Identification of unknowns in atmospheric aerosols using comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometer (GC×GC-TOF-MS)

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Organic aerosols contain thousands of organic compounds and contribute to 20-90 wt% of the total fine aerosol mass (Kanakidou et al., 2005). Comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometer (GCxGC-TOF-MS) is a powerful tool to analyze chemical compounds in a highly complex sample (Kallio et al., 2006). Thus, it is suitable for analysis of atmospheric aerosols, particularly, identification of unknowns in atmospheric aerosols. In this study, unknowns filtered by principal component analysis in the atmospheric aerosols are identified.

PM2.5 samples were collected on the roof of the Asan engineering college, Ewha Womans University, Seoul, Republic of Korea (37.56 ℃N, 126.94 ℃E, 20 m above ground level). A total of 68 samples were obtained during summer (August 2014) and winter (January and February 2014) with a PUF sampler (Tisch, TE-1000) on quartz fiber filters. Filters were extracted using accelerated solvent extractor with a mixture of dichloromethane and methanol (3:1, v/v). Total extracts were blown down to 0.5 mL using a nitrogen evaporator (Turbo Vap II, Caliper Life Sciences).

For data processing, analytes in the PM2.5 samples were divided into 4 groups depending on their retention time in the two dimensions for their volatility and polarity (Welthagen et al., 2003). All the areas of the peaks in each group were summed and the variance of total area in each group was compared to each other. Area of each compound in each group was processed by principal component analysis to characterize each group and select meaningful unknowns in atmospheric aerosols.

Table 1. Property of divided group depending on retention time.

Group	1st R.T (min)	2nd R.T (sec)	Property	
			Volatility	polarity
1	7-32	2-4	High	High
2	32-57	2-4	Low	High
3	7-32	0-2	High	Low
4	32-57	0-2	Low	Low

In summer, the areas of group 2, 3 and 4 contributed different fraction day by day. However, the area of group 1 showed consistently low value. In winter, compounds of group 3 and 4 dominated most of aerosol while compounds of group 1 and 2 showed low intensity. The area of group 2 showed a large difference between summer and winter. In terms of area, the area in summer is three time higher than in winter.

By using the area of each analyte in each group including both knowns and unknowns, principal component analysis are processed to choose meaningful unknowns in the principle component for identifying. Chosen unknowns are identified by manual identification or extra measurement and analysis.

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