

Study on On-line Trace Analysis Technique for SG Tube Leakage Monitoring

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1. Introduction

In recent days, a leakage symptom of the steam generator tube of domestic nuclear power plants (NPPs) is emerging in accordance with aging NPPs due to the long-term operation and increasing numbers of power plants. The possibility of leakage of steam generator tube is gradually increasing because the equipment gets aged as it operates overtime. NPPs steam generator leakage monitoring method is mainly adopted in the world. Since this method is using nuclear fission product of certain radionuclides (¹⁶N, ³H, Xe, etc.), it is only available when the reactor power is more than 20%. Therefore, it requires alternative techniques of real-time leakage monitoring under a variety of operation conditions such as start-up, abnormal environment of NPPs, etc [1-3].

Boron (B) which exists mostly nonionic particle state has been weakly ionized, revealing the lowest anionic tendency in aqueous phase ($\text{SO}_4^{2-} > \text{Cl}^- > \text{F}^- > \text{SiO}_2^- > \text{HBO}_3^-$) [4]. In general, B has been titrated with a NaOH solution into a new compound forming a strong alkaline anion after being dissociated with addition of a polyhydric alcohol. And that has been also measured amplified conductivity that reacting directly polyhydric alcohol by conductivity detector. GE (General Electric Company) has applied monitoring equipment of ultrapure water production by using mannitol reagent as polyhydric alcohol, which is detected less than 20 ppb of boron in the semiconductor company.

However, the separation of boron among the secondary water system has been regarded as a critical issue because it contains a lot of impurities and particulate materials which are N₂H₄, NH₃, ETA and component of the iron in the system. This study is a follow-up study concerning the separation of boron peak presented at the 2013 Korean Nuclear Society [1]. This study indicates the possibility of analysis of trace-level boron. The study performed a new method, which is considering the conditions of on-line monitoring such as a single peak, a short analysis time, a low pressure for durability and maintenance of operation parts, to separation of some anion peaks in terms of on-line monitoring.

2. Methods and Results

In this part, includes the results of experiments concerning the separation of boron and anion peaks. The forms of boron in liquid phase and mechanism which reacts between boron and polyhydric alcohol are also described.

2.1 Materials and Methods

All solutions were prepared with deionized (DI) water. Boric acid (H₃BO₃, 99.5%, Sigma Aldrich), sodium fluoride (NaF, 99%, Sigma Aldrich), sodium hydroxide (NaCl, 2N in H₂O) and sodium sulfate (Na₂SO₄, 99.0%, Sigma Aldrich) were selected at 1 ppm, respectively. The following solvents are used as eluent: Mannitol (C₆H₁₄O₆, 98%, Sigma Aldrich) and methan sulfonic acid (MSA; CH₃SO₃H, 99.5%, Sigma Aldrich). They were diluted to 20 and 60 mM, respectively. Boron was analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES; Thermo Fisher Scientific Inc. iCAP6300). The concentration of anions was detected by Ion chromatography (IC; DIONEX ICS-500).

Figure 1 shows a flow-sheet to separate of boron peak with anion peaks in this study. This system comprises ion chromatography (DX-120, Dionex corp.) equipped with C_B column. C_B column is composed of chelate-type resin which is selectively trapped with boron ion. This study was carried out in 3 steps: load, rinse and injection mode. The first sample was obtained from a solution passed through the C_B column. In the load mode, the C_B column is concentrated at 5 mL/min from an outlet side. Through this step, the other anion is released immediately from the C_B column, while boron is only remained in this column. Subsequently, anion remained on the line can be completely removed at the rinse step. Finally, the boron trapped in the column was obtained by through MSA and mannitol dissociating the complexation bond between boron and resin in the injection mode.

Moreover, it was also performed using the heating sample in the range of 10 to 60°C due to special molecular characteristic of ionization with different temperature.

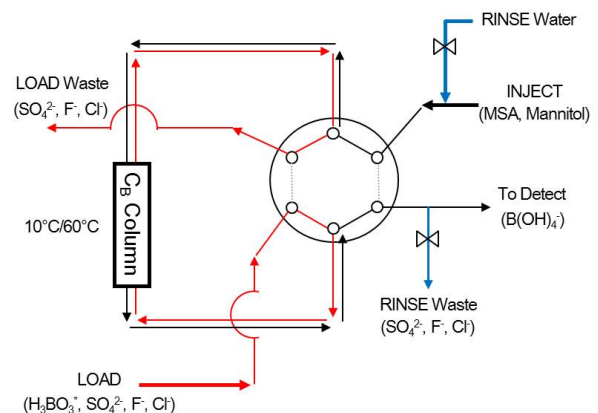


Fig. 1. Schematic diagram of trace-level borate determination

2.2 Characteristic of the C_B Column

As shown in Table I, the end result of this process using C_B column indicated that the concentration of B³⁺, F⁻, Cl⁻ and SO₄²⁻ were 0.004, 1.16, 1.04 and 0.58 mg/L in load mode, respectively. B³⁺ was removed 99.58% by the chelate-type resin in the C_B column. And F⁻ and Cl⁻ had been almost released in column. After completely rinsing the interfering anion presented on the line, each concentration of B³⁺, F⁻, Cl⁻ and SO₄²⁻ in injection mode was 0.55 mg/L, ND, ND and 2.53 mg/L, respectively (Table II). This result was caused by the manual method that could not calculate the dilution ratio of remaining demi-water on the line. Accordingly, boron in the C_B column would be extracted mostly from the outlet. The concentration of SO₄²⁻ was influenced by MSA not using the suppressor. The pressure of the process mode remained constant 228±2 psi in load mode and 345±2 psi in injection mode, respectively.

Table I: Concentration of B³⁺, F⁻, Cl⁻ and SO₄²⁻ in load mode

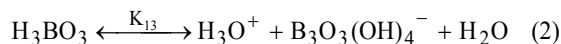
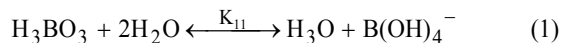
Conc.	B ³⁺	F ⁻	Cl ⁻	SO ₄ ²⁻
Initial	0.964	1.23	1.26	1.36
Final	0.004	1.16	1.04	0.58

Table II: Concentration of B³⁺, F⁻, Cl⁻ and SO₄²⁻ in inject mode

Conc.	B ³⁺	F ⁻	Cl ⁻	SO ₄ ²⁻
Initial	0.951	1.17	1.19	1.29
Final	0.55	ND	ND	2.53

2.3 Boron's Ionization with Temperature

Most of the inorganic chemicals exists ionic status in solution. Likewise, boric acid (H₃BO₃) exists monoborate [B(OH)₄⁻] and triborate [B₃O₃(OH)₄⁻] in the water.



Ionization constants K₁₁ and K₁₃ were changed depending on different temperature as shown in Table III. As the replacement ratio of boron and resin in the column increases, the boron concentration of effluent goes down at the influent temperature 10°C. Since the amount of triborate is increased, while the amount of monoborate is decreased in the influent. When the influent temperature is 60°C, the boron concentration of effluent rises because the amount of monoborate is increased and the amount of triborate is decreased in the influent. This mechanism was in accord with in Table III below.

Table III: Comparison of B conc. with different temperature

Blank	10°C	60°C
0.512 ppm	0.151 ppm	0.489 ppm
0.457 ppm	0.166 ppm	0.546 ppm

2.4 Reaction of Boron and Polyhydric alcohol

The combined reaction of boric acid and a polyhydric alcohol forms a new compound being decreased 9.1 to 4.1 at pKa value. The lowest pKa value in terms of ion chromatography has a tendency to stay a long time in the column due to high ionic strength. Therefore, it indicates a high conductivity because of a long retention time [5]. For example, if boron 50 ppm is added to the polyhydric alcohol, mannitol, pH value is decreased from 4.8 to 3.5 and increased conductivity about 100 fold. By considering mannitol as the representative polyhydroxy compound, the following equilibria can be considered together with the acid dissociation of boric acid.

4. Conclusions

The study investigated the separation of boron peak with anion through 3-steps mode. In previous studies, the problem of peaks overlap has been solved through the rinse process completely removing the interfering ions presented on the line. The combination of mannitol and MSA was dissociated from the strong compound between boron and a chelating type resin in the C_B column. In particular, the C_B column will be able to operate at low pressure of 1/10 than typical ion chromatography, and be maintained the equipment easily due to long term durability as a single column. Even if the injection mode before entering the mobile phase in column requests an enough cleansing process to remove remaining impurity materials, the analysis time takes less than 10 minutes per each session. Therefore, this research showed the possibility to analyze the trace-level boron and use field application in the NPPs, which is only single peak, without additional analytical column.

ACKNOWLEDGMENTS

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