
APPLICATION IRON AND ALUMINUM ELECTRODES IN EMISSION SPECTROGRAPH FOR ANALYZING BORON AND CADMIUM IN URANIUM NUCLEAR FUEL

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ABSTRACT

APPLICATION OF IRON AND ALUMINUM ELECTRODES IN SPECTROGRAPH EMISSION FOR ANALYZING BORON AND CADMIUM IN URANIUM NUCLEAR FUEL. Analysis of boron and cadmium in nuclear fuel was carried out using iron and aluminum electrodes as well as X-ray film photographic for thorax in emission spectrograph. DC arc excitation source could not be used for iron and aluminum electrodes, since both electrodes melt even at current less than 10 ampere and excitation time less than 2 seconds. AC sparks excitation source using iron and aluminum electrodes could be used for analyzing boron and cadmium after extraction of uranium in nuclear fuel using TBP-kerosene solution. Graphite electrode was also utilized to analyze boron and cadmium with ac sparks method for comparison. X-ray film photographic for thorax was used to replace glass photographic film SA-1. Halogens elements could not be analyzed using this method because they needed higher temperature for excitation. Calibration curves for boron and cadmium were prepared for each electrode for quantitative analysis, sensitivity calculation and detection limit. It was found that the sensitivity for cadmium metal using aluminum electrode was higher than that using iron electrode, even with respect to graphite electrode. Limit of detection of cadmium using aluminum electrode was the lowest although its intercept was the highest. On the other hand, limit of detection of boron using graphite electrode was the lowest but its intercept was the highest.

FREE TERMS: Iron and aluminum electrodes, Emission spectrograph, Graphite electrode

ABSTRAK

PENGGUNAAN ELEKTRODE BESI DAN ALUMINIUM PADA SPEKTROGRAFI EMISI UNTUK ANALISIS BORON DAN KADMIUM DALAM BAHAN BAKAR NUKLIR URANIUM. Analisis boron dan kadmium dalam bahan bakar nuklir dilakukan menggunakan elektrode besi dan aluminium serta pelat film sinar-X untuk toraks pada spektrografi emisi. Sumber eksitasi dc arc tidak dapat digunakan untuk elektrode besi dan aluminium karena kedua elektrode tersebut meleleh meskipun arus kurang dari 10 A dan waktu eksitasi kurang dari 2 detik. Sumber eksitasi ac sparks menggunakan elektrode besi dan aluminium dapat digunakan untuk analisis boron dan kadmium setelah uranium dalam bahan bakar nuklir diekstraksi menggunakan larutan TBP-kerosin. Elektrode grafit juga digunakan untuk analisis boron dan kadmium dengan menggunakan sumber eksitasi ac sparks sebagai perbandingan. Pelat film sinar-X untuk toraks digunakan untuk menggantikan film gelas fotografi SA-1. Unsur-unsur halogen tidak dapat dianalisis dengan metode ini karena unsur-unsur halogen membutuhkan suhu yang lebih tinggi untuk eksitasi. Kurva kalibrasi untuk boron dan kadmium dibuat untuk setiap elektrode untuk analisis kuantitatif, perhitungan sensitivitas dan batas deteksi. Hasil menunjukkan sensitivitas untuk logam kadmium menggunakan elektrode aluminium lebih tinggi dibandingkan elektrode besi, bahkan terhadap elektrode grafit. Batas deteksi kadmium

menggunakan elektrode aluminium paling rendah tetapi nilai titik potongnya paling tinggi. Sebaliknya, batas deteksi boron menggunakan elektrode grafit paling rendah tetapi nilai titik potongnya paling tinggi.

KATA KUNCI: Elektrode besi, Elektrode aluminium, Spektrografi emisi, Elektrode grafit

I. INTRODUCTION

Nuclear fuel that is widely used in nuclear reactor is uranium oxide or uranium metal. Mining and milling is the first step of the nuclear fuel cycle, in which uranium ores are first crushed and ground. The product of a uranium mill is not directly usable as a nuclear fuel in reactor. The end products of leaching processes are not only extracts of uranium but also several other metals like Fe, Pb, As, Se and Cd, as well as nonmetals like F, Cl, Br, I, B and Si. Uranium as a nuclear fuel should be free from impurity elements, especially strong neutron absorbers such as B and Cd.

The flow chart diagram below gives a general view of the process as a part of nuclear fuel cycle and the main streams of impurity analysis in nuclear fuel cycle. If the purified uranyl-nitrate material or sample is nuclear grade, the sample will go to fabrication, otherwise the sample will be purified again, as shown in Figure 1. Spectrograph emission is used as a quality control of purified uranyl-nitrate [1,2,3,4].

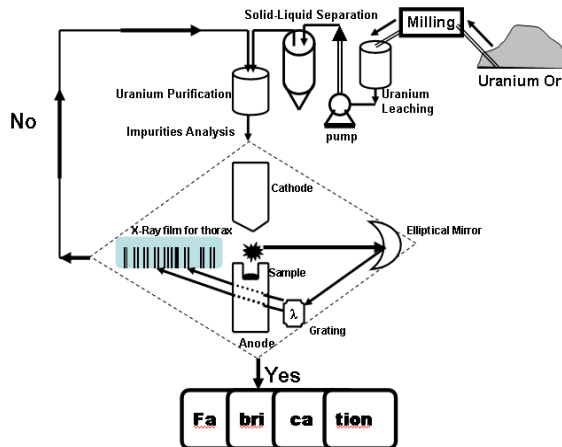


Figure 1. Flowchart of a part nuclear fuel cycle and the main stream impurities analysis

There are some sensitive techniques which can be included in the flowchart decision, such as Atomic Absorption and Inductively Coupled Plasma (ICP) which are able to analyze some impurity elements in uranium quantitatively after removing all uranium in the sample^[5]. The application of Optical Emission Spectrograph (i.e. dc arc) in direct analysis of impurity elements in uranium oxide has been done conventionally. In any case, the selection of graphite electrode and photographic glass plate for impurities analysis in uranium oxide has to take into account physical and chemical parameters such as melting point, conductivity, purity and range of concentration. The use of graphite electrode and photographic glass plate SA-1 is

recommended. The problems of using graphite electrode and photographic glass plate SA-1 as a detector are they are difficult to obtain in the market and also very expensive. To overcome these limitations, the graphite electrode has to be replaced with iron and aluminum electrodes whereas photographic glass plate SA-1 has to be replaced with X-ray film for thorax. Iron and aluminum metals physically can easily be formed as an electrode for emission spectrograph. These metals have good electrical and thermal conductivity, are strong and can be heated up to high temperature. So, both iron and aluminum can replace graphite electrode. Since iron and aluminum emit their spectra, iron electrode is used as an electrode for analyzing aluminum, and vice versa.

Metals and nonmetals will emit resonance line when samples are put in hot condition. Resonance line of metals will emit in long wavelength, while nonmetals will emit in short line. Moreover, nonmetals especially halogens are not easy to excite because of their physical properties, and therefore special equipment is needed in order to meet this experiment. On the other hand, aluminum monohalogenes will emit their resonance lines on ultraviolet region such as AlCl and AlBr that emit at wavelengths of 2614 Å and 2790 Å respectively, which are close to metal resonance lines. All resonance lines could be recorded by X-ray film for thorax.

This paper presents the limitations of iron and aluminum electrodes as a replacement of graphite electrode and X-ray film for thorax as a replacement of photographic glass film SA-1 as a detector for analyzing impurities of nuclear fuel oxide uranium. It also describes the applicability and versatility of iron and aluminum electrodes for simultaneous determination of boron and cadmium in aqueous phase as impurities of nuclear fuel simulations.

II. EXPERIMENTAL

2.1. Materials

1. Uranium dioxide (CAMPT), HNO₃ (Merck), TBP, kerosene (Fisher)
2. AgCl, Ga₂O₃ (Spec Industries)
3. Iron and aluminum rods (CAMPT)
4. Standard solution of boron 10 ppm, as H₃BO₃ (Spec Industries)
5. Standard solution of cadmium 10 ppm, as CdO (Spec Industries)
6. Standard solution of chloride 10 ppm, as HCl (Spec Industries)
7. Standard solution of bromine 10 ppm, as HBr (Spec Industries)

2.2. Equipment

1. pH Meter (Mettler)
2. Oven and furnace
3. Emission spectrograph 3.4 m (Jarell-Ash)
 - Slit width : 10 µm
 - Grating : 590 grooves mm⁻¹
 - Exposure time : 25 seconds (for ac spark)
 - Electrode gap : 2 mm
 - Current : 10 A
 - Voltage : 220 V
 - Excitation : Jarell-Ash model various source dc arc and ac sparks
 - Electrodes : Iron and aluminum electrodes were formed into ring-O drof. The lower electrode (anode) had a sample cavity of 4.5×5.5 mm while the upper electrode had pencil-shape.

- Photographic plates : X ray film for thorax (Kodak)
4. Densitometer (Jarell-Ash). The system was also equipped with microphotometer: Jarell-Ash, microphotometer with 7 μm slit and 0.5 mm slit height for measurement blackening.

2.3. Procedure

A solution of uranyl nitrate hydrate ($\text{UNH} = 250 \text{ g/L}$) in 3 M HNO_3 was divided into two parts. One part of the uranyl nitrate sample solution was dried completely before being changed into U_3O_8 in furnace at 600 $^\circ\text{C}$ for 3 hours. Furthermore, impurities Cl, Br, I, B, Si, Cd, Al, Fe, Cr, Ni and Pb in U_3O_8 were analyzed directly using dc arc method. The other one was to be extracted by TBP-kerosene as an organic phase. An aqueous phase containing impurity elements was evaporated until a moist mass remained. The residue was dissolved in dilute HNO_3 and the volume was made up to 5 mL. Standards were prepared by mixing standards solution above and evaporated until a moist mass remained. The residue was dissolved in dilute HNO_3 and the volume was made up to 5 mL.

100 mg of U_3O_8 sample was blended with 2% of mixture AgCl and Ga_2O_3 in a mortar. Sample was placed into iron and aluminum cup or sample cavity lower electrode. Venting was used in order that each sample in lower electrode hole did not pour out during the excitation process. Iron or aluminum upper electrodes were situated in the upper electrode which had pencil-shape. The spectrographic emission was operated in dc arc at a fixed voltage of 220 V.

Samples and standards solutions were analyzed by ac spark spectrographic emission method. They were then dropped to cup of lower iron and aluminum electrodes and dried slowly. The spectrographic emission was operated in ac spark at a fixed voltage of 220 V. Calibration curve of each metals and nonmetals impurities were made based on the intensities or the amount of darkening or blackening of their analyte lines in the range of concentrations in each standard.

Photographic plates used X-ray film for thorax. X-ray film for thorax was cut in the dark room with the same width and length as those of glass film SA-1 in order to be suitable for glass film SA-1 box. Emitted lines on recorded film for thorax were measured by densitometer qualitatively for all elements mentioned above and quantitatively for elements which could be analyzed and whose intensities were at least three times higher than their background.

III. RESULTS AND DISCUSSION

Analysis of impurity elements in uranium as a nuclear fuel is divided into two methods, one is in solid condition or dc arc method and the other is in solution condition or ac spark method. Analyzing impurity elements in triuranium octaoxide U_3O_8 , in solid condition by dc arc method using iron and aluminum electrode is not satisfying because both electrodes melt, even in less than 2 seconds of excitation when the power is 220 V and 10 A. So this method or direct method is not suitable for analyzing impurity elements in U_3O_8 because dc arc excitation produces high temperature and needs much time for exposure. On the other hand, iron and aluminum electrodes are not strong enough for high temperature. The lower arc current 8 A method might be useful for iron and aluminum electrodes, but unfortunately iron and aluminum electrode still melt in less than 2 seconds. Melted iron and aluminum electrodes will worsen excitation system because the distance between anode and cathode will be longer, and analyzed samples will pour out of the electrode. If iron and aluminum electrodes were used in

excitation system, samples and standards would not be analyzed in standard condition. Ideally, excitation system should be stable during the excitation process for samples and standards because intensity of samples will be compared to calibration curve of standards. This is a disadvantage of iron and aluminum as an electrode in emission spectrograph besides the fact that each of them emits its spectrum.

3.1. Optimization

Synthesized solution of standards above was placed on lower cavity of iron and aluminum electrodes, and X-ray film was used as a detector to replace glass film SA-1. Synthesized solutions were dried slowly and excited by ac spark method. Power of excitation such as voltage, current and time of exposure was varied. The voltage was found to be 220 V and the exposure time 25 seconds. The size of X-ray film before and after excitation process was the same. Iron and aluminum electrodes after excitation process do not change physically at all, so samples can be compared to standards solutions. Qualitative analysis was done for metallic elements such as aluminum (using iron electrode), cadmium, chromium, lead, and nickel, and also for nonmetallic elements such as silicon, boron and halogen. Fortunately, boron and cadmium could be analyzed using iron and aluminum electrodes qualitatively and quantitatively. On the other hand, other elements could not be detected even qualitatively for halogen needs high temperature and special equipment to lessen air absorption in spectrograph emission. Other elements lines might be interfered by each electrode line.

3.2. Preparation of Impurity Element Solution

Impurity elements and triuranium octaoxide U_3O_8 were dissolved in 3 M HNO_3 . After extraction with TBP-kerosene, uranyl nitrate was in organic phase meanwhile all impurities were still in aqueous solution. Aqueous solutions and standards were dropped and dried slowly to lower iron and aluminum electrode. Solutions on lower cavity iron and aluminum electrodes were dried slowly in order to increase the impurity elements that could be excited and to have stable excitation process. Stable condition process during excitation necessitates this condition because standards will be used as a calibration curve and sample will be calculated based on calibration curve, otherwise comparison will not be correct. Measurements of intensity of samples and standards were taken under 220 V, 10 A and 25 seconds of excitation which was the optimum operating condition by means of ac spark method using iron and aluminum electrode. Based on the above conditions, the calibration curve of each element was formed and the concentration of each impurity element could be calculated, as shown in Figure 3.

3.3. Analysis of Impurity Elements with Graphite Electrode

As a comparison, graphite electrode was also done as iron and aluminum electrodes. Standards were dropped and dried slowly to lower graphite electrode and were excited under 220 V, 10 A and 25 seconds of excitation as it was done to iron and aluminum electrodes. X-ray film as a detector was also used in this method and the result can be seen in Figure 2.

3.4. Detector

X-ray film can interact as well as glass film SA-1 with emitted lines after diffracting in spectrograph emission. Calibration of lines has been done previously^[10,11] so detectors of X-ray film were treated as a glass film SA-1 in developing and fixing in the dark room.

Measurement of density of each analyzed element in the X-ray film was also done in densitometer as in glass film SA-1.

3.5. Choice of Spectra Lines

Since iron and aluminum electrodes are strong enough for using ac sparks as a source of excitation and nonmetals silicon and boron emit their resonance lines in air, both of them could be analyzed by emission spectrograph. Iron and aluminum resonance lines were recorded in the X-ray for thorax as a detector, and some resonance lines of iron will interfere with boron resonance lines. Resonance line B(I) 2497,73 Å will be located close to Fe(II) 2497,82 Å, but those lines are well separated. Meanwhile Fe(I) 2497,72 Å has low intensity and it will not enhance the intensity of B(I) 2497,73 Å. Fortunately, all interference resonance lines have low intensity, as a comparison the intensity of B(I) is 500. Boron spectra are nonmetal impurities which have high nuclear cross section, and will be recorded in the X-ray for thorax as a detector and they can easily be analyzed since other spectra which are close to boron can be ignored. Boron emits two resonance lines, which are B(I) 2497,73 Å and B(I) 2496,78 Å as a consequences of transition electron $^2S_{1/2} - ^2P_{3/2}$ and $^2S_{1/2} - ^2P_{1/2}$ respectively. Silicon emits its lines in Si(I), so it will not interfere with boron lines, because the grating ($590 \text{ lines mm}^{-1}$) used is strong enough to separate those lines.

Cadmium as a metal which is also a strong absorber will emit resonance in many wavelengths, but only one of them has strong intensity. Cadmium which emits resonance lines above 3000 Å which have weak intensities and they can be ignored, but cadmium resonance line 2288,022 Å has strong intensity and it is accompanied by Fe(II) 2287,250 Å and As(I) 2288,12 Å which have weak intensities. So resonance lines of Cd(I) 2288,022 Å can be assumed as a results of Cd alone. Resonance lines of Cd and their interferences can be described in Figure 2.

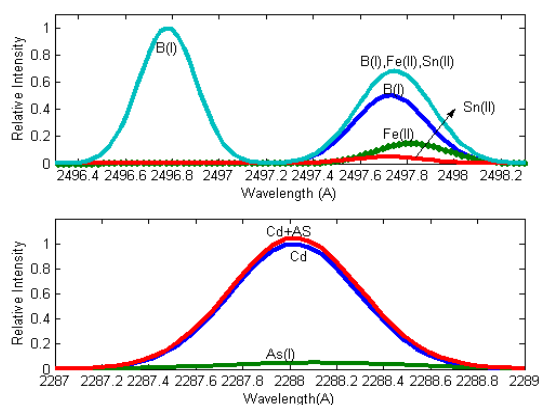


Figure 2. Spectra of strong neutron absorbers boron and cadmium with their interferences

When accurate analysis of impurity elements in uranium oxide at ppm level is needed but using iron and aluminum as an electrode in emission spectrograph, ac sparks should be used as a source of excitation because this source does not destroy iron or aluminum as an electrode when impurity elements of uranium oxide sample are analyzed. Metals and

nonmetals emit the resonance lines including iron and aluminum as an electrode. Since most elements in the excitation-deexcitation system are iron and aluminum, both elements will be recorded with nonmetal and metal impurities. Nonmetal and metal impurities are accompanied by strong resonance lines of electrode. Iron and aluminum are not the object to analyze because both of them have low neutron absorber. Element which has strong neutron absorber is the object to analyze and its interferences, because they will increase the intensity of element to be analyzed. As mention above, boron will emit resonance lines close to Fe resonance lines. So theoretically boron 2497,8 Å will not be analyzed using iron electrode; on the other hand, boron 2496,78 Å is free of interference and can be used for analyzing boron using of iron electrode.

3.6. Comparison of Calibration Curves

Emission spectrograph method is a comparison method which means sample and standard were treated as close as possible. Since the objective of this experiment is to study the possibility of using iron and aluminum as an electrode in emission spectrograph, impurity element of uranium oxide was used as a sample. Graphite electrode was also used as a comparison for the same sample and operation condition. Boron and cadmium standards solution were prepared from standard material of H_3BO_3 , CdO, HCl and HBr, in which each standard solution contained 0.1 – 1 µg mixture standard material above which were then excited and their intensities were measured. Iron electrode was the least sensitive for analyzing cadmium. Analytical calibration curves were generated by measuring intensities of boron and cadmium lines emitted when synthetic reference solution was excited in emission spectrograph. The analytical wavelengths were evaluated and selected, so that no spectral interference correction was made. Analysis was performed using the 6-point calibration approach and measurements were made in triplicate. The quality of the curves was indicated by the value of the correlation coefficient, that is the slope of the calibration curve. In addition, the use of closely matched standard and samples is recommended to reduce or to minimize the error in analysis. For analyzing cadmium, aluminum electrode is better than graphite and iron because it is the most sensitive calibration curve. Iron electrode is the least sensitive for analyzing cadmium., and the use of aluminum electrode is more sensitive than the other electrodes (iron and graphite), as indicated in Figure 3.

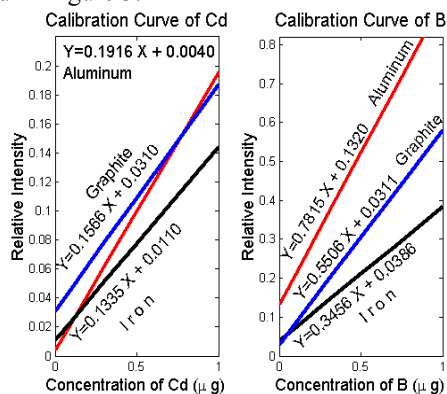


Figure 3. Calibration curves of cadmium and boron with aluminum and iron as an electrode, with graphite electrode as a comparison

It should be noted that the calibration curves of boron analysis with iron and aluminum electrodes were promoted, especially with aluminum electrode. From analytical point of view, the sensitivity of boron analysis with aluminum electrode is so high in comparison with iron electrode. The sensitivity of calibration curve of boron using aluminum electrode was 0.7815, which was a very promoting numerical value.

For low concentration, however, iron electrode is better than aluminum electrode because the background of iron is lower than that of aluminum electrode. Both calibration curves are not linear for high concentration, boron calibration curve with iron curved faster than aluminum electrode. Thus for analyzing boron at high concentration, aluminum electrode is recommended and for low concentration iron electrode is recommended.

Under standard conditions, analyses of cadmium metal in standards and samples were also carried out using iron and aluminum electrodes. The analytical results obtained so far are not very promoting because from calibration point of view, the sensitivity of both calibration was not high. Sensitive calibration curve is required for analyzing cadmium in nuclear fuel since cadmium is a strong neutron absorber. Calibration curves of cadmium have low sensitivity, 0.1335 for iron electrode and 0.1916 for aluminum electrode. There is actually no minimum sensitivity for calibration curve. Those calibration curves could be used for high cadmium concentration, with aluminum electrode more sensitive than iron electrode.

Based on the calibration curves above, the concentration of boron and cadmium could be calculated. The measurements were repeated five times, and the range of concentrations was obtained with the final result given as the average value. Samples which were synthesized are shown in Table 1.

Table 1. Analysis results of boron and cadmium in synthesized uranium sample

Element \ Electrode	Cadmium (added 0.5 μg)	Boron (added 0.6 μg)
Aluminum	Range of concentration 0.39 – 0.56 μg Average 0.4569 μg	Range of concentration 0.45 – 0.61 μg Average 0.5320 μg
Graphite	Range of concentration 0.39 – 0.65 μg Average 0.5280 μg	Range of concentration 0.50 – 0.68 μg Average 0.5660 μg
Iron	Range of concentration 0.38 – 0.67 μg Average 0.5500 μg	Range of concentration 0.34 – 0.60 μg Average 0.5040 μg

The results show that the average for analyzing cadmium using aluminum electrode is lower but higher using iron and graphite. On the other hand, for analyzing boron all electrodes produce lower result. The range of concentrations for boron, however, covers the added value of synthesized sample.

3.7. Detection Limit

One of the main issues in micro chemical analysis is detection limit. According to International Union Pure and Application Chemistry (IUPAC), limit of detection (LoD) expressed as the concentration, c_L or q_L , is derived from the smallest measure, x_L , that can be detected with reasonable certainty for a given analytical procedure. The value of x_L is given by the equation $x_L = x_{bl} + k s_{bl}$, where x_{bl} is the mean of the blank measures, s_{bl} is the standard deviation of the blank measures, and k is a numerical factor chosen according to the confidence level desired. Numerical factor k was chosen as 3, so under the optimized operating condition, the measurements of the blanks for iron and aluminum electrodes were done. Detection limit of cadmium and boron is shown in Table 2.

Table 2. Detection limit of cadmium and boron using aluminum, iron and graphite electrodes

Electrode	Cadmium (μg)	Boron (μg)
Aluminum	0.1174	0.0845
Iron	0.2831	0.1233
Graphite	0.3459	0.0692

From limit of detection point of view, aluminum is the best electrode for analyzing cadmium and boron in low concentration and the intercept of calibration curve of cadmium was low but boron calibration curve was the highest. The performance of aluminum electrode was opposed to graphite electrode whereas iron electrode was in between of aluminum and graphite. Therefore, the use of graphite electrode is suitable for low concentration of boron but not for low concentration of cadmium. On the other hand, aluminum electrode had low limit of detection for analyzing boron but its calibration curve had highest intercept, which was the weakness of aluminum electrode.

IV. CONCLUSION

1. Iron and aluminum electrodes cannot be used as an electrode for dc arc method even at low power source because they melt. However, both can be used as an electrode for ac spark source because their form do not change at all.
2. Iron and aluminum electrodes are only used in ac spark and sample form should be in a liquid dried form.
3. The application of iron and aluminum electrodes for the determination impurity elements in U_3O_8 is severely limited due to low temperature to excite sample in ac spark method, so the amount of sample excited is also limited.
4. Boron and cadmium resonance lines are not close to iron and aluminum lines when the source is ac spark. This is the advantage of using iron and aluminum electrodes, and ac spark source.
5. The weakness of these methods is that only limited number of excited analytes is produced, so that the sample concentration should be high enough in order to get enough number of excited analytes.
6. Halogens cannot be analyzed by this method. Special treatment and instrument are needed to record the halogen spectra.

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