An Improvement of Graphite Rod Electrode of Used Primary Cell
for Analyzing Boron And Cadmium in Thorium Oxide Using
Emission Spectrograph Method
(Sahat Simbolon**)**

AN IMPROVEMENT OF GRAPHITE ROD ELECTRODE OF USED PRIMARY CELL FOR ANALYZING BORON AND CADMIUM IN THORIUM OXIDE USING EMISSION SPECTROGRAPH METHOD

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ABSTRACT

AN IMPROVEMENT OF USED PRIMARY CELL GRAPHITE ROD ELECTRODE FOR ANALYZING BORON AND CADMIUM IN THORIUM OXIDE USING EMISSION SPECTROGRAPH METHOD. Analysis of boron and cadmium in synthetic thorium oxide fuel using emission spectrograph method was carried out. Used primary cell graphite rod electrodes (UPCGREs) receiving (chemical and physical) treatment and standard electrodes (Spex) were used as an electrode in the emission spectrograph method. The graphite rod electrodes of used primary cells comprised 50 graphite rod electrodes soaked in water for 2 weeks, 50 graphite rod electrodes soaked in 0.1 N nitric acid for 1 week (chemical treatment), and 50 graphite rod electrodes heated in an oven at 300 °C for 2 hours (physical treatment). Pure thorium oxide was obtained synthetically through thorium nitrate solution extraction using organic solution TBP-kerosene, followed by stripping, drying and calcination. Standards were made from a mixture of synthetic thorium oxide, CdO and H_3BO_3, and distillation carrier. 100 mg of standards was introduced into the hole of the chemically and physically treated sample-carrying electrodes as well as the standard electrodes (Spex). The operating condition was established using a current of 10 A, an excitation time of 25 seconds, and a gap of 4 mm between electrodes. It was found that when the chemically treated UPCGREs were used as an electrode, the relationship between the concentration and the intensity of boron and cadmium was not in order. Meanwhile, when the physically treated UPCGREs were used as an electrode, the relationship between the concentration and the intensity of boron and cadmium in thorium oxide was linear, therefore it could be used as a calibration curve. It was discovered that the calibration curve of the standard electrodes (Spex) was more sensitive than the calibration curve of the physically treated UPCGREs. However, the calibration curve for boron and cadmium of the standard electrodes (Spex) contained higher background. Therefore, for thorium oxide having low concentrations of boron and cadmium, the use of the physically treated UPCGREs was more favorable than the standard electrodes (Spex).

FREE TERMS: used primary cell graphite rod electrode, sample-carrying electrode, boron, cadmium, thorium oxide

ABSTRAK
PERBAIKAN BATANG ELEKTRODE GRAFIT BATU BATERAI BEKAS UNTUK ANALISIS BORON DAN KADMIUM DALAM TORIUM OKSIDA DENGAN METODE SPEKTROGRAF EMISI. *Telah dilakukan analisis boron dan kadmium di dalam bahan bakar nuklir torium oksida sintesis dengan menggunakan metode spektrograf emisi. Batang elektrode grafit batu baterai bekas setelah perlakuan (secara kimia dan fisika) dan elektrode standar (Spex) sebagai pembanding digunakan untuk*

elektrode pada metode spektrograf emisi. Batang elektrode grafit dari batu baterai yang digunakan mencakup 50 batang elektrode grafit yang direndam dalam air selama 2 minggu, 50 batang elektrode grafit yang direndam dalam 0,1 N asam nitrat selama 1 minggu (secara kimia), dan 50 batang elektrode grafit yang dipanaskan dalam tungku pada suhu 300 °C selama 2 jam (secara fisika). Torium oksida murni disintesis melalui ekstraksi larutan torium nitrat dengan menggunakan larutan organik TBP-kerosin, diikuti stripping, pengeringan dan kalsinasi. Standar dibuat dari campuran torium oksida sintesis dengan CdO dan H_3BO_3, serta campuran pengemban sulingan. 100 mg standar dimasukkan ke dalam lubang elektrode standar (Spex), maupun elektrode hasil metode kimia dan fisika. Kondisi operasi untuk semua percobaan adalah arus 10 A dengan waktu eksitasi 25 detik dan jarak antar elektrode 4 mm. Hasil percobaan menunjukkan bahwa hubungan antara konsentrasi dan intensitas boron serta kadmium di dalam torium oksida dengan elektrode yang dibuat dengan metode kimia tidak teratur. Sementara itu hubungan antara konsentrasi dan intensitas boron serta kadmium di dalam torium oksida dengan elektrode yang dibuat dengan metode fisika merupakan garis linear yang dapat digunakan sebagai kurva kalibrasi. Adapun kurva kalibrasi boron dan kadmium dengan menggunakan elektrode standar (Spex) masih lebih sensitif dibandingkan dengan elektrode yang diperoleh metode fisika. Akan tetapi latar elektrode standar (Spex) lebih tinggi daripada elektrode yang diperoleh dengan metode fisika. Oleh karena itu untuk torium oksida dengan konsentrasi boron dan kadmium yang rendah lebih baik digunakan elektrode yang diperoleh metode fisika daripada elektrode standar (Spex).

KATA KUNCI: *batang elektrode grafit batu baterai bekas, elektrode kerja, boron, kadmium, torium oksida*

I. INTRODUCTION

Thorium is one of the most abundant nuclear materials found in the Earth's crust. Although thorium-232 is not a fissile material, it is a good candidate as a fertile material. Thorium-232 will be converted into uranium-233, which is a fissile material, through neutron absorption in conventional reactor[1,2]. Therefore, thorium-232 which is placed in a nuclear reactor core must possess good chemical purity like nuclear fuel uranium-235, which is having low concentrations of elements with large neutron absorption cross section, such as cadmium and boron. Consequently, thorium oxide which is inserted into the core has to be chemically analyzed first.

The use of emission spectrograph as one of the sensitive techniques for analyzing impurity elements in thorium oxide in powder form is attractive, since thorium oxide matrix and its impurity elements can be analyzed without the need for a separation process. The emission spectrograph method can be set up using thorax film as a detector and high thermal electrodes as a source of excitation. Thorax film as a detector has been used successfully for replacement of standard glass film[3]. Electrodes consist of a counter and a sample-carrying or working electrode are essential components in emission spectrograph because they are used as an atomizer. Due to the function and high temperature of excitation process, the electrodes should have a high melting point, good hardness, electrical conductivity, heat resistance, inertness, ease to fabricate and ease to find. These represent requirements for electrodes in emission spectrograph method.

Studies show that metallic electrodes such as iron and aluminum electrodes have some limitations to be used as an electrode in the emission spectrograph method, as both can only be employed as an electrode with an ac spark source. Due to the melting points of iron and

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82/Akred-LIPI/P2MBI/5/2007

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aluminum electrodes, these metallic electrodes are not capable of using a dc arc method[3]. An improved experiment has been established by using used primary cell graphite rod electrode (UPCGRE) for analyzing impurity elements in nuclear fuel after extraction with TBP-kerosene solution. The untreated UPCGREs can be used directly to analyze impurity elements (B and Cd) with a dc arc source. Based on the evaluation of boron element analysis in triplicate, the experiment was not good enough for analyzing boron, though satisfactory for cadmium analysis[4].

Triggered by the results found above and the number of UPCGREs, the use of UPCGRE in emission spectrograph is a challenge. Moreover, modern technology has been used to purify electrode graphite in battery until 99.9% C prior to fabrication. Boron and cadmium elements which have a high neutron absorption cross section are not found in the primary cell graphite rod electrode analysis[5,6]. Therefore, UPCGRE can be used as a source of graphite electrode.

The purpose of this paper is to explore the improvement of UPCGRE as an electrode for analyzing impurity elements of boron and cadmium in thorium oxide by two approaches, which are chemical and physical treatments. For chemical treatment, to decontaminate any unwanted elements the UPCGREs were soaked in water or in low concentration of nitric acid for some time. The decontamination of the UPCGREs were also done through physical treatment in an oven at 300 °C for 2 hours. The UPCGREs can be used to solve future problem in analyzing the impurity elements in nuclear fuel.

II. EXPERIMENTAL
2.1. Material
The materials used in the experiment were as follows:
1. Thorium nitrate (CAMPT), HNO_3 (Merck), TBP (Merck), kerosene (Fisher)
2. Distillation carrier: AgCl (950 mg), Ga_2O_3 (10 mg), LiF (40 mg) (Spex Industries)
3. Thorium oxide ThO_2 (Impurity standard) has 22 multi elements CRM No.66 (1-7) New Brunswick Laboratory Certified Reference Materials (U.S Department of Energy - New Brunswick Laboratory)
4. Film for thorax, Developer D19B and Kodak rapid fixer
5. Used primary cell graphite rod electrode (UPCGRE)
6. Standard powder of cadmium oxide (0.011423 g) (Spex Industries)
7. Standard powder of boric acid (H_3BO_3) (0.005719 g) (Spex Industries)

2.2. Equipment
The equipment used in the experiment consisted of glassware, beaker glasses, Erlenmeyer flasks, extraction separator; vial polyethylene for standards and samples; balance Sartorius 2405; pH Meter (Mettler); oven; Lathe – Horizon M-300; emission spectrograph 3.4 m Ebert type (Jarell Ash); and densitometer (Jarell Ash).

The operating conditions are as follows:

- Spectrograph 3.4 m Ebert type Jarell-Ash
- Grating : 590 lines mm^{-1}
- Slit width : 10 μm
- Current : 10 A
- Exposure time : 25 s

- Electrode: Used primary cell graphite rod electrodes (UPCGREs) were formed into a pencil-shape (counter electrode) and the sample-carrying electrode or working electrode had a hollow or hole of 4.5×5.5 mm
- Electrode gap: 4 mm
- Excitation: Jarell-Ash model with various dc arc sources
- Detector: X-ray for thorax (Kodak)
- Jarell-Ash, microphotometers with 7 μm slit and 0.5 mm slit height for measurement blackening.

2.3. Procedure

2.3.1. Preparation of samples and standards

A 600 mL solution of thorium nitrate was heated on a hotplate at $60 - 80$ °C until a crystalline structure was formed. About 100 mL of 1M HNO_3 was added to the crystalline $Th(NO_3)_4$ and heated again on a hotplate until the crystalline $Th(NO_3)_4$ was dissolved. The thorium nitrate solution obtained was filtered to obtain a clear thorium nitrate solution. A 100 mL thorium nitrate solution above was added into a 100 mL organic solution of TBP (30 %)-kerosene (70 %). The mixture was stirred for 10 minutes and the organic solution was separated from the aqueous solution. This step was performed three times. All organic phase were collected in a beaker glass, and then 250 mL of 3M HNO_3 was added and mixed for 1 hour, and eventually the organic and the aqueous phases separated. Striping process was performed by adding 250 mL of demineralized water and heating at a temperature of $60 - 70$ °C for about 1 hour. The organic phase was separated from the aqueous phase in a funnel separator. The thorium solution was then dried using a hot plate, and the thorium nitrate obtained was calcinated in a furnace at 850 °C for 3 hours.

2.3.2. Preparation of distillation carrier

950 mg of AgCl, 10 mg of Ga_2O_3 and 40 mg of LiF were weighed, and then mixed and homogenized in a mortar for 2 hours.

2.3.3. Preparation of standard boron and cadmium in ThO_2 matrix

0.011423 g of CdO and 0.988577 g of ThO_2 were weighed, and then mixed and homogenized in a mortar for 1 hour. The same procedure was repeated for 0.05719 g of H_3BO_3 and 0.942806 g of ThO_2. It was found that the amount of each standard cadmium and boron was 10000 ppm in the ThO_2 matrix. 50 mg of each standard boron and cadmium was weighed and mixed with 450 mg of ThO_2 matrix, and 1000 ppm of boron and cadmium was obtained. 50 mg of each standard (1000 ppm) was weighed and mixed with 400 mg of ThO_2, and 100 ppm of boron and cadmium was found in the ThO_2 matrix. The above powder mixture was subsequently diluted with ThO_2 and homogenized to obtain a series of standards which contained 0.3, 0.5, 0.7, 1, 3, 7 and 10 ppm of boron and cadmium in the ThO_2 matrix.

2.3.4. Preparation of electrodes

150 used primary cell graphite rod electrodes (UPCGREs) were collected, cleaned with purified water, and then dried. They were then divided into 3 groups: the first two groups were chemically treated and the third group was physically treated. The first and the second groups were soaked in water for 2 weeks and in nitric acid of low concentration for 1 week,

ISSN 1907–2635
82/Akred-LIPI/P2MBI/5/2007

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Emission Spectrograph Method
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respectively. The third group was heated in an oven at 300 °C for 2 hours. These treatments were intended to remove the impurities.

The chemically and physically treated UPCGREs were divided into two groups respectively. One group was shaped with lathe into a pencil-shape to be used as a counter electrode, and the other was made into a sample-carrying electrode with a sample cavity of 4.5 × 5.5 mm. The UPCGREs soaked in water and in nitric acid of low concentration were more difficult to obtain than the UPCGREs heated in the oven.

2.3.5. Operating condition and position of electrodes

100 mg of standards of ThO_2 were blended with 2% of AgCl and Ga_2O_3 mixture in a mortar. Standards of ThO_2 which contained various concentrations of boron and cadmium were introduced into the hole of the sample-carrying of the UPCGRE. The UPCGRE which had a pencil-shape was positioned in the upper electrode, meanwhile the sample-carrying electrode was in the lower electrode.

The source of the spectrographic emission was a dc arc with a current of 10 A, a voltage of 220 V and an exposure time of 25 seconds. The gap between the electrodes was 4 mm, which was kept the same during the excitation process. The detector of the X-ray film for thorax was cut as wide and long as a photographic glass plate of SA1. It was used to record the emitted spectra. Photographic emulsion and latent image were treated in a dark room and then exposed in recording spectra of the spectrograph.

The design of the counter and sample-carrying electrodes plays an important role in chemical and physical changes of the samples or standards, as shown schematically in Figure 1.
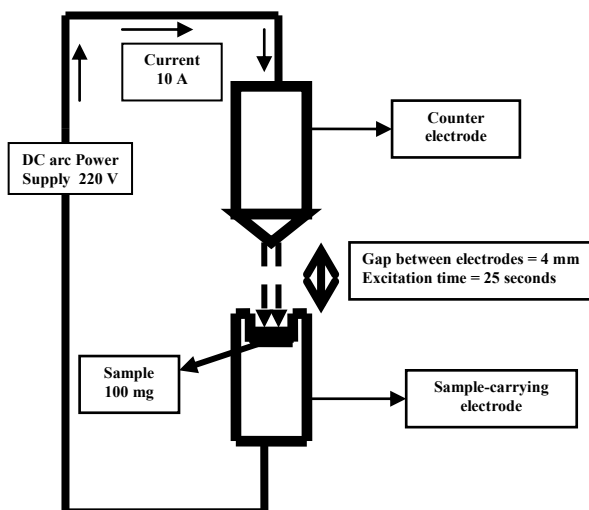

Figure 1. Counter and sample-carrying electrodes with sample and plasma.

III. RESULTS AND DISCUSSION

The first objective of the present study is to show the performance of UPCGRE for analyzing impurities boron and cadmium elements in thorium oxide, both qualitatively and quantitatively. The study is to establish whether the UPCGRE performance is sufficient to

analyze B and Cd elements in ThO_2. Qualitative analysis of B and Cd in thorium oxide is based on the wavelength emitted due to high temperature of the electrode. It can be applied to detect the presence or absence of B and Cd in thorium oxide sample. Quantitative analysis of B and Cd in thorium oxide is based on the intensities of B and Cd lines in the detector which can be tested by using calibration criteria.

3.1. Chemically Treated Used Primary Cell Graphite Rod Electrode (UPCGRE)

The nature of the UPCGRE is potentially exposed to some impurity elements which can enter into the inside of graphite through liquid or solution to contaminate graphite. Consequently, the UPCGREs used as an electrode in emission spectrograph has to be purified before it can be used for analyzing impurity elements. In others words, it is important to reduce the impurity elements in the UPCGRE either chemically or physically. In these experiments, chemical treatments were done by soaking some of the UPCGREs in nitric acid of low concentration for 1 week and in water for 2 weeks respectively. Of the total UPCGRE chemically treated, some were successfully machined to form as a standard graphite electrode which consists of working or sample-carrying electrode and counter electrode. So there was various collection of UPCGREs. Great care must be taken to ensure that all UPCGREs were accurately formed as a counter and sampling-carrying electrode. Fortunately, the size of UPCGREs is the same as that of the standard graphite electrode for emission spectrograph method, hence it is helpful in forming as an electrode. Since the sample and standards were in powder form, the design of sample-carrying electrode should have a hole at the end of the electrode where the sample or standard is introduced and kept during excitation. Sample-carrying electrode is acting as an atomizer of the sample where atoms of the analyte are produced, so the design of the sample-carrying electrode must have a constant hole.

If sample-carrying electrodes were formed properly, the thorium oxide sample and its impurities in powder form could be stable inside the sample-carrying electrode during excitation. Chemical and physical changes of the sample takes place in short time at a high temperature in the sample-carrying electrode. Therefore, ideal excitation process undergoes when no sample could pour out of the sample-carrying electrode during excitation. It is essential to have good design and quality of material of sample-carrying electrode where the sample is kept during the excitation. If the design of the sample-carrying electrode is not good and the material quality is not strong enough for high temperature, the sample will overflow out of the sample-carrying electrode. If this happens, then the analysis result will not be valid because it contains a gross error. Therefore, the quality and good design of the sample-carrying electrode are important in emission spectrograph. The amount of the sample in the sample-carrying electrode is also essential. In this experiment, the volume of 100 mg of sample ThO_2 is appropriate in sample-carrying electrode hole.

3.2. Complexity of High-speed Raising Temperature

When the button power of instrument was pressed and the arc was established, the electrons flowed from the counter electrode to the sample-carrying electrode Electrical energy was transformed into electrothermal energy, where ~30 % of the heat was in the counter electrode and 70% in the working or sampling-carrying electrode. From thermal excitation process point of view, higher temperature produces higher number of atoms that are excited, as given by the Saha equation:

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82/Akred-LIPI/P2MBI/5/2007

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$$N_j = N_o \ \frac{P_j}{P_o} \exp(-\frac{\Delta E}{kT})$$

where N_j = number of atoms in excited state
        N_o = number of atoms in ground state
        P_j = statistical factor in excited state
        P_o = statistical factor in ground state
        ΔE = energy difference between states
        K   = Boltzmann constant
        T   = temperature (Kelvin)

Chemical and physical performance of the sample or the reaction mechanism in sample-carrying electrode is very complex. The property of this experiment is unique as the change in the temperature of the system is so fast that the chemical and physical changes of the samples should be performed for a short time around 25 seconds. As a comparison, the Graphite Furnace Atomic Absorption Spectrometry (GFAAS) method requires three steps. Firstly, to dry the sample requires 20 seconds, which raises the temperature to 125 °C; secondly, to destroy the organic materials requires 60 seconds, which raises the temperature to 1600 °C; and thirdly, to atomize the analyte requires 10 seconds, which raises the temperature to 2100 °C. Overall, it takes ± 100 seconds for one experiment. In this experiment, the change in temperature from room temperature to the highest temperature of the electrode, which could reach ± 1000 °C, practically took 25 seconds. High-speed raising temperature of the electrothermal system would give rise to temperature variation in the sample-carrying electrode where the samples or standards were placed. Fortunately, the amount of sample was small so there was not much difference in temperature of the sample. Moreover, the operating conditions were kept constant during the excitation, so homogeneous temperature could be attained. Chemical and physical changes of the samples were assumed complete since the temperature in the sample-carrying electrode was homogeneous, the size of the sample was small, and the sample was assumed to be highly homogeneous.
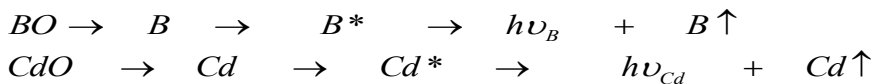
3.3. Performance of Chemically Treated UPCGREs

In these experiments, most UPCGREs used as a counter electrode were still in good shape but some of UPCGREs used as a sample-carrying or working electrode melted slightly after 10 seconds of arcing. It was different from the standard graphite counter electrode and the sample-carrying electrode that were still in good shape until 25 even 40 seconds of arcing. Based on the UPCGRE performance, the experiment should be done in less than 10 seconds in order to maintain the shape of the counter electrodes and the sample-carrying electrodes. In others words, the sample would not overflow out of the sample-carrying electrode during the 10 seconds of arcing. Less than 10 seconds of arcing results in less temperature of arcing, therefore the number of boron and cadmium excitation process in plasma will be low and their intensities will also be very weak. Eventually, low intensities will not produce good sensitivity for a calibration curve. On the other hand, excitation conditions with a current of 6 A, an arcing time of 40 second and a gap of 4 mm between electrodes produced maximum analysis of boron[7]. This indicates that the time of excitation is important. Generally, the abrupt increase of temperature will trigger chemical reactions of boron and cadmium oxide in thorium oxide in

J. Tek. Bhn. Nukl.
Vol. 5 No. 2 Juni 2009: 53–105

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82/Akred-LIPI/P2MBI/5/2007

sample-carrying electrode unexpectedly. Eventually, this is one of the sources of errors in chemical analysis.

3.4. Assumptions and Mechanisms of Chemical and Physical Changes of the Samples

The amount of samples or standards in the sample-carrying electrode in each experiment was small and assumed to be a highly homogeneous mixture. So reduction reaction would take place homogeneously in all samples or standards. They underwent chemical and physical changes completely because the temperature in the sample-carrying electrode was also assumed homogeneous. Therefore, the absorbance of each analyte was proportional to the number of analyte atoms in the samples or standards. Moreover, chemical reaction for atomization was assumed first order, where boron and cadmium atoms were produced. Excitation (physical change) took place in plasma where boron (B*) and cadmium (Cd*) were produced. They then emitted their specific wavelengths respectively before being released from the system. The overall chemical and physical changes for boron and cadmium oxide are as follows

$$BO \rightarrow \quad B \quad \rightarrow \quad B* \quad \rightarrow \quad h\upsilon_B \quad + \quad B\uparrow$$
$$CdO \quad \rightarrow \quad Cd \quad \rightarrow \quad Cd* \quad \rightarrow \quad h\upsilon_{Cd} \quad + \quad Cd\uparrow$$

where: B* and Cd*   = in excited condition
            h   = Planck's constant
            υ_B, υ_{Cd} = frequency of boron and cadmium respectively
            B$\uparrow$ and Cd$\uparrow$ = out of the system

Theoretically, the amount of analyte in plasma reflects the amount of analyte in the sample. Therefore, to increase the intensities of boron and cadmium, either using of the standard graphite electrode or the UPCGRE, the amount of the sample or standard to be excited has to be increased. Unfortunately, the amount of sample is limited due to the size of the cup in the sample-carrying electrode. If the amount of sample is increased, a larger cup size is required. So, the design of the sample-carrying electrode where the sample is placed will have to be altered. An increase of the intensities of the analyte will cause an increase of the sensitivity of the analysis method, which will lower the minimum detection limit.

3.5. Ideal Relationship between Intensity and Concentration

Since this method was a physical measurement, comparison approach was used for the determination of the analyte concentration in the sample. Firstly, the intensities of the standards were measured, as well as the intensities of the samples with similar operating condition. One of the important criteria for a physical measurement is the components of the standard and the sample should be as close as possible. By comparing the intensities of the analyte in the sample and the standard, the concentration of the analyte in the sample could be determined. The simplest comparison between the analyte intensity of the sample and the standard is through linear relationship. In general, the calculation using a calibration curve that forms a straight line, can mathematically be written as follows:

$$y = m\,x + a,$$

where   y   = intensity
          m   = sensitivity

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82/Akred-LIPI/P2MBI/5/2007

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x = concentration of analyte
a = intercept (intensity when the standard has no analyte)

From the experiments, the data of boron and cadmium intensities at various concentrations can be seen in Table 1.

Table 1. Experimental values of boron and cadmium intensities of UPCGREs soaked in water and acid.

No	Concentration (ppm)	I – B – Water	I – B – Acid	I – Cd – Water	I – Cd – Acid
1	0.3	0.161	0.163	0.039	0.043
2	0.5	0.197	0.122	0.011	0.038
3	0.7	0.089	0.155	0.024	0.008
4	1	0.052	0.149	0.011	0.008
5	3	0.118	0.122	0.005	0.033
6	7	0.152	0.239	0.003	0.049
7	10	0.182	0.189	0.007	0.047

Note: I – B – Water = Intensity of boron using UPCGREs soaked in water
I – B – Acid = Intensity of boron using UPCGREs soaked in acid
I – Cd – Water = Intensity of cadmium using UPCGREs soaked in water
I – Cd – Acid = Intensity of cadmium using UPCGREs soaked in acid

The data was divided into two groups, which were boron and cadmium. Each was depicted in Figure 2. The relationship between the concentration of boron and cadmium and their intensity for the UPCGREs treated in water and nitric acid was not linear or even exponential or logarithmic.
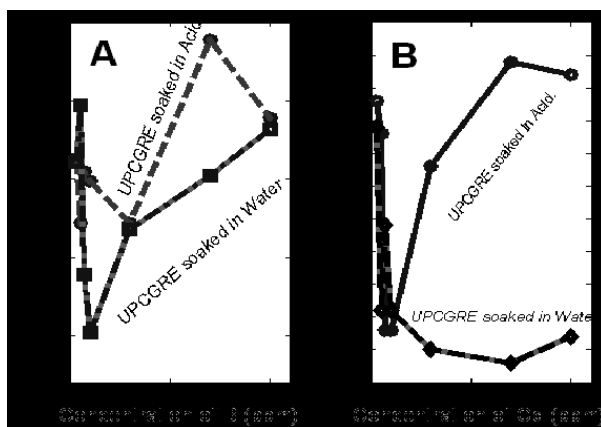

Figure 2. The relationship between concentration of boron and cadmium and the intensity

Since the relationship between concentration and intensity is not linear, exponential or logarithmic, consequently the sensitivity, precision, accuracy, range of linear and detection limit of both elements above, which are important criteria in analytical chemistry, could not been determined. Slightly melted sample-carrying electrode during a given period time of arcing did result in an obscure relationship between the concentration and the intensity. A gross

J. Tek. Bhn. Nukl.
Vol. 5 No. 2 Juni 2009: 53–105

ISSN 1907–2635
82/Akred-LIPI/P2MBI/5/2007

error occurred when using chemically treated UPCGREs, as the chemical and physical changes were not complete or the excitation process was not similar for all experiments. From the relationship between concentration and intensity, it can be seen that chemical treatment for UPCGRE was not successful to analyze boron and cadmium in thorium oxide with a dc arc source. This is a drawback for analyzing boron and cadmium by using of the UPCGRE treated chemically either with water or nitric acid of low concentration. The UPCGRE should be stable during the excitation process, as it is necessary. These limitations arise from the inability of the UPCGRE chemically treated at high temperature for 40 seconds. The shape of the UPCGREs after excitation process, especially the sample-carrying electrodes, can be used as a primary test to determine whether the experiment was correct or had a gross error.

3.6. Physically Treated Used Primary Cell Graphite Rod Electrode (UPCGRE)

Pure and strong electrode is an important criterion for analyzing impurity elements, besides hardness, melting point, ease/difficulty to prepare an electrode, and the required number of electrodes. Higher purity and hardness of UPCGRE can be made by physical treatment. Some of the UPCGREs were put in an oven at 300 °C for 2 hours. Carbon in graphite is not yet reactive with oxygen when treated at 300 °C for 2 hours, therefore simple physical treatment of the UPCGRE could be accomplished. For a temperature higher than 300 °C and a duration longer than 2 hours, some carbon in the graphite reacts with oxygen. The higher the temperature of the oven and the longer the sample in the oven, the easier it is for carbon in the UPCGRE to react with oxygen. Special equipment is needed to protect graphite from oxygen when UPCGRE is heated especially at a temperature greater than 300 °C for more than 2 hours. Physical parameters for having better UPCGRE, which are temperature and heating time, must be taken into account.

The UPCGRE developed in-house should undergo a complete performance as the standard graphite electrode in the emission spectrograph. If the performance of the UPCGREs is similar or at least close to that of the standard graphite electrode, the analytical important criteria can be determined through a calibration curve. To evaluate the performance of the physically treated UPCGREs for analyzing boron and cadmium in thorium oxide, the same experiment as that for the chemically treated UPCGREs was performed. The data obtained for boron and cadmium concentrations and their intensities using the physically treated UPCGREs and the standard electrode (Spex) can be seen in Table 2.

ISSN 1907–2635
82/Akred-LIPI/P2MBI/5/2007

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Emission Spectrograph Method
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Table 2. Experimental values of boron and cadmium intensities of physically treated UPCGREs and standard electrode (Spex)

No	Concentration (ppm)	I – B – Oven	I – B – Spex	I – Cd – Oven	I – Cd – Spex
1	0.3	0.125	0.259	0.026	0.125
2	0.5	0.130	0.265	0.027	0.137
3	0.7	0.137	0.276	0.034	0.149
4	1	0.143	0.291	0.038	0.155
5	3	0.152	0.328	0.060	0.194
6	7	0.171	0.387	0.086	0.252
7	10	0.182	0.432	0.108	0.309

Note: I – B – Oven   = Intensity of boron using UPCGREs treated in oven
       I – B – Spex   = Intensity of boron using standard electrode (Spex)
       I – Cd – Oven   = Intensity of cadmium using UPCGREs treated in oven
       I – Cd – Spex   = Intensity of cadmium using standard electrode (Spex)

The data could be used to obtain a calibration curve as shown in Figure 3. It is evident from the figure that the agreement between the concentration and the intensity for boron and cadmium is quite satisfactory. A very good agreement is observed between boron and cadmium calibration curves using the physically treated UPCGREs. As it can be seen in Figure 3, the calibration curves for boron and cadmium using the standard electrode have higher sensitivity than those using the physically treated UPCGREs. From calibration curve point of view, the physically treated UPCGREs possess lower background than the standard electrode (Spex). The utility of the physically treated UPCGREs is better than the standard electrode when the sample has low concentration.
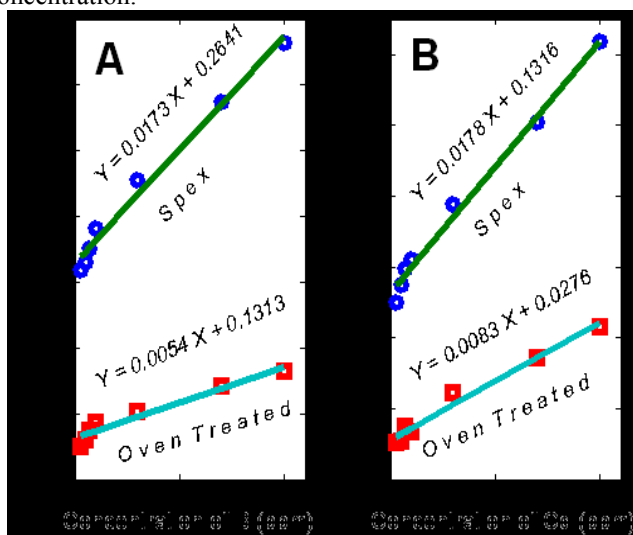

Figure 3. Calibration curves of boron and cadmium

Changing the design or the size of the electrode is an alternative method to increase the amount of sample, which is proportional to the number of impurity elements excited when

the exciting process takes. In order to enhance the intensities of boron and cadmium in thorium oxide using UPCGRE, the amount of sample in the sample-carrying electrode should be increased significantly. A new design and a larger sample-carrying of the physically treated UPCGRE are necessary.

IV. CONCLUSIONS

1. Physically, the combination of dc arc as a source of excitation, powder sample and the chemically treated UPCGRE as alternative electrode can be used as long as the exposure time is less than 10 seconds. This method is applicable for high concentration only.
2. Chemically, an exposure time of less than 10 seconds will not produce a good calibration curve, since the temperature for arcing is not high enough to initiate the chemical and physical changes where the excitation process is based on.
3. An exposure time of less than 10 seconds requires a different design and a change in the size of the sample-carrying electrode with a greater volume of sample-carrying hole.
4. The physically treated UPCGRE can be used for analyzing boron and cadmium in thorium oxide if the concentration of the sample is low.
5. The physically treated UPCGRE should be carried out in a special oven in order to obtain similar physical and chemical properties as those of the standard graphite electrode.

V. ACKNOWLEDGEMENT

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