-	96-76-4	C ₁₄ H ₂₂ O	Substituted aromatic OVOC	20:15.2	00:01.3	
Analyte 504			Unknown	34:16.8	00:01.3	
Analyte 271			Unknown	21:24.0	00:01.4	
Analyte 420			Unknown	30:12.0	00:01.2	
Furan, 2-pentyl-	3777-69-3	C ₉ H ₁₄ O	Cyclic OVOCs	08:36.0	00:00.9	
2-Nonanone	821-55-6	C ₉ H ₁₈ O	Linear and branched OVOC	10:55.2	00:01.1	
2-Octanone	111-13-7	C ₈ H ₁₆ O	Linear and branched OVOC	11:30.7	00:01.1	
Octanal	124-13-0	C ₈ H ₁₆ O	Linear and branched OVOC	08:51.6	00:01.0	
Nonanal	124-19-6	C ₉ H ₁₈ O	Linear and branched OVOC	11:01.2	00:01.1	
Heptanoic acid, methyl ester	106-73-0	C ₈ H ₁₆ O ₂	Linear and branched OVOC	09:18.8	00:01.0	
2-Octenal, (E)-	2548-87-0	C ₈ H ₁₄ O	Linear and branched OVOC	10:12.0	00:01.1	
Octanoic acid, methyl ester	111-11-5	C ₉ H ₁₈ O ₂	Linear and branched OVOC	11:41.7	00:01.1	

Table 2. Chemical information of analytes in factor 3 in winter.

Compound	CAS no	Molecular formula	Class	1st RT	2nd RT	Chemical group separation
Benzo[a]pyrene	207-08-9	C ₂₀ H ₁₂	PAHs	40:10.6	00:02.9	HP-NVOC
(E)-2-formylcinnamaldehyde	61650-52-0	C ₁₀ H ₈ O ₂	OPAHs	21.88	2.02	
9H-Fluoren-9-one	486-25-9	C ₁₃ H ₈ O	OPAHs	25:10.1	00:02.0	
1,2-Naphthalic anhydride	5343-99-7	C ₁₂ H ₆ O ₃	OPAHs	26.75	1.87	
Phthalic anhydride	85-44-9	C ₈ H ₄ O ₃	OPAHs	30:07.2	00:02.6	
1-Phenanthrenecarboxaldehyde, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1S-(1,4a,10a)]-	13601-88-2	C ₂₀ H ₂₈ O	OPAHs	29:52.8	00:01.5	
Phenanthrene	85-01-08	C ₁₄ H ₁₀	PAHs	25.94	1.73	HP-SVOC
Fluoranthene	206-44-0	C ₁₆ H ₁₀	PAHs	35:28.8	00:02.3	
Naphthalene, 2-phenyl-	612-94-2	C ₁₆ H ₁₂	PAHs	29:09.6	00:01.9	
Pyrene	129-00-0	C ₁₆ H ₁₀	PAHs	31:06.0	00:02.1	
Benzo[ghi]fluoranthene	203-12-3	C ₁₈ H ₁₀	PAHs	35:28.8	00:02.3	
Chrysene	218-01-9	C ₁₈ H ₁₂	PAHs	36.37	2.26	
1-Penten-3-one, 1-phenyl-	3152-68-9	C ₁₁ H ₁₂ O	Substituted aromatic OVOCs	21:57.6	00:02.2	
Analyte 709				43:50.4	00:00.5	LP-NVOC
n-Hexadecanoic acid	00:00.0	C ₁₆ H ₃₂ O ₂	Linear and branched OVOCs	28:32.5	00:01.3	
Octadecanoic acid	00:00.0	C ₁₈ H ₃₆ O ₂	Linear and branched OVOCs	31:44.3	00:01.3	
Pentadecane	629-62-9	C ₁₅ H ₃₂	Linear and branched VOCs	30:25.8	00:01.0	LP-SVOC
Eicosane	112-95-8	C ₂₀ H ₄₂	Linear and branched VOCs	26:45.0	00:00.9	
Heneicosane	629-94-7	C ₂₁ H ₄₄	Linear and branched VOCs	28:53.6	00:01.0	

compounds. PAHs included both PAHs and oxygenated PAHs (OPAHs).

In summer, 4 factors were extracted each of which explained more than 10% of variance each and analytes having more than 0.6 of factor loadings. The number of extracted analytes in factor 1 was 30. Table 1 shows chemical information and classification of each analytes in factor 1. 21 out of 30 analytes were classified as OVOCs and 2 analytes were unknowns. In factor 2, the number of analytes was 28. Among them, 12 analytes were classified as unknowns and other analytes were evenly distributed in OVOCs, VOCs and PAHs. In factor 3, 24 analytes were extracted. Unknowns and OVOCs were similarly contributed in factor 3, 10 and 9, respectively. In factor 4, 18 analytes showed strong correlation with factor 4. Of them, 13 analytes were OVOCs and 2 analytes were unknowns. In other words, OVOCs were dominant in 4 factors in summer except factor 2. It is not clear what were the major sources of each factor in summer.

In winter, 3 factors were extracted with more than 10% of variance. In factor 1, 55 analytes indicated more than 0.6 of factor loadings. Number of unknowns was 22 and was the highest followed by OVOCs, 17. In factor 2, 30 analytes were extracted and 29 of them were unknowns except only one analytes. In factor 3, 19 analytes showed high factor loadings and 13 analytes were identified in PAHs (Table 2). Its suggested that factor 3 in winter might be related to primary emission sources because PAHs are representative markers for primary organic aerosols. In addition to factor 3, factor 1 in winter appeared to be related to specific sources. Since factor 1 contained mostly unknowns and OVOCs, factor 1 might be related to secondary organic aerosols.

Through PCA, a large number of analytes in the atmospheric aerosols could be grouped according to presence of correlation between each other. In case of winter, each factors showed certain characteristics through chemical class. While, in case of summer, clear characteristics of each factor were not found though the presence of dominant OVOCs might suggest relationship with secondary organic aerosols.

3.4 Limitations of the Results

There are a few limitations in the chemical grouping analysis. First, there might be inconsistency between theory and practice. We carried out the chemical grouping under the assumption that analytes would be sepa-

rated in gas chromatography depending on their volatility and polarity sequentially. However, some analytes might not be separated as expected. Matrix effect is one of the reasons. Generally, most studies analyzing chemical compounds have been focused on specific target compounds and, thus, appropriate analytical method was adopted to eliminate matrix interference. However, in this study, some compounds were not separated as expected. For example, most PAHs which were non-polar in the atmospheric samples were identified as high polarity compounds (HP-SVOC group). Also, many oxygenated volatile organic compounds which should be polar since an n-alkane compound was used as polarity standard (oxygenated compounds are theoretically more polar than n-alkanes) were classified as low polarity compounds (LP-SVOC group).

Also, instrumental limitation might be also one of reasons. We used two columns filled with similar stationary phase used in Welthagen *et al.* (2003) to have similar analysis conditions. Among them, DB-17MS which was second column was known to be less reliable to separate chemical compounds depending on their polarity than DB-WAX. However, since DB-WAX has lower maximum temperature limit (240°C) than DB-17MS (320°C), DB-WAX could not be used in this study. It might influence on separation ability of analytes depending on polarity.

Other effect is certain patterns obtained from GC × GC data depending on their chemical class. As mentioned before, in GC × GC analytes separated in first column are focused in modulator and released to the second column. The difference with conventional 1-dimensional GC was that, since each analyte in each peak is modulated into several second-dimension peaks, same analytes can be observed in different retention time. Considering this property, we summed all peak areas of same analytes and chose the last retention time for chemical group separation. Therefore, this data processing could be influenced on chemical group separation. Furthermore, same chemical class (for example, n-alkanes and PAHs) are detected in a series of retention time in GC × GC data. In this case, analytes that should be classified in the same chemical class could be included in different chemical groups.

Finally, there are “too many” analytes to be separated according to several standards. Each analytes has its own characteristics such as emission source, chemical structure, etc. Since they were not separated clearly from their

other properties, partial analytes in chemical group can already have relationship with other analytes in different chemical separation group. This was indicated when we applied chemical separation group to the PCA results. Fig. 1 also shows scheme of correlation between partial analytes in different chemical separation group with PCA results. Grouping by PCA means that each analyte has correlation each other. Then grouping of these correlated analytes by “chemical group separation” means that each analyte has their own correlation according to other parameters including chemical property.

Though there were several possible limitations in the approach used in this study, this approach is promising one and further studies are warranted such as more detailed and advanced library and dual oven system to accommodate each column.

4. CONCLUSIONS

In this study, we carried out two kinds of analysis for characterization of unknown peaks in the atmospheric aerosols one of which was chemical and the other was statistical analysis. We applied chemical group analysis as a new approach using GC × GC data referred as Welthagen *et al.* (2003). Based on principle of GC × GC, analytes in 2D data were divided into 6 chemical group depending on their volatility and polarity. Specific analytes were chosen for separation standards. Naphthalene and benzo[a]pyrene were used for separation depending on their volatility. Hentriacontane was used for separation depending on their polarity. Using these classification standards, all analytes were classified as one of 6 chemical groups, HP-VOC, LP-VOC, HP-SVOC, LP-SVOC, HP-NVOC and LP-NVOC.

To investigate whether this chemical grouping is related to emission source or formation of secondary organic aerosol, relationship between the sum of the peak areas of the chemical groups with other variables such as the concentrations of OC, EC, OC_{POC}, OC/EC and OC_{SOC} were studied. However, no apparent relationship was observed.

For statistical analysis, the principle component analysis (PCA) was carried out. The factors explaining more than 10% of variance in summer and winter were separated. The OVOCs were dominant compounds in 3 out of 4 factors in summer. In winter, factor 1 was related to secondary organic aerosol and factor 3 was related to pri-

mary emission sources. Through PCA, information of unknowns about source of atmospheric aerosols could be obtained, though partially.

The proposed approach looks promising in characterization of chemical groups but have limitations at current stage. Further studies are warranted to fully utilize the proposed approach.

ACKNOWLEDGEMENT

This work was supported by National Research Foundation of Korea (NRF-2017R1A2B4006760).

REFERENCES

- Alam, M.S., West, C.E., Scarlett, A.G., Rowland, S.J., Harrison, R.M. (2013) Application of 2D-GCMS reveals many industrial chemicals in airborne particulate matter. *Atmospheric Environment* 65, 101–111, DOI: 10.1016/j.atmosenv.2012.10.014.
- Choi, N.R., Ahn, Y.G., Lim, H.B., Lee, J.Y., Jung, C.H., Kim, Y.P. (2018) Particulate nitrosamines in the atmosphere at Seoul and their major sources. *Air Quality, Atmosphere and Health*, 11(7), 855–865, DOI: 10.1007/s11869-018-0594-0.
- Choi, N.R., Lee, S.P., Lee, J.Y., Jung, C.H., Kim, Y.P. (2016) Speciation and source identification of organic compounds in PM₁₀ over Seoul, South Korea. *Chemosphere* 144, 1589–1596, DOI: 10.1016/j.chemosphere.2015.10.041.
- Dallüge, J., Vreuls, R.J., Beens, J., Brinkman, U.A.T. (2002) Optimization and characterization of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection (GC × GC-TOF MS). *Journal of Separation Science* 25(4), 201–214, DOI: 10.1002/1615-9314(20020301)25:4<201::AID-JSSC201>3.0.CO;2-B.
- Goldstein, A.H., Galbally, I.E. (2007) Known and unexplored organic constituents in the earth's atmosphere. *Environmental Science & Technology* 41(5), 1514–1521, DOI: 10.1021/es072476p.
- Hallquist, M., Wenger, J., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N., George, C., Goldstein, A. (2009) The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmospheric Chemistry and Physics* 9, 5155–5236, DOI: 10.5194/acp-9-5155-2009.
- Kallio, M., Hyötyläinen, T., Lehtonen, M., Jussila, M., Hartonen, K., Shimmo, M., Riekkola, M.-L. (2003) Comprehensive two-dimensional gas chromatography in the analysis of urban aerosols. *Journal of Chromatography A* 1019, 251–260, DOI: 10.1016/S0021-9673(03)01238-X.
- Kallio, M., Jussila, M., Rissanen, T., Anttila, P., Hartonen, K., Reissell, A., Vreuls, R., Adahchour, M., Hyötyläinen, T. (2006) Comprehensive two-dimensional gas chromatog-

- raphy coupled to time-of-flight mass spectrometry in the identification of organic compounds in atmospheric aerosols from coniferous forest. *Journal of Chromatography A* 1125(2), 234–243, DOI: 10.1016/j.chroma.2006.05.050.
- Kanakidou, M., Seinfeld, J., Pandis, S., Barnes, I., Dentener, F., Facchini, M., Dingenen, R.V., Ervens, B., Nenes, A., Nielsen, C. (2005) Organic aerosol and global climate modelling: a review. *Atmospheric Chemistry and Physics* 5, 1053–1123, DOI: 10.5194/acp-5-1053-2005.
- Lee, J.-Y., Lane, D.A., Huh, J.-B., Yi, S.-M., Kim, Y.P. (2009) Analysis of organic compounds in ambient PM_{2.5} over Seoul using thermal desorption-comprehensive two dimensional gas chromatography-time of flight mass spectrometry (TD-GC × GC-TOFMS). *Journal of Korean Society for Atmospheric Environment* 25(5), 420–431, DOI: 10.5572/KOSAE.2009.25.5.420.
- Lim, H.-J., Turpin, B.J. (2002) Origins of primary and secondary organic aerosol in Atlanta: Results of time-resolved measurements during the Atlanta supersite experiment. *Environmental Science & Technology* 36(21), 4489–4496, DOI: 10.1021/es0206487.
- Mauderly, J.L., Chow, J.C. (2008) Health effects of organic aerosols. *Inhalation Toxicology* 20, 257–288, DOI: 10.1080/08958370701866008.
- Ramanathan, V., Crutzen, P., Kiehl, J., Rosenfeld, D. (2001) Aerosols, climate, and the hydrological cycle. *Science* 294(5549), 2119–2124, DOI: 10.1126/science.1064034.
- Weggler, B.A., Ly-Verdu, S., Jennerwein, M., Sippula, O., Reda, A.A., Orasche, J.r., Gröger, T., Jokiniemi, J., Zimmermann, R. (2016) Untargeted identification of wood type-specific markers in particulate matter from wood combustion. *Environmental Science & Technology* 50(18), 10073–10081, DOI: 10.1021/acs.est.6b01571.
- Welthagen, W., Schnelle-Kreis, J., Zimmermann, R. (2003) Search criteria and rules for comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry analysis of airborne particulate matter. *Journal of Chromatography A* 1019, 233–249, DOI: 10.1016/j.chroma.2003.08.053.
- Xu, X., Stee, L., Williams, J., Beens, J., Adahchour, M., Vreuls, R., Brinkman, U., Lelieveld, J. (2003). Comprehensive two-dimensional gas chromatography (GC × GC) measurements of volatile organic compounds in the atmosphere. *Atmospheric Chemistry and Physics* 3, 665–682, DOI: 10.5194/acp-3-665-2003.
- Zheng, M., Cass, G.R., Schauer, J.J., Edgerton, E.S. (2002) Source apportionment of PM_{2.5} in the southeastern United States using solvent-extractable organic compounds as tracers. *Environmental Science & Technology* 36(11), 2361–2371, DOI: 10.1021/es011275x.