Evaluation of uncertainties measurement in EDXRF for air filter analysis

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Abstract. Energy Dispersive X-Ray Fluorescence (EDXRF) is one of the nuclear analytical techniques that has been widely used for elemental analysis, especially for air filter analysis. EDXRF Epsilon 5 has been installed in BATAN Bandung laboratory, Indonesia. EDXRF Epsilon 5 is an analytical instrument that is used to determine trace elements in many kinds of materials, especially in air filter samples. Measurement conditions have to be set up to determine several elements. Uncertainty evaluation was different according to the instrument used in each laboratory. This activity is aimed to calculate and evaluate the uncertainty measurement associated with EDXRF Epsilon 5 for air filter analysis. Evaluation of uncertainties measurement in EDXRF Epsilon 5 was carried out following the guides to express uncertainty: JCGM 100:2008 and EURACHEM. The uncertainty evaluation focused on 10 elements: Na, Si, S, K, Ca, Ti, Fe, Zn, Br, and Pb that generally existed in airborne particulate samples. The uncertainties results for 10 selected elements measured with Epsilon 5 were in a good correlation, with % relative uncertainty were ranged from 2% to 32%.

1. Introduction

Nuclear analytical techniques (NATs) have been widely used for elemental analysis in many fields. EDXRF is one of the NATs that generally used to analyze trace elements in many kinds of samples. An EDXRF named Epsilon 5 has been installed in the Center for Applied Nuclear Science and Technology-BATAN Bandung. Epsilon 5 with its 3-dimensional polarizing optics is used to analyze trace elements in samples especially dedicated to air filter analysis. EDXRF can be used for both qualitative and quantitative analysis with minimum sample preparation.

Before EDXRF Epsilon 5 being used to analyze samples, the method must be set to optimize the measurement condition according to the element to be analyzed. After the sample is measured, then it is analyzed both qualitative and quantitative. Calibration standards become an important thing for quantitative analysis. The optimized method that had been made was then used to measure samples. From the measurement then the software calculated the peak intensity of the element to be determined and converted to concentration according to the calibration curve that had been made and optimized [1].

Epsilon 5 software only showed the raw intensity and corrected intensity then they were calculated and converted to concentration automatically by the software. There were no uncertainty values showed in the final results showed in the software. Therefore, this study is aimed to calculate and estimate uncertainty from the measurement [2]. Uncertainty evaluation was calculated using the basic theory of calculating the uncertainty in XRF, especially for air filter analysis.
2. Experimental Method

2.1. Air filter analysis
Airborne particulate sampling was carried out using Gent Stacked Sampler in several locations in Indonesia. The filter used in this activity were nucleopore polycarbonate filters. The sampler can be used for collecting particulate matter for two different size fractions: fine and coarse. Sampling was performed at a flow rate of 15-18 liters/min for 24 hours.

All the exposed samples were collected and then stored in a clean room for at least 24 hours then continued to be weighed using microbalance to determine the masses of the fine and coarse fractions. Then the Black Carbon (BC) concentrations were measured using an EEL Smoke Stain Reflectometer (Diffusion System, Ltd., model 43M). The elemental determination for air filter was performed using EDXRF Epsilon 5.

2.2. Instrumentation
The instrument used in this study is 3-dimensional polarizing optics EDXRF Epsilon 5 with a maximum power of 600 Watt (100 kV and 24 mA). Epsilon 5 also has 10 secondary targets and 6 sample trays that can accommodate up to 48 samples. Its 3-dimensional polarizing optics was used to optimize the energy excitation [3, 4].

2.3. Method setup
The method should be set before Epsilon 5 is used to measure samples. There were several parameters to set the application in Epsilon 5’s software such as tube voltage and current (kV and mA), analysis time, and also secondary target corresponding to the elements to be measured [5].

2.4. Calibration
The calibration was set by measuring micromatter standards. The standards used for making the calibration curves were thin-film standards from Micromatter Technologies Inc. This method used 85 micromatter standards for several elements’ measurement. The concentrations were ranged from 17-64 µg/cm². There was no sample preparation for measuring micromatter standards. The standards were placed into the holder and measured using the method that had been set. The micromatter standards were measured as standards and then will be calculated by the software automatically and plotted as calibration curves.

There are two main calibration factors: The D and E values. The D value is the constant term in the main intensity to concentration conversion equation (intercept). The E value is the coefficient of the linear term in the main intensity to concentration conversion equation (angle of the regression line or slope). These values should be calculated by using regression from the calculation program window [6, 7].

2.5. XRF analytical uncertainties
The analytical uncertainties were calculated using international standards: JCGM 100:2008 and EURACHEM, customized according to the instrument used in the laboratory, in this case, EDXRF Epsilon 5. The process of measurement uncertainty estimation schematically is shown in Figure 1.

XRF analytical uncertainties in EDXRF Epsilon 5 calculated following an international method [2, 9, 10, 11]. The mass loading of each element for EDXRF Epsilon 5 (ng/cm²), Cₑ₅, is quantified using Equation (1):

\[ C_{E5} = \frac{I_{net} - I_{blk}}{E} \]  

where \( I_{net} \) is the net intensity of X-rays emitted by the sample (cps/mA) and \( I_{blk} \) is the net intensity of a blank filter (cps/mA) and \( E \) is the calibration factor [(cps/mA)/(ng/cm²)], calculated as the slope of the
linear regression between elemental loadings of calibration standards and their blank subtracted (net) intensities.

\[
\begin{align*}
\text{Figure 1.} \text{ The uncertainty estimation process [8].}
\end{align*}
\]

The combined analytical uncertainty of EDXRF Epsilon 5 (\(u_{ES}\)) was estimated applying GUM (Guide to Express the Uncertainty of Measurement 2008, JCGM 100:2008) methodology to Equation (1), as shown in Equation (2):

\[
\begin{align*}
\nu_{E5} &= \sqrt{\sum \left( \frac{\partial E_{ES}}{\partial x} \right)^2 u_x^2} \\
&= \sqrt{\sum (E \times u_{I_{net}})^2 + (E \times u_{I_{blank}})^2 + \left( (u_{I_{net}} - u_{I_{blank}}) u(E) \right)^2}
\end{align*}
\]

where \(x\) is the components of Equation (1) and \(u_x\) is the uncertainty of each component. The uncertainties of \(I_{net}\) and \(I_{blank}\) were estimated as the standard deviation of the replicated sample and blank filter analysis, respectively. The uncertainty of calibration factor, \(u(E)\), was estimated from the uncertainty of Micromatter standard that was used in the method and the deviation of the linear curve based on software calculation. The combined uncertainty is converted into expanded uncertainty (\(U_{ES}\)) by using a coverage factor, \(k\), as shown in Equation (3):

\[
\begin{align*}
U_{E5} &= k \sqrt{\sum (E \times u_{I_{net}})^2 + (E \times u_{I_{blank}})^2 + \left( (u_{I_{net}} - u_{I_{blank}}) u(E) \right)^2}
\end{align*}
\]
The coverage factor takes into account the distribution of uncertainties possible for a given measurement and, in this work, a coverage factor of 2 is used to give approximately the 95% confidence interval on the uncertainty value \((k = 1.96 \text{ at 95\% confidence level for a normal distribution})\) [10].

3. Results and Discussion

3.1. Measurement application

Optimum excitation conditions were set up as shown in Table 1. The method was set up for 26 elements divided in five conditions, but in this discussion only focused on the evaluation of 10 elements: Na, Si, S, K, Ca, Ti, Fe, Zn, Br, and Pb that generally existed in airborne particulate samples.

There were several parameters should be optimized in the method to generate an optimum excitation in each condition [4, 12]. The application had five conditions with different settings according to the characteristic energy for each element [13].

| No. | Parameter | Conditions |
|-----|-----------|------------|
| 1.  | Tube voltage (kV) | 40, 75, 75, 90, 90 |
| 2.  | Tube current (mA) | 15, 8, 8, 6, 6 |
| 3.  | Secondary target | CaF₂, Fe, Ge, Zr, CeO₂ |
| 4.  | Detector setting | high resolution, standard, high intensity, high intensity |
| 5.  | Energy range (keV) | 0-20, 0-20, 0-20, 0-20, 0-40 |
| 6.  | Analysis time (s) | 600, 400, 400, 600, 400 |
| 7.  | Elements analyzed | Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Pb, Sn, Sb, Ba |
| 8.  | Analysis line | Kα, Kα, Kα, Kα (except Pb using Lβ1) |

3.2. Calibration standards

The calibration parameters used in this study are presented in Table 2. In quantitative analysis, the net intensities are converted into concentration using a calibration standard [14]. There are several parameters: D value, E value, and also correlation was used in calibration. Those values are determined by linear regression that is calculated automatically from the software. The correlations for 10 elements were in good results according to the data shown in Table 2.

There were good correlations between the expected concentrations and count rates with the correlation value close to one. The ability of an X-ray to penetrate an aerosol deposit depends on the energy of the X-ray, composition, and thickness of the deposit. As a characteristic of light elements, lower-energy X-rays are absorbed in samples greater than higher energy. However, attenuation factors for PM₂.₅ samples are generally negligible even for the lightest element. PM₂.₅ samples contain particles small enough so that no self-absorption corrections are needed [13].
Table 2. Calibration parameters of the method in EDXRF Epsilon 5 spectrometer.

| No. | Elements | D value | E value   | Correlation |
|-----|----------|---------|-----------|-------------|
| 1   | Na       | 0       | 1.16E+04  | 0.9997      |
| 2   | Si       | 0       | 7.58E+02  | 1           |
| 3   | S        | 0       | 3.38E+02  | 1           |
| 4   | K        | 0       | 9.04E+01  | 1           |
| 5   | Ca       | 0       | 1.32E+02  | 1           |
| 6   | Ti       | 0       | 1.04E+02  | 1           |
| 7   | Fe       | 0       | 1.71E+02  | 1           |
| 8   | Zn       | 0       | 7.64E+01  | 1           |
| 9   | Br       | 0       | 2.03E+02  | 1           |
| 10  | Pb       | 0       | 5.38E+02  | 1           |

3.3. XRF analytical uncertainties

Uncertainty evaluation is an essential part of quantitative analysis because analytical results should always be expressed with its corresponding uncertainty value [15]. In the present EDXRF uncertainty determination, the main source of uncertainty could be identified from counting statistics (gross or raw intensity, blank, and subtracted intensity) which were correlated with the calibration function. The counting statistic parameters become essential in calculating uncertainty because they were contributed to the conversion of intensity to concentration.

Generally, the element concentrations in air filter samples were very small (trace elements). Therefore, the role of the blank becomes important [16]. In this study, the blank was measured as a blank while the samples were measured as routine according to the software of Epsilon 5. The blank intensity then used to subtract the raw intensity of samples.

Table 3. Uncertainty values from air filter samples.

| No. | Elements | Atomic Number (Z) | Concentration Range (ng/cm²) | Relative Uncertainty (%) | Correlation |
|-----|----------|-------------------|------------------------------|--------------------------|-------------|
| 1   | Na       | 11                | 92.6-1015                    | 22.5                     | 0.96        |
| 2   | Si       | 14                | 49.3-1528                    | 7.78                     | 1.00        |
| 3   | S        | 16                | 530-3739                     | 2.44                     | 0.91        |
| 4   | K        | 19                | 70.5-756                     | 1.58                     | 1.00        |
| 5   | Ca       | 20                | 16.4-1119                    | 3.61                     | 1.00        |
| 6   | Ti       | 22                | 0.28-43.4                    | 25.4                     | 0.99        |
| 7   | Fe       | 26                | 33.5-808                     | 26.5                     | 1.00        |
| 8   | Zn       | 30                | 4.66-1031                    | 4.49                     | 1.00        |
| 9   | Br       | 35                | 1.39-36.6                    | 30.8                     | 0.98        |
| 10  | Pb       | 82                | 8.99-299                     | 31.9                     | 1.00        |

In this study, the blank filter was the clean filter before being used to collect the dust samples. The blank filter measured as blank in the application then used to subtract the air filter samples and it was set automatically in the software. The results from EDXRF Epsilon 5’s software were the counting statistics data: net intensity (cps/mA), corrected intensity (cps/mA), and concentration (ng/cm²). The analytical uncertainties in this paper were calculated using Equation (2) and Equation (3) for expanded uncertainty. There were three main sources of uncertainties according to the Equation (1) to get the mass loading of the air filter samples in ng/cm²: net intensity (I_{net}), blank intensity (I_{blk}), and slope from standard calibration (E).
Figure 2. Total uncertainty estimation for 10 elements: (a) Na, (b) Si, (c) S, (d) K, (e) Ca, (f) Ti, (g) Fe, (h) Zn, (i) Br and (j) Pb.
The uncertainties evaluation results for 10 elements were illustrated in Figure 2. The figure shows that generally, the results of uncertainty measurements were in good correlation when compared with the concentration. The average uncertainty calculation was shown in Table 3. The results were varied from one to another elements. The averages of uncertainties from 10 elements were ranged from 2 to 32\%. These results showed that uncertainties of EDXRF measurements depended on the concentration of elements that existed in the samples. The uncertainties for X-ray attenuation losses, although based on an extreme range of deposit compositions, are reasonable and conservative estimates; only exhaustive, actual measurement of particle composition and size distribution would allow calculation of more accurate values [17].

4. Conclusion
The uncertainty evaluation results demonstrate that the EDXRF Epsilon 5 spectrometer is applicable for air filter analysis both qualitatively and quantitatively and gave reliable results. Uncertainty evaluation is an essential part of quantitative analysis because analytical results should always be expressed with its corresponding uncertainty value.

Evaluation of uncertainties measurement in EDXRF Epsilon 5 was carried out following the guide to express uncertainty. The uncertainties evaluation results for 10 selected elements were in a good correlation, with \% relative uncertainty were ranged from 2-32\%. The results of this analysis can be utilized to determine the uncertainty value for air filter samples measured using EDXRF Epsilon 5, especially for 10 elements: Na, Si, S, K, Ca, Ti, Fe, Zn, Br, and Pb.

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