Case study | 001964

Ion chromatography

Nuclear industry water analysis: Sizewell B Nuclear Power Plant Chemistry Laboratory, EDF UK

Thermo Scientific Dionex CR-CTC III Continuously Regenerated Cation Trap Column enhances detection of anions in ammoniated condensate samples

"Managing water chemistry with IC is critical. A nuclear plant is supposed to be operational for a minimum of 40, if not 60, years, so ensuring our plant equipment stays healthy is essential. Anionic contaminants such as chloride and sulfate, even at µg/L levels, can cause stress-induced corrosion cracking. Thermo Scientific IC systems can be optimized for a wide range of chemistry monitoring methods. Whether its sub-ppb or -ppm levels of cations and anions, IC can detect them accurately and reliably so we can ensure contaminants aren't causing corrosion, reducing plant lifetime, and ultimately causing lost generation."

—Peter O'Brien, Chemistry Lab Team Leader, Sizewell B Nuclear Power Plant, EDF UK

Introduction

Nuclear power plants are an important source of electrical energy in the U.S and Europe. Successful operation of these facilities requires careful control and monitoring of water chemistry in primary coolant dosed with boron and lithium, steam generator tubes dosed with ammonia, and closed cooling water systems dosed with nitrite. Plant operators dose these systems to minimize corrosion to reduce maintenance costs and lost production. Trace anionic and cationic impurities, in particular, can catalyze corrosion and, therefore must be monitored at low or sub-µg/L (ppb) concentrations.

Ion chromatography (IC) is an accurate, reliable, and rapid method for monitoring µg/L (ppb) and mg/L (ppm) levels of anions and cations, including transition metals, in nuclear power plant waters. IC is safer than alternate methods such as flame photometry which relies on highly explosive reactive compressed acetylene gas. However, matrix components such as borate and lithium in pressurized water reactor (PWR) samples and ammonia in boiling water reactor (BWR) samples, interfere with IC-based quantification of ionic compounds. Thermo Scientific™ Dionex™ IC systems can automatically perform inline removal of these

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interferences using reagent-free IC (RFIC) and a Thermo Scientific™ Dionex™ Continuously Regenerated Cation Trap Column (CR-CTC), enabling accurate and reproducible quantitation of the analytes of interest.

Using the Dionex CR-CTC to remove interferences in mg/L (ppm) concentrations of lithium in lithium-borated water and ammonia in ammoniated condensate samples, the Sizewell B Nuclear Power Plant Chemistry Laboratory at EDF measures fluoride, chloride, and sulfate with low µg/L (ppb) sensitivity and good repeatability. This case study showcases how the laboratory improved IC method sensitivity from ppm to 10-ppb levels with inline removal of ammonia over versions of Dionex trap columns: the Thermo Scientific™ Dionex™ CR-CTC Continuously Regenerated Cation Trap Column II and Thermo Scientific™ Dionex™ CR-CTC Continuously Regenerated Cation Trap Column III.

Analytical challenge

The presence of high levels of interferences in nuclear power plant waters presents a significant analytical challenge. In facilities that use a PWR, boric acid is added to the coolant as a water-soluble neutron absorber to control the nuclear reaction. Boron concentrations at the beginning of the fuel cycle may be as high as 2,500 mg/L (ppm), corresponding to 1.4% boric acid. At the high temperatures and pressures in the PWR, boric acid can cause crud buildup due to deposition of metal oxides on the fuel rods. To prevent this, lithium hydroxide is added up to 4 mg/L to increase the pH to 6.9 or higher. Other components, including dissolved hydrogen or hydrazine (added at ppb levels to scavenge oxygen), zinc (added to suppress radiation), and transition metals from crud burst (sudden loosening of crud deposits following a chemical, hydraulic or temperature transient), likewise challenge analytical methods.

A BWR includes a secondary circuit that generates steam to drive a turbine to produce electricity. Samples from this circuit—for example, condensate—can contain up to 10 mg/L ammonia that, as in the primary circuit, is added to control pH and prevent crud deposition on components. Similarly, compounds such as hydrazine, morpholine (added to inhibit corrosion), and particulate iron from crud buildup may also be present in condensate samples. Ammonia interferes with anion analysis, and iron (Fe^{3+}) binds with the phosphate in guard columns, impeding its measurement. As Peter O'Brien, Chemistry Lab Team Leader, Sizewell B Nuclear Power Plant, EDF UK explained, "the challenge is to determine fluoride, chloride, sulfate, and sodium in systems dosed with high levels of corrosion inhibitors and that contain high levels of iron burden. Without a suitable method, analysis of inorganic anions in the presence of ammonia can yield poor accuracy of results, especially with fluoride."

Inline sample preparation provides a solution

Lithium-borated and ammoniated water can be accurately and reproducibly measured for low-µg/L fluoride, chloride, and sulfate concentrations using the Dionex CR-CTC to pretreat samples inline (Figure 1). Though originally introduced to continously remove ionic contaminants from eluents without offline chemical regeneration, the Dionex CR-CTC also removes interferences caused by mg/L concentrations of lithium or ammonia when placed in the sample stream (Figure 1) in samples. An inline filter is used to remove any iron particles that would interfere with phosphate measurement.

> "The cation trap column is important because it helps us deal with challenging sample matrices. In our condensate samples for example, it helps remove the 10-ppm ammonia, and in our primary site, it removes the 3-ppm lithium. Eliminating these interferences helps us get good analytical results. In addition, the continuously regenerating nature of the cation trap column makes it reagent-free. That means there is minimal upkeep and maintenance to worry about."
>
> —Peter O'Brien

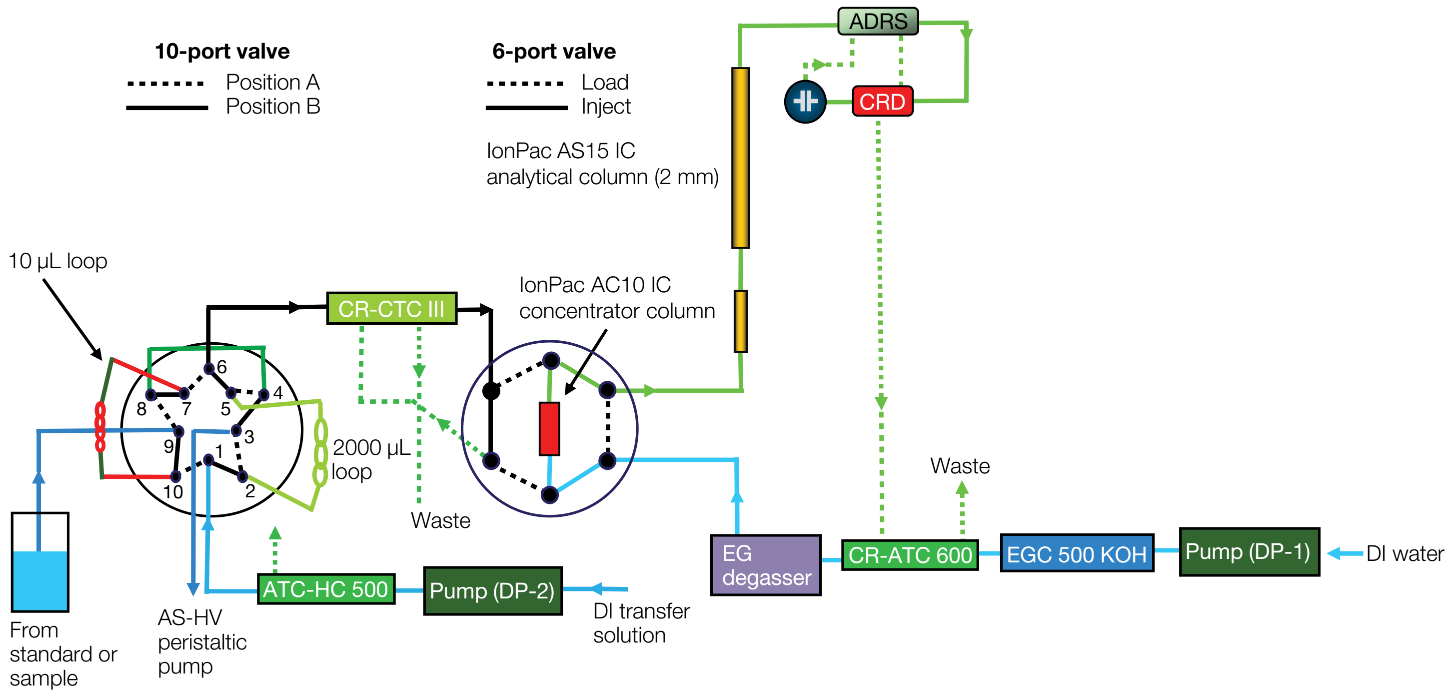

Figure 1. Example of the inline Dionex CR-CTC setup to pretreat samples to remove interfering levels of lithium and ammonia. The Thermo Scientific™ Dionex™ CR-CTC III removes interfering anions from the eluent during automatic generation. For analyses of cationic contaminants, the Dionex CR-CTC can be configured to ensure the eluent itself is free of interfering cations.

Amoniated sample matrices

Figure 2 illustrates how well the Dionex CR-CTC reduces interferences from the ammonia matrix when placed inline to treat samples prior to IC separation. "Without the CR-CTC III, the fluoride and chloride peaks elute later, and their response is reduced—fluoride significantly so. This can cause misidentification of peaks and underestimation of amounts," said O'Brien.

"A low-tech option is to use a cation resin column to strip out the ammonia, but that approach has a limited life of a few hours before it needs to be replaced or regenerated, and it increases sulfate contamination. Overall, the CR-CTC method is much easier, automated, and performs better."

Thermo Scientific Dionex CR-CTC continuously regenerated trap columns

> "We've got a pretty clean system here, so we are looking at really low-ppb levels for our condensate and primary site chemistry. Using the Dionex CR-CTC III at sample loading removes up to 10 ppm ammonia and restores the fluoride peak that would be lost otherwise. It's been a good investment."
>
> —Peter O'Brien

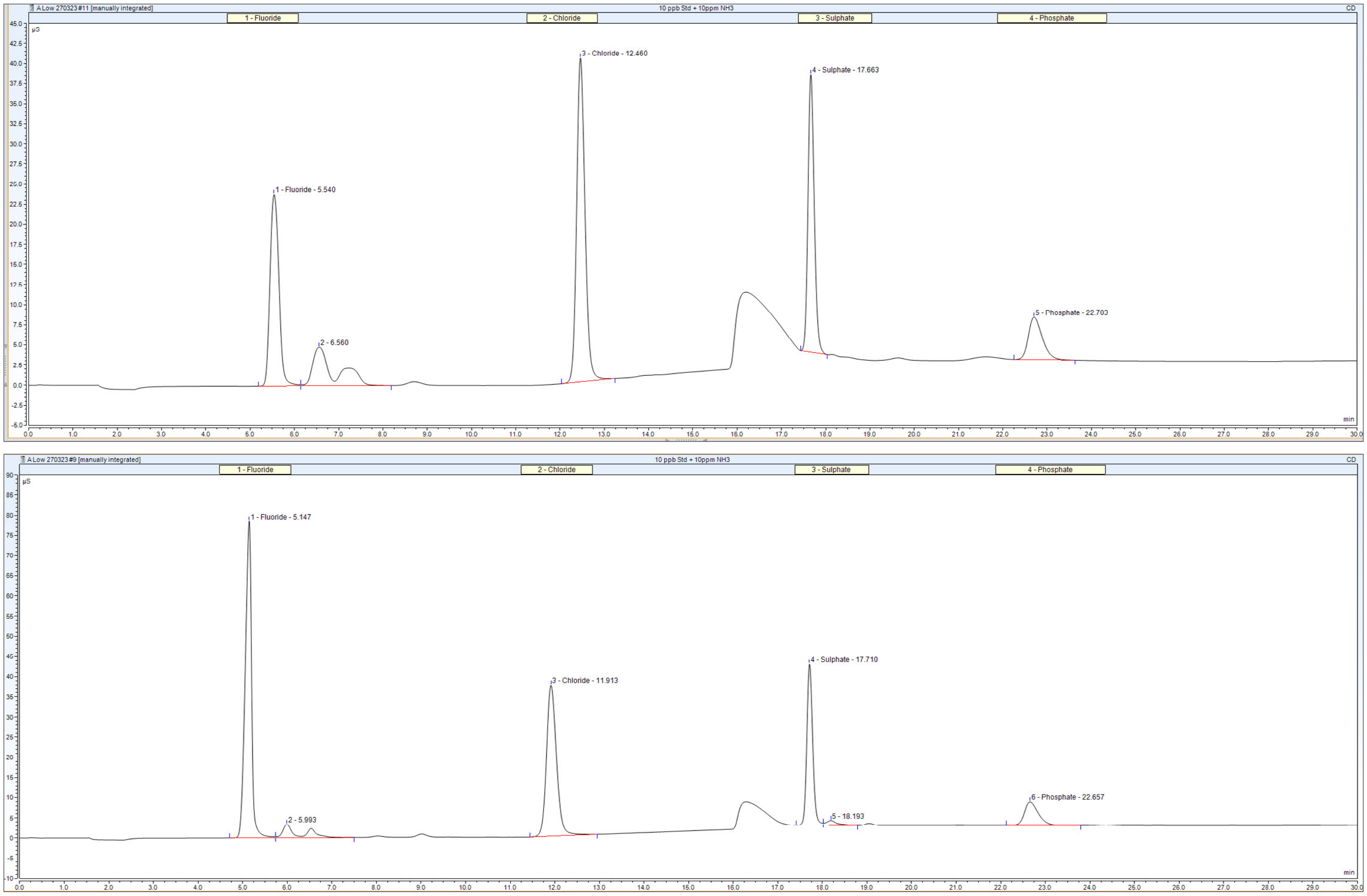

Figure 2. Chromatograms from the analysis of a 10-ppb mixed anion standard (fluoride, chloride, sulfate, and phosphate) in 10-ppm ammonia matrix with (bottom) and without (top) sample treatment on the Dionex CR-CTC III. Without using the Dionex CR-CTC III to clean up the ammonia matrix, the fluoride and chloride peaks elute later, and their response is reduced, particularly for fluoride. This can result in misidentified peaks and inaccurate quantitation.

Evolution of Dionex CR-CTC improves method performance

Due to improvements in continuous generation capabilities, each successive generation of the Dionex CR-CTC has improved method performance, particularly for fluoride measurement. To demonstrate, O'Brien compared the results from analyses of a 10-ppb anion check standard using the Dionex CR-CTC II or Dionex CR-CTC III to perform inline removal of ammonia from condensate.

The instrument configuration used, including consumables, is listed in Table 1 and shown in Figure 3. The configuration is the same as the one the laboratory normally uses to monitor condensate waters for anionic contaminants. The various Dionex CR-CTC devices were positioned after the Dionex AXP Auxiliary Loading Pump and operated in sample preparation mode. When switched on, the Dionex CR-CTC continuously regenerates and flushes via a second 6 port valve which allows ultrapure water to pass through it when not in use, and then switches to sample when loading. To reduce iron particulate load, an inline high-pressure filter housing with a 0.5 µm frit was installed after the AXP auxiliary loading pump, with a second filter installed before the guard column.

The check standard consisted of fluoride, chloride, sulfate, and phosphate at 10 ppb in 10 ppm ammonia with 50 ppb hydrazine. This resulted in a pH of 10 and a conductivity of approximately 25 µS/cm. During normal laboratory operations, the check standard sample is injected each workday to verify the calibration and instrument performance. Check standard results between 9 and 11 ppb are considered acceptable. If the result is between 8.5 and 9, or between 11 and 11.5, then it is flagged yellow. If more than one result is flagged, the calibration standards are rerun. Values below 8.5 or greater than 11.5 are unacceptable, flagged red, and require a recalibration.

Table 1. IC configuration and consumables used to compare Dionex CR-CTC models.

IC systems and consumables	Description
IC systems	Thermo Scientific™ Dionex™ Integrion™ HPIC™ System
Sample and reagent delivery	Thermo Scientific™ Dionex™ AXP Auxiliary Pump (P/N 063973)
CR-CTC	Dionex CR-CTC II (P/N 066262) or Dionex CR-CTC III (P/N 104-60001)
Filter (iron)	Dionex high pressure inline filter kit (P/N 074505)
Guard column	Thermo Scientific™ Dionex™ IonPac™ AG15 Guard Column
Analytical column	Thermo Scientific™ Dionex™ IonPac™ AS15 IC Analytical Column, 2 x 250 mm (P/N 053941)
Concentrator column	Thermo Scientific™ Dionex™ IonPac™ AC10 IC Concentrator Column, 4 x 50 mm (P/N 043133)
Suppressor	Thermo Scientific™ Dionex™ ADRS 600 Anion Dynamically Regenerated Suppressor, 2 mm (P/N 088667CMD)
Eluent generation	Thermo Scientific™ Dionex™ EGC 500 KOH Potassium Hydroxide Eluent Generator Cartridge (P/N 075778) with Dionex CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662) and high-pressure EG degasser

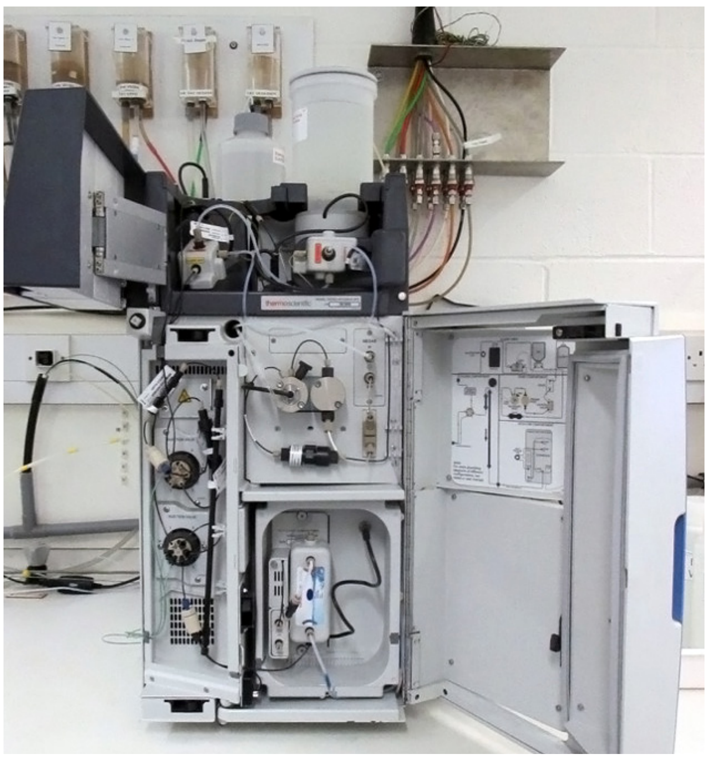

Figure 3. Dionex Integrion HPIC system configuration for monitoring anions in condensate samples. Photo courtesy of EDF.

The comparative performance of the various Dionex CR-CTC devices is shown in Tables 2 and 3. Though both the Dionex CR-CTC models reduced ammonia inferences, the Dionex CR-CTC III increased method performance significantly more than its predecessor. Describing the results, O'Brien noted that "the data demonstrate how each generation of Dionex CR-CTC became more effective at regeneration. Because we run a lot of ammonia samples, without sufficient regeneration it becomes saturated with ammonia and the fluoride in the check standard suffers. The data from the new generation Dionex CR-CTC III shows that no matter how hard we hit it with samples, the fluoride in the standard is measured accurately and more repeatably."

As shown in Table 4, The fluoride in the check samples pretreated with Dionex CR-CTC III remained within spec for over 50 days, indicating that ammonia continued to be removed and did not hinder fluoride response. The Dionex CR-CTC III enables the laboratory to run samples about twice as long without recalibrating, which is a huge productivity benefit "because it's a bit of work to perform calibration," noted O'Brien.

“We improved our level of precision and accuracy measuring sub-µg/L concentrations of primary-coolant and feed-water anions and cations using the continuously regenerating cation trap columns. Regeneration is automatic and requires no interaction. It’s very easy running a sample—it loads, it runs and then you go on to the next sample.”

—Peter O’Brien

Automatic regeneration for continuous productivity

During typical operating conditions, the laboratory may only run one or two samples daily to check the performance of the plant’s online monitors. However, during planned plant outages, for example, for refueling, the laboratory may continuously monitor about 20 to 30 samples daily. O’Brien commented that “we ran the Dionex CR-CTC III continuously and had no problem whatsoever with the number of samples. Our next goal is to further improve our sub-µg/L limit of detection using an autosampler to enhance our sample preparation and dilution.”

Table 2. Results from a 10-ppb anion check standard using the Dionex CR-CTC II for inline removal of ammonia. Check sample was injected daily on workdays. Results highlighted in orange indicate an out-of-spec result. Results in red are unacceptable and indicate that recalibration is needed.

Sample number	QC Standard (ppb) - Certified Concentration = 10 ppb			
	Fluoride	Chloride	Sulfate	Phosphate
1	10.43	10.67	10.45	10.91
2	10.16	9.27	10.62	10.87
3	8.87	10.07	10.05	9.86
4	9.63	9.85	9.87	9.66
5	8.90	9.92	10.00	9.82
6	10.11	10.28	10.43	10.22
7	10.99	10.04	10.18	10.11
8	10.45	10.24	10.36	10.40
9	9.90	10.09	10.04	10.24
10	10.81	10.09	10.04	9.02
11	10.24	9.95	9.77	10.03
12	10.46	10.04	10.14	9.74
13	9.12	10.58	10.37	10.09
14	10.26	10.70	10.73	10.10
15	8.95	10.22	10.21	10.85
16	9.07	10.54	10.49	10.65
17	9.54	10.53	10.57	10.51
18	9.04	10.19	10.19	10.96
19	9.25	10.50	10.58	10.91
20	9.02	10.72	10.72	10.14
21	9.01	10.15	10.16	8.00
22	9.27	10.34	10.33	10.09
Average	**9.70**	**10.23**	**10.29**	**10.14**
RSD	**7.12%**	**3.33%**	**2.62%**	**6.73%**

Table 3. Results from a 10-ppb anion check standard using the Dionex CR-CTC III for inline removal of ammonia. Check sample was injected daily on workdays. Even after 50 check sample injections, none of the results were out of spec.

Sample number	QC Standard (ppb) - Certified Concentration = 10 ppb			
	Fluoride	Chloride	Sulfate	Phosphate
1	9.65	10.00	9.86	9.47
2	9.81	10.41	10.42	10.16
3	9.44	10.06	9.76	9.01
4	9.57	9.95	9.85	9.58
5	9.57	9.97	9.94	9.78
6	9.78	10.03	9.98	9.87
7	10.11	10.09	10.10	10.06
8	9.97	10.01	9.95	9.49
9	9.49	9.96	9.75	9.61
10	9.79	10.56	10.25	9.95
11	9.42	10.06	9.90	9.64
12	9.05	10.24	10.05	9.58
13	9.49	9.94	9.93	9.55
14	9.86	10.01	10.01	9.48
15	10.07	9.50	10.55	10.59
16	10.02	9.45	10.07	10.47
17	9.24	9.58	9.43	9.03
18	9.77	9.80	9.85	9.65
19	9.22	9.99	9.89	9.76
20	9.14	9.60	9.54	9.55
21	9.33	9.89	9.88	9.92
22	9.16	9.87	9.60	9.23
23	9.30	9.91	9.75	9.71
24	9.23	10.01	9.80	9.89
25	9.46	10.17	10.06	9.72

Sample number	QC Standard (ppb) - Certified Concentration = 10 ppb			
	Fluoride	Chloride	Sulfate	Phosphate
26	9.01	9.45	9.38	9.43
27	9.44	9.95	9.86	9.49
28	9.30	9.79	9.61	9.16
29	9.28	10.46	9.85	9.22
30	9.16	10.60	9.99	9.28
31	9.39	10.63	10.04	9.67
32	9.44	10.15	10.06	9.63
33	9.45	9.80	9.57	9.20
34	9.96	10.17	10.07	9.81
35	9.48	9.78	9.57	9.37
36	9.38	10.23	9.72	9.40
37	9.66	9.87	9.84	9.61
38	9.14	9.62	9.36	9.09
39	9.52	9.91	9.79	9.56
40	9.56	10.06	10.02	9.87
41	9.27	9.93	9.87	9.78
42	9.29	9.89	9.89	9.64
43	9.35	10.04	9.96	9.44
44	9.33	10.32	10.08	9.47
45	10.11	9.49	10.51	10.59
46	9.55	9.82	9.82	9.89
47	9.15	10.02	9.85	9.73
48	9.19	9.70	9.59	9.53
49	9.41	9.72	9.76	9.87
50	9.49	9.97	9.98	10.08
Average	**9.485**	**9.9686**	**9.8842**	**9.6512**
RSD	**3.02%**	**2.78%**	**2.51%**	**3.64%**

"We use IC for a variety of different water chemistry applications. The applications are challenging but working together with Thermo Scientific we developed the methods we use today, and they are working well. Over the past 6 years, we've had no issues with our setups. We've only changed the consumables on a yearly basis, proactively, so it's possible that the consumables could even last longer."

—Peter O'Brien

Figure 4. At the Sizewell B Nuclear Power Plant Chemistry Lab, Dionex Integrion HPIC systems are dedicated to the analysis of either cations or anions in condensate samples. Photo courtesy of EDF.

IC handles range of nuclear power plant water applications

"Nothing compares to a Thermo Scientific Dionex IC system for the determination of trace concentrations of ionic impurities in nuclear power plant waters," said O'Brien. That's why the Chemistry Lab uses several Thermo Scientific Dionex IC systems for their monitoring applications. According to O'Brien, these applications include "measuring inorganic cations and anions in systems dosed with ammonia or lithium hydroxide, boric acid, and sodium nitrite. We also use IC to monitor transition metals, zinc injected to suppress radiation dosage, and sodium in systems dosed with NaOH to control corrosion which can cause pinhole leaks that can allow sea water into condensate water or other plant support systems. Some cooling water systems themselves are cooled by seawater and any pinhole leaks can be detected with IC."

IC leadership adds confidence

As the technology leader in IC for over 45 years, laboratories can be confident that they are getting the best with Thermo Scientific Dionex IC systems, consumables, service, and support. "Thermo Scientific IC systems have always done what we've needed. We have eight IC instruments—four Dionex Integrion HPIC systems, two Dionex Aquion IC systems, a Dionex ICS-5000$^+$ HPIC system, and a Dionex ICS-6000 HPIC system—that meet all our needs for doing our different applications. They're quite modular with the different columns, the suppressors, concentrators, and eluent generators, so they are suitable for a wide range of applications. And we've never had an issue with them, so that's why we've stuck with them," explained O'Brien.

About Peter O'Brien

Peter O'Brien is a Chemist and Systems Engineer at EDF Energy's Sizewell B Nuclear Power Plant with more than 16 years of experience using IC. In 2006, he joined EDF as a chemistry apprentice and graduated as a shift chemistry technician before progressing into the position of Chemistry Lab Team Leader. O'Brien worked with Thermo Scientific to move the laboratory's lithium and sodium determination away from flame atomic absorption to the far safer IC method.

About EDF

EDF is helping Britain achieve Net Zero and tackle climate change by leading the transition to a cleaner, low-emission, electric future. The company is the UK's largest producer of low-carbon electricity and supplies millions of customers with electricity and gas. EDF generates low-carbon electricity from five nuclear power stations, more than thirty onshore wind farms, and two offshore wind farms. EDF is part of EDF Group, the world's largest electricity generator. In the UK, the company employs around 11,000 people at locations across England, Scotland, Wales, and Ireland. The Sizewell B Nuclear Power Plant produced a quarter of the zero-carbon electricity coming from EDF's fleet of stations which reached 40 TWH (40 million-million watts) in 2022. It is the UK's only pressurized water reactor (PWR) and the most modern nuclear power station in the UK. In 2022, the station recorded 99% load factor, making it one of the most reliable power stations in the UK with availability to deliver power 99% of the time.

Additional resources

- Thermo Fisher Scientific. Thermo Scientific Application Update AU-000610 Determination of trace organic acids and inorganic anions in boric acid-treated power plant waters using an automated reagent-free ion chromatography system. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/au-000610-ic-an185-trace-acids-anions-water-nuclear-au000610-na-en.pdf. Feb. 2022.
- Thermo Fisher Scientific. Thermo Scientific Application Note AN-277 Fast and sensitive determination of transition metals in power industry waters using ion chromatography. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-277-ic-transition-metals-power-industry-water-an71554-en.pdf. Oct. 2017.
- Thermo Fisher Scientific. Thermo Scientific Application Note AN-73852 Determination of trace anions in high purity waters using a large-volume direct injection. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-73852-ic-trace-anions-high-purity-water-direct-injection-an73852-en.pdf. Nov. 2020.
- Thermo Fisher Scientific. Thermo Scientific Application Note AN-1058 Determination of Polyacrylic Acid in Nuclear Power Plant Pressurized Water Reactor Secondary Feed Water. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AN-1058-IC-Polyacrylic-Acid-Nuclear-Power-Plant-Water-AN70566-EN.pdf. Aug. 2016.

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