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Determination of Boron in Zircaloy by using ICP-AES and Colorimetry

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1. Introduction

Zircaloy has been being widely used in the nuclear industry because of the low cross section of Zirconium against a thermal neutron.

Accurate composition data of Zircaloy for Hf, B, and so on having a high cross section against thermal neutron is important to use it as a nuclear material. Accordingly proper determination methods of these elements in Zircaloy are needed.

In this study, the application of two methods[1,2], ICP-AES and a colorimetry using methylene blue were investigated in order to establish a proper analysis method of Boron in the range from tens to hundreds ug B/g sample of Zircaloy.

2. Experimental

2.1. ICP-AES method

Five 0.25g of Zr-4 (SRM , <5 ug B/g) samples with 0, 10, 30, 50, 100ug of Boron (SRM) were dissolved with the procedure of ASTM E 146 and the final volumes were made up to 10ml. The emission intensities for Boron of the solutions were measured at the wavelengths, 208.893, 208.959, 249.773nm and were compared to the intensities for the standard Boron solutions without Zr.

The same procedure as above was again performed against 0, 1, 3, 5, 10ug of Boron (SRM) with four 0.25g of Zr-4 (SRM , <5 ug B/g) samples.

2.2. Colorimetry method

Two different amounts of Zr-4 (SRM , <5 ug B/g) samples(one is 0.1g and another 0.2g) with 0, 1, 2, 5, 10ug of Boron (SRM) were dissolved and treated with HF, methylene blue to make the Boron BF_4^--methylene blue complex and a final volume of 10ml. The BF_4^--methylene blue complex in the solutions was extracted with 10ml of 1.2-dichloroethane and measured at a wavelength 650nm by using a spectrophotometer.

Calibration curves were prepared for the two cases above of different amounts of Zr-4 and for pure Boron standards.

3. Results and discussion

3.1. ICP-AES method

In order to investigate the matrix effect of Zircaloy, from the experimental results of 2.1., relation curves of the measured values of five Zr-4 (SRM , <5 ug B/g) samples to calculated values of the pure Boron standard solutions were prepared(Fig.1,2).

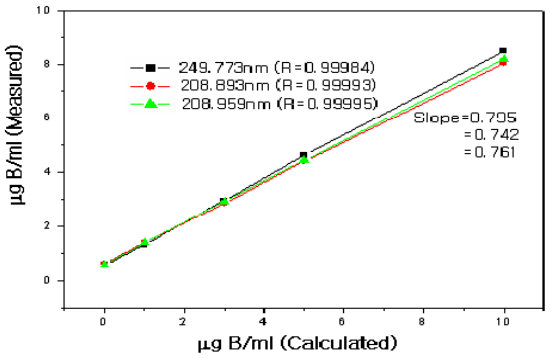

Fig. 1. Relation curve between the calculated and measured values for 0 - 10 ug B/ml(standard) in the Zr-4 matrix.

Fig. 1. shows that the relation between the calculated and measured values are all more than 0.999 at the three wavelengths, 208.893, 208.959, 249.773nm.

It indicates that the dynamic range of ICP-AES is good in the range of 0 - 10 ug B/ml in the Zr-4 matrix.

But the ratios, measured values to calculated values, are 0.742, 0.761, 0.795 at each wavelength. It indicates that the matrix effect of zircaloy is not small when Boron is measured in the Zircaloy matrix by using ICP-AES directly.

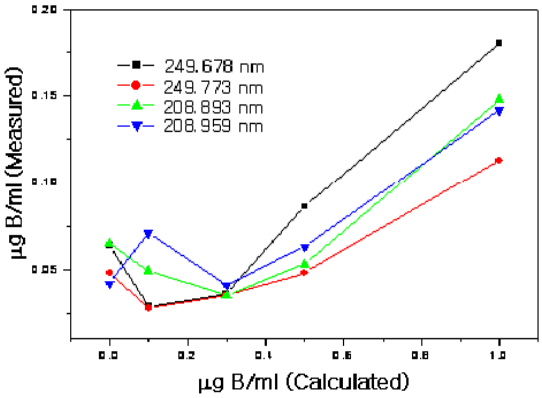

Fig. 2. Relation curve between the calculated and measured values for 0 - 1 ug B/ml(standard) in the Zr-4 matrix.

Fig. 2. shows that the degree of relation between the calculated and measured values looks poor. And the ratios, measured values to calculated values, are less than 0.2. It indicates that the matrix effect of zircaloy is big in the range of 0 - 1 ug B/ml in the Zr-4 matrix.

From the experiments as shown Fig.1, Fig.2, the ICP-AES method gives a proper result in the range of 0 - 10 ug B/ml in the Zr-4 matrix, while on the other hand it is not adequate in the range of 0 - 1 ug B/ml in the Zr-4 matrix .

3.2. Colorimetry method

In order to investigate matrix effect of Zircaloy when colorimetry of BF_4^--methylene blue complex is used, calibration curves against two cases of different amount of Zr-4 and plus against pure Boron standard solutions are prepared from the experimental results of 2.2. (Fig.3.).

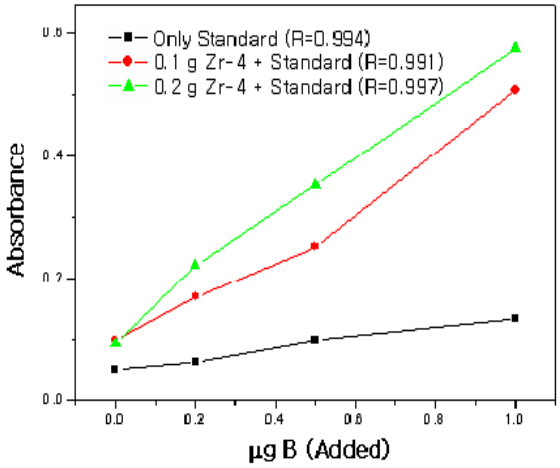

Fig. 3. Calibration curves depending on the amount of Zircaloy

Fig. 3. shows that the slopes of the calibration curves vary depending on the sample matrix composition. Especially the absorbance increases in the Zircaloy matrix compared to the case of only the standard Boron. It indicates that the matrix effect of zircaloy exists in some analysis steps of this colorimetric method, that are a complexation step or a extraction step.

In spite of the matrix effect, the colorimetry method using methylene blue could be used for a relatively low level of a Boron concentration sample.

4. Conclusion

For the determination of Boron in Zircaloy, the ICP-AES method can be used for a relatively high concentration of 0 - 10 ug B/ml in the Zircaloy matrix and a colorimetry method using methylene blue can be used of 0 - 1 ug B/ml in the Zircaloy matrix. Both methods need to apply a standard addition method to overcome the matrix effect.

REFERENCES

[1] Bernhard A. Zarcinas and Brian Cartwright, "Acid Dissolution of Soils and Rocks for the Determination of Boron by Inductively Coupled Plasma Atomic Emission Spectrometry", ANALYST, Vol.112, 1987.
[2] "Analysis of Zirconium and its Alloys", JAERI 4050, 1969