Characterization ionic species fine particulate samples in Indonesia by ion chromatography

Indah Kusmartini, Natalia Adventini, Syukria Kurniawati, Diah Dwiana Lestiani, Endah Damastuti, Dyah Kumala Sari

Center for Applied Nuclear Science And Technology
National Nuclear Energy Agency of Indonesia (BATAN)
Bandung, Indonesia
E-mail: indahkus@batan.go.id

Abstract. Particulate is one indicator of air pollutants derivative from a complex mixture of large and small particles that are decomposed. Particulate diameter at 2.5 to 100 mm consists of dust originating from agriculture, building construction, and vehicles. Particulates with a diameter of less than 2.5 mm are generally made from fossil fuels and vehicle exhaust containing various specific chemicals or ions. In this activity, characterization of chemical content and specific ions in fine particulates was carried out in fine air particulate samples by ion chromatography. Sampling was carried out in several regions in Indonesia such as Pekanbaru, PalangkaRaya, Manado, Ambon, Jayapura, Denpasar, and Surabaya. The validation methods using reference materials. On the other hand, verification of measurements is carried out regularly with ED-XRF therefore accurate and precise quality can be obtained. The results of this activity obtained several cations and anions such as Ca$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$, SO$_4^{2-}$, NO$_3^-$, F$^-$, and Cl$^-$.

1. Introduction
Air quality in several cities in Indonesia is influenced by several industrial sources including fuel for electricity generation, transportation, industry, biomass generation and primary emissions other than biogenic sources [1]. Air pollution occurs because of contamination due to industrial activities which are released directly into the environment. This contamination enhances the ability of the environment to deal with and process it [2]. Excessive contamination will accumulate in the air. Air pollution containing industrial activities can consist of carbon monoxide (CO), carbon dioxide (CO$_2$), nitrite, nitrate, ammonia, SO$_x$ and chloride [3]. This polluted air will accumulate in the atmosphere. One of the main pollutants that serves as an indicator of air quality is air particulates [4]. Particulates are a mixture of dense and liquid droplets in the air including smoke, dust and ash. Atmospheric aerosols and air particles are very important in environmental problems related to climate, air quality, visibility, atmospheric chemistry and adverse effects on human health. In a previous study conducted by Stafoggia, M et al. Declared that air pollution as air particulate matter (PM) was one of the pollutants that caused death [5][6]. Has been estimated by the world health organization about there were 4.2 million deaths by air discussions worldwide and based on a Global Study on the number 6 cause of death worldwide due to air particulates [4]. Aerosol sulfate and nitrate from SO$_2$ and nitrogen oxides condense in the atmosphere (Kumar and Joseph 2006) [7]. Previous research that has been proposed by Sen-chao et al. (2007) namely sulfate and nitrate are secondary particles in investigating chemical
species as an indicator of debate over sources of air pollutants[8]. Research related to the investigation of pollutant sources through the characterization of chemical elements in particulates has previously been carried out Al-momani, et al (2017) and Bouhila Z., et al (2015) with Nuclear Analysis Techniques (TAN)[9]. The characterization of anions and cations is difficult to do with nuclear analytical techniques, it is necessary to coordinate with sulfates and nitrates can be done by ion chromatography method[10]. Ion chromatography is a method of measurement that has high sensitivity, selectivity and accuracy. The purpose of this study was to identify anions and cations in fine air particulate samples in several cities in Indonesia with ion chromatography.

2. Methodology
2.1 Sampling Site
Sampling was conducted in several cities in the Territory of Indonesia, namely Ambon, Denpasar, Jayapura, Manado, PekanBaru, PalangkaRaya, and Surabaya.

2.2 Sampling
Before being used for sampling, the filter is conditioned in a clean room to be weighed for at least 24 hours. Clean room is a dust-free room equipped with a dehumidifier and Air Conditioning to control room air humidity at a humidity level of 40 - 60% with a temperature of 18-25°C [11]. PM2.5 and PM10 ambient air particulate sampling was performed using the GENT Stacked Filter Unit Sampler (Gent SFU Sampler) is an air sampling device consisting of two main parts, namely a black container and a vacuum pump. The Gent Sampler is equipped with a timer, rotameter, air volume indicator and unite stacked filter, a dichotomous sampler. In each sample capture two types of polycarbonate filters are used which are fine filters (porous 0.4 µm) and coarse filters (porous 0.8 µm). The sampling was carried out at a height of 6 to 20 meters above the ground at a flow rate of 16-18 L / min for 24 hours. From this sampling will produce air particulate samples with sizes up to 2.5 µm in fine filters and between 2.5-10 µm in coarse filters. Fine filter and coarse filter after sampling are conditioned in a clean room then weighing [12], [13].

2.3 Determination of air particulate mass concentration
The determination of air particulate mass is done gravimetrically, namely the determination of air particulate concentrations based on differences in filter weight before and after sampling in order to obtain air particulate mass. Fine and coarse filters before sampling are weighed using Mettler Toledo micro balance (6 digits) for 3 repetitions so that the filter weight is obtained which shows the value that is not much different. The same is done for the filter filter after sampling. Fine air particulate matter (PM2.5) is obtained from the weight measurement results of the fine filter sample in equation (1), while PM10 is obtained from the sum of the mass of airborne particles from fine and coarse in equation (2) [13].

\[
PM_{2.5} = \frac{W_{\text{sample, fine filter}}(\mu g)}{Volume_{\text{air}}(m^3)} \times 1000 \tag{1}
\]

\[
PM_{10} = PM_{2.5}(\mu g/m^3) + \frac{W_{\text{sample, coarse filter}}(\mu g)}{Volume_{\text{air}}(m^3)} \times 1000 \tag{2}
\]

2.4 Determination concentration of anions and cations by ion chromatography
2.4.1 Preparation equipment of ion chromatography. Equipment used in ion chromatography methods include injection valves, sample loops, protective columns, separation columns and fiber or membrane suppressors, small volume conductivity cell detectors with temperature compensation (6uL or less), and graphical recording strips capable of scale response full of 2s or less. The ion chromatography method is capable of producing 2 to 5 mL of eluents / minute at pressures of 1400 to
In the separation column between anion and anion exchange resin with styrene divinylbenzene material and has a low capacity and is able to determine Br, Cl, NO3, SO42-. Separating column to protect from particulate or organic impurities. The fiber exchanger or membrane exchange cation exchange membrane can continuously change the eluent and the separated anion into its acidic form.

2.4.2. Reagents. Deionized water, filtered through a 0.2 um filter to avoid column clogging with conductance <0.1 uS / cm. Preparation of Standard Solutions, preparation of E-Merck IC anion F, Cl, SO4, NO3 pipette as much as 20 mL into a 100 mL volumetric flask, then a gradual dilution is obtained to obtain a solution concentration of 1 ppm, 2 ppm, 5 ppm, 7.5 ppm and 10 ppm. Whereas the cations were obtained from standard maternal solutions of Ca, Mg, Na and K then gradual dilution obtained a completion concentration of 2, 4, 6, 8 ppm.

2.4.3. Procedure. The equipment of ion chromatography system is turned on and adjusted the eluent flow rate to close to separation is achieved at around 2 mL / min. The detector is adjusted to 10 to 30 uS conductivity and the system is left to reach a balanced condition. The detector is offset to zero eluent conductivity with a fiber or membrane suppressor adjusting the regeneration flow rate to maintain stability of 2.5 to 3 mL / min.

Making a calibration curve is done by injecting a standard containing one anion or mixture and determining the estimated retention time. Observed time varies with conditions but if standard eluents and anion separation columns are used, retention is always in the order of Cl, NO3, SO4. The filter sample is divided into four parts, extracted with deionized water using an ultrasonic device for 15 minutes. The extracted filter is then filtered and measured by ion chromatography. For determination of a fine filter sample filtered with a 0.2 um membrane filter. Use prewashed syringes with capacities of 1 to 10 mL which are equipped with appropriate samples or injection standards. The sample is injected to water the sample loop several times; 0.1 mL sample loop injects 1 mL.

3. Result and Discussion
Filtered and homogeneous air particulate samples were injected into the ion chromatography column and the particle size was smaller than 0.45 µm. Samples were flowed by eluent and pumped through an ion chromatography system. The separation of anions is based on their affinity from the chromatographic column material. The conductivity reading of the detector is used to calculate concentration [14]. Concentration of the ionic species on the filter, as well as their precision estimates, can be calculated using a computer spreadsheet program according to the following steps. Table 1 show determine the lineer regression slope and intercept of the relation between standard concentration and detector response. In this activity a calibration curve with high concentrations (eg 0, 1.0, 2.0, 5.0, 7.5, and 10.0 ppm) is made from a mixture of standard solutions that have known concentrations. The lowest point in making this calibration curve is 1.0 ppm in this approach for samples with low concentrations will not be read by the tool, therefore to re-analyze air particulate samples with concentrations lower than 1.0 ppm can use calibrations with low concentrations 0-1.0 ppm

| Analyte | Range (ppm) | Linearity (R²) |
|---------|-------------|----------------|
| F       | 1 - 10      | 0.9965         |
| Cl      | 1 - 10      | 0.9970         |
| SO4     | 1 - 10      | 0.9981         |
| NO3     | 1 - 10      | 0.9973         |
| Na      | 2 - 8       | 0.9915         |
| Mg      | 2 - 8       | 0.9996         |

External standard calibration methods are applied for all determinations [15]
Eight-point calibration curves are determined by analyzing multi-element reference standards prepared from stock solutions (E-Merck Standard). These results indicate that the IC method for determining air particulate content has good linearity with a value of R² close to 1.

\[
\begin{array}{ccc}
\text{K} & \text{2 - 8} & 0.9954 \\
\text{Ca} & \text{2 - 8} & 0.9883 \\
\end{array}
\]

Figure 1. Chromatogram for calibration standard cation

Figure 1 shows the chromatogram for the anion of the standard calibration curve. In the picture it can be seen that fluoride and chloride anions have the similar retention time therefore columns with solid extraction can be used to hold organic acids and pass organic anions. On the other hand anions that have high concentrations can overlap with other anionic species. In this condition can be reduced by diluting air particulate samples with reagent water [14].

Table 2. Concentration ionic species dalam SRM 1468a and reference material

| Analyte | Concentration (ppm) | Certificate Value (ppm) | Recovery |
|---------|---------------------|-------------------------|----------|
|         | RM 172 10x | SRM PU | RM 172 10x | SRM PU | 172 10x | SRM PU |
| Mg      | 6          | 7085   | 6.24       | 8130   | 94     | 87     |
| NO₃     | 94         |        | 112.22     |        | 84     |        |
| K       | 6          |        | 7.02       |        | 89     |        |
| Ca      | 50         | 57334  | 52.4       | 58400  | 95     | 98     |

Method validation was carried out using the SRM 1648 Particulate Matter and Rainwater Reference material footage. The results of ionic analysis in SRM and RM use ion chromatography. From Table 2 it can be seen that the value of the results of the ionic analysis when compared with the value of the certificate shows a fairly good value with% recovery were in the range of 84-98%. These values were in the% recovery of acceptance criteria for 10 ppm concentration of 80-110% [16].
From the figure 2, it can be seen that there is a closeness of the results of the calculation of elemental levels in the sample with the ion chromatography and XRF methods, this shows the results of the measurement of the elemental levels in the samples from the two methods give results that are not significantly different. 

PM$_{2.5}$ concentrations in several cities in Indonesia can be seen in Figure 3, which shows the cities of Palangkaraya 2, and Denpasar are at a fairly high concentration of 350.88 and 72.34 µg/m$^3$ compared to other cities, respectively. PM$_{2.5}$ values in the cities of PalangkaRaya and Denpasar have exceeded the concentration standards set by the concentration set by the United State Environmental Protection Agency (USEPA) of 35 µg/m$^3$. While the PM$_{10}$ concentration of Palangkarata 2 city has the highest value of 759.29 µg/m$^3$. This value is 5 times higher and is above the standard set by USEPA of 150 µg/m$^3$. If it exceeds the standard set, it will affect health because the particles can pass through the body's normal resistance mechanism and penetrate deep into the alveoli of the lungs [17][7].

The sodium concentration in Table 1 shows that Jayapura city has the highest value compared to other cities, while for Mg ion cities Palangkaraya 2, Jayapura, Denpasar and Surabaya have higher values compared to the cities of PekanBaru and Manado. For calcium and potassium ions. The cation can be said to be 'light element' because it is related to substances that come from burning garbage and plant vegetation which contains a lot of dust (soil or dust particles and can be emitted back into the atmosphere)[18].

**Figure 2.** Elemental content curves in air particulate samples by ion chromatography and XRF methods

**Figure 3.** Concentration of PM$_{2.5}$ and PM$_{10}$ in several cities in Indonesia
### Table 3. Ion Concentration (ng/m$^3$) of fine particulate in several cities in Indonesia

| City          | Na  | Mg  | K   | Ca  | F   | Cl  | SO$_4$ | NO$_3$ |
|---------------|-----|-----|-----|-----|-----|-----|--------|--------|
| Palangkaraya 1 | 28.425 | 11.7 | 19.8 | 49.1 | 38 | 71  | 199    | 84    |
| Palangkaraya 2 | 47.693 | 38.5 | 10.7 | 119.4 | 130 | 121 | 379    | 117   |
| Palangkaraya 3 | 49.085 | 19.7 | 14.9 | 57.1 | 36 | 102 | 311    | 135   |
| Pekanbaru 1   | 18.291 | 11.7 | 13.5 | 51.5 | 122 | 96  | 349    | 98    |
| Pekanbaru 2   | 45.913 | 10.1 | 6.1  | 54.2 | 52 | 83  | 194    | 108   |
| Ambon         | 22.471 | 27.7 | 14.7 | 120.0 | 77 | 146 | 139    | 83    |
| Denpasar      | 32.196 | 32.5 | 64.1 | 91.4 | 173 | 724 | 659    | 486   |
| Jayapura      | 367.239 | 60.7 | 55.0 | 216.6 | 5 | 19  | 28     | 17    |
| Menado        | 6.199  | 1.4  | 0.8  | 8.2  | 9  | 131 | 279    | 98    |
| Surabaya      | 30.308 | 28.0 | 14.2 | 121.5 | 129 | 103 | 247    | 84    |

Ion fluoride in the city of Manado has the lowest value compared to other cities, however the determination of the F-concentration is not recommended on a matrix whose concentration is unknown. Based on studies that have been done previously show that precision is not good, this happens due to the F- difficult to quantize at low concentrations caused by negative concentrations of the main "water immersion", in addition to the presence of simple organic acids (formic, carbonate, etc.) it will interfere eluted close to fluoride. To determine the precision and accuracy of fluoride before sample analysis can be determined accurately by ion chromatography with dilute elution or gradient elution using eluent NaOH.[14].

While the highest concentration of Cl ion is in the cities of Denpasar, Manado, Surabaya and Ambon. High concentration of Cl in the areas of Denpasar, Manado, Surabaya, and Ambon because the location is on the coast so that the high concentration of Cl comes from sea water. SO$_4$ and K anion concentrations in table 1 for Palangkaraya and Pekanbaru city are quite high compared to other cities because of the presence of forest fires. Based on previous research conducted by Ofosu, F et al and Froehlich potassium and sulfate decomposed in air particulate aerosols is a key element indicator in forest fires. While the highest nitrate concentration in the city of Denpasar was 486.2 ug/m$^3$[19][20]. Previous research conducted by Vaconcellos, et al in Brazil (2007) showed concentration values of Na, K, Ca, Mg, F, Cl, NO$_3$, and SO$_4$ respectively 550, 720, 1130, 120, 50, 1210, 4170, 5210. This value is significantly different from the results conducted in this study, it is caused by several factors such as differences in wind direction, regional topography, temperature, and air humidity [21].

### 4. Conclusion
The results of this activity obtained several cations and anions namely Ca$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$, SO$_4^{2-}$, NO$_3^-$, F, and Cl$. Determination of the concentration of anions and cations can be used as data to identify sources of pollutants in several regions in Indonesia and is expected to be used as a basis and scientific-based reference data for regional / national in formulating, taking appropriate and directed actions and policies to solve the problem of air pollution.

### References
[1] G. Engling, J. He, R. Betha, and R. Balasubramanian, “Assessing the regional impact of indonesian biomass burning emissions based on organic molecular tracers and chemical mass balance modeling,” *Atmos. Chem. Phys.*, vol. 14, no. 15, pp. 8043–8054, 2014.

[2] I. F. Al-momani and W. M. Shatnawi, “Chemical Characterization and Source Determination of Trace Elements in PM2 . 5 and PM10 from an Urban Area , Northern Jordan,” vol. 5, no. 4, pp. 103–108, 2017.
[3] H. Wang and G. Han, “Chemical composition of rainwater and anthropogenic influences in Chengdu, Southwest China,” *Atmos. Res.*, vol. 99, no. 2, pp. 190–196, 2011.

[4] Y. Feng, Y. Li, and L. Cui, “Critical review of condensable particulate matter,” *Fuel*, vol. 224, no. March, pp. 801–813, 2018.

[5] M. Stafoggia, T. Bellander, S. Bucci, M. Davoli, K. De Hoogh, F. De Donato, C. Gariazzo, A. Lyapustin, P. Michelozzi, M. Renzi, M. Scortichini, A. Shtein, G. Viegi, I. Kloo, and J. Schwartz, “Estimation of daily PM 10 and PM 2.5 concentrations in Italy, 2013–2015, using a spatiotemporal land-use random-forest model,” *Environ. Int.*, vol. 124, no. November 2018, pp. 170–179, 2019.

[6] Z. S. Ahmed and S. S. Abozed, “Functional and antioxidant properties of novel snack crackers incorporated with Hibiscus sabdariffa by-product,” *J. Adv. Res.*, vol. 6, no. 1, pp. 79–87, 2015.

[7] J. K. Nagar, A. B. Akolkar, and R. Kumar, “A review on airborne particulate matter and its sources, chemical composition and impact on human respiratory system,” vol. 5, no. 2, pp. 447–463, 2014.

[8] L. A. I. Sen-chao, Z. O. U. Shi-chun, C. A. O. Jun-ji, L. E. E. Shun-cheng, and H. O. Kin-fai, “Characterizing ionic species in PM 2.5 and PM 10 in four Pearl River Delta cities, South China,” vol. 19, pp. 939–947, 2007.

[9] L. H. Bouhila Z, Mouzai M, Azli T, Nedjar A, Mazouci C, Zergoug Z, Boukhadra D, Chegrouche S, “Investigation of aerosol trace element concentrations nearby Algiers for environmental monitoring using instrumental neutron activation analysis,” *Atmos. Res.*, vol. 166, pp. 49–59, 2015.

[10] M. R. Facchini Cerqueira, M. F. Pinto, I. N. Derossi, W. T. Esteves, M. D. Rachid Santos, M. A. Costa Matos, D. Lovinsohn, and R. C. Matos, “Chemical characteristics of rainwater at a southeastern site of Brazil,” *Atmos. Pollut. Res.*, vol. 5, no. 2, pp. 253–261, 2014.

[11] D. D. L. Indah Kusmartini, Djoko Prakoso DA, Syukria Kurniawati, Endah Damastuti and Putar, “Estimasi ketidakpastian konsentrasi pm 2,5 dan pm 10 dalam cuplikan partikulat udara ambien,” *Proceeding Semin. Nas. dan Teknol. Nukl. 2015 Aula Timur ITB*, 2015.

[12] M. S. Indah Kusmartini, Natalia Adventini, Dyah Kumala Sari, Syukria Kurniawati, Diah Dwiana Lestiani and Putar, “KARAKTERISASI UNSUR PM 2,5 PADA PERIODE KEBAKARAN HUTAN DI PEKANBARU DENGAN TEKNIK ANALISIS AKTIVASI NEUTRON Indah,” *J. Sains dan Teknol. Nukl. Indones.*, vol. ISSN 1411, pp. 9–23, 2019.

[13] D. K. Muhayatun, Diah Dwiana, Syukria, Endah, Djoko, Indah, Natalia, Woro, *LAPORAN KEGIATAN BERSAMA 2016-2017*. 2017.

[14] A. Public and H. Association, “APHA Method 4110: Standard Methods for the Examination of Water and Wastewater,” vol. 552, 1992.

[15] J. G. Watson, “Ion chromatography in elemental analysis of airborne particles,” no. January 1999, 2014.

[16] A. G. Gonza, “A practical guide to analytical method validation, including measurement uncertainty and accuracy profiles,” vol. 26, no. 3, pp. 227–238, 2007.

[17] M. Ahmed, X. Guo, and X. Zhao, “Determination and analysis of trace metals and surfactant in air particulate matter during biomass burning haze episode in Malaysia,” *Atmos. Environ.*, vol. 141, pp. 219–229, 2016.

[18] Y. N. Samsonov, V. A. Ivanov, D. J. Merae, and S. P. Baker, “Chemical and dispersal characteristics of particulate emissions from forest fires in Siberia,” *Int. J. Wildl. Fire*, vol. 21, no. 7, pp. 818–827, 2012.

[19] F. G. Ofosu, P. K. Hopke, I. J. K. Aboh, and S. A. Bamford, “Biomass burning contribution to ambient air particulate levels at Navrongo in the Savannah zone of Ghana,” *J. Air Waste Manage. Assoc.*, vol. 63, no. 9, pp. 1036–1045, 2013.

[20] I. F.-F. M.G. Froehlich, S. Chatterjee, M. Li, T. DeSilva, J. McDonald, S. Rockliff, “Airborne Particulate Matter Pollution in the Australian Capital Territory,” 2015.

[21] P. C. Vasconcellos, “Water-Soluble Ions and Trace Metals in Airborne Particles Over Urban Areas of the State of São Paulo, Brazil: Influences of Local Sources and Long Range Transport,” pp. 63–73, 2007.
