X ray Fluorescence in Member States

Application of ED XRF in supporting national program of air quality improvement in Indonesia

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Abstract

Since 1997, the National Nuclear Energy Agency, BA-TAN has been involved in the IAEA's RAS projects for the application of nuclear analytical techniques to characterize airborne particulate samples. The measurement of the elemental composition of the particulate matters is a key factor in utilization of the data for the determination of possible sources, which the process of identification and apportionment of pollutants to their sources is an important step in air quality management. Nuclear analytical methods such as XRF and PIXE are suitable for characterizations and need to be applied to produce large data sets of elemental compositions of APM. To maintain the sustainability of research in supporting the national program of air quality improvement in Indonesia, in 2011, BATAN has proposed new equipment, Energy Dispersive X-Ray Fluorescence (ED-XRF) Epsilon 5. During the last two years, based on MoU between BATAN and the Ministry of Environment, the assessment and monitoring of air quality has been expanded into 15 cities in Indonesia. In this review, we present the research activities related to the application of XRF in APM samples characterization.

Introduction

In Indonesia, air pollution control programs have been conducted through several actions i.e unleaded gasoline policy, vehicle emission testing, car free day and launching environmental programs in national and local regions such as blue sky program and urban Air Quality improvement (UAQi). But, increased air pollution is still present in several cities and needs serious attention from the government, stakeholders and the public, in order to avoid health impact and greater financial losses.

The National Nuclear Energy Agency of Indonesia, BA-TAN has contributed in solving air pollution problems through the application of nuclear analytical techniques for the characterization of airborne particulate samples. BATAN is involved in regional research activities in application of nuclear analytical techniques in airborne particulate matter characterization and source identification under IAEA cooperation in RAS project since the 1990s.

Fig. 1. Sampling locations

NAT's such as neutron activation analysis, X-Ray Fluorescence and particle induced X-ray emission have simultaneous capabilities to detect various elements present in airborne particulate matter with fraction sizes less than 2.5 μm (PM$_{2.5}$), producing a set of data concentration of 25-30 key elements in identification of air pollutant sources.

In this review, the elemental composition analysis of airborne particulate matters by EDXRF Epsilon 5 and comparison with the Particles Induced X-ray Emission - PIXE results from the same samples will be presented. Quality assurance of the method using standard reference material SRM NIST 2783 airborne particulate on filter media and the detection limit of elements are also discussed.

Sampling activities

The APM samples were collected using a Gent stacked filter unit sampler [1]. During the last two years, the sampling locations covered 12 cities in Indonesia, i.e: Sumatra (Pekanbaru), Java (Jakarta, Serpong, Bandung, Yogyakarta, Semarang, Surabaya), Borneo (Palangka Raya, Sulawesi (Makassar), Bali (Denpasar), Maluku (Ambon) and Papua (Jayapura), and in the end of 2013 the sites were expanded into other 3 cities: Lombok, Menado and Balikpapan. Sampling activities were carried out once a week in each location, in a year that will be totally 780 pairs of samples collected, consisting of fine filter (PM$_{2.5}$) and coarse filter (PM$_{10-2.5}$).

Sampling activities were done by the local EPA in each region whose staff has been trained and supervised before in a national training/workshop. After sampling, samples were sent back to BATAN Bandung to be analyzed for gravimetric and black carbon concentrations, then analyzed for elemental compositions.

Fig. 2. Characterization of APM using Epsilon5 in BATAN Laboratory

Elemental composition using ED-XRF Epsilon5

The elemental composition analysis was all carried out at BATAN Bandung which has implemented ISO/IEC 17025:2005 accredited by the National Accreditation Body since 2006. The analysis was conducted using an Epsilon 5 EDXRF spectrometer from Panalytical, which has a 100kV excitation source and a polarising optical path, giving detection limits in the low ng/cm^2 range for most elements [2].

A special sample insert enables air filters to be fitted directly into the sample cup. No additional sample preparation is needed and the sample changer makes continuous analysis possible. The calibration was set up using a multi standard reference material, standard Micromatter® and a blank standard for each element, Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As and Pb. The method validation of this application was done by analyzing the SRM NIST 2783. The EDXRF Epsilon 5 installed at BATAN Bandung has 9 secondary targets i.e: Al$_2$O$_3$, Fe, CaF$_2$, Ge, Zr, CeO$_2$, Mo, Ag and Al. EDXRF Epsilon 5 with its polarization method produces an indirect exitation/secondary target excitation giving significantly lower background.

For method validation, the result for SRM 2783 is shown in Figure 3, it has a good agreement with the certificate value with ratio 0.92-1.09.
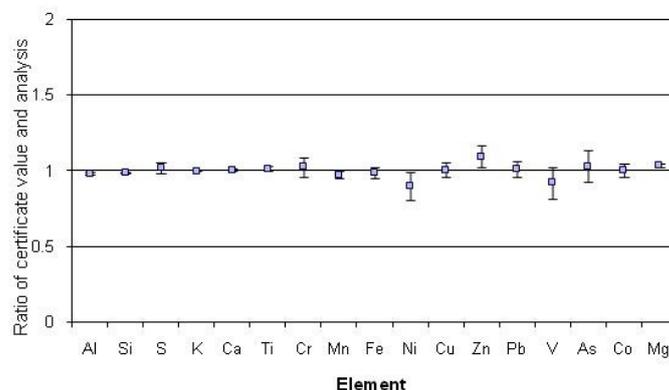

Fig. 3. The ratio of certificate value of SRM NIST 2783 and the analysis result by ED-XRF[3].

To ensure the analysis method, beside method validation using SRM NIST 2783, the comparison with the Particles Induced X-ray Emission - PIXE results was also carried out from the same samples. The comparisons for some elements are shown in Figure 4. PIXE analysis to the same samples was done previously in the Geological Nuclear Science, New Zealand. It can be seen for some elements such as S, K, Fe and Mn were in good agreements between EDXRF and PIXE method as shown in the figure. PIXE offers higher sensitivity and quicker analysis time than ED-XRF which requires long time measurement to meet the good results and low detection limit. At present, a PIXE accelerator based nuclear analytical technique facility is not available in Indonesia. Using PIXE, it could analyze one filter of APM in 5-6

minutes compared with XRF that will need times around 1-1.5 hours.

The results of elemental analysis of Pb concentrations during 2013 are shown in Figure 5. The box represents 25 to 75% of the distributions of the concentration. The box represents 25 to 75% of the value. The horizontal bar in the box indicates the median and the plus symbol (+) denotes the mean data. The points lying outside the range defined by the whiskers are plotted as outlier dots. From this figure, it can be stated that Surabaya sampling sites is detected for lead pollution which is higher than Serpong area. Preliminary results related to Pb pollution in Serpong showed that the highest concentration of Pb in

the $PM_{2.5}$ and $PM_{2.5-10}$ in industrial areas, respectively 5 and 8 times higher than the residential area.

Identification of pollutant source analysis showed that more than 80% concentrations of Pb in $PM_{2.5}$ are estimated from the metal smelting process [3]. The Pb concentrations in Surabaya from this monitoring could be beneficial to show an early warning of lead pollution in Surabaya, and quick response should be taken to control this pollution. Lead concentrations during the period ranged from 11.0 to 1911 ng/m^3 with an average of 427.3ng/m^3. Some samples were almost in violation to the 24–hour Indonesian standard for total suspended particles, 2 μg/m^3.
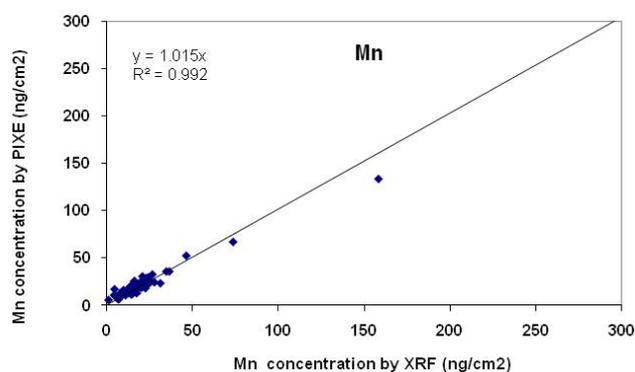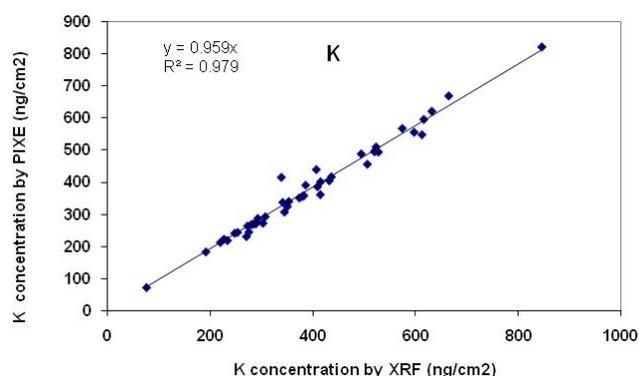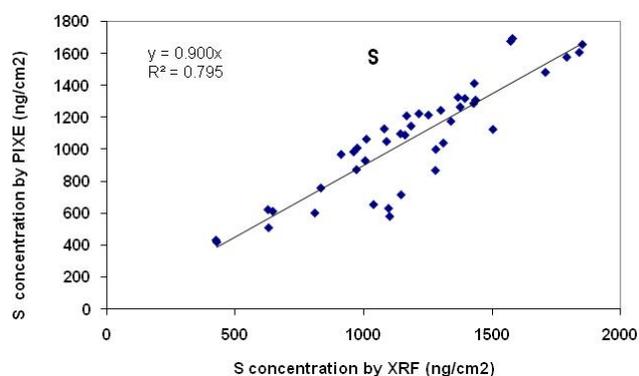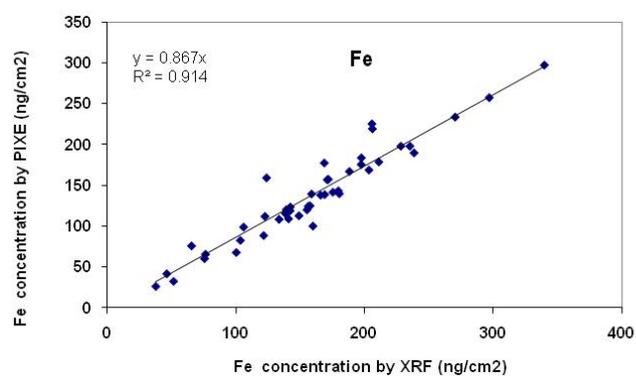

Fig. 4. Comparison of element Mn, K, S and Fe by PIXE and EDXRF

The pollution of heavy metals in Surabaya was also detected for Fe and Zn as shown in Figure 6. The concentrations of Fe and Zn in Surabaya were higher than in other cities. This could be attributed to industrial

sources, for more detail and comprehensive discussion, source identification research related to this matter is needed.
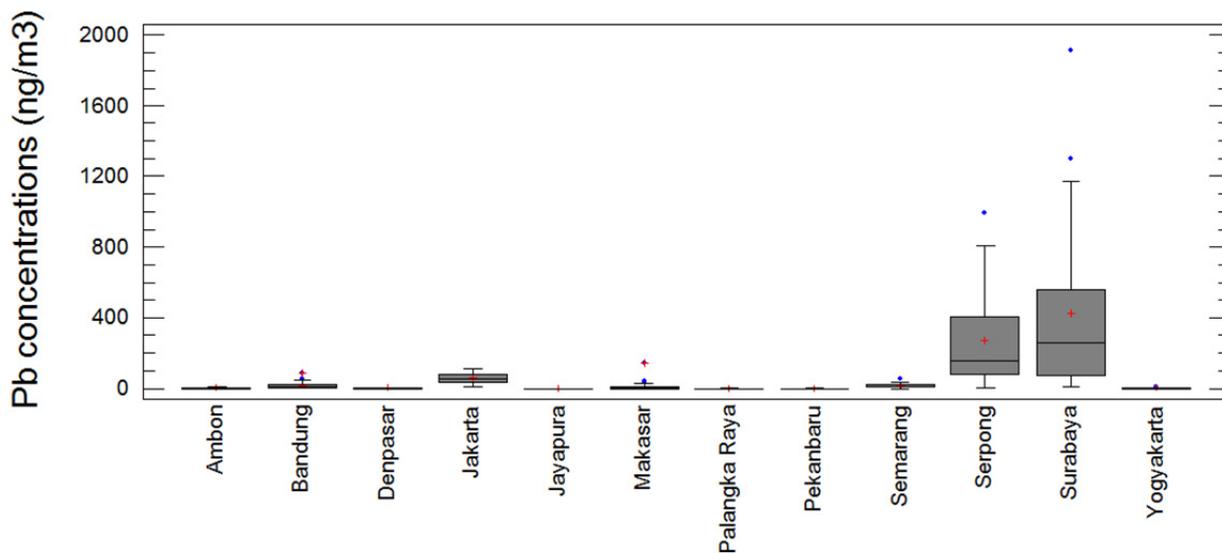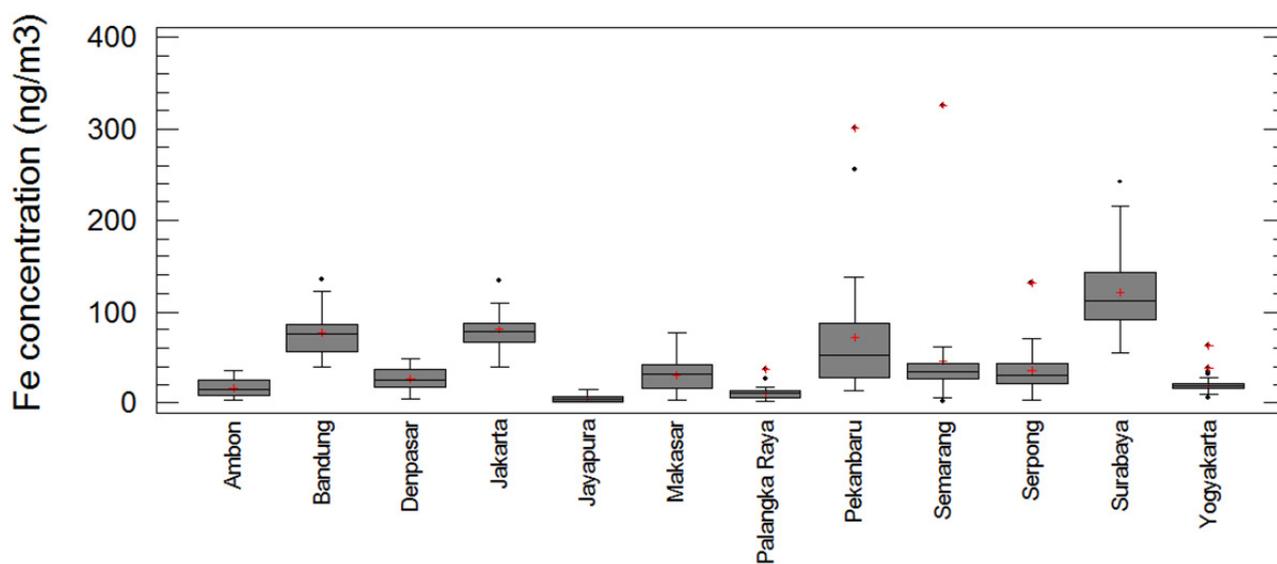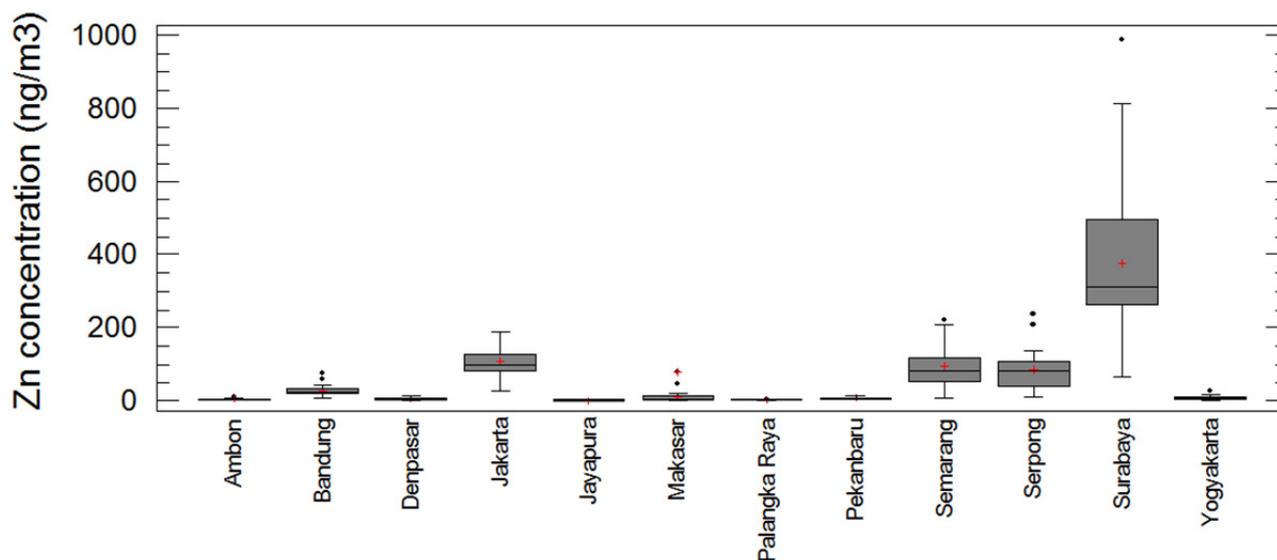
Fig. 5. Pb concentrations in PM$_{2.5}$ at several sampling locations
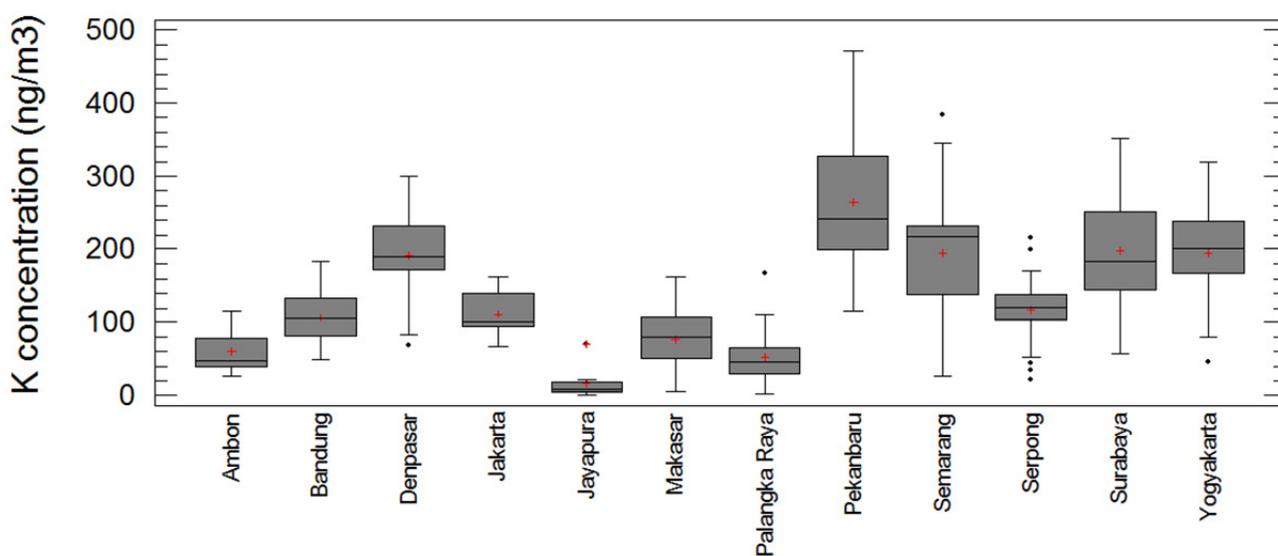

(a)   Fe concentrations

(b)   Zn concentrations

Fig. 6. Fe and Zn concentrations of PM$_{2.5}$ during 2013 in several locations

S and K concentrations are shown in Figure 7. From the figure it can be seen that Pekanbaru has higher S and K concentrations. This could be related to forest fires which occurr occasionally. Pekanbaru is one of the cleanest big cities in Indonesia. In 2011, it received the "Adipura" ('clean city') award in the category of large city for the seventh consecutive time.

However, Pekanbaru regularly suffers from smoke or smog due to forest fires, particularly in the dry season. Forest fires from uncontrolled burning of large areas of lands are a major problem for air quality. Tropical peat/forest fires in Indonesia are generally caused by illegal human activities including land clearing, converting to agricultural lands through heavy logging

and slash and burn techniques [5]. Most of the fires are intentionally started but often unintentionally grow dangerous. The highest concentrations of S and K were observed in Pekanbaru, and those elements are assumed to originate from peat forest fires. Peat is the earliest stage of transition from compressed plant growth to the formation of coal and contains high amounts of sulfur [6]. K concentrations were also high in Denpasar, despite of lower mass concentrations (PM$_{2.5}$ ranged 3.44 - 14.74 μg/m^3). Potassium was also high in Semarang, Surabaya and Yogyakarta. More comprehensive research related to this matter is needed and still on going.

(a) K concentrations in PM$_{2.5}$
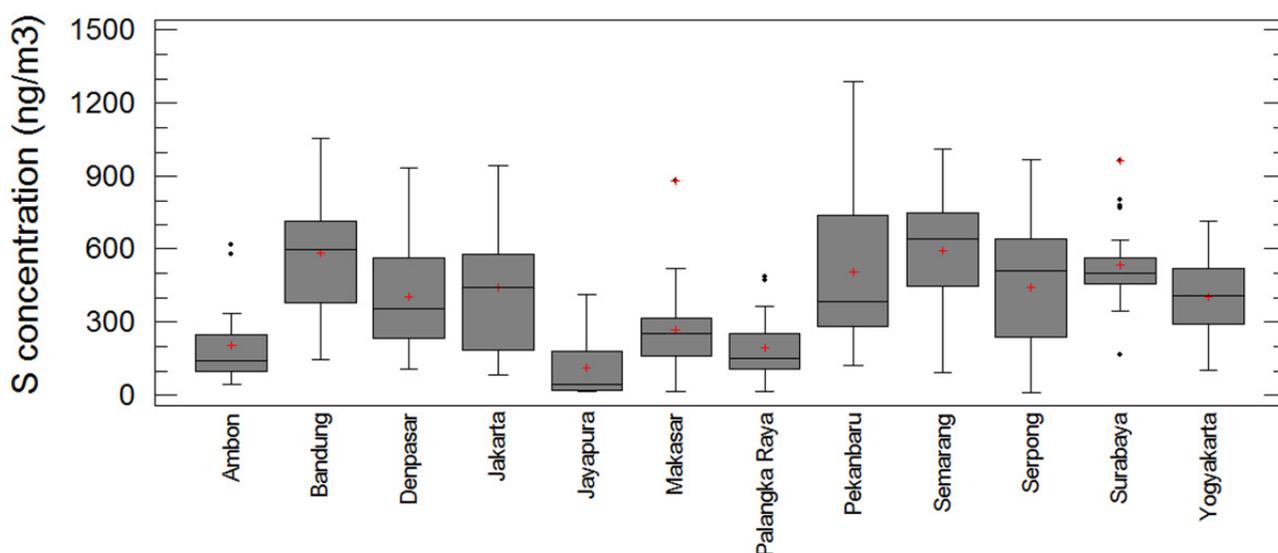
(b) S concentrations in PM$_{2.5}$

Fig. 7. Concentrations of S and K in PM$_{2.5}$ at several sampling locations

Source Apportionment

Source identification of pollutants has been applied to several cities data in Indonesia, using Positive Matrix Factorization (PMF). One of the source apportionment results in Serpong has been published [3], and it reveals that more than 80% of Pb concentrations in PM$_{2.5}$ are estimated to originate from the metal smelting process. Figure 8 shows the source apportionment in Serpong, and the first factor shows a high value of lead. The lead in this factor dominates more than 80% of lead in the samples. It should be noted that S also appears along with Al, Ca, Fe, and Si suggesting contaminated road dust. This factor could be represented by lead industry mixed with road dust that represented 12% of fine fraction composition. There are industrial facilities involved in metal lead processing and battery recycling plant to the northwest of sampling sites.

The source apportionment in Jakarta, Bandung and Lembang has been published elsewhere, and the source apportionment needs the large data sets of elemental concentrations [7,8].

Conclusions and future plans

The application of nuclear analytical techniques such as XRF contributed to the national air quality program of Indonesia. The results of our research have shown that ED-XRF is an effective tool and enables the characterization of multi elemental composition and could produce large data sets for source identification. However, to meet good sensitivity and low detection limit, it needs longer measurement times than accelerator based nuclear techniques such as PIXE. In the next three-five years, the air quality assessment research will be expanded into 33 cities covering all the capital of province in Indonesia, therefore to cover and accomplish the project it will need other complimentary analysis tools that enable characterization in a short time and with good quality. To make this project sustain, BATAN will assess the possibility of PIXE development in Indonesia. Some visibility studies have been conducted and hopefully in the near future, PIXE will be available in BATAN Indonesia to be utilized for environmental, materials, and other related research to emphasize the role of nuclear analytical techniques in a broad field, to solve national problems through enhancing the collaboration with several numbers of end users.
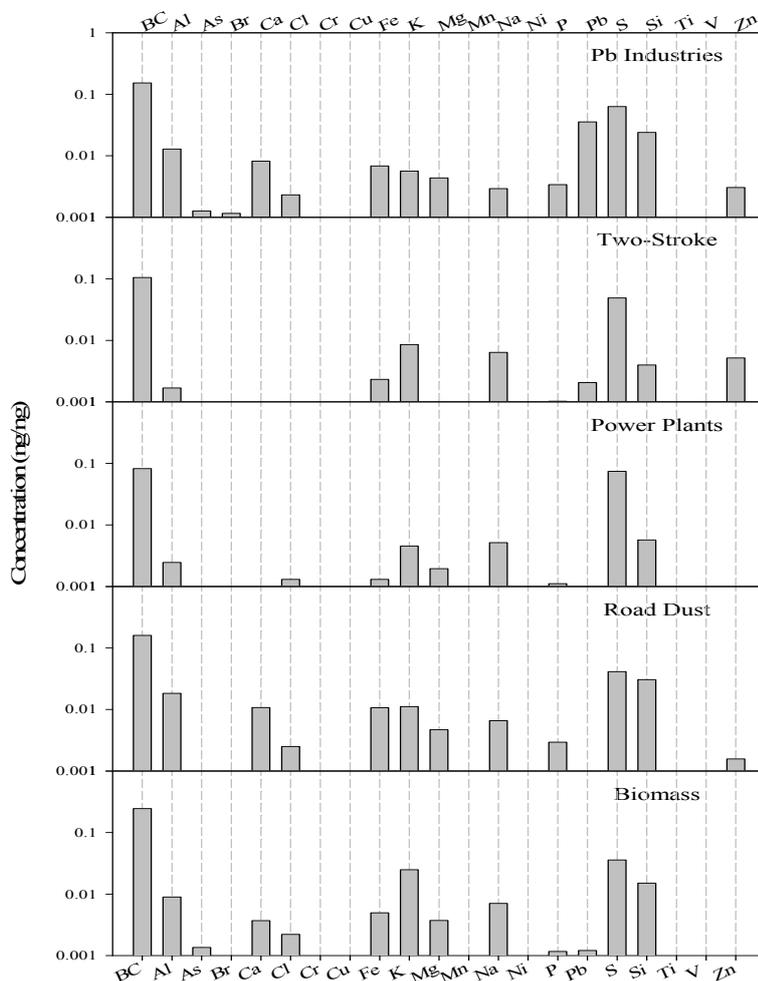

Fig.8. Source apportionment in Serpong area [3].

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Italy

Portable EDXRF in a multi-technique approach for the analyses of large paintings

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Energy-dispersive X-ray fluorescence (EDXRF) with its portable capability, generally characterized by a small X-ray tube and a Si-PIN or Si-drift detector, is particularly useful to analyze works of art. The main aspect that characterizes the EDXRF technique is its non-invasive character.

This characteristic that makes the technique so powerful and appealing is on the other hand the main source of uncertainty in XRF measurements on Cultural Heritage. This problem is even more evident when we analyze paintings because of their intrinsic stratigraphic essence.

As a matter of fact a painting is made of several layers: the support, which can be mainly of wood, canvas, paper; the preparation layer, mainly gypsums, white lead or ochre; pigment layers and at the end the protective varnish layer. The penetrating power of X rays allows that most of the times the information of all the layers reaches the detector. Most of the information that is in the spectrum arrives from deep layers of which we have no clue. In order to better understand this concept, let us use the equation of A. Markowicz [1]:

$$\sigma^2_{tot} = \sigma^2_{sample\ representation} + \sigma^2_{sample\ collection} + \sigma^2_{sample\ handling} + \sigma^2_{sample\ preparation} + \sigma^2_{analysis}$$

in which the various uncertainties that influence the analyses with portable EDXRF are reported.

Let us adjust this equation for *non invasive* portable EDXRF analysis. The second, the third and the fourth term do not exist, for obvious reasons. Only the first and the last term influence the total uncertainty of an EDXRF analysis. The ways to reduce the influence of the fifth term is known by any scientist: good stability of the system, long measuring time, correct standard samples, good energy resolution etc. But what about the first term when we are executing a non invasive analysis?

An example that shows the influence of the sample representation in the increasing of the uncertainty of a XRF analysis is the case in which we are asked to determine the original pigments used in a painting. If we have no clue of where restoration areas are dislocated on the painting, the probability of analyzing a "wrong" pigment is surely high and therefore high is the probability of having a high uncertainty in our results. Without a good representation of the painting to analyze, the total uncertainty could be very high even applying correctly all the analytical procedures for XRF analysis.

The only way to reduce the influence of the sample representation in the EDXRF technique is to backup the EDXRF analysis with different kinds of techniques that help reduce the total uncertainty. These techniques, totally non invasive such as EDXRF, can be the imaging techniques such as UV light, IR reflectography and X radiography. These techniques have already an independent application in Cultural Heritage with their own proto-