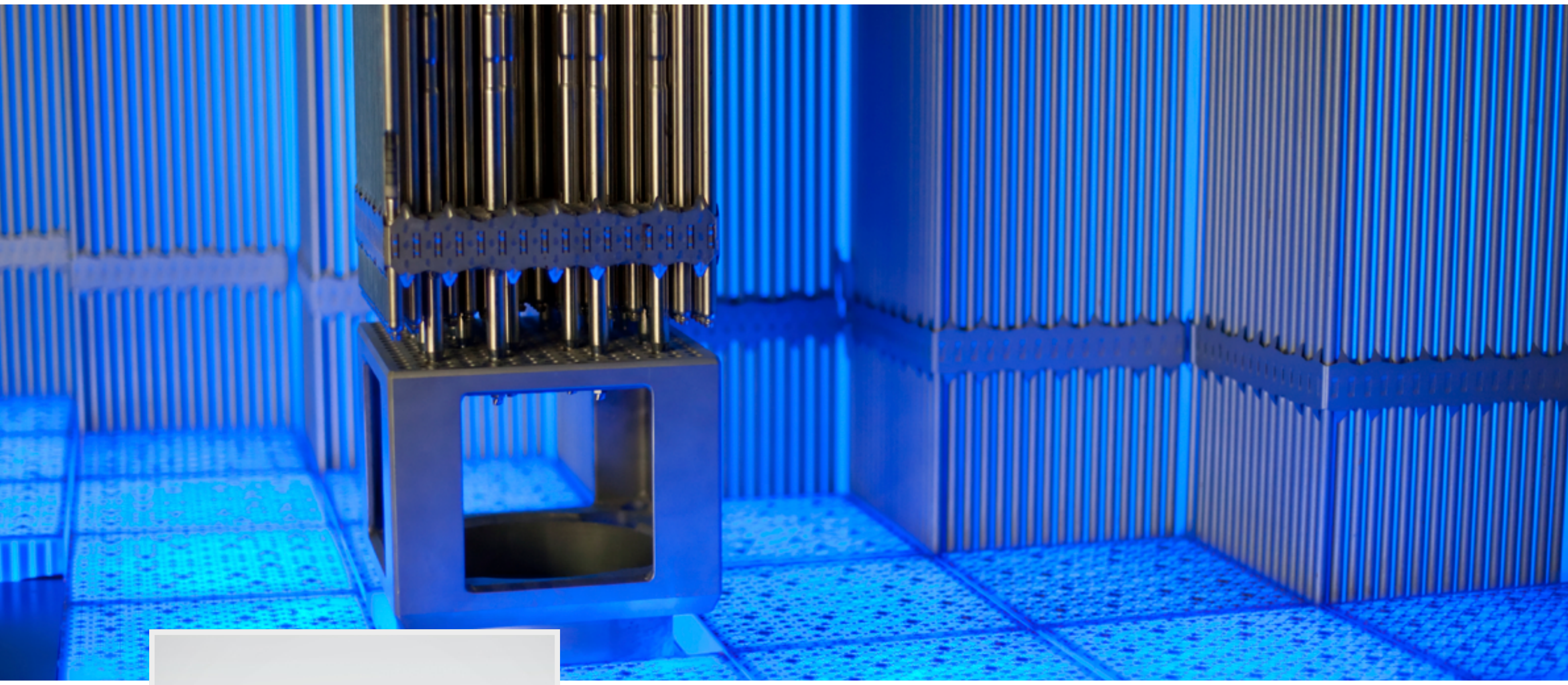

Challenge

Monitoring the cooling water of a nuclear reactor for safe and efficient operation

Solution

Simple and robust ICP-MS performance with accurate isotopic analysis

Determination of Trace Elements and Isotope Ratios in Borated Cooling Water of a Nuclear Power Plant

Introduction

Nuclear power plants are an important and efficient source of electrical energy, supplying over 12% of the world's electricity. Many modern plants use a pressurized water reactor (PWR) due to their improved safety and self-regulating capability. The reactor coolant plays a very important role in the process. In a PWR, the primary coolant (water) is pumped under high pressure to the reactor core where it is heated by the energy generated by the fission of atoms. The higher water pressure enables more heat to be carried from the reactor and the heated, radioactive water then flows to a steam generator where it transfers its thermal energy to a secondary system. Here, non-radioactive steam is generated which drives the turbines for the electric generator.

Like all thermal reactor designs, PWR require the fast fission neutrons to be slowed down in a process called 'moderation' in order to interact with the nuclear fuel and sustain the chain reaction.

In PWRs, the coolant water is also used as a moderator by letting the neutrons undergo multiple collisions with light hydrogen atoms in the water, losing speed in the process.

Boron is often added in the form of boric acid to the reactor coolant as a neutron absorber to control the nuclear reactivity in the primary reactor. The neutron absorption cross-section, reported in the unit 'barns' is a measure of how likely a neutron will react with the nucleus. ^{10}B isotope is known for being a strong neutron absorber and has a much higher neutron absorption cross section than ^{11}B.

The pH of the coolant is also crucial in maintaining the system as a pH lower than 6.9 at elevated temperatures of 300 °C can cause accelerated corrosion of the fuel rod cladding. As boric acid is weakly acidic, lithium hydroxide is regularly added to the coolant to achieve the desired pH.

Instrumentation

A PlasmaQuant MS ICP-MS in combination with a Cetac ASX-520 autosampler was used for the sample analysis.

Table 1: Instrument settings – PlasmaQuant MS

Parameter	Settings
Plasma Gas Flow	9.0 L/min
Auxiliary Gas Flow	1.05 L/min
Nebulizer Gas Flow	1.08 L/min
Plasma RF Power	1.4 kW
Dwell Time	30ms
Spraychamber Temp.	3°C
Ions Optics	Optimized for low masses
Pump Rate	10rpm (black-black PVC pump tubing)
Nebulizer type	Micromist (0.4ml/min)
Torch type	Standard quartz torch with 2.3mm id injector
Replicates	4
Scans per replicate	20
Integrated Collsion Reacton Cell (iCRC) gas flow	110mL/min H_2 gas for Al, Mg and Ca 120mL/min He gas for Na, Ni, Zn, Cr, Co
Accessories	Cetac ASX 520 autosampler with ESI OneFAST

Samples and Reagents

All solutions were made up in deionized water (18.2 MΩ/cm, Millipore MilliQ, Billerica, MA, USA) and nitric acid NORMATOM Suprapur 60%, VWR.

Calibration standards

Calibration solutions were prepared from Merck multi-elements standard and were made up in high purity 1%HNO_3.

Table 2: Concentration of Calibration Standards

	Std 1	Std 2	Std 3	Std 4	Std 5
Al, Ca, Na, Mg, Ni, Zn, Cr, Co (µg/L)	0.1	0.5	1	10	100

Sample preparation

Samples consisted of 2.5 g/L of boric acid and 2 mg/L of lithium as lithium hydroxide and acidified in 1% HNO_3

Internal standard

An internal standard solution containing 20 µg/L ^{45}Sc, ^{89}Y, ^{103}Rh and ^{193}Ir was prepared and added online to the sample line via a Y-piece

Note: Standards were not matrix match to the samples to reduce the risk of contamination.

Results and Discussion

For the primary coolant to transfer heat and moderate the core effectively, chemical controls are required. This includes the measurement of elements that can effect corrosion, indicate cladding failure or produce crud formation. For example:

- Na can increase corrosion and indicates contamination or possible leak
- Ca and Mg contamination can contribute to crud deposition
- Zn additives injected into coolant for corrosion suppression
- Cr, Ni, Co in stainless steel and other metal-alloy components, fuel rod and pressure vessel cladding
- Al from Al_2O_3 coatings or leaching of B_4C-Al_2O_3 pellets during initial reactor burn-in

Two samples containing 2.5 g/L H_3BO_3 in 2 mg/L Li were analyzed directly on the PlasmaQuant MS. The samples were also spiked with 1 µg/L of all elements to check for matrix effects and the results are shown in table 3.

Table 3: Results of two spiked and unspiked samples.

Isotope	Sample 1 H_3BO_3 + Li (µg/L)	Sample 2 H_3BO_3 + Li (µg/L)	Sample 1 + 1ppb Spike H_3BO_3 + Li (µg/L)	Sample 2 + 1ppb Spike H_3BO_3 + Li (µg/L)	Average Recovery
^{23}Na	5.45	5.29	6 .53	6.48	101.7%
^{24}Mg	0.059	0.042	1.07	1.08	102.4%
^{27}Al	0.670	0.555	1.80	1.78	110.9%
^{40}Ca	0.195	0.092	1.33	1.10	107.3%
^{52}Cr	0.005	0.011	0.979	0.978	97.1%
^{59}Co	-0.002	-0.004	0.969	0.968	97.1%
^{60}Ni	0.0054	0.003	0.960	0.971	96.1%
^{66}Zn	0.142	0.071	1.03	1.04	93.1%

Benefits of using hydrogen within the iCRC

Given the very high presence of Boron in the samples, significant interference from $^{11}B^{16}O$ would be expected on the monoisotopic element of aluminium at mass 27. Using hydrogen within the iCRC effectively removes this interference allowing trace level measurement of aluminium at below the parts per billion level in a high boron matrix.

Isotope ratio measurements

The isotope ratios of Li, B and U were measured using a calibration standard to demonstrate the precision possible with the PlasmaQuant® MS quadrupole based ICP-MS. The high sensitivity and excellent abundance sensitivity performance of the PlasmaQuant® MS achieves isotope ratio precision ranging from 0.13% to as low as 0.01% for adjacent isotopes, as shown in table 4.

National Institute of Technology and Standards, Reference Material 951a, Boric Acid Isotopic Standard was also measured to demonstrate the accuracy of isotope ratio measurements as shown in table 5. No corrections were applied to the isotope ratio results.

Table 4: Measured isotope ratios of Li, B and U

Isotope Ratio	**$^{6}Li/^{7}Li$**	**$^{10}B/^{11}B$**	**$^{235}U/^{238}U$**
Measurement 1	0.077735	0.26838	0.004309527
Measurement 2	0.077753	0.26842	0.004298298
Measurement 3	0.077753	0.26844	0.004299815
Measurement 4	0.077767	0.26844	0.004310240
Measurement 5	0.077758	0.26838	0.004299788
Average	**0.077753**	**0.26841**	**0.004303533**
Theoretical value	**0.081081**	**0.24844**	**0.004216867**
Accuracy	**4%**	**8%**	**2%**
Precision (RSD)	**0.02%**	**0.01%**	**0.13%**

Table 5: Measured isotope ratio of boron in NIST 951a

NIST 951a (10B/11B)	**Measured value**	**Certified value**
Dwell Time [ms]	50	
Isotope Ratio	0.24958*	0.2473 ± 0.0002
Standard deviation n=20	0.000145	
Precision (RSD)	0.0581%	

*no corrections have been applied

Conclusion

This application demonstrates the important role an ICP-MS plays in ensuring the safe and efficient operation of a pressurized water nuclear reactor. The ability of the PlasmaQuant MS to quickly and easily analyze reactor coolant in a 2.5g/L boric acid matrix, highlights the robustness of the plasma system and the effectiveness of the iCRC interference management system.

The option to rapidly switch between helium collision gas and hydrogen reaction gas within the integrated Collision Reaction Cell (iCRC) offers the most effective removal of spectroscopic interferences. The specific polyatomic interference of boron oxide ($^{11}B^{16}O$) on ^{27}Al demonstrates the importance of hydrogen reaction gas in eliminating this particular interference and allowing lower limits of detection to be achieved for aluminium.

The ICP-MS technique also offers the additional benefit of isotopic analysis, with the PlasmaQuant MS demonstrating accurate and precise measurement of the B10:B11 isotope ratio.

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