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OPTIMIZATION FOR METHOD IN DETERMINATION OF CHLOR CONCENTRATION IN $PM_{2,5}$ USING EDXRF EPSILON 5

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ABSTRACT

OPTIMIZATION FOR METHOD IN DETERMINATION OF CHLOR CONCENTRATION IN $PM_{2,5}$ USING EDXRF EPSILON 5. Airborne particulate matter with aerodynamics diameter less than 2.5 µm, $PM_{2.5}$, is one of air pollutant parameter which have adverse impacts for human health and environment. To minimize those adverse impacts, elemental composition of $PM_{2.5}$ needs to be characterized so that can be estimated their sources. One of instruments for characterize $PM_{2.5}$ is Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer. EDXRF was used for measuring the elemental composition of $PM_{2.5}$ in Indonesia. This study focused in determination of chlor concentration in $PM_{2.5}$ since the optimal condition of chlor quantification using EDXRF spectrometer has not been obtained yet, whereas chlor is one of key element which is needed for source identification of air pollution. Concentration of chlor were determined using calibration curve and sensitivity curve methods. Both of curves were performed using Micromatter standards. The multi-element International Atomic Energy Agency (IAEA) reference materials were used for evaluating the accuracy and precision of the procedure. Our measurements result showed good agreement between observed value and certified value. Their accuracy and precision are more than 90%, to ensure the reliability of analytical results, the comparison with the Particles Induced X-ray Emission (PIXE) results from the same samples were also carried out. The result showed that there was good correlation between EDXRF and PIXE results, this is evidenced by the value of R^2 is 0.9592. It can be concluded that calibration curve and sensitivity curve can be used to quantify of chlor in $PM_{2.5}$ accurately.

Keywords: Chlor, $PM_{2.5}$, EDXRF Epsilon 5, Calibration Curve, Sensitivity Curve

ABSTRAK

OPTIMISASI UNTUK METODEPENENTUAN KADAR UNSUR KLOR DALAM $PM_{2,5}$MENGGUNAKAN EDXRF EPSILON 5. Partikulat udara dengan diameter aerodinamis kurang dari 2,5 µm disebut $PM_{2,5}$, merupakan salah satu polutan udara yang keberadaannya memiliki dampak buruk bagi kesehatan manusia dan lingkungan. Dalam upaya meminimalisasi dampak buruk tersebut perlu dilakukan identifikasi $PM_{2,5}$ melalui karakterisasi kandungan berbagai unsur di dalamnya sehingga dapat diperkirakan sumber penghasilnya. Salah satu instrument untuk karakterisasi $PM_{2.5}$ adalah Spektrometer *Energy Dispersive X-Ray Fluorescence* (EDXRF). EDXRF telah digunakan untuk analisis multi unsur $PM_{2,5}$ di Indonesia. Penelitian ini difokuskan pada penentuan kadar unsure klor dalam $PM_{2,5}$ karenakondisi optimal identifikasi unsure klor menggunakan spektrometer EDXRF belum diperoleh, sedangkan klor merupakan salah satu unsure penanda sumber pencemar. Penentuan kadar unsure klor dilakukan menggunakan kurva kalibrasi dan kurva sensitivitas. Standar *Micromatter* digunakan untuk memperoleh kurva sensitivitas dan kurva kalibrasi. Uji akurasi dan presisi dilakukan menggunakan *Certified Reference Material* (CRM) dari *International Atomic Energy Agency* (IAEA). Hasil yang diperoleh menunjukan terdapat kesesuaian yang baik antara nilai terobservasi dengan nilai sebenarnya pada sertifikat,

dengan akurasi dan presis lebih dari 90%.Untuk memastikan hasil analisis, perbandingan dengan *Particles Induced X-ray Emission* (PIXE) dari sampel yang sama juga dilakukan. Hasilmenunjukanterdapatkorelasi yang baikantarahasilanalisis EDXRF dan PIXE, ini terbukti dengan nilai R^2 sama dengan 0,9592. Hal ini menunjukan bahwa kurva kalibrasi dan kurva sensitivitas dapat digunakan secara akurat untuk kuantifikasi unsure klor dalam $PM_{2,5}$.

Kata kunci: Klor, $PM_{2,5}$,EDXRF Epsilon 5, Kurva Kalibrasi, Kurva Sensitivitas

1. INTRODUCTION

This Airborne particulate matter (APM) is a solid, liquid, or mixture of solid and liquid particles suspended in the air (1). Airborne particulate matter with aerodynamic diameter less than 2.5 μm ($PM_{2.5}$), can be inhaled into the human respiratory system (2).Several studies have reported that air pollutant causes adverse human health effects. In the study by WHO (3), $PM_{2.5}$ increasing mortality caused by respiratory diseases. Furthermore, the presence of $PM_{2,5}$ also has adverse impacts for living things and its surroundings. $PM_{2.5}$can also cause visibility reduction and changes in earth's radiation balance (4).

In order to minimize those adverse impact, elemental composition of $PM_{2.5}$ need to be characterize. Various analytical instruments for elemental composition analysis have been applied in environmental studies, such as Atomic Absorption Spectrometry (AAS), Neutron Activation Analysis (NAA) and Particle Induced X-Ray Emission (PIXE).These techniques have advantages and disadvantages. AAS technique require further sample treatment which is involving sample destruction with the result that sample was contaminant. AAN technique require irradiation process. Both NAA and AAS cause sample destruction. PIXE requires a nuclear particle accelerator (5) and Indonesia still does not have its instrument.

A good alternative is the Energy Dispersive X-ray Fluorescence (EDXRF). The EDXRF spectrometry is a multi-element analysis technique with basic X-ray emission principles that can measure up to the nanogram order (6). It is a relatively low cost non-destructive technique that does not require further sample treatment (5) and used in a wide range of applications (APM, vegetal species, electronic components, etc.). Another advantage of EDXRF is the simultaneous measurement. The setups involve three dimensional geometry in combination with a polarized X-ray beam to reduce the background signal. This is important because trace element concentrations especially chlor is very low in $PM_{2.5}$ in Indonesia. The Epsilon 5 has been used for quantitative analysis of $PM_{2.5}$ with samples collected in Indonesia (7).

In some trace elements contains in $PM_{2.5}$, this spectrometer is not optimal yet to quantifying chlor elements using calibration curve in instrument. This is because the lack of standard reference material which have nanogram order and low concentration of analyte in $PM_{2.5}$. Sensitivity curve is a good alternative to be used for determining concentration of chlor element. Therefore, calibration and sensitivity curve to determine chlor concentration were studied in this paper.

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Sensitivity is defined as being the net intensity obtained per unit of concentration (8).

Chlor element was needed to be quantified because the concentration of this element can be use as one of informations to identify the source of the air pollutant through statistical data processing (9).In addition, this element has adverse impacts for living things and its surroundings. Chloraffects atmospheric reactivity and canimpact the formation of ozone and secondary organic aerosol(10).Faxon and Allen (11) reported that chlor can destroy stratospheric ozone. Indonesia still does not set minimum levels of chlor in $PM_{2.5}$ in the air. However, some countries have monitored the characteristics of $PM_{2.5}$, as has been done by Santoso et al. over the last ten years in Indonesia (12).

This paper was focused on quantitative determination of chlor element concentration using EDXRF Spectrometer through two methods, calibration curve and sensitivity curve. To obtain the reliable result, not only the validation of a method is carried out, but a comparison with Particle Induced X-Ray Emission (PIXE) analysis techniques is also performed. This study was performed with an EDXRF Epsilon 5, instrument from the National Nuclear Energy Agency in Bandung, Indonesia.

2. METHODOLOGY

EDXRF EPSILON 5 Set Up

The EDXRF Epsilon 5 was applied for the determination of the chlor element in $PM_{2.5}$. The X-ray tube anode operates with accelerating voltages of 40 kV and currents of 15 mA, with a maximum power of 600 W. The primary target is W and secondary target is CaF_2 to analyze of chlor. The three dimensional polarized-beam geometry reduces the incidence of spurious scattered radiation from the X-ray tube into the detector, thus reducing the background and allowing the measurement of light and heavy elements at very low concentration. A Si(Li) detector with resolution of 124 eV for Mn Kα was used.

Determine of calibration and sensitivity curve

Calibration curve was made by measuring standards from Micromatter (see Table 1) using EDXRF Epsilon 5 spectrometer. Use X axis for chlor concentration and Y axis for intensities in curve.

Table 1.Standards were used to made calibration curve for chlor element

Standards	Certified concentration (ng/cm^2)
13-35205-KCl	8370
15-33731-KCl	21590
14-33730-KCl	22446
02-33724-NaCl	30149

Sensitivity curve was made by use X axis for elemental atomic number (Z) and Y axis for elemental sensitivity. It was used to determine the elemental sensitivity of the EDXRF spectrometer system for chlor elements and made by measured the standard Micromatter (see Table 2). According to Bacet al. (13), The elemental sensitivities (Sen_i) were defined as follows:

$$Sen\_i = (N.Fi)/(Ti\,me.Current\,.C) \quad [1]$$

Where,

Sen_i : Sensitivity of i-th element in the sample ($counts.ng^{-1}.cm^2.s^{-1}.mA^{-1}$),

N_i : Net peak area of i-th elemental characteristic X-ray (counts),

F_i : Absorption factor of i-th element, (≈1),
Time : Live time of the spectrum acquirement (measurement time, sec),
Current : Current of X-ray tube (mA),
C : Elemental concentration in the standard sample (ng/cm^2).

Table 2. Standards were used to determine elemental sensitivity for chlor element using sensitivity curve

Element	Range of Certified Concentration (ng/cm^2)
Mg	44.23 – 20366
Al	309.1 – 50800
Si	5824.5 – 33830
P	15377 – 15592
S	634.1 – 6900
K	632.2 – 9230

Method validation

Method validation was conducted using reference materials airborne particulate matter on filter media from International Atomic Energy Agency (IAEA). These reference materials were analyzed in the same experimental conditions used in the sample analysis. Method validation established to evaluate the precision and accuracy of the analysis results by using calibration and sensitivity curve of EDXRF. The accuracy was evaluated by recovery. The expression below refers to the calculation of the recovery according to Ventura et al. (14) :

$$\frac{\text{Observed value}}{\text{Expected value}} \text{x}100\% \quad [2]$$

To assess the recovery was used an average of the ten result of the observed values. Meanwhile, the precision was evaluated by the relative standard deviation (RSD) within ten result of the observed values. According to Ventura et al. (14), RSD were defined as follows:

$$\%\text{RSD} = \frac{\text{Deviation Standard}}{\text{Mean}} \quad [3]$$

Quantification of chlor concentration

Concentration of chlor element in the unknown sample (Ci) through calibration curve were calculated from following equation:

$$N_i = a\ Ci + b \quad [4]$$

Concentration of chlor elements in the unknown sample (Ci) through sensitivity curve, according Bac*et al*. (13), were calculated from following equation :

$$Ci = (Ni * Fi)/(Time * Current * Sen\_i) \quad [5]$$

Where,

a : Slope of curve,
b : Intercept,
Sen_i : Sensitivity of i-th element in the sample (counts.ng^{-1}.cm^2.s^{-1}.mA^{-1}),
N_i : Net peak area of i-th elemental characteristic X-ray (counts),
F_i : Absorption factor of i-th element, (≈1),
Time : Live time of the spectrum acquirement (measurement time, sec),
Current : Current of X-ray tube (mA),
Ci : Cl concentration(ng/cm^2).

Comparison method with PIXE

To ensure the analysis method, beside method validation using IAEA reference materials, the comparison with the Particles Induced X-ray Emission (PIXE) on the same samples also carried out. Elemental analysis of samples was performed using PIXE at the Institute of Geological and Nuclear Sciences (GNS), New Zealand. Samples were mounted on the positioning system and irradiated with 2.5 MeV proton beam in a vacuum chamber.

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The beam current was 10 mA and beam was accumulated for a preset charge of 60 µC. Emitted X-rays were detected by Si(Li) X-ray detector located at 135° angle according to incident proton beam. The X-ray spectra were analyzed using the computer code GUPIX. Calibration of the PIXE system was performed by irradiating the suitable Micromatter thin target standards (15).

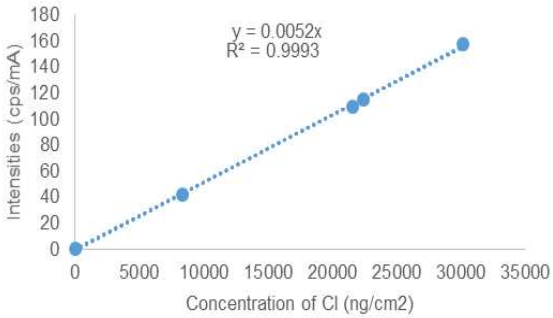

Figure 1.Calibration curve of chlor element by EDXRF Epsilon 5

3. RESULT AND DISCUSSION

Calibration curve

To determine the chlor element content in $PM_{2.5}$ by EDXRF spectrometry, a calibration curve was made. This method uses a series of standards of a certain level. To determine the calibration curve of chlor, the standard Micromatter have been measured. The calibration curve for chlor element are shown in Figure 1 with the corresponding linear fitting. The adjusted R-square coefficient found is 0.9993 means that as much as 99.93% changes in the intensity is influenced by the chlor concentration. Correlation coefficient found is 0.9996. According to Discenza et al. (16), 0.9996 was included in the category of very strong correlation. Thus the correlation between intensity to concentration is very strong. We have got the equation to calculate chlor element concentration Y=0.0052X [6]

Sensitivity curve

In order to use an instrument method, one needs to have one or more standards with a matrix similar to the unknown samples or at least a set of standards that contain the analyze elements. There are many situations in which standards do not exist. This is particularly true in laboratories developing new materials and those involved in one of a kind and/or trouble shooting production problems. Meanwhile, there is the lack of calibration curve, which is analyte in the sample do not exist in the range concentration of standards in calibration curve. Analyte concentration in $PM_{2.5}$ usually exist in nanogram order, meanwhile the standards exist in order bigger than nanogram. For this reason, there is a large demand for a standardless fundamental parameter method. Theconcept is elemental sensitivity which contains the instrumen sensitivity. Using this sensitivity, one can analyze unknowns without any standard or prior knowledge of the unknown sample matrix.

In this paper, the chlorconcentration in $PM_{2.5}$ is also determined using the sensitivity, throughsensitivity curve. The sensitivity curve for XRF is obtained by plotting the atomic number of the element and its sensitivity (17). To obtain the sensitivity of the chlor element, an interpolation technique was used. The standards for elements such as Mg, Al, Si, P, S and K have been measured to determine

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the corresponding elemental sensitivities. The elemental sensitivities (Sen_i) were defined as equation [1].

Fitting the experimental values we obtained following equations for calculating the elemental sensitivity for elements with Z < 20. After fitting the experimental values of Sen_i, we have got the equation to calculate elemental sensitivity for chlor element:

$$Y = 2E-13X^{8.4746} \quad [7]$$

where Y is sensitivity, X is Z, 17 for chlor element.

The sensitivity curve shown in Figure 2 provides a better response for light elements, but for XRF there is an increase in sensitivity function for heavier elements. The trends in the sensitivity curve similar with the study from Ivosevic in 2014 (17). The regression equation obtained can be used to calculate the sensitivity of the chlor element from an unknown sample. The value of chlor sensitivity as Y will be known by inserting atomic number to X value at equation $Y = 2 \times 10^{-13}X^{8,4746}$. Based on calculated, sensitivity of chlor element is 0,005353 $counts.ng^{-1}.cm^2.s^{-1}.mA^{-1}$.

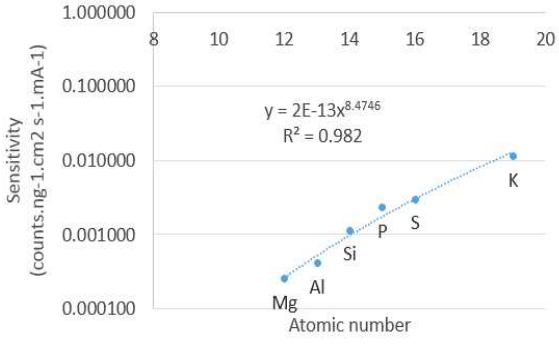

Figure 2. Sensitivity curve for determine sensitivity of chlor element by EDXRF Epsilon 5

Method validation

Method validation has been performed by measurements of IAEA reference materials air particulate on filter media. Equation from sensitivity curve and calibration curve were used to recalculate the concentrations of these reference materials. The calculated results showed quite good agreement comparing to the given certified values (see Table 3). The accuracy value is quite good and still accepted based on the Association of Official Agricultural Chemists (AOAC).

RSD values were in the range of 2.75-3.80% for the both determination, respectively for calibration curve and sensitivity curve. The value of RSD is still acceptable, because in a very critical method, it is generally acceptable if RSD should be more than 2% (18). The RSD values has an acceptable RSD less than or equal to 10% of the required X-ray fluorescence spectrometers and sometimes more than 10% for the constraints of elements of a certain concentration (18).

Our data suggest that calibration curve and sensitivity curve are an acceptable methods for the determination of chlor in $PM_{2.5}$. Calibration curve is recommended for routine analysis which is involve many sample. In the other hand, sensitivity curve is very benefit when the standards do not exist.

Comparison method with PIXE

To ensure the analysis method, the comparison with the PIXE results from the same samples also carried out. There are 33 PM samples have been measured using sensitivity curve method. The obtained spectra were processed using Epsilon 5 software. The concentrations of chlor element

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were calculated from equation [7] through sensitivity curve. PIXE analysis to the same samples was done previously in the Geological Nuclear Science, New Zealand. The comparison provided a good correlation between EDXRF and PIXE as shown in the Figure 3. This is evidenced by the value of R^2 is 0.9592.

From the observation of the distribution of chlor element analyzed by EDXRF and PIXE as shown in Table 4. It can be seen that chlor concentration obtained by EDXRF were lower than the distribution by PIXE. There are several possible explanations about this. First, this could be due to a non homogenous distribution of the mass on the surface of filter (15). Second, this could be due to different x-ray spectra fittings, and to sample and blanks inhomogeneities, because of the different area covered by proton and excitation x-rays beam (19). Although there are some systematic difference between both techniques, but based on the accuracy and precision through validation, the EDXRF was quite good for chlor quantification, therefore EDXRF data are preferred, while PIXE does not exist in Indonesia.

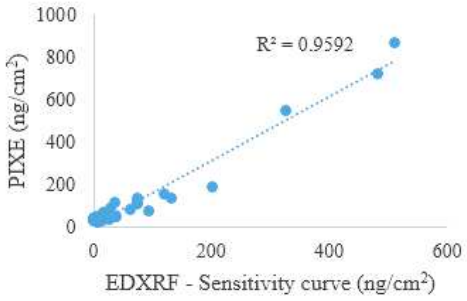

Figure 3. Comparison of chlor in $PM_{2.5}$ by measuring between EDXRF through sensitivity curve and PIXE's result

Table 3. Accuracy and Precision

Method	Reference Material	CRM Id (n=10)	Certified Value (ng/cm^2)	Measurement value (ng/cm^2)	Accuracy (%)	RSD (%)
Calibration Curve	IAEA	Prague	57.0	65.8	115	3.80
		Vienna	92.1	88.0	95.5	2.75
Sensitivity Curve	IAEA	Prague	57.0	63.9	112	3,80
		Vienna	92.1	85.5	92.8	2.75

Table 4. Ratio of chlor element analyzed by EDXRF and PIXE

Instrument	Mean of Cl concentration (ng/cm^2)	Ratio
EDXRF	73	0.6
PIXE	122	

4. CONCLUSIONS

Calibration curve and sensitivity curve methods in EDXRF for quantify chlor concentration have been studied and tested carefully. Applicability of these method have been demonstrated through analyzing 33 $PM_{2.5}$ samples deposited on nucleopore filters. The accuracy and precision of the calibration curve and sensitivity curve to find chlor concentration were verified by measuring IAEA reference materials. Our measurements are in good agreement with the certified value, respectively for calibration and sensitivity curve methods. Meanwhile, there were good correlation between EDXRF and PIXE method. This study has shown that calibration curve and sensitivity curve methods in EDXRF are still be reliable method to quantify concentration of chlor element in $PM_{2.5}$. But there are many situations in which standards do not exist and the lack of calibration curve. For this reason, sensitivity curve is recommended in these situations which standards do not exist.

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