Determination of Ca, Na, Mg Impurities in Demineralized Water Bandung Triga 2000 Reactor using Flame Atomic Absorption Spectrophotometry

Natalia Adventini*, Endah Damastuti, Neni Ratnawati, Fuji Octa Indah Suciati, Woro Yatu Niken Syahfitri
Center for Applied Nuclear Science and Technology-BATAN, Tamansari 71, Bandung, West Java, Indonesia

*nadventinigm@gmail.com

Abstract. Demineralized water is commonly used as cooling water, neutron moderator and as a radiation shield in a nuclear reactor such as Bandung Triga 2000 Reactor. According to its function, demineralized water has to fulfilled some requirements as stated in Safety Analysis Report (SAR) of Bandung Triga 2000 Reactor. The requirements were impurities of Ca, Na and Mg, pH and conductivity electricity in demineralized water reactor. Determination of Ca, Na and Mg as impurities were carried out using Flame Atomic Absorption Spectrophotometry (FAAS). In this activity, instrument and method verification were carried out as quality control. Instrument verification determined were sensitivity, precision and detection limit of FAAS. Method verification was carried out by using spike demineralized water with Na, Ca, and Mg standard. Accuracy and precision of the method were in the acceptance criteria according to AOAC then implemented to determined impurities of Ca, NA, Mg in demineralized water reactor samples. Na and Mg in demineralized water using FAAS gave values less than 1 mg/L, pH values were in the range 5.5-6.5 meanwhile conductivity electricity gave values were less than 3 µmho fulfilled the requirements in SAR. These results were indispensable to support the performance of Bandung Triga 2000 Reactor which needed by public and university for the development of science and its application in the industry, health, environment and other fields.

1. Introduction
Low power research reactors such as Bandung Triga 2000 reactor commonly used in many fields. Bandung Triga 2000 reactor could be implemented in various fields such as health, environment, industry and other applications that provide many benefit to mankind [1]. Bandung Triga 2000 Reactor and other type of reactor require water which is its function as water coolant, neutron moderator and radiation shield [2]. Water sources of Bandung Triga 2000 Reactor were Perusahaan Daerah Air Minum (PDAM) and groundwater that were processed using a water softening system and purified using reserve osmosis process [3]. Both water sources caused demineralized water reactor may contain elements of calcium and chlorine derived from PDAM and elements of ground water such as magnesium, iron and many compounds such as carbonate-bicarbonate and sulphate meanwhile Na originated from the ion exchange process. Demineralized water used by Bandung Triga 2000 Reactor must meet requirements such as pH, conductivity and Si, Ca, Mg, Na content which values were stated in the Safety Analysis Report (SAR).
Determination of mineral impurities in demineralized water reactor could be done using Flame Atomic Absorption Spectrophotometry (FAAS) and other methods. Samin et al. and Supriyanto et al. studied the demineralized water reactor quality using FAAS Meanwhile Neutron Activation Analysis was used by Elisabeth R et al. [4, 5, 6, 7]. AAS method had been common used for determination elements in various sample matrices [8, 9] such in environment field. In this activity, FAAS method was used for determination impurities of Ca, Na, Mg in demineralized water Bandung Triga 2000 Reactor. FAAS instrument and the used method must be checked before sample measurement were carried out. Instrument verification includes were sensitivity, precision, and limit of detection (LOD). Method verification of the specified method includes the accuracy and precision parameters of Ca, Na and Mg in spike demineralized water based on the acceptance criteria of accuracy and precision from AOAC [9].

In this activity, determination of Ca, Na, Mg impurities, pH values and conductivity parameter in demineralized water Bandung Triga 2000 reactor was carried out periodically since 2017 after having a new operating permit from national nuclear energy regulatory body (Bapeten) for 2017-2027 period. The purpose of this activity is to observe the characteristics and dissolved chemical concentration in reactor demineralized water for the study of reactor safety assessment and the study of Bandung Triga 2000 reactor aging [10,11] in suppotting performance of Bandung Triga 2000 Reactor to develop science and its applications.

2. Materials and methods

2.1. Instrumentation/procedures
Flame atomic absorption spectrophotometer (FAAS) from GBC Avanta P, Australia, equipped with Deuterium (D₂) background corrector was used as main device. To reach optimum absorbance signal of each elements, the device was set as follows: setting of flow rate (mL/minutes), the height of burner and adjusting of gas flow rates (oxidant and fuel). Calcium, Sodium and Magnesium hollow cathode lamps were used as light sources. Instrumental parameters used was listed in Table 1.

| Analyte | Wavelength (nm) | Slit width (nm) | Lamp current (mA) | Flame | Optimum working range of FAAS (mg/L) |
|---------|-----------------|-----------------|------------------|-------|--------------------------------------|
| Ca      | 422.7           | 0.5             | 5.0              | C₂H₂-air | 0.01 – 4.0                          |
| Na      | 589.0           | 0.5             | 5.0              | C₂H₂-air | 0.01 – 0.7                           |
| Mg      | 285.2           | 0.5             | 3.0              | C₂H₂-air | 0.01 – 0.4                           |

2.2. Reagents
All reagents such as HNO₃ 65%, stock standard solutions Ca, Na, Mg Titrisol (1000 ± 0.002mg) each were obtained from E. Merck pro analysis (pa) grade. Deionised water with ± 18,1 MΩ resistivity was used throughout the experimental work produced by AriumPro deionised water machine from Sartorius, Germany. Laboratory glasswares/plasticwares were soaked overnight in 5 N HNO₃ solution. All of the apparatus then were washed with deionised water and dried.

2.3. Demineralized water reactor sampling
Demineralized water reactor samples were collected from the surface of reactor tank and bulk shielding using plastic measuring cup then placed into the plastic bottles 100 mL volume. Before the samples keep in the refrigerator, a drop of HNO₃ 65% was added.
2.4. Preparation of working standard solution series

FAAS working standard solution series was made according to the optimum working range of the instrument. Stock standard of Ca prepared to be a mix working standard solution into 0.1; 0.2; 0.3; 0.4; 1; 2; 3 mg/L meanwhile Na, Mg were prepared into 0.1; 0.2; 0.3; 0.4mg/L with HNO$_3$ 0.1 N used in adjusting standard solution in 100 mL volumetric flask. Strontium 50,000 mg/L solution then added to have 2000 mg/L for each concentration of mix working standard solution. Strontium (Sr) 2000 mg/L in the mix working standard solution was meant as a releasing agent in Ca analysis.

2.5. Preparation of blank solution for instrument verification

Reagent blank was made from 0.1 N HNO$_3$ by adding strontium solution until the concentration was 2000 mg/L.

2.6. Preparation of spike demineralized water as Ca, Na, Mg method verification

Ten mL of Ca standard, 1 mL of Na and 2 mL Mg standards with concentration of 10 mg/L each were added into a 100 mL volumetric flask, added by releasing agent 2000 mg/L Strontium and adjusted using demineralized water. Concentration of spike standards in demineralized water were 1; 0.1; 0.2 mg/L for Ca, Na and Mg respectively. Demineralized water as sample also included in the measurement process.

2.7. FAAS instrument verification

Instrument verification was carried out by constructing standard curve of Ca, Na, Mg using working solution series with 10 replicates each to determine instrument sensitivity and precision of each element while measuring. Blank solution then aspirated to determine LOD of the instrument. Sensitivity was determined as follow:

\[ S = 0.0044 \times \frac{C}{A} \]  

where \( S \) = sensitivity; \( C \) = analyte concentration in standard solution; \( A \) = mean analyte absorbance of standard. The sensitivity values (mg/L) of the instrument were stated in GBC Avanta P Series AAS method manual book [10] as reference sensitivity. Ratio sensitivity observed to sensitivity reference must be \( \leq 125 \) as our laboratory criteria acceptance.

Precision which is stated as Relative Standard Deviation (RSD) was calculated using this formula:

\[ \text{RSD} = \frac{\text{SD}}{\text{mean}} \times 100\% \]  

Limit of detection is the smallest amount of analyte in the blank solution that can still be detected by the instrument which calculated with formula:

\[ \text{LOD} = \text{mean blank concentration} + (3 \times \text{SD blank concentration}) \]  

In addition to LOD, the limit of quantification (LOQ) is also determined according to the LOQ formula:

\[ \text{LOQ} = 10 \times \text{LOD} \]  

LOQ is intended to determine the smallest analyte signal in a blank solution that can be quantified. Both unit are in mg/L.

2.8. Method verification

Method verification was carried out by 2 parameters those were accuracy and precision using spike standards in demineralized water. Accuracy is expressed as percent recovery was calculated according to the formula as follow:

\[ \%\text{Rec} = \frac{a-b}{c} \times 100\% \]  

where: \( a \) = concentration of demineralized water + concentration of standard addition (mg/L); \( b \) = demineralized water sample concentration (ppm); \( c \) = theoritic concentration of standard addition (mg/L).

Precision of method verification is stated as Horwitz precision (RSDr) calculated from the equation:

\[ \text{RSDr} = 2^{(1-0.5 \log C)} \]
where C is concentration fraction. For example: concentration fraction of ppm is $10^{-6}$. Precision acceptance is set by our laboratory as HorRat value as much as 0.3–0.67 as fully acceptable recommended range according to Association of Official Analytical Chemists (AOAC) [11].

HorRat values is calculated as follow:

$$\text{HorRat} = \frac{\%\text{RSD}}{\text{RSDr}}$$

(7)

2.9. Quantitative calculation

Analyte concentration in demineralized water reactor samples were calculated using this formula:

$$C_{\text{sample}} = a \times F$$

(8)

Where a= concentration (mg/L) of the element in the demineralized water reactor sample was obtained from calibration curve, F=dilution factor of the sample; concentration sample unit in mg/L.

3. Result and discussion

Verification parameters for sensitivity, precision and LOD of Ca, Na and Mg can be seen in Table 2 below. From Table 2 it showed that Ca was in good agreement with the sensitivity and precision acceptance criteria of instrument verification. Unfortunately, Natrium and Magnesium sensitivity values were out of criteria acceptance but they had good results in precision.

| Table 2. Instrument verification of Ca, Na and Mg |
|-----------------------------------------------|
| Parameters | Ca | Na | Mg | References Values | Unit |
| Sens.Obs  | 0.020 | 0.016 | 0.0038 | - | mg/L |
| Sens. Ref | 0.020 | 0.004 | 0.0030 | - | mg/L |
| Sens. (Obs/Ref) | 100 | 288 | 127 | ≤ 125 | - |
| Precision | 0.700 | 0.600 | 0.640 | ≤ 1 | % |
| LOD       | 0.020 | 0.007 | 0.0007 | - | mg/L |
| LOQ       | 0.20 | 0.07 | 0.007 | - | mg/L |

Sensitivity problem may caused not only by instrument flow rate which was not suitable for Na and Mg but also corrosive nebulizer. These conditions, will decrease instrument sensitivity and resulted in LOD values were increased. Chemical interferences in air-acetylene flame can be reduced by addition of a releasing agent 2000 mg/L Strontium to remove the interference [10]. This step can minimized sensitivity problem.

Method verification using spike demineralized water with standards presented in Table 3. Accuracy refers to how close a measurement is to the true value which is stated in percent recovery as a function of analyte concentration [11].

| Table 3. Method verification using spike demineralized water |
|----------------------------------------------------------|
| Element | Spike conc. (mg/L) | Demin conc. (mg/L) | Std conc. (mg/L) | Theoretical Conc. (mg/L) | %Rec | %RSD | %RSDr | HorRat |
| Ca      | 2.90 | 0.80 | 1.05 | 1.85 | 112 | 4.88 | 13.63 | 0.36 |
| Na      | 0.20 | 0.07 | 0.12 | 0.19 | 71 | 8.66 | 20.40 | 0.43 |
| Mg      | 0.19 | 0.02 | 0.19 | 0.21 | 78 | 8.32 | 20.58 | 0.40 |

Accuracy Ca at 2,90 mg/L concentration obtained 112% Recovery meanwhile Na and Mg at concentration 0.2 ppm and 0.19 mg/L had 71 and 78% Recovery respectively. It meant that accuracy of Ca, Na, Mg in spike demineralized water were suitable with the percent recovery range values
determined by AOAC. HorRat values from Table 3 were in the range 0.36 up to 0.43. The results showed that accuracy and precision of the method fulfilled the value as AOAC recommendation so it could be implemented to determine impurities of Ca, Na, Mg in demineralized water of Bandung Triga 2000 reactor.

Tables 4 presented impurities of all elements in spike demineralized water reactor samples which collected from reactor tank and bulk shielding. The results showed that concentration of the impurities throughout 2017-2019 were in the range 0.01-0.96 mg/L. Based on the Table 2 it can be seen that the LOQ concentration of blank solution for the three elements had values were 0.2; 0.07; 0.007 mg/L for Ca, Na, Mg which indicated that these concentrations of blank solution signal could be quantified properly as analyte by the instrument.

**Table 4. Minerals impurities in demineralized water Bandung Triga 2000 reactor 2017-2020**

| Date    | Samples      | Ca (mg/L) | Mg (mg/L) | Na (mg/L) |
|---------|--------------|-----------|-----------|-----------|
| Apr-17  | Water tank   | 0.51      | 0.02      | 0.26      |
| Apr-17  | Bulk shielding | 0.50     | 0.03      | 0.21      |
| Mei-17  | Water tank   | 0.26      | 0.03      | 0.37      |
| Mei-17  | Bulk shielding | 0.96     | 0.08      | 0.91      |
| Sep-17  | Water tank   | 0.31      | 0.03      | 0.50      |
| Sep-17  | Bulk shielding | 0.37     | 0.02      | 0.11      |
| Feb-19  | Water tank   | 0.28      | 0.01      | 0.23      |
| Feb-19  | Bulk shielding | 0.28     | 0.01      | 0.27      |
| Jan-20  | Water tank   | LOD       | LOD       | LOD       |
| Jan-20  | Bulk shielding | LOD     | LOD       | LOD       |
| Jun-20  | Water tank   | LOD       | LOD       | LOD       |
| Jun-20  | Bulk shielding | LOD     | LOD       | LOD       |
| Jul-20  | Water tank   | LOD       | LOD       | LOD       |
| Jul-20  | Bulk shielding | LOD     | LOD       | LOD       |

However, since 2020 concentration of three elements were less than LOD presented in Table 2. It means, the smallest blank concentrations of Ca, Na, Mg which could be detected by the instrument were 0.02; 0.007 and 0.0007 mg/L respectively. This could be stated that the blank solution signal was a noise signal. Measurement results which provided values around the lower limit of the working range will be better if method detection limit (MDL) is also determined as a study by Rona M. Napitupulu etal, 2019 [12]. Table 4 showed that minerals impurities in demineralized water Bandung Triga 2000 reactor was less then 1 mg/L. Low mineral content will reduce corrosion rate up to maximum and moves the primary cooling system. This condition not only to minimize reaction between source radiation against dissolved chemical particles but also to prevent radioactive contamination on all components of the primary cooling system from excessive radiation exposure.

Other parameters that supported reactor demineralized water quality presented in Figures 1 and 2 in time series.
Based on the SAR of the Bandung TRIGA 2000 reactor, document No. R 093/KN 01 01 /SNT 4, Revi 0, Issue 2, 2017, water (H₂O) as one of the components in the primary cooling system must have several requirements. Figure 1 presented pH values through 2017-2020 were in the range 5.5-6.5 while conductivity were less than 3 µmhos as showed in Figure 2. To maintain the quality of primary cooling water, inside the reactor during operation, demineralized water is cleaned continuously using a water purification system designed separately from the primary cooling system. This system consists of filters and resins. Filter system must be able to filter particles up to 5 μm while mixed-bed resin system purify water until demineralized water’s conductivity is less than 3.5 µmhos. The values of pH and electrical conductivity need to be determined because they are demineralized water impurities indicators which are influenced by dissolved chemical species in the water. While the reactor is not operating, purifier system is operated periodically and at least once a month the cooling water parameters must be measured to ensure demineralized water reactor quality is always maintained. From the obtained data, these activities were needed for safety reactor assessment and study of the Bandung TRIGA 2000 reactor Aging [13,14].
4. Conclusion
Determination impurities of Ca, Na and Mg in demineralised water Bandung Triga 2000 reactor using FAAS gave a good results meanwhile pH and conductivity gave values were in the range between lower and upper level. These data could be used for Assessment Periodic Safety and Study of Bandung TRIGA 2000 reactor aging in supporting performance of Bandung Triga 2000 Reactor.

References
[1] Sayed A. El-Mongy, Overview of reactor research worldwide and their applications, Nuclear regulatory authority of Egypt, Article May, 2018.
[2] J Tominaga, Advances in Steam Turbines for Modern Power Plants, Science Direct, (2017) : 41-56
[3] F.N. Kemmer; The Nalco water handbook; 2. Edition; 1988
[4] Samin, Pemutakhiran Metode SSA, UV-VIS dan Potensiometri-ESI untuk Kontrol Kualitas Air Tangki Reaktor, Prosiding Pertemuan dan Presentasi Ilmiah – Penelitian Dasar Ilmu Pengetahuan dan Teknologi Nuklir 2014 Pusat Sains dan Teknologi Akselerator – BATAN, Yogyakarta, 10-11 Juni 2014
[5] Supriyanto C, Iswani G, Kualifikasi Air Tangki Reaktor (ATR) Kartini Berdaarkan Data Dukung Metoda Nyala Spektrometri Serapan Aatom (SSA_ dan Ion Selective ElecTrode (ISE), Prodising PPI-PDIPTN (2007).
[6] Elisabeth R, M. Gading Permadi, Dicky Tri Jatmiko, Analisis Unsur Pengotor di dalam Air Pendingin Primer Reaktor RSG-GAS, Jurnal Forum Nuklir 9JFN) Vol. 12, Nomor 2 (2018).
[7] Elisabeth Ratnawati, Dihay Erlina Lestari, T. Rina Mulyaningsih, Studi Pengotor Pada Pendingin Primer Reaktor RSG GAS Setelah 30 Tahun Beroperasi, Jurnal Iptek Nuklir Ganendra, Vol. 22 No. 1 (2018): 17-24
[8] Alfan Hidayatulloha, Taslimaha, Abdul Harisa, Penentuan Kandungan Logam Magnetik Komponen Penyusun Abu Layang Batubara, Jurnal Kimia Sains dan Aplikasi 14 (1) (2011) 1 – 3
[9] Idha Yulia Ikhsani, Eki Naidania Dida, Sri Yudawati Cahyarini, Evaluasi Penggunaan Spektrofotometri Serapan Atom Nyala (FAAS) untuk Analisis Konsentrasi Sr/Ca dalam Karang Porites dari Teluk Ambon dan Pulau Jukung, Jurnal Ilmu dan Teknologi Kelautan Tropis, Vol 9, No. 1 (2017) 247-255
[10] GBC Avanta P Series AAS method manual book, May 2009.
[11] Standard Format and Guidance for AOAC Standard Method Performance Requirement Document, Version 12.1, 31 Januari 2011
[12] Rona M. Napitupulu, Dirgarini Julia, Aman Sentosa Panggabean, Validasi metode penentuan Mn dalam oli lubrikan dengan metode pengenceran langsung menggunakan spektrofotomeer serapan atom, Indo. J. Chem. Res., vol. 16, no. 2, 2019, pp. 94-100.
[13] Peraturan Kepala Badan Pengawas Tenaga Nuklir Nomor 2 Tahun 2015 tentang Verifikasi dan Penilaian Keselamatan Reaktor NonDaya
[14] Peraturan Kepala Badan Pengawas Tenaga Nuklir Nomor 8 TAHUN 2008 tentang Ketentuan Keselamatan Manajemen Penuaan Reaktor NonDaya