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1.21 ELEMENTAL QUANTIFICATION OF AIRBORNE PARTICULATE MATTER BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS AND INDUCED COUPLED PLASMA MASS SPECTROMETRY ANALYSIS

Achmad Hidayat, Harjoto Djojosubroto, Rukihati and Sutisna
Indonesian National Nuclear Energy Agency

ABSTRACT. ELEMENTAL QUANTIFICATION OF AIRBORNE PARTICULATE MATTER BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS AND INDUCED COUPLED PLASMA MASS SPECTROMETRY ANALYSIS. Airborne particulate were collected using Gent sampler for PM 10 and using high volume sampler for total suspended particulate (TSP). PM 10 sampling was carried out in Bandung during period of January to December 1997. Whereas TSP samples were collected at Serpong (rural area) and Jakarta (urban area) during period of May and July 1995. The concentration of the PM 10 in the air is independent to the level of the rainfall. The levels of the PM 10 and the PM 2.5 are lower than the maximum permissible levels set by the US Environmental Protection Agency in July 1997. The element detected using short lived radioactivity measurement in PM 10 and PM 2.5 were Al, Na, V, Mn, Br and Cl. Bromine concentration in both coarse and fine fractions was high, and the enrichment factor for bromine in these fraction was found between 2000 – 10,000. The elemental concentrations of particulate matter obtained by ICP-MS was found that the Ag, Al, As, Ba, Cd, Co, Cr, Cs, Cu, Fe, In, K, Mg, Mn, Na, Ni, Pb, Rb, V and Zn in samples from Serpong area, were lower than those in samples taken from Jakarta area. The level of Pb concentrations in TSP samples from Serpong and Jakarta area were lower than Pb concentration proposed Indonesian standard of 2 $\mu g/m^3$. The data obtained by INAA no significant different to those obtained by ICP-MS. Therefore comparative data can be obtained by these techniques.

INTRODUCTION

Through industrialization, Indonesia has achieved remarkable economic development over the last twenty-five years, which has improved the quality of live the Indonesian people. Economic and industrial developments are also accompanied by side effects. Urbanization and economic activities in specific urban areas have caused degradation of environmental quality. Pollution of air, water and ground resources may have a potential impact on human health and upon natural ecological systems. In this respect it was observed for example, that the incidence of coronary heart disease in Indonesia is increasing without significant correlation to the incidence of conventional risk factors.

Declining of air quality induces serious impact to environment and human health. The total cost of health impact for Jakarta is estimated by World Bank to be

more than 250 million US $ per year [1]. Environmental Impact Management Agency (BAPEDAL) which was established in June 1990, is an agency responsible for environmental protection in Indonesia. In order to improve and to control air quality in four provinces (Jakarta, West Java, Central Java and East Java), in July 1992 Bapedal Introduces Blue Sky program [1].Managing these environmental impacts has long been a high priority for Government of Indonesia.

To monitor and to solve problems on air quality in Jakarta region, Bapedal received technical assistance from Australian Nuclear Science and Technology Organization (ANSTO) and Japan International Co-operation Agency (JICA). In these activities, quantification of trace elements in airborne particulate samples is one of the particular concerns[2,3,4]. The samples were collected using a sampler that separated fine (< 2.5 μm aerodynamic diameter) from coarse (2.5 – 10 μm aerodynamic diameter) fractions. Toxic materials in the fine fraction are more hazardous to human health than those in coarse fraction.

In the present study the distribution of airborne particulate matter in the fine and the coarse fraction and elemental concentration in these fractions will be determined. The quantification of the elements will be performed by instrumental neutron activation analysis (INAA). To ensure that comparative data has been obtained, a comparison study on elemental quantification by INAA and induced coupled plasma – mass spectromectric (ICP-MS) analysis was performed. The ICP-MS is a highly sensitive technique for elemental analysis and achieves detection limit comparable to neutron activation analysis.

DESCRIPTION OF THE WORK

Airborne particulate matter was deposited on Nuclepore filters from an urban area in Bandung, i.e. Center for Research and Development of Nuclear Technique. These filters were placed in a catridge of a Gent [5] sampler and were used to collect the two fractions of PM 10, i.e. PM 2.5 (fine fraction) and a course fraction of aerodynamic diameter 2.5 – 10 μm. The cartridge of the Gent sampler was placed on the roof of a two story building, about 10 m above ground level and 50 m from the nearby street. The sampling period was 24 hours, or shorter if the fine filter was clogged. The quantity of

the deposited matter on the Nuclepore filter were determined by weighing the filters using a semi micro balance following equilibration these filters in a " clean" chamber to avoid dust particle contamination at 25 ^{0}C and 50 % relative humidity.

The amount of airborne particulate deposition Nucleporc filters was on the order of 1 mg, or sometimes less than 1 mg. That is why for comparison the INAA and ICP-MS study the particulate matter was deposited using a high volume air sampler on a nitro-cellulose membrane filter (Toyo Rushi Kaisha, Ltd., 203 x 254 mm, 5.0 mm pore size). During the particulate matter collection, the membrane filter was backed-up by a piece of filter made of pure poly tetra fluoro ethylene resin. The sampling duration was 24 hours at 1200 m^3 min^{-1}. The amount of the deposit was determined by weight different after and before sample collection following equilibration of the membrane filter for 24 hours in a preconditioning chamber at 20^{0}C and 50 % relative humidity. The filters were cut into eight parts, and the two of one eight part filters were used for the INAA and ICP-MS measurements. The samples were taken during May – July 1995 from Pulo Gadung (a very dense traffic site), Bandengan (business area) and a residential and rural area in Serpong.

Elemental quantification in the deposits on Nuclepore filter by short lived radio activity was performed in Yogyakarta Nuclear Research Center by exposing the samples and mixed standards for 5 minutes in a neutron flux of 10^{11} n cm^{-2} sec^{-1} and promptly counted the γ-ray spectra using a high purity Ge (HPGe) γ-ray spectrometer equipped with Accuspec emulation system. The levels of elements that produced long lived radionuclides were determined by exposing the samples for 30 minutes in a neutron flux of 10^{13} n cm^{-2} sec^{-1} in Multi Purpose Reactor in Serpong. The irradiated samples were cooled for 1-2 weeks, then counted by a high-resolution γ-ray spectrometer coupled with Aptec emulation system. The spectral resolution of the spectrometer system used in this study was better than 2 keV (full width at half maximum) and peak to Compton ratio of better than 35 for 1332 keV line emitted by ^{60}Co.

For the INAA technique, the one eight part of the membrane filter was placed in a high-density polyethylene vial. Sample and standard were packed into one irradiation container. The samples were exposed to thermal neutron flux of about 10^{13} n cm^{-2} scc^{-1} in Multi Purpose Reactor in Serpong. The γ-ray emission from the irradiated samples

was counted by a high resolution HPGe detector (Canberra, NIGC-18190, resolution 1.9 keV at 1.33 MeV of ^{60}Co, and peak to Compton ratio of 44) coupled to Nuclear data multichannel analyzer.

For the ICP-MS analysis, the one eight of the filtered sample was placed in a sealed Teflon vessel, to which were added 6 ml of concentrated HNO_3 and 2 ml of concentrated HF. The mixture was digested in a microwave oven (Milstone). The mixture was then transferred to a teflon beaker and evaporated to dryness. The residue was redissolved in 50 ml of 2 % HNO_3. A blank was also prepared; this is analyzed in a similar matter as the samples. Metal elements of this solution were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Sciex-Perkin Elmer, Elan model 250/5000).

RESULTS AND DISCUSSIONS

The concentration of the coarse and fine particulate matter during 1997 and the respective amount of rainfall and wind speed during this period are depicted in Figure 1. It seems that the concentration of the particulate matter in the air is independent to the level of the rainfall. The concentration of coarse fraction was slightly higher than the fine fraction. In all cases the levels of the PM 10 and PM 2.5 are lower than the maximum permissible levels set by the US Environmental Protection Agency in July 1997 (maximum permissible levels for PM 2.5 = 65 mg/m^3 and PM 10 = 150 mg/m^3).

Figure 2 and 3 represent the variation of the concentration of several elements in the airborne particulate matter, respectively in fine and coarse fraction. From this figures were observed that the aluminum concentration was the highest and vanadium was the lowest, either in fine or in coarse fractions. In most cases bromine concentration in both fraction was high, and the enrichment factor for bromine in these fractions was found between 2000 – 10,000. That is why it was concluded, bromine was released by anthropogenic source(s).

As illustrated in Figure 4 it was found that the data obtained by INAA showed no significant different to those obtained by ICP-MS. Therefore, comparative data can be obtained by these techniques.

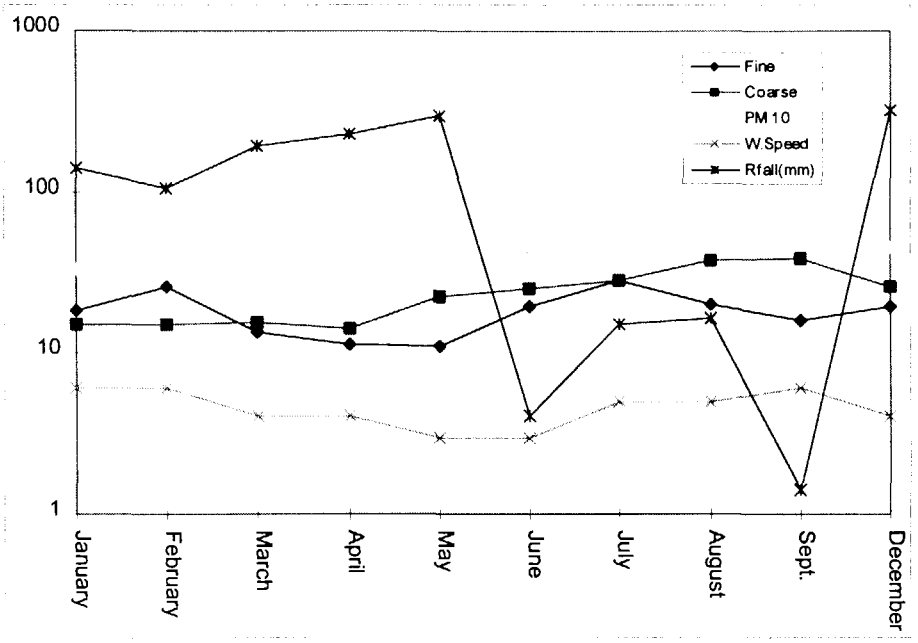

Figure 1. Levels of fine and coarse fraction of particulate matter ($\mu g/m^3$).

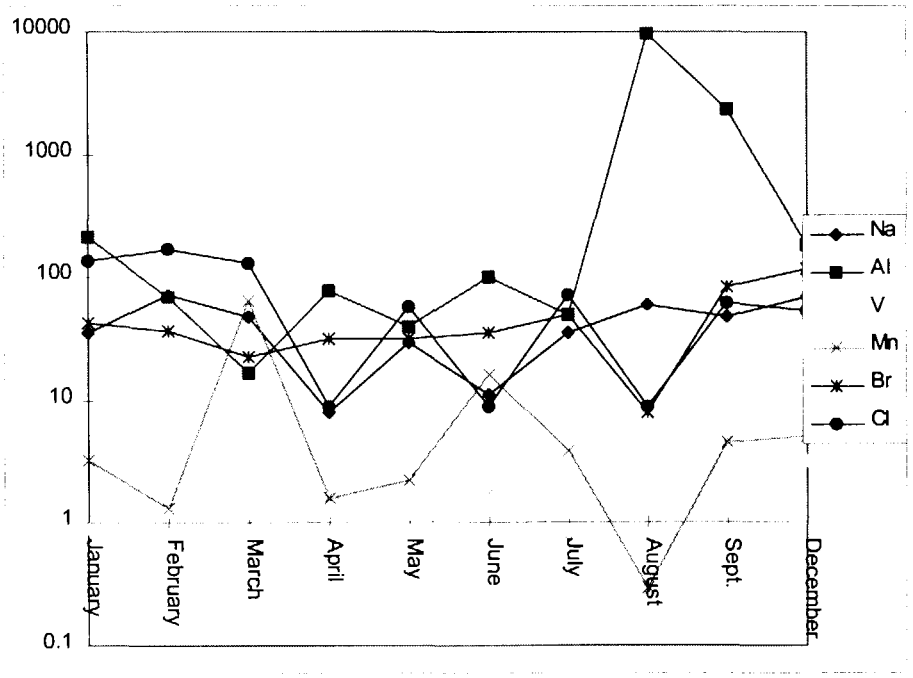

Figure 2. Elemental concentration in fine fraction (ng/m^3).

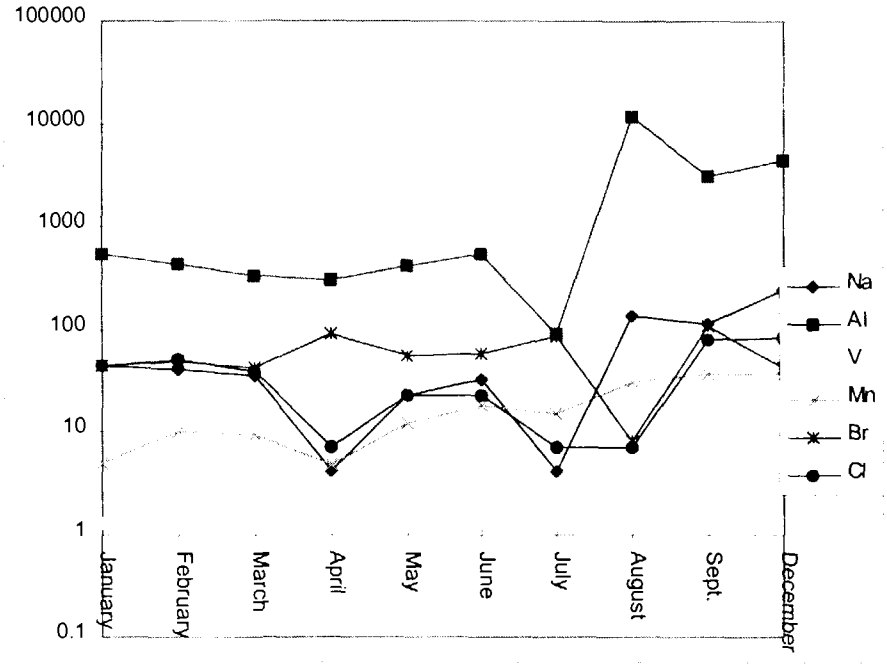

Figure 3. Elemental concentration on coarse particles (ng/m^3).

The elemental concentrations of particulate matter obtained by ICP-MS technique for samples from Serpong and Jakarta areas were shown in Figure 5, 6 and 7. It was found that the elemental concentrations of Ag, Al, As, Ba, Cd, Co, Cr, Cs, Cu, Fe, In, K, Mg, Mn, Na, Ni, Pb, Rb, V and Zn in samples from Serpong area were lower than that in samples taken from Jakarta area, except for Cu. The concentration of Cu at Serpong area was 6-10 times higher than that in the samples from Jakarta area. The high Cu concentration in samples from Serpong area might be due to erosion of copper electrode in the motor of the high air volume sampler.

Although the airborne particulate samples from Jakarta and Bandung were taken from different environment and different sampler, it was observed that the concentration of aluminum in the samples is the highest. By ICP-MS was found that the concentration of lead (Pb) in the sample from Jakarta was 0.7 - 1.7 μg/m^3 (lower than the maximum permissible level set by Indonesian Standard, 2 μ/m^3). Lead is very difficult to

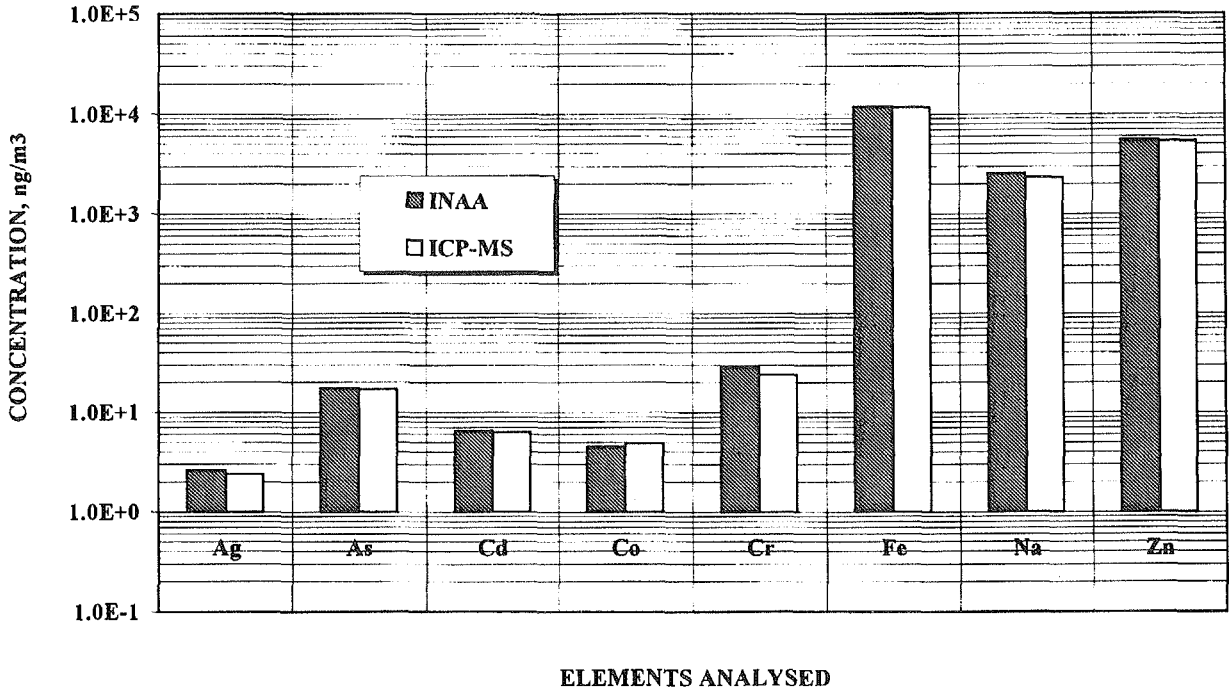

FIGURE 4 . COMPARISON OF ANALYTICAL RESULTS OF INAA AND ICP-MS

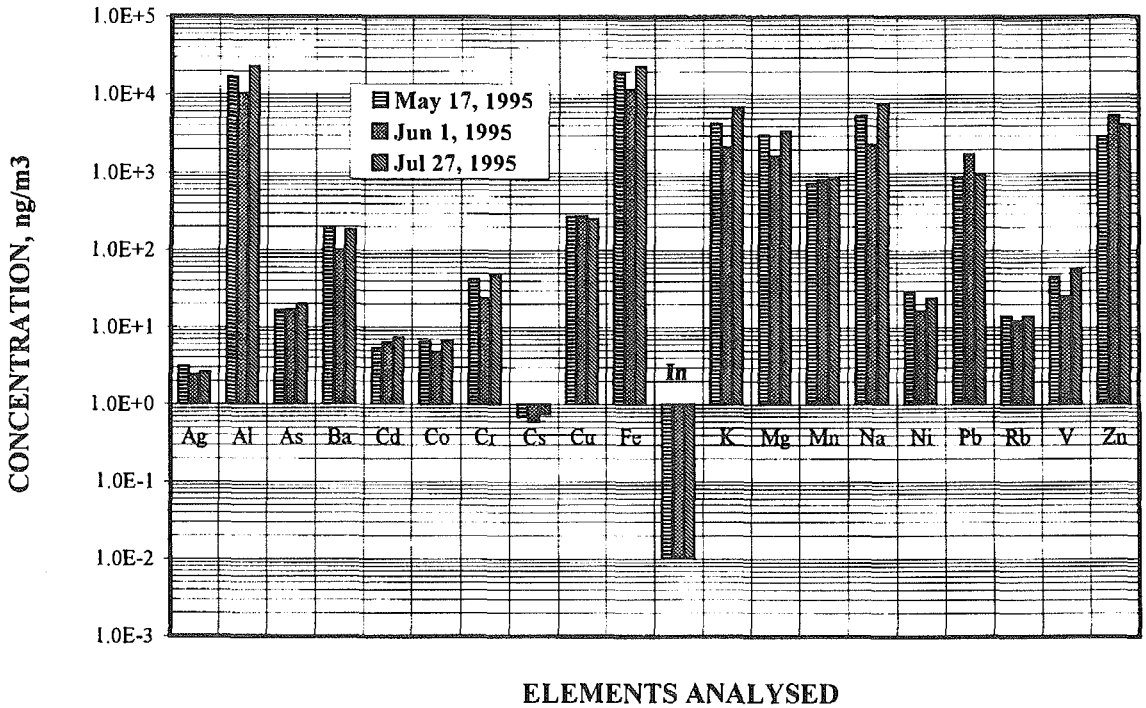

FIGURE 5. ELEMENTAL CONCENTRATION OF TSP SAMPLES FROM JAKARTA (POLUGADUNG) MEASURED BY ICP-MS

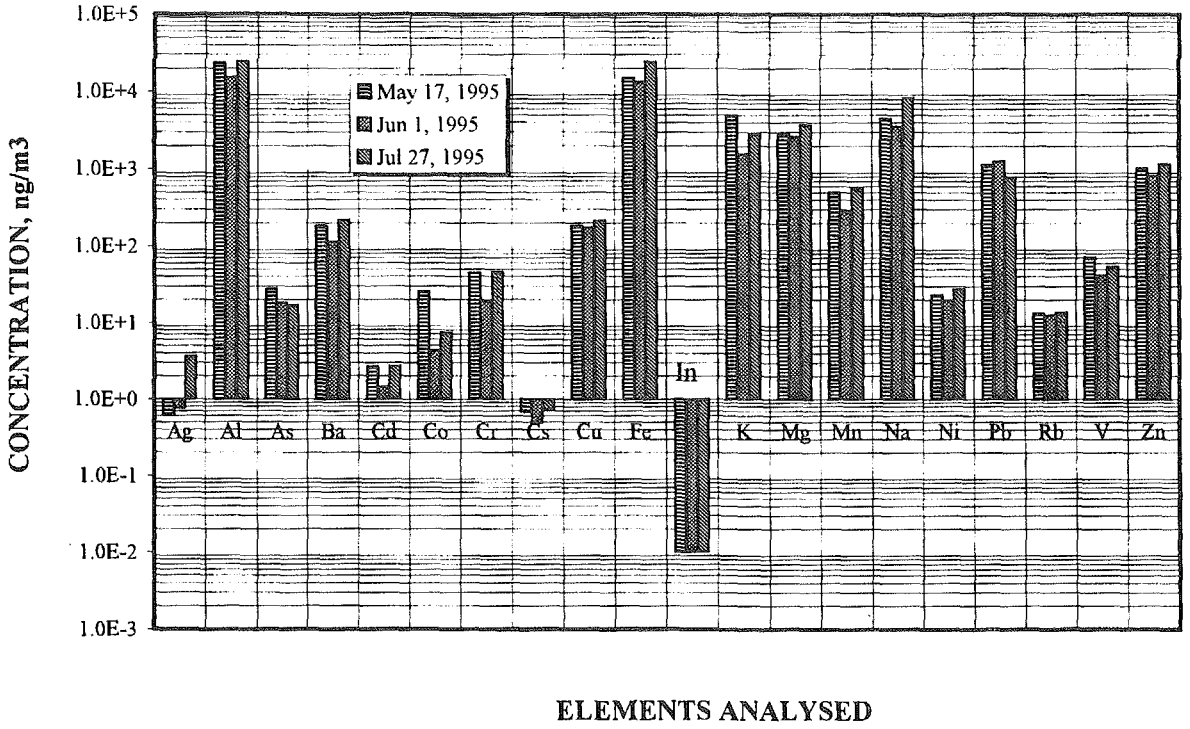

FIGURE 6. ELEMENTAL CONCENTRATION OF TSP SAMPLES FROM JAKARTA (BANDENGAN) MEASURED BY ICP-MS

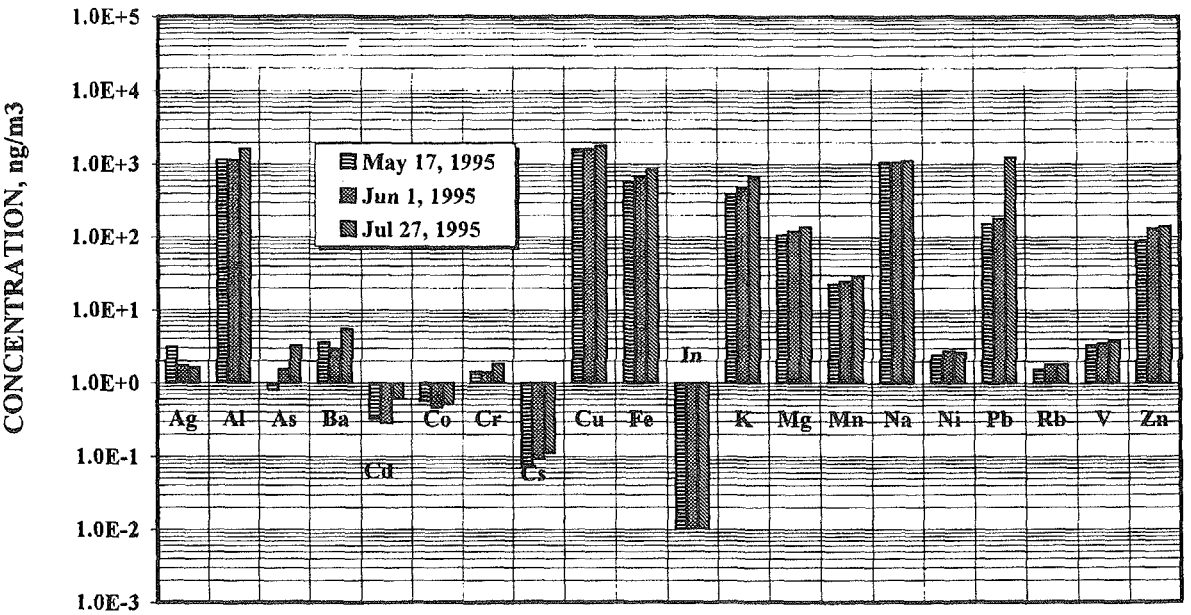

FIGURE 7. ELEMENTAL CONCENTRATION OF TSP SAMPLES FROM SERPONG MEASURED BY ICP-MC

determine by neutron activation analysis. In addition there are several elements that are simpler if determined by ICP-MS. In this respect it was obvious that the ICP-MS and (I)NAA are complementary each other.

CONCLUSION

The data of experiment showed that the concentration of the particulate matter in the air is independent to the level of the rainfall. The levels of the PM 10 and PM 2.5 are lower than the maximum permissible levels set by US Environmental Protection Agency in July 1997. Bromine concentration in both fine and coarse fraction was high and the enrichment factor for bromine in these fractions between 2000 – 10,000. It was concluded that bromine was released by anthropogenic sources.

The data obtained by INAA no significant different to those obtained by ICP-MS. Therefore comparative data can be obtained by this techniques.

REFERENCES

1. The Integrated Air Quality Management for Metropolitan Areas of Indonesia, Technical Proposal - One Day Seminar on Air Quality Monitoring Under Blue Sky Program, Bapedal, Jakarta, February 17, 1997.

2. Shinosuke, E., *Seminar for the study on Intregated Air Quality Management for Jakarta Metropolitan Area*, Japan International Co-operation Agency (JICA)-Environmental Impact Management Agency (Bapedal) the Republic of Indonesia, Jakarta, 1997, 1.

3. Mowle, M.G., *Seminar Study of Atmospheric Particles in the Jakarta Region*, Jakarta, 1995.

4. Study of Fine Atmospheric Particles and Gases in the Jakarta Region, *Consultants Report No. 2*, Physics Division ANSTO, Atmospheric Research, CSIRO, The Bapedal and East Java Pollution Control Implementation (PCI) Project, Internal Report J22, July 1996.

5. IAEA, Training Course Series No. 4, Vienna, Austria, 1992.