ANALYSIS OF BORON, CADMIUM AND IRON IN THORIUM NITRATE BY ICP-AES METHOD AFTER MATRIX SEPARATION USING TRIBUTYL PHOSPHATE

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ABSTRACT

ANALYSIS OF BORON, CADMIUM AND IRON IN THORIUM NITRATE SOLUTION BY ICP–AES METHOD AFTER MATRIX SEPARATION USE OF TRIBUTYL PHOSPHATE. Analysis impurities elements in aqueous phase after thorium extraction with TBP-kerosen by ICP-AES method were carried out. A series of synthesized standards mixture of boron, cadmium and iron were prepared and each standards were measured 7 (seven) replicates for each elements for setting up calibration curve of boron, cadmium and iron. Aqueous samples solutions containing thorium less than 100 ppm and impurities elements boron, cadmium and iron solutions were analyzed by ICP-AES. All impurities elements were analyzed in optimum condition. It was found that minimum detection limit for boron 0.5 ppm, for cadmium 0.4 ppm and for iron 0.2 ppm. Boron, in three of the five samples, could be detected their presence but it could not be quantified statistically, and in two other samples their presence could be detected and quantified statistically. Boron concentrations were also calculated by first and second order of calibration curve and the difference between them was also depicted. It was found that cadmium had lower concentration than its minimum detection limit in all samples. On the other hand, It was found that iron had higher concentration than its minimum detection limit in all samples. Boron concentrations were also calculated by deterministic and probabilistic model. It was found that range of lower and upper concentration as a result of the prediction formula calculation is the widest and the shortest interval is caused by confidence formula, meanwhile samples measured seven times is closed to confidence formula.
Keywords: Analysis, boron, cadmium, iron, thorium nitrate, tributyl phosphate, ICP-AES.

ABSTRAK

ANALISIS BORON, KADMIUM DAN BESI DI DALAM LARUTAN TORIUM NITRAT DENGAN METODA ICP-AES SETELAH PEMISAHAN MATRIKS MENGGUNAKAN TRI BUTIL FOSFAT. Telah dilakukan analisis unsur-unsur takmurnian di dalam fasa air setelah ekstraksi torium dengan campuran TBP-kerosin menggunakan metoda ICP-AES. Satu seri larutan standar sintesis yang terdiri dari campuran boron, kadmium dan besi dan setiap standar diukur 7 (tujuh) kali untuk setiap unsur dipersiapkan untuk membuat kurva kalibrasi setiap unsur. Larutan cuplikan yang mengandung torium lebih kecil dari 100 ppm dan unsur–unsur takmurnian dianalisis dengan ICP-AES. Semua unsur takmurnian dianalisis dalam kondisi optimum. Didapatkan batas deteksi minimum untuk boron 0,5 ppm, kadmium 0,4 ppm dan besi 0,2 ppm. Keberadaan boron, di dalam tiga cuplikan dari lima cuplikan tidak dapat ditentukan secara kuantitatif dan dua cuplikan lainnya terdeteksi dan dapat

ditentukan secara kuantitatif. Konsentrasi boron juga ditentukan dengan menggunakan kurva kalibrasi orde pertama dan kedua dan perbedaannya juga digambarkan. Didapatkan bahwa kandungan unsur kadmium lebih rendah daripada batas deteksi untuk kelima cuplikan. Sebaliknya, didapatkan bahwa kandungan unsur besi pada semua cuplikan lebih besar daripada batas deteksinya. Konsentrasi boron juga dihitung dengan menggunakan model deterministik dan probalilistik. Diperoleh hasil bahwa kisaran konsentrasi antara yang paling rendah dan paling tinggi sebagai hasil dari model prediksi merupakan interval terluas dan lebih sempit jika digunakan model konfidens (kepercayaan), sedangkan cuplikan yang diukur tujuh kali diselesaikan dengan model kepercayaan.
Kata kunci*: Analisis, boron, kadmium, besi, thorium nitrat, tributil fosfat, ICP-AES*

I. INTRODUCTION

To fulfilling the world's energy demand, nuclear energy has been used in many countries because it has advantageous in free of greenhouse effect which is able to change climate over the world. From future point of view, thorium is a nuclear fuel in the future because its abundance is higher than uranium and thorium is not much used for nuclear fuel reactor right now. Thorium is not fissile but it is fertile material, therefore thorium should be prepared for fissile material for nuclear fuel[1,2].

Simplified of thorium cycle can be described as follows. Monazite sand is dissolved in hot concentrated sulfuric acid or sodium hydroxide, and the residue found is separated from solution. Thorium solution is then extracted by organic solution and stripped. Calcination process is done after thorium solution was mixed with oxalate acid and finaly ThO_2 is found. By mixing ThO_2 with anhidrous HF, ThF_4 compund is found. Converting $_{90}Th^{233}$ becomes $_{92}U^{233}$ is done in a molten-salt nuclear reactor after ThF_4 was mixed with molten fluoride salt carrier. Fission product and $_{90}Th^{233}$ found in unloaded irradiated fuel from molten-salt reactor should be separated from fissile material $_{92}U^{233}$. Furthermore, $_{90}Th^{233}$ can be fed back into molten salt nuclear reactor again. Fission product is stored up in waste

disposal, meanwhile $_{92}U^{233}$ is then fabricated to for another nuclear fuel[3,4,5]. Reaction of thorium with neutron is described as follows, $_{90}Th^{233} + _0n^1 \rightarrow _{90}Th^{233} \rightarrow _{91}Pa^{233} \rightarrow _{92}U^{233}$, $_{90}Th^{233}$ release gamma ray, $_{91}Pa^{233}$ and $_{92}U^{233}$ release $_{-1}\beta^0$ respectively[6]. Thorium used, therefore, should be free of impurities elements especially which have large cross-section of thermal neutron absorbance such as B (767 barns), Cd (2450 barns) and some of rare earth elements such as Gd (49,000 barns), Sm (5922 barns) [7]. Thorium nitrate used in this experiment might be consist of impurities elements such as B, Cd, Cu, Cr, Mn, Fe, Si and Al etc.

Some analytical methods have been used for the determination of impurities in nuclear fuel compound, such as ThO_2. Emission spectrograph analysis based on dc arc on graphite electrode and distillation carrier mixture of Ga_2O_3, LiF and Ag_2O has been used to analyze impurities elements in nuclear fuel because it is sensitive method[8]. Matrix of the sample and standard should be matching and stable in high temperature, because it goes on high temperature. So, impurities elements in matrix ThO_2 in high temperature emit their specific wavelength which can be used for qualitative and quantitative analysis. The advantages of this method, the sample is quite small, simultaneous analysis and direct determination. Impurities elements and its

matrix ThO_2 are not needed to separate during analysis. Sample could be in solid or liquid form. On the other hand, the disadvantageous of this method, sample preparation takes time and tedious because sample in powder form. Linearity of calibration curve is limited and detection limit is high, rather low precision. Graphite standard as an electrode and as a cup of the sample are not easy to find in the market. From spectroscopy point of view, the presence of matrix ThO_2 even though chemically stable in high temperature but it also emits high background. Reading lines of impurities elements in a glass or plastic film which is used as a detector is not easy because lot of spectral lines are also recorded. It needs lot of experience. Since many spectral lines and high background of thorium spectra interference spectral analyte lines in complex atomic emission spectra, so error of analysis is quite possible. In addition, overlaping spectra between spectral analyte lines and spectral others lines are not rare in emission spectrograph, the analyst should take care of it[8]. Therefore, it is necessary to analyze impurites element as a metal such as iron, transition metal cadmium and metaloid boron simultaneously and increase analytical capabilities such as sensitive, reproducible, rapid, simultaneous, high precision, low detection limit and accurate. Lowering detection limit especially for large cross-section of absorbance thermal neutron elements in thorium is desirable because quality of nuclear fuel is heavily dependent of quality of analyses of boron and cadmium. It will be possible only with an increase the sensitivity of the calibration curve. Although analysis boron, cadmium and iron in all samples were carried out, but for other impurities elements are also important to analyze.

Modern analytical instrument such as ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) has been widely used for trace elements analysis because it is quite sensitive, reproducible, rapid, simultaneous, high precision, low detection limit and accurate. Linearity of calibration curve with ICP-AES method is wider than emission spectrograph method. ICP-AES method is based on high temperature of argon plasma which is created by radio frequency generator and argon gas flowing. Tesla unit ignites a brief discharge arc and then it initiates ionization process which produces high temperature. It could analyze impurities elements in solution and solid sample form. Temperature in the center of the argon plasma could be reach between 5000 K and 9000 K which brings about most elements exist as singly charge ions. Population of analyte which emits characteristic lines is proportional to the amount in the sample and the temperature, the higher temperature of plasma will produce the higher its intensity. For quantitative analysis purposes, a series of standards and samples are measured on the same condition. Ideally, matrix and chemical composition of the sample and standard should be same chemically and physically or as close as possible[9,10,11].

Solvent Extraction

Analyzing impurities elements in a aqueous and solid solution form was done after solvent extracting of thorium process. Ideally, thorium should be extracted by supercritical fluid extraction with organic compound such as TBP (tributyl phosphate) due to reduce unwanted chemical substances. Unfortunately, instrument for supercritical fluid extraction with CO_2 is very expensive, so traditional extraction was used because of its rapidity, high yield which is almost 99 % for three times extractions and it

is simplicity to separate thorium from others elements. Furthermore, an aqueous solution form of the samples were analyzed by ICP-AES in optimum condition[12,13].

In order to have a good signal of analyte spectral lines of impurities elements, separation techniques should be done due to major elements in the samples, otherwise analytes spectral lines produced will be weak leads to high detection limit. Moreover, they will be interfered by complex atomic emission spectra of matrix thorium. Some sepration techniques have been already done to separate impurities elements from thorium, one of them is liquid-liquid extraction. It is used to separate impurities elements from matrix thorium because it is suitable for small sample sizes. There are some of organophosphorus solvents which can be used as an extraction solvent, TBP with kerosene as a diluter was used for extracting thorium nitrate from its impurities because it is suitable extraction solvent and much easier to find in a market.

The aim of this research is to apply analysis technique for gaining information of large cross-section of absorbance thermal neutron impurities elements such as boron (metaloid), cadmium (transition) concentration and iron (metal) elements which is assumed have high concentration in thorium after extracting process by ICP-AES method.

II. METHODOLOGY

2.1. Apparatus and reagents

The ICP-AES Plasma 40, Perkin Elmer and glasswares. Reagents: Fe_2O_3, CdO and H_3BO_3 (Spex Industries), Ar gas (HP) and Nitrogen gas (HP), HNO_3 (Merck), TBP (Merck), Kerosen (Fisher)

A standard solution of boron, cadmium and iron were prepared by dissolving H_3BO_3, CdO and Fe_2O_3 in nitric acid 25 mL concentrated nitric acid, was then diluted with pure water. Each solutions series was made up from 0 ppm until 4 ppm of boron, cadmium from 0 ppm until 1 ppm and iron from 0 ppm until 40 ppm.

Operation Condition of ICP-AES
RF power   : 1 kW
Argon Flow Rate   : 12 L min^{-1}
Sample Flow Rate   : 1 mL min^{-1}

2.2. Procedure

Each of a three-stock solutions of $Th(NO_3)_4$ and each of a two-solid of $Th(NO_3)_4$ were mixed separetely with HNO_3 solution in each an erlenmeyer flask for 60 minutes in order to have a good homogeneous solution. Pure water was used to dilute $Th(NO_3)_4$ and HNO_3 solution, and filtered by a filter paper to remove unwanted residue. After filtering, each solution was diluted until volume solution 100 mL. Fifty mL of each aqueous solution was poured into an erlenmeyer flask and mixed with 50 mL mixed of organic substance (TBP-kerosen, 70%:30% v/v) by a magnetic stirrer for 30 minutes. Separation process between an aqueous and organic phase was carried out in a separatory funnel which had already been put on a ring which was hold by stopcock. It took a while for waiting equilibrium condition. Sample an aqueous solution **A** was extracted with mixed organic solution (TBP-kerosen, 70% : 30% v/v) by a magnetic stirrer for 45 minutes twice. Sample an aqueous solution **B** was extracted with mixed organic solution (TBP-kerosen, 70% : 30% v/v) by a magnetic stirrer for 45 minutes three times. Sample an aqueous solution **C** was extracted with mixed organic solution (TBP-kerosen, 70%:30% v/v) by a magnetic stirrer for 45 minutes twice. Sample an aqueous solution **D** was extracted with mixed organic solution (TBP-kerosen, 70% :

30% v/v) by a magnetic stirrer for 45 minutes three times. Sample an aqueous solution **E** was extracted with mixed organic solution (TBP-kerosen, 70% : 30% v/v) by a magnetic stirrer for 45 minutes once. Aqueous solution found assumed to be representative of the sample for ICP-AES, its thorium concentration in each sample was analyzed by XRF (X-Ray Fluorescence) method and EDTA titration. It was found that its concentration was about less than 100 ppm. All samples were prepared in Centre for Accelerator and Material Process Technology (CAMPT) in Yogyakarta and all samples analyses were conducted in Centre for Nuclear Fuel Technology (CNFT) in Serpong - Banten with ICP-AES method. A laboratory-synthesized aqueous standards solution was prepared by mixing boron, cadmium and iron solution with variation concentration and blanks. Ideally, samples, standards preparation and measurements should be done in one laboratory, in this work.

III. RESULTS AND DISCUSSION

As mentioned above, this research was run in limited of funding, the number of sample and the number of impurities elements analyzed was chosen based on scale of priority of how large nuclear cross-section and concentration assumed is. Boron and cadmium elements were chosen because both of them have large neutron absorbance cross-section (767 barn and 2450 barn respectively). Even though iron has neutron absorbance cross-section Fe (2.56 barn), but from concentration point of view, iron was chosen because its concentration was assumed high and its spectral line are closed to spectral lines of boron and cadmium. Meanwhile the others element such as Cu (3.78 barn) and Cr (3.1 barn) are medium

and Si (0.171 barn) and Al (0.232 barn) are small neutron absorbance cross-section[4]. If B, Cd and Fe are analyzed directly from high concentration thorium solution by ICP-AES method, it will bring about interfered intensities of boron, cadmium and iron because of thorium matrix. Thorium which has 90 electrons will emit much more wavelengths than combine boron which has 5 electrons, cadmium 42 electrons and iron 26 electrons. Some of thorium spectra causes high background emission from continuous or recombination anion and cation in excitation system. From matrix point of view, thorium spectral lines will interference B, Cd and Fe spectral lines because of physical, chemical and spectral interference of thorium as matrix. Overlapping of spectra lines is often encountered in spectroscopy analysis. Strong cadmium spectral line for example has two lines, Cd(I) (2288.022 Å) its intensity 1500 and Cd(II) (2286.15 Å) its intensity 1000, meanwhile cobalt spectral line which close to cadmium spectral line is Co(II) (2286.14 Å) its intensity is 1000. Fortunately, cobalt concentration was so small in samples, so its interference was able to ignore. Another element which has closed spectral line to Cd is Fe(I) (2287.250 Å) its intensity is 150. Boron has two high intensity spectral lines, they are B(I) (2496.77 Å) and B(I) (2497.73 Å) their intensities 1000 respectively, meanwhile spectra line of iron is Fe(I) (2496.533 Å) its intensity is 600. Those spectral lines which has closed to analyte spectral lines will interfere analyte spectral lines. Due to high temperature of argon plasma which has temperature 5000 ^{o}C until 9000 ^{o}C where sample or standard excites, a number of spectral lines could be detected. This is an disadvantages of this method because all metal and nonmetal elements in hot condition such argon plasma

J.Tek. Bhn. Nukl.
Vol. 8 No. 2 Juni 2012: 67 - 122

ISSN 1907 – 2635
416/AU2/P2MI-LIPI/04/2012
(Masa berlaku Akreditasi s/d April 2015)

will emit so many spectral line. Spectral line interferences and overlap problem can be solved by resolution of optics system or separation technique of analyte elements from its matrix. Those interactions will increase the detection limit.

In order to have a high validation quantitative analysis factors, analysis method for the determination B, Cd and Fe should not be analyzed in thorium solution directly with ICP-AES method. High background of matrix of thorium concentration spectra will suppress B, Cd and Fe spectral lines. Ideally, the number of thorium ion in aqueous solution after separation process should be closed zero and the number of boron, cadmium and iron in aqueous solution should not be changed before and after extraction. Since ICP-AES emits all spectra of atoms in a sample and their intensities are proportional to their amount or concentration in sample.

3.1. Extraction Model

Organophosphorus solvents such as TBP forms a stable complex with cation oxidation state 4+ and 6+, on the other hand, TBP does not form complex with cations which oxidation state 3+ and 2+ [14]. Model of $Th(NO_3)_4$ in HNO_3 solution and TBP extraction actually is complex. Reaction between $Th(NO_3)_4$ in HNO_3 and TBP brings about physically separation between thorium nitrate in organic phase meanwhile their impurities elements are still in aqueous phase. The overall reaction model thorium extraction can be written as follows,

$$4[TBP.H_2O]_{(org)} + Th(NO_3)_{4(Aq)} \longrightarrow [Th(NO_3)_4.4TBP]_{(org)} + 4\ H_2O_{(Aq)} \quad (1)$$
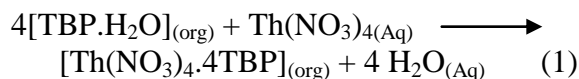
Reaction between impurities elements in aqueous phase with TBP-kerosen do not occur, but in very small amount, it might be carried over to organic solution during the extraction process. So it can be assumed that impurities elements concentration in an aqueous solution do not change or it might be slightly change. Ideally, all thorium nitrate in aqueous phase have to be moved to organic phase and impurities elements are still in aqueous phase, followed by analyzing impurities elements in aqueous phase. Ideal condition above is not easy to meet, impurities elements in aqueous phase could be analyzed in minimum thorium nitrate by ICP-AES. In these experiments, thorium nitrate were extracted once until four times or thorium concentration less than 100 ppm. Boron, cadmium and iron could be analyzed in solution form containing thorium concentration as low as possible.

3.2. ICP-AES Analysis

ICP-AES provides multi elements analysis, less inter elements interference, its advantageous over other methods such as atomic emission spectrometry method which is time consuming. For quantitative analysis, modern instrument such as ICP-AES heavily depends on comparison between analyte signal or measured signal of a series of known concentration and unknown analyte signal or measured signal. As mentioned above, iron has 2 spectral lines which are close to spectral line of Cd and B. It was found that its calibration curve for iron was $Y = 15.67\ X + 9.443$ where Y is measured signal, X is concentration and its correlation coefficient r was 0.9940 and its detection limit was 0.2 ppm. All samples had concentration from 44 ppm until 189 ppm of iron. A simple seven-point calibration curve was set up by measuring a series of standards solutions from reference material containing mixture of boron, cadmium and iron solution which were measured in optimum condition. A series of standards solution containing Cd from 0 ppm (blank) until 1 ppm was used to

prepare a simple calibration curve. It was found that simple calibration curve of cadmium was Y = 21.9872 X + 2.6708 and correlation coefficient was 0.9771 and its detection limit of cadmium was 0.4 ppm. Analytical figures of merits, all samples can be calculated from comparison between cadmium intensities in each sample and cadmium calibration curve. It was found the highest cadmium concentration was 0.4 ppm and the lowest was 0.1 ppm. So, analytically Cd element in all samples could not be detected because their concentrations were less than its detection limit and so, their measured signals are assumed as a background.

A series of standards solution containing boron from 0 ppm (blank) until 4 ppm was used to set up a simple nine-point calibration curve, each point was measured seven times (seven replicates) and the results found was shown in Tabel 1[15].

Tabel 1. Relationship between concentration of boron (ppm) and its intensity.

Boron Concentration (ppm)	Intensity (mean value)
0.0	0.094
0.1	6.143
0.2	10.714
0.3	21.429
0.4	24.571
0.8	28.000
1.0	44.000
2.0	91.000
4.0	177.000

Although there are various mathematically relationship between boron concentraion and its intensity can be figure out, this paper addresses two kinds of relationship. First, its application of the traditional calibration curve or simple linear regression deterministic model for analysis of

boron element was set up by a least-square regression first order form and it was found in general mathematically form is $Y = 44.2039\,X + 0.0773$, where Y is meassured signal or intensity, X is concentration, this equation is the first order. Second, since the computer has been widely used in all aspects, mathematically the second order equation of above calibration curve was found as $Y = 0.4146\,X^2 + 42.5677\,X + 0.7978$. When both calibration curves first order and second order are plotted will look the same or both lines are completely overlapped each other as shown Figure 1 [a]. If the calibration curve is extrapolated until concentration of boron over 10 ppm, there will be significant differences between them. Since the calibration curve was constructed for the highest boron concentration was 4 ppm, so both calibration curve are not easy to differentiate each other. Figure of merit, however, there are small differences boron concentration among the samples when calculated by first and second order equation as shown in Figure 1 [b].
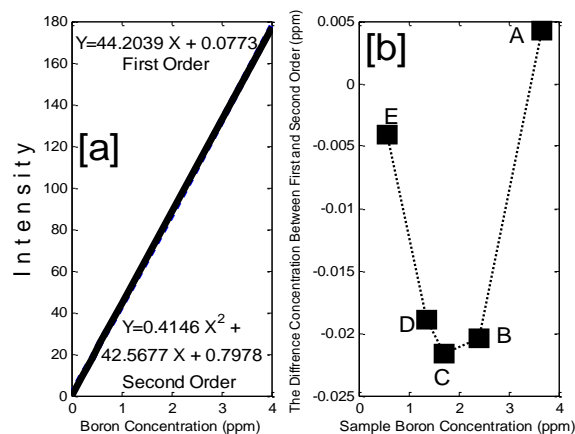

Figure 1. The plotted first and second order calibration curve and the difference concentration among the samples calculated by first and second order calibration curve.

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Vol. 8 No. 2 Juni 2012: 67 - 122

ISSN 1907 – 2635
416/AU2/P2MI-LIPI/04/2012
(Masa berlaku Akreditasi s/d April 2015)

3.3.   Detection Limit.

Limit of detection concept in analytical chemistry is used to describe the lowest determined concentration of a sample statistically. Relationship between limit of detection and the lowest concentration determined reliably is set up through background signal of blank solution. Theoretically, there are two types of error in analyzing at the lowest concentration. Type I or false positive, analyte as present when it is not and type II, false negative, analyte as not present when it is. Generally, analysis impurities elements such boron and cadmium in nuclear fuel at very low concentration is not easy to do. Because, it is a difference between analyte in small amount and background signal. In order to analyze of detectable boron, cadmium and iron concentration in all samples, background of the sample fluctuations have to be measured several times (seven replicates) in the same condition as the samples measured. The statistically calculation of background fluctuation of blank solution brings about limit of detection and quantitation. If the analyte signal is lower than signal the limit of detection its presence will be called not detected, furthermore if the analyte signal is between limit of detection and limit of quantitation range its presence will be called detected but not qualified statistically quantified. Analyte signal is in over limit quantitation can be reliably statistically quantified and it is less free of random measurements.

Statistically, the value of detection limit is 3 sigma or standard deviation of background plus concentration of background. Mathematically, it is written by $C_b + 3\ \sigma$ (sigma), where C_b is background concentration as shown in Figure 2. In chemical analysis, limit of quantitation is one of the important validation parameters,
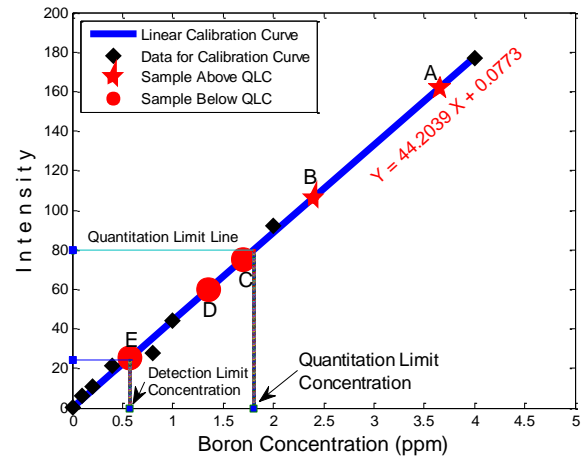

Figure 2. Relationship between Boron Concentration and its Intensity for Calibration Curve

mathematically is written as $C_b + 10\ \sigma$ (sigma). Based on the experiments done for blanks which were measured 7 times, it was found that limit of detection was 0.5 ppm of boron and limit of quantitation was 1.8 ppm of boron. Therefore all the sample measured between 0 until 0.5 ppm was considered as a background. Sample C, D and E were lied on calibration curve between detection limit and quantitation limit, it means boron could be detected in sample C, D and E but they could not be qualified determined quantitatively. On the other hand, sample A and B were lied on linear range of calibration curve and above quantitation limit, so both samples could be qualified determined statistically, as shown in Figure 2.

3.4.   Precision and Accuracy

In order to evaluate precision and accuracy, the calibration curve used for boron and iron should show excellent linearity with correlation coefficient r above 0.98 and intercept as small as possible or close to origin. Since boron, cadmium and iron were synthesized standards and they were mixed together in a series of bottle,

their calibrations curves were set up separately. Unfortunately, cadmium concentration in all samples were less than its detection limit concentration. Therefore, their precision and accuracy would not be investigated anymore. Standards mixture boron, cadmium and iron were available in synthetic form, therefore, the accuracy of analyses boron was done by measuring standard in the range of interest calibration curve. The precision of ICP-AES was evaluated as the relative standard deviation of boron 5 % for 2 ppm of standard which indicates good stability and reproducibility for trace element. It was also found that this method was good precision for analysis of boron and iron. In evaluating accuracy, it was found 96 % for 10 ppm of iron and 98 % 2 ppm of boron respectively.

3.5. Probabilistic Model Calibration Curve

Based on the measurements uncertainty, regression line of calibration curve above contains error, statistically the consequences of calibration curve error gives rise all samples concentration measurements uncertainty [15]. Statistically, there are two kinds of calibration curves, they are deterministic and probabilistic model. Deterministic model was used to calculate detection and quantitation limit, concentration calculation with deterministic model is easier than probabilistic model. However, probabilistic model will accommodate an error. Equation of probabilistic model can be written as $Y = b_0 + b_1 X \pm \varepsilon$ where $b_0 + b_1 X$ is linear component and ε is the random error component. Based on statistically calculation, probabilistic model has two kinds, they are confidence level and which can be written as follows,

$$Y = b_0 + b_1 X \pm t\,(ESD)\sqrt{\frac{1}{n} + \frac{(X_p - \bar{X})^2}{S_{xx}}} \qquad (2)$$

and prediction level which can be written as follows,

$$Y = b_0 + b_1 X \pm t\,(ESD)\sqrt{1 + \frac{1}{n} + \frac{(X_p - \bar{X})^2}{S_{xx}}} \qquad (3)$$

For comparison, relationship between Y and X when use of simple linear regression calibration curve and prediction level were shown in Figure 3 below. Since prediction and confidence limit lines are very closed each other, and confidence limit were lied between prediction limit line, so confidence levels lines were not shown in Figure 3. Despite confidence levels lines were not shown in Figure 3, information about interval concentration of boron after analyzing use of simple calibration curve, prediction line and confidence line numerically was written in Tabel 2. The confidence interval of the expected value of Y is narrower than the prediction interval for the same given value of X. Moreover, detection and quantitation limit use of upper prediction line was also increased significantly as shown in Figure 3. When quantitation limit was calculated based on upper prediction line concentration, the quantitation limit value becomes increase as shown in Figure 3.

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ISSN 1907 – 2635
416/AU2/P2MI-LIPI/04/2012
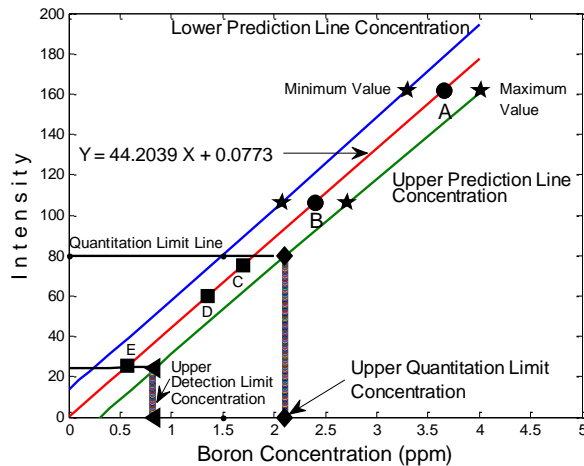(Masa berlaku Akreditasi s/d April 2015)

Figure 3. Estimation Calibration Curve, Limit of Detection, Limit of Quantitation and Prediction line (upper and lower).

All concentrations of the samples have been calculated based on the confidence level formula,

$$x = \left(\frac{Y_{unk} - b_0}{b_1}\right) \pm t \frac{(ESD)}{b_1} \sqrt{\left[\frac{1}{n} + \left(\frac{Y_{unk} - \bar{Y}}{b_1}\right)^2 / S_{xx}\right]} \quad (4)$$

There are two others formula which can be used to calculate boron concentration in samples. Prediction formula can be written as

$$x = \left(\frac{Y_{unk} - b_0}{b_1}\right) \pm t \frac{(ESD)}{b_1} \sqrt{\left[1 + \frac{1}{n} + \left(\frac{Y_{unk} - \bar{Y}}{b_1}\right)^2 / S_{xx}\right]} \quad (5)$$

this formula is valid for samples which are measured once, furthermore, when samples are measured several times (k) the formula can be writtern as

$$x = \left(\frac{Y_{unk} - b_0}{b_1}\right) \pm t \frac{(ESD)}{b_1} \sqrt{\left[\frac{1}{k} + \frac{1}{n} + \left(\frac{Y_{unk} - \bar{Y}}{b_1}\right)^2 / S_{xx}\right]} \quad (6)$$

Where:
Y : boron intensity

Y_{unk} : is the sample boron intensity measured

$\bar{y}$: is the average intensity of the boron standards.

X : boron concentration

X_i : are the boron concentration of standards

$\bar{X}$: average boron concentration of all standards

X_p : boron concentration to be determined

b_0 : intercept of calibration curve

b_1 : slope of calibration curve

t : student's t distribution with (n-2) degree of freedom

ESD : Error Standard Deviation

n : number of standards used to be built calibration curve

k : number of sample measured (replicates)

The results calculated based on the three equations above, they are for confidence level, prediction level and prediction interval for seven measurements done for each samples is shown in Tabel 2. There are significantly differences interval among them, the results found from confidence level is the narrowest, and the widest interval is prediction level, however when the samples were measured seven (7) replicates the prediction interval value is closed to confidence interval for the same given of Y. In other words, the addition of value of one (1) in square root for confidence interval will produce prediction formula causes rather high interval difference between them, on the other hand by measuring 7 replicates each sample also causes slightly difference interval. If the $(y_{unk} - \bar{y})$ value is zero or close to zero the error component of X value will be the narrowest. However, $(y_{unk} - \bar{y})$ value could be engineered by arranging synthesized standards.

Tabel 2. Boron Concentration Based on Estimation Calibration Curve and Confidence (95 %),
Prediction One Measurement and Prediction Seven Replicates (ppm)

Sample	Based on Estimation Y=44.2039 X+0.0773 (ppm)	Based on Confidence (95 %) (ppm)		Based on Prediction One Measurement (ppm)		Based on Prediction Seven Replicates (ppm)	
		Lower	Upper	Lower	Upper	Lower	Upper
A	3.6580	3.4353	3.8807	3.3031	4.0129	3.4120	3.9040
B	2.3980	2.2574	2.5386	2.0880	2.7080	2.2228	2.5731
C	1.6990	1.5929	1.8051	1.4030	1.9950	1.5501	1.8479
D	1.3530	1.2572	1.4488	1.0606	1.6454	1.2113	1.4947
E	0.5760	0.4780	0.6739	0.2828	0.8691	0.4328	0.7192
DL	**0.5140**	0.4423	**0.6401**	0.2477	**0.8347**	0.3974	**0.6850**
QL	**1.8080**	1.6975	**1.9185**	1.5105	**2.1056**	1.6560	**1.9601**

D L = Detection Limit; **Q L**= Quantitation Limit

When detection limit (DL) and quantitation limit (QL) were measured use of probabilistic model the results found in bold and underline numbers in Tabel 2. The highest value was prediction interval for one measurement sample. The higher concentration of boron in a sample it is, the wider of interval for probabilistic model it is as shown in Tabel 2. The wider of interval a measured given sample is heavily dependent on the position of sample in calibration curve. If the ($Y_{unk} - \bar{Y}$) value is zero, or signal of the sample is closed to mean signal value of the standards concentration error will be minimum. In other words, precision of analyses could be engineered. Confidence and prediction levels will overlap with estimation calibration curve if coefficient correlation r is one and all points of standard calibrations are lied on the estimation calibration curve. It is hard to find such estimation calibration curve, it needs extra careful experiments. Eventually, detection and quantitation limit are affected by carefully measurements, in this experiments, detection and quantitation limit increases 0.1 ppm respectively. Cadmium and iron concentrations were carried out as the same as boron calculation.

IV. CONCLUSION

Simple method for analyzing, boron, cadmium and iron in an aqueous solution containing small amount of thorium by ICP-AES have been developed. Instrument condition plays one of the most important roles in measuring standards in order to get low detection limit, another which also plays important role is standard preparation. Preparation samples, in extraction treatment for 25 minutes, were done by machine (magnetic stirrer) and human hand for separation were helping for precision and accuration. Eventhough the descripencies analysis result by using first order calibration curve and second order calibration were not much, second order calibration curve is not used for chemical analysis. First order calibartion curve is always used eventhough the discrepencies of analysis result in this experiment were exits. Further works are needed to determine other impurities, because analytical methodology

developed has been a strong argument and it is also under control. Estimation calibration curve found for boron analysis was very good but when probabilistic model is applied, interval differences among them will be significantly high. An engineering calibration curve and concentration determined could be utilized to do good precision.

V. ACKNOWLEGMENT

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