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Applicability of EDXRF for elemental analysis in airborne particulate matter (APM): assessment using APM reference material

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Abstract. Nuclear analytical technique such as EDXRF has been widely used for elemental analysis of airborne particulate matters (APM). EDXRF Epsilon5 has been installed and commissioned in Center for Applied Nuclear Science and Technology-BATAN Bandung, Indonesia. Measurement conditions has to be set up to determine several elements: Al, Ca, Cu, Fe, K, Pb, S, Si, Ti and Zn. Optimization was carried out by optimizing the excitation conditions covering the tube voltage, tube current, secondary target, and analysis time. Method validation of EDXRF Epsilon5 was determined using Standard Reference Material (SRM) NIST 2783 Air Particulate on Filter Media for ensuring the reliability on APM analysis. Four measurement conditions with variation setting of tube voltage, tube current, secondary target, and analysis time were defined for several elements. The results of the selected elements were in a good agreement with the certified values. Replication of analysis using air particulate on filter media reference material using EDXRF Epsilon5 were considered as valid, accurate and reliable data.

1. Introduction

Airborne particulate matter (APM), consists of a mixture of solid particles and liquid droplets that are suspended in the air for long periods of time, varying microscopic in size, composition and origin [1]. The composition of airborne particulate matter (APM) with aerodynamic diameters less than 2.5 μm ($\text{PM}_{2.5}$) has received considerable research interest. These fine particles are small enough to penetrate deep into the human lung, most effective at scattering light and have a great effect on visibility and also have direct access to the blood stream with obvious health impacts. However, neither the responsible component for, nor the mechanism of adverse health effects is currently known. Therefore, more data on chemical composition of size fractionated APM are needed [2], [3]. The suitable methods for airborne particulate matter are hardly needed to solve the air pollution problem. The nuclear analytical technique such as X-ray Fluorescence (XRF) is one of suitable instruments to characterize chemical composition of all kinds of materials. The materials can be in solid, liquid, powder, filtered or other form. XRF can also sometimes be used to determine the thickness and composition of layers and coating. The method is fast, accurate and non-destructive, and usually requires only a minimum of sample preparation [4]. Nuclear techniques such as XRF also have been applied to the characterization of airborne particulate matter [5].

Laboratory of Center for Applied Nuclear Science and Technology, National Nuclear Energy Agency (BATAN) Bandung has been installed an Energy Dispersive X-Ray Fluorescence (EDXRF) Epsilon5 spectrometer which is used for research on supporting the national program of air quality



improvement in Indonesia [6]. Before EDXRF Epsilon5 used to characterize some elements and calculate the concentration, we should set up the application first. The application is like an integrated program, contains all information required to run a conventional analysis. The user can be led via a wizard through the assembly of an application which contains the program used to measure the samples.

Reliability of analysis results depend on instrument's performance as well as personal capability, and were proven by its method validation. In this study, APM application in EDXRF Epsilon5 was determined by conducting method validation of EDXRF for ensuring the reliability on analysis results. Optimization was carried out by optimizing the excitation conditions covering the tube voltage, tube current, secondary target, and analysis time. The points that will be reviewed are the common validation criteria, which are trueness (accuracy and bias) and also data precision. Quality assurance assessment of EDXRF Epsilon5 was carried out using standard reference material (SRM) NIST 2783 air particulate on filter media. Results from these studies will provide information about QA and QC in trace elements analysis for airborne particulate matter using EDXRF Epsilon5.

2. Experimental Method

2.1. Instrumentation

The XRF used is 3-dimensional EDXRF Epsilon5 (PANalytical), equipped with Sc/W tube as X-ray generator (600 W X-ray tube, max. 100 kV and 24 mA, W anode with 26° take off angle, Be window with 150 μm thickness), a high resolution Germanium detector with 30 mm^2 collecting area, 10 secondary targets and 6 sample trays that can accomodate up to 48 samples. EDXRF Epsilon5 also has 3-dimensional polarizing optics to improve detection limits by reducing spectral background. In 3-dimensional EDXRF Epsilon5, the primary radiation from the X-ray tube strikes the secondary target, which then emits characteristic radiation and generates some scattered bremsstrahlung radiation. The emitted radiation is pseudomonochromatic and the degree of monochromaticity is further enhanced by secondary target [7]. The 3-dimensional polarized optical design gives very low background, even for samples with a very low density where the background scatter is usually high [8].

2.2. APM application setup

The APM application was set up using standards for several elements. Standards used for calibration consist of single or two non-interfering elements deposited as thin film standards from Micromatter Technologies Inc., P220-Prague and also V149-Vienna thin glass film standards. The micromatter standards are prepared using nuclepore polycarbonate aerosol membranes by vacuum deposition resulting in highly uniform deposits [9]. P220-Prague is a reference air filters of target values of elements contents for proficiency testing while V149-Vienna is a reference material IAEA-NAT-3, Urban Dust Artificially Loaded on Air Filters [10, 11].

Optimization was carried out by optimizing the excitation conditions covering the tube voltage, tube current, secondary target, and analysis time. Six different analysis conditions applied during a single analysis run to maximize sensitivity to the full range of elements. In this APM application used six different secondary targets: Al, CaF_2 , Fe, Ge, Zr and also Al_2O_3 . The micromatter standards were placed in the sample holders and loaded into the trays of EDXRF Epsilon5 spectrometer.

2.3. Calibration

Calibration of the EDXRF Epsilon5 analyzer was performed using the standards. Each type of standard sample media has a corresponding blank membrane that must be analyzed and used for blank subtraction. The standards are selected in the application, and the software calculates the theoretical relative intensities of the standards listed in the standards file using the operating and deconvolution parameters in the selected application; this calculation will be most accurate when the full composition of the standards is entered. The software then performs least-squares regression with the theoretical and measured intensities forcing the intercept to zero for each element. At least two standards for each element are required, preferably spanning the range of concentrations expected in the APM samples.

The calibration factors (slopes of linear regression) for the elements are stored within the application on the XRF's computer [12].

There are three calibration factors: the D and E values, and also correlation coefficient. 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. In the software, they can be viewed on the calculation program, calibration graph and calibration report windows. The correlation coefficient is also calculated during regression analysis [13].

2.4. Method validation

The method validation of this application was applied by analyzing the SRM NIST 2783 [15]. SRM NIST 2783 was measured as a routine and employed as quality control (QC). Ten elements: Al, Ca, Cu, Fe, K, Pb, S, Si, Ti and Zn were obtained. Method validation is determined by calculating the trueness (accuracy and bias) and also precision. The results of SRM NIST 2783 Air Particulate on Filter Media analysis were compared with its certificate value and evaluated its accuracy and precision by % recovery and %CV calculation.

Table 1. Certificate value of SRM NIST 2783
Air Particulate on Filter Media.

No.	Elements	Concentration (ng/cm ²)	Uncertainty (ng/cm ²)
1	Al	2330	53
2	Ca	1325	171
3	Cu	40.6	4.2
4	Fe	2661	161
5	K	530	52
6	Pb	31.8	5.4
7	S	105	26
8	Si	5884	161
9	Ti	150	24
10	Zn	180	13

3. Results and Discussion

3.1. Selection of optimum conditions

APM application was set up using several parameters as shown in Table 2. The application was set up for 31 elements divided in six conditions, but in this discussion only focus on 10 elements: Al, Ca, Cu, Fe, K, Pb, S, Si, Ti and Zn that generally exist in airborne particulate samples.

In order to generate intense characteristic radiation from secondary target, the tube kV should be two to three times the K absorption-edge energy of the element from which the secondary target is made. The K-lines are used, as they offer the highest fluorescence yield, which means that there are lower losses than with other line series. Generally, K-lines are more intense than L-lines, which are more intense than M-lines and so on [5, 8]. All elements in this application used K-lines except for lead (Pb), it used L-line. The measurement of Pb used L-line because the K-line characteristic energy of Pb is higher than its L-line energy and the EDXRF Epsilon5 can not reach its K-line energy. The highest kV used in this application is 90 kV and that value is still lower than the maximum kV that can be set in Epsilon5 spectrometer.

Table 2. Optimum excitation conditions of the APM application in EDXRF Epsilon5 spectrometer.

No.	Parameter	Condition Names					
		Mg	Si-K	Ti-Cr	Cu-Zn	Rb_Re-Tl	Xe-La
1.	Tube voltage (kV)	25	40	75	75	90	90
2.	Tube current (mA)	24	15	8	8	6	6
3.	Secondary target	Al	CaF ₂	Fe	Ge	Zr	Al ₂ O ₃
4.	Detector setting	high resolution	high resolution	standard	standard	high intensity	high intensity
5.	Energy range (keV)	0-20	0-20	0-20	0-20	0-20	0-80
6.	Analysis time (s)	600	600	400	400	600	400
7.	Elements analyzed	Na	Mg, Al, Si, S, Cl, K, P	Cr, Ca, Sc, Ti, V	Fe, Co, Ni, Cu, Mn	As, Se, Pb, Zn, Br, W, Au	Sb, Ag, Ba, Rh, Pd, Sn, Te, La
8.	Analysis line	K α	K α	K α	K α	K α (except Pb used L β 1)	K α

3.2. Calibration standards

The calibration results for the several elements are presented in Table 3. There are three calibration parameters presented in Table 3: D value, E value and also correlation. All the calibration parameters can be seen in calibration graph, for example calibration graph of Pb as shown in Figure 1. Across a limited range, the curve can be approximated by a straight line given by $C = D + E \cdot R$, where the D and E are determined by linear regression [4]. From Table 3, it can be seen that almost all the D value were zero except for Ca and Zn. The D value can be locked as zero, made a better result and it was applied for another eight elements. The E value were vary for all elements according to the concentration conversion equation in EDXRF Epsilon5's software.

Table 3. Calibration standards of the APM application in EDXRF Epsilon5 spectrometer.

Elements	Energy (keV)	Conditions	Concentration range (ng/cm ²)	D value	E value	Correlation
Al	1.486	Si-K	1.3252E+02 – 3.7457E+03	0	1.66E+03	0.9304
Si	1.739	Si-K	2.2224E+02 – 3.3830E+04	0	8.57E+02	0.9949
S	2.307	Si-K	1.2720E+02 – 2.6887E+03	0	4.23E+02	0.9401
K	3.312	Si-K	2.4052E+02 – 2.4754E+04	0	88.8	1
Ca	3.690	Ti-Cr	50.0300 – 2.4947E+04	2.07E+02	1.26E+02	0.9997
Ti	4.508	Ti-Cr	7.2400 – 4.7100E+04	0	1.04E+02	1
Fe	6.398	Cu-Zn	62.4900 – 1.7400E+04	0	1.64E+02	0.9988
Cu	8.040	Cu-Zn	3.1000 – 4.8300E+04	0	90.3122	0.9995
Zn	8.630	Rb_Re-Tl	32.1800 – 1.7243E+04	11.99	1.77E+02	0.9999
Pb	12.612	Rb_Re-Tl	17.7000 – 5.3300E+04	0	4.36E+02	1

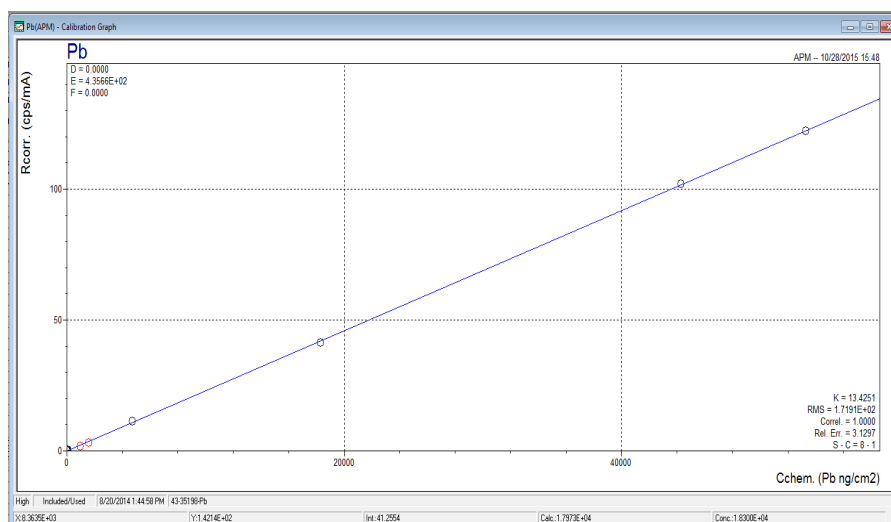


Figure 1. Pb calibration graph.

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 and composition and thickness of the deposit. In general, lower energy X-rays, characteristic of light elements are absorbed in matter to a much greater degree than higher energy X-rays. However, attenuation factors for PM_{2.5} samples are generally negligible even for the lightest element. PM_{2.5} samples contain particles small enough so that no self-absorption corrections are needed [3].

3.3. Method validation

The validation results of the elements in the NIST 2783 are presented in Table 4. These results showed that EDXRF Epsilon 5 was accurate with acceptable accuracy (%recovery) [16].

Table 4. Validation results.

No.	Elements	Analysis Results (ng/cm ²)		Certificate (ng/cm ²)		%Bias	%Recovery	%CV
		Concentration	Unc.	Concentration	Unc.			
1	Al	2316	43	2330	53	0.60	99.4	0.94
2	Ca	1314	95	1325	171	0.83	99.2	3.61
3	Cu	40.2	2.3	40.6	4.2	0.84	99.2	2.84
4	Fe	2608	150	2661	161	1.99	98	2.87
5	K	527	29	530	52	0.50	100	2.77
6	Pb	31.4	4.5	31.8	5.4	1.21	98.8	7.23
7	S	108	10	105	26	-1.99	102	4.76
8	Si	5851	71	5884	161	0.56	99.4	0.60
9	Ti	147	16	150	24	1.43	98.6	5.32
10	Zn	181	10	180	13	-0.47	100	2.69

In order to guarantee the analysis results accurate and reliable, the analytical method must be validated. The validation results of SRM NIST 2783 Air Particulate on Filter Media as listed in Table 4. It showed that the result obtained are in good agreement with certified values. Analytical accuracy,

described as %recovery (%rec), were in the range 98–102%; while the difference of the reported value from the accepted value, described as %bias were in the -1.99–1.99%. The results of analytical accuracy were acceptable according to acceptable recovery percentages depending on the analyte level [16]. The precision results of SRM NIST 2783 Air Particulate on Filter Media showed as %CV as listed in Table 4. It showed that the result obtained are in good agreement with certified values [17].

Method validation is done once, but to find out the performance of the method analysis used is still in accordance with destination (fit for purpose), it needs to be done verification method. Method verification carried out using reference materials. Analysis can also use reference materials as a form of monitoring of data accuracy from the analysis. Reference material plays an important role in the guarantee the quality of a chemical test. Several elements in the SRM NIST 2783 were detected and the results were then compared with its certificate values. The ratio between the analysis results obtained using EDXRF Epsilon5 method and the certificate values of Al, Ca, Cu, Fe, K, Pb, S, Si, Ti and Zn are shown in Fig. 2. These analysis results had a good agreement with the value quoted in the NIST certificate. The ratio between the analysis value and the certificate indicates the values with a ratio between 0.86 and 1.10.

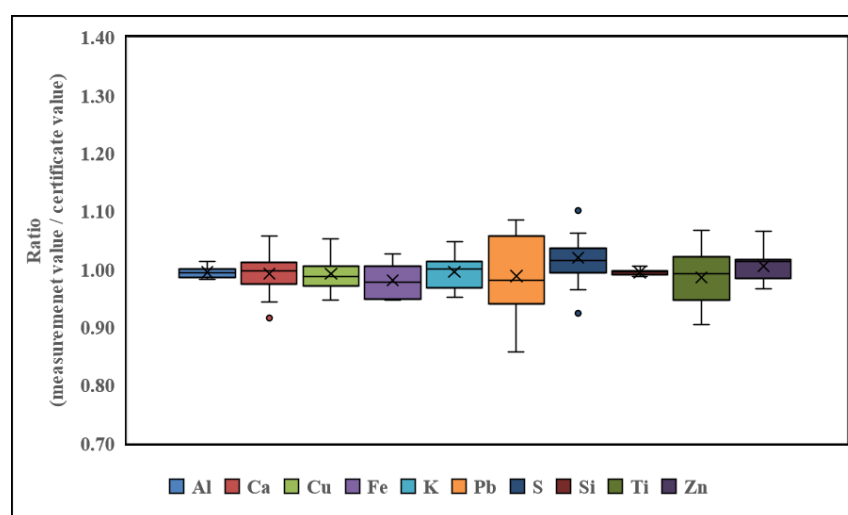
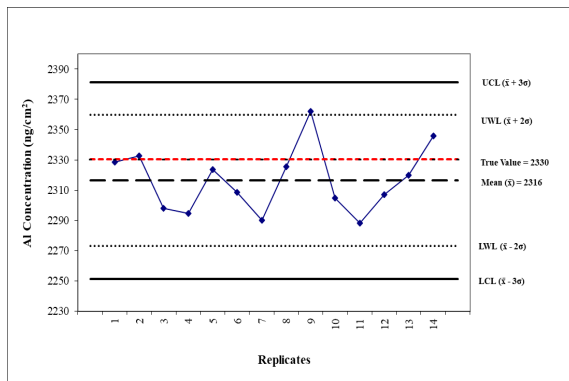
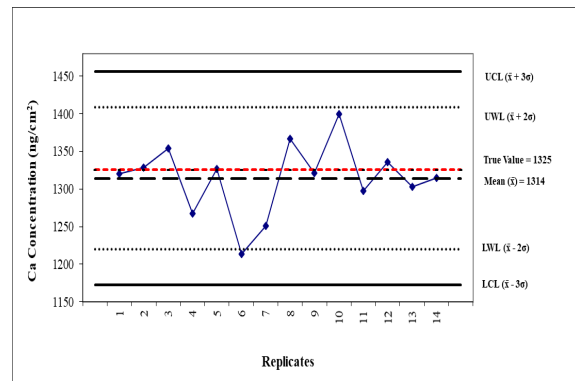


Figure 2. The ratio between analysis and the certificate values NIST 2783 Air Particulate on Filter Media.

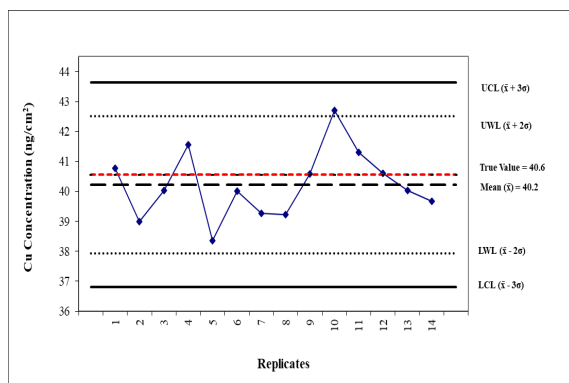
In addition to analysis using reference materials, internal quality control includes replication analysis that is generally done use QC (Quality Control) samples which aims to monitor performance day to day analysis or from batch to batch. QC samples are a kind of sample which is stable and available in quantities enough to be analyzed inside a long period of time. Generally, the results of monitoring QC samples expressed in the control chart. Control chart is a tool for monitoring quality of analysis. Analysis replication control chart in a batch analysis can be utilized to find out if there is an error or drift. Analysis replication control chart shows good results and does not occur systemic error where the results of each analysis replicas are distributed randomly in a range acceptable value [18].



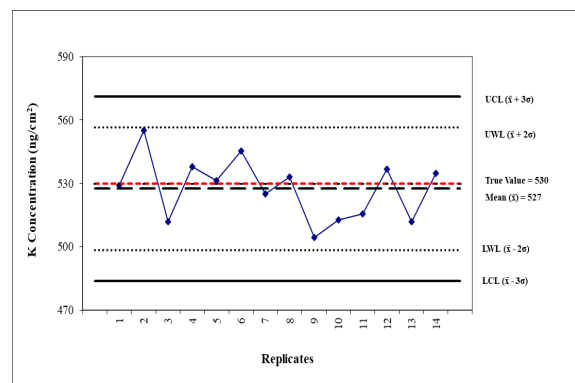
(a)



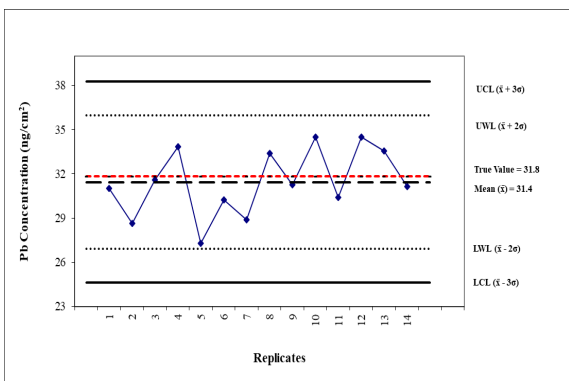
(b)



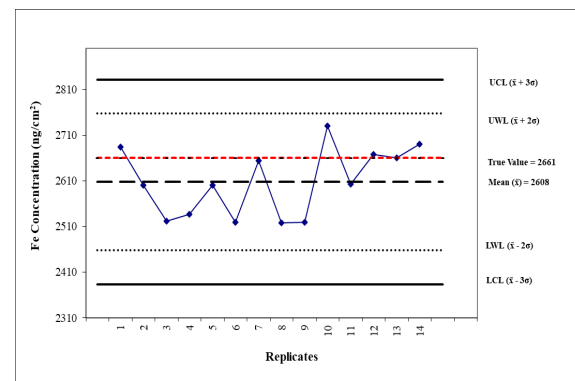
(c)



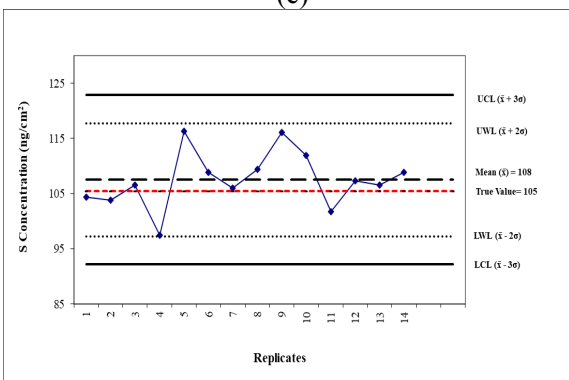
(d)



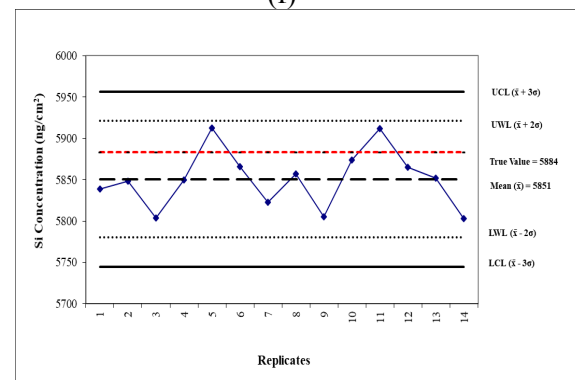
(e)



(f)



(g)



(h)

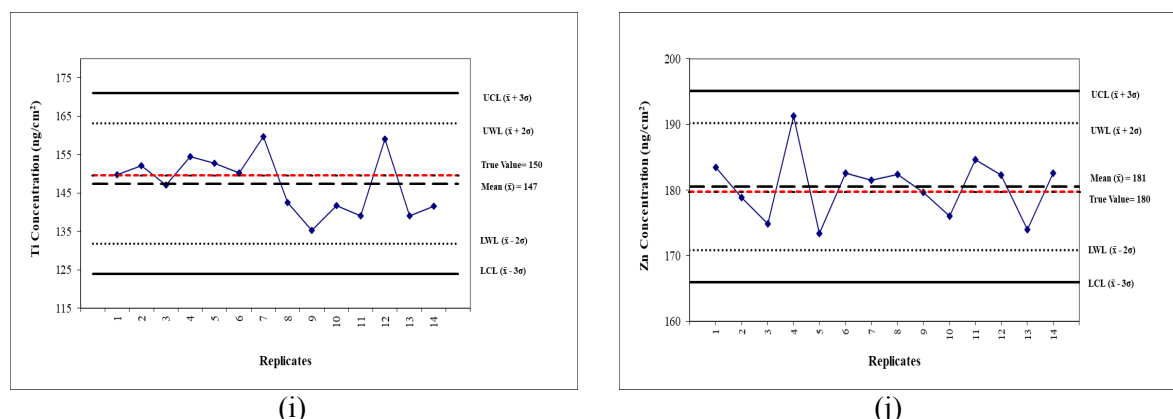


Figure 3. Control charts for elemental analysis: (a) Al, (b) Ca, (c) Cu, (d) K, (e) Pb, (f) Fe, (g) S, (h) Si, (i) Ti and (j) Zn.

Monitoring control charts of the results for periodic testing (intermittent) of APM reference material, NIST 2783 Air Particulate on Filter Media are shown in Figure 3. From the control charts, it can be seen that the test results at some points have fairly good accuracy and precision because the elemental levels of the test results of the standard reference materials of APM for Al, Ca, Cu, Fe, K, Pb, S, Si, Ti and Zn were in good results. As long as the value of the QC sample goes into the accepted range, then the results of the analysis from the sample on the same batch as the QC sample is considered as reliable data.

4. Conclusion

The results from this study demonstrate that the EDXRF Epsilon 5 spectrometer was applicable for airborne particulate matter analysis. The results of this analysis can be utilized to determine the composition of airborne particulate matter, especially for Al, Ca, Cu, K, Pb, Fe, S, Si, Ti and Zn. The assessment results for selected elements were in a good agreement with the certified values, with %recovery ranged from 98 to 102%.

Replication of analysis using airborne reference materials, SRM NIST 2783 Air Particulate on Filter Media indicated values that were in the range of acceptable value. It can be concluded that data of elemental analysis in APM reference material NIST 1567a 2783 Air Particulate on Filter Media using EDXRF Epsilon5 were considered as valid, accurate and reliable data.

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