

# REPLACEMENT AND COMMISSIONING OF THE NEW INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETER (ICP-MS) AT THE GEOCHEMICAL LABORATORY, GEOLOGICAL SURVEY OF NEWFOUNDLAND AND LABRAODR

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## ABSTRACT

*The Geochemical Laboratory of the Geological Survey of Newfoundland and Labrador uses Inductively Coupled Plasma Spectrometry as its primary instrumentation for trace- and major-element analysis of rock, till, lake and stream sediment, and water. The in-service X-Series II Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), purchased in 2011, is no longer supported by the vendor; therefore, a replacement instrument was required. To ensure any replacement instrument would seamlessly continue and maintain existing analytical methods, comparisons were made between the existing ICP-MS and a Thermo Fisher Scientific iCAP-RQ ICP-MS. This included validating the method migration to the new ICP-MS by looking for occurrences of bias (if any) between the methods on the two instruments, comparing Certified Reference Material (CRM) results, and verifying stability over time, by comparing internal standard recovery. The Thermo Fisher Scientific iCAP-RQ instrument proved an acceptable replacement.*

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## INTRODUCTION

The Geochemical Laboratory of the Geological Survey of Newfoundland and Labrador (GSNL) has analyzed samples for trace- and major-elements in a variety of media for over forty-five years. Several generations of instruments have been used during this period, the most recent of which is the Thermo Fisher's X-Series II Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). On October 15, 2019, the laboratory received notification from Thermo Fisher Scientific that this instrument would reach its End of Guaranteed Service (EOGS) by March 31, 2020.

This EOGS notice meant that Thermo Fisher would no longer be able to provide a service contract for the ICP-MS after this date, nor would they be able to guarantee the availability of replacement parts going forward.

Since the commissioning of the X-Series II ICP-MS in the early 2000s, the laboratory has developed methods to analyze trace elements in rock, soil and sediment using Lithium Metaborate Fusion and Four Acid Digests, having a focus on rare-earth elements (REE). A method for the analysis of natural waters was also developed and implemented. Therefore, any replacement instrument had to meet these specifications to ensure there would be no interruption to the analytical services to the GSNL.

## REPLACEMENT CONSIDERATIONS

It was determined that any replacement ICP-MS would be required to meet or exceed a number of requirements, including:

- 1) The replacement instrument had to be made available in a timely manner to ensure no interruptions of analytical services;
- 2) The replacement to meet budgetary parameters;
- 3) The ability to migrate existing analytical methods to the new instrument with minimal research and development;
- 4) The ability to maintain the synergies between existing Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), with respect to software and combination of methods;
- 5) The functionality to maintain or improve upon analytical parameters, such as detection limit (DL), linearity, stability and matrix effects; and
- 6) Either maintain or reduce operational costs.

After notification of the EOGS, the laboratory director contacted several vendors to obtain specifications on their products. Specifications requested were to meet or exceed the current ICP-MS system, with a hard deadline for delivery and “plugged in” on the laboratory floor on, or before, March 31, 2020.

After reviewing the specifications provided and obtaining budgetary quotations from the potential vendors, the preferred choice of instrumentation started to become clear. Elimination of some vendors resulted because their technology was mature and becoming obsolete. Other vendors did not meet analytical specifications that the laboratory required. The final decision was to purchase a Thermo Fisher Scientific iCAP RQ ICP-MS.

## RESULTS OF REPLACEMENT CONSIDERATIONS

1) *The replacement to be available in a timely manner to ensure no interruptions in analytical output.* The selected replacement instrument was sourced from the Thermo Fisher Scientific factory for mass spectrometers located in Bremen, Germany. A purchase order for the iCAP RQ ICP-MS was issued on February 19, 2020, and the instrument was delivered to the laboratory on March 17, 2020. The requirement of delivery before fiscal year-end was achieved, and the EOGS date for the old ICP-MS was no longer of concern, as the replacement instrument met the end-of-fiscal year deadline, thereby ensuring continuity of analytical services.

2) *The replacement to meet budgetary parameters.* Budgetary quotes were received from various vendors. As noted, Thermo Fisher Scientifics ICP-MS was the lowest cost, while also meeting or exceeding defined specifications.

3) *The ability to migrate existing analytical methods to the new instrument with minimal research and development.* To aid with the migration of the laboratory’s analytical methods to the replacement ICP-MS, the old ICP-MS was kept online during transition. This enabled the export and printing of all the associated analytical parameters to aid in building the analytical methods on the new ICP-MS. Testing was undertaken to validate the method migration to the new ICP-MS, by looking for the occurrence of bias between the methods on the two instruments. This was accomplished by comparing Certified Reference Material (CRM) results between the two instruments. Table 1 shows a comparison between United States Geological Survey’s CRM STM-1, as analyzed by the laboratory’s ICP-MS Trace Element Lithium Metaborate Fusion package (Finch *et al.*, 2018). There are significantly fewer data for the iCAP RQ (n=8) than for the X-Series II (n=78), but the initial results indicate strong agreement.

The migration of methods from the old to the new ICP-MS was accomplished with only minor adjustments in calibration strategies due to innate differences in the iCAP-RQ software.

4) *The ability to maintain the synergies between existing Inductively Coupled Plasma-Optical Emission Spectro-*

**Table 1.** Results STM-1 iCAP-RQ, Series II

|                          | N  | Ga<br>ppm | Ge<br>ppm | Rb<br>ppm | Sr<br>ppm | Y<br>ppm  | Nb<br>ppm | Sn<br>ppm | Cs<br>ppm | La<br>ppm |
|--------------------------|----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| X-Series II (Old ICP-MS) | 8  | 39        | 5         | 103       | 683       | 40        | 238       | 7.8       | 1.3       | 146       |
| iCAP RQ (New ICP-MS)     | 78 | 42        | 5         | 110       | 718       | 42        | 237       | 7.6       | 1.4       | 155       |
| Relative Error %         | %  | 5.1       | 5.5       | 4.7       | 3.3       | 3.0       | 0.3       | 2.0       | 6.4       | 4.0       |
|                          | N  | Ce<br>ppm | Pr<br>ppm | Nd<br>ppm | Sm<br>ppm | Eu<br>ppm | Tb<br>ppm | Gd<br>ppm | Dy<br>ppm | Ho<br>ppm |
| X-Series II (Old ICP-MS) | 8  | 255       | 24.9      | 79        | 12.0      | 3.4       | 1.4       | 9.3       | 7.9       | 1.4       |
| iCAP RQ (New ICP-MS)     | 78 | 267       | 26.3      | 84        | 12.7      | 3.6       | 1.5       | 9.3       | 8.4       | 1.5       |
| Relative Error %         | %  | 3.0       | 3.5       | 4.3       | 3.6       | 3.6       | 2.1       | 0.2       | 3.8       | 0.2       |
|                          | N  | Er<br>ppm | Tm<br>ppm | Yb<br>ppm | Lu<br>ppm | Hf<br>ppm | Ta<br>ppm | W<br>ppm  | Th<br>ppm | U<br>ppm  |
| X-Series II (Old ICP-MS) | 8  | 4.3       | 0.6       | 4.2       | 0.63      | 26.7      | 18.7      | 4         | 28.8      | 8.2       |
| iCAP RQ (New ICP-MS)     | 78 | 4.5       | 0.6       | 4.4       | 0.57      | 29.5      | 15.8      | 3         | 28.8      | 8.4       |
| Relative Error %         | %  | 2.4       | 2.1       | 3.4       | 5.6       | 6.7       | 10.6      | 8.1       | 0.1       | 1.8       |

meter (ICP-OES), with respect to software and combination of methods. The laboratory provides combination analytical packages of elements analyzed by ICP-MS and ICP-OES. The previous instrumentation configuration had synergies between the two instrument's operational software. These synergies enable ease of exporting raw data from both instruments, to be combined for offline calculation of the data. The new ICP-MS retained this functionality within the software. This was quite important as the laboratory did not have to rewrite any of the existing spreadsheets and reports that are used to produce final versions of the datasets.

5) *The functionality to maintain or improve upon analytical parameters, such as detection limit (DL), linearity, stability and matrix effects.* Detection limits (DL) are evaluated on real-digestion blanks or fusion blanks. A series of blanks are analyzed with every sample batch. These blanks are then calculated and the DL is based upon 3 standard deviations of the blank values. Table 2 lists DLs for elements analyzed by the laboratory's ICP-MS Trace Element Lithium Metaborate Fusion package (Finch *et al.*, 2018). Table 2 shows favourable agreement between DLs obtained by both the old and new instrumentation.

Linearity for ICP-MS generally spans many orders of magnitude for intensity in counts per second (cps) of signal *vs.* concentration for the full mass range analyzed. The calibration regime applied by the laboratory uses a zero standard and at least two other standards for calibration with one standard at 10% concentration of the highest standard. Standards are prepared to cover the full range of expected concentrations and beyond. The degree of linearity for the calibration working range can be expressed as the correlation coefficient ( $R^2$ ) of the linear regression of cps *vs.* con-

centration. For all calibrations  $R^2=1$ . This illustrates that all calibration curve fits are perfectly linear leaving no concerns for linearity of signal over expected working range.

Stability over the time can be measured by internal standard recovery. To measure stability, the recovery of the internal standard is measured over time in real samples. Figure 1 shows a chart of Internal Standard Recovery *vs.* Time for a sample run of ICP-MS trace elements prepared by Lithium Metaborate Fusion. This matrix has high total dissolved solids. The effect of the matrix on the sample introduction system should cause drift over time with a decline in signal response. The iCAP-RQ uses interchangeable sample cone inserts to optimize the sensitivity of the instrument depending on the total dissolved solids (TDS) of the matrix. These inserts come in three variations, from high sensitivity, to high matrix, to robust design. They achieve optimal sensitivity based on matrix, reducing the amount of cone maintenance and drift due to salt deposition on the cones. In this case (Figure 1), even in a harsh sample matrix, the drift displayed is acceptable.

Since the introduction of the first ICP-MS instrumentation, the biggest analytical issue concerns the correction of polyatomic interferences. High TDS that are prevalent in geological samples and the fluxes used in the preparation of the solutions lead to polyatomic interferences that require correction. With the high sensitivity of the ICP-MS instrumentation, dilution of the sample can lower the overall effect of the matrix contribution to the interference profile. This may help with some minor interference but correction equations need to be developed to remove any interference present. The process involves many solutions and many equations to carry out adequate correction of the interfer-

**Table 2.** Detection Limits ICP-MX Trace X-Series II, iCAP-RQ

|                   | <b>Ga</b><br><b>ppm</b> | <b>Ge</b><br><b>ppm</b> | <b>Rb</b><br><b>ppm</b> | <b>Sr</b><br><b>ppm</b> | <b>Y</b><br><b>ppm</b>  | <b>Nb</b><br><b>ppm</b> | <b>Sn</b><br><b>ppm</b> | <b>Cs</b><br><b>ppm</b> | <b>La</b><br><b>ppm</b> | <b>Ce</b><br><b>ppm</b> |
|-------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| X-Series II (Old) | 0.3                     | 1.0                     | 0.3                     | 0.5                     | 0.1                     | 0.3                     | 0.3                     | 0.1                     | 0.2                     | 0.1                     |
| iCAP RQ (New)     | 0.1                     | 0.1                     | 0.3                     | 0.7                     | 0.1                     | 0.4                     | 0.6                     | 0.1                     | 0.1                     | 0.1                     |
|                   | <b>Pr</b><br><b>ppm</b> | <b>Nd</b><br><b>ppm</b> | <b>Sm</b><br><b>ppm</b> | <b>Eu</b><br><b>ppm</b> | <b>Tb</b><br><b>ppm</b> | <b>Gd</b><br><b>ppm</b> | <b>Dy</b><br><b>ppm</b> | <b>Ho</b><br><b>ppm</b> | <b>Er</b><br><b>ppm</b> | <b>Tm</b><br><b>ppm</b> |
| X-Series II (Old) | 0.1                     | 0.1                     | 0.1                     | 0.04                    | 0.02                    | 0.1                     | 0.1                     | 0.04                    | 0.1                     | 0.03                    |
| iCAP RQ (New)     | 0.1                     | 0.1                     | 0.1                     | 0.06                    | 0.03                    | 0.1                     | 0.1                     | 0.09                    | 0.1                     | 0.09                    |
|                   | <b>Yb</b><br><b>ppm</b> | <b>Lu</b><br><b>ppm</b> | <b>Hf</b><br><b>ppm</b> | <b>Ta</b><br><b>ppm</b> | <b>W</b><br><b>ppm</b>  | <b>Tl</b><br><b>ppm</b> | <b>Bi</b><br><b>ppm</b> | <b>Th</b><br><b>ppm</b> | <b>U</b><br><b>ppm</b>  |                         |
| X-Series II (Old) | 0.05                    | 0.1                     | 0.1                     | 0.9                     | 0.3                     | 0.05                    | 0.1                     | 0.1                     | 0.05                    |                         |
| iCAP RQ (New)     | 0.11                    | 0.1                     | 0.1                     | 0.1                     | 0.3                     | 0.11                    | 0.1                     | 0.1                     | 0.1                     |                         |

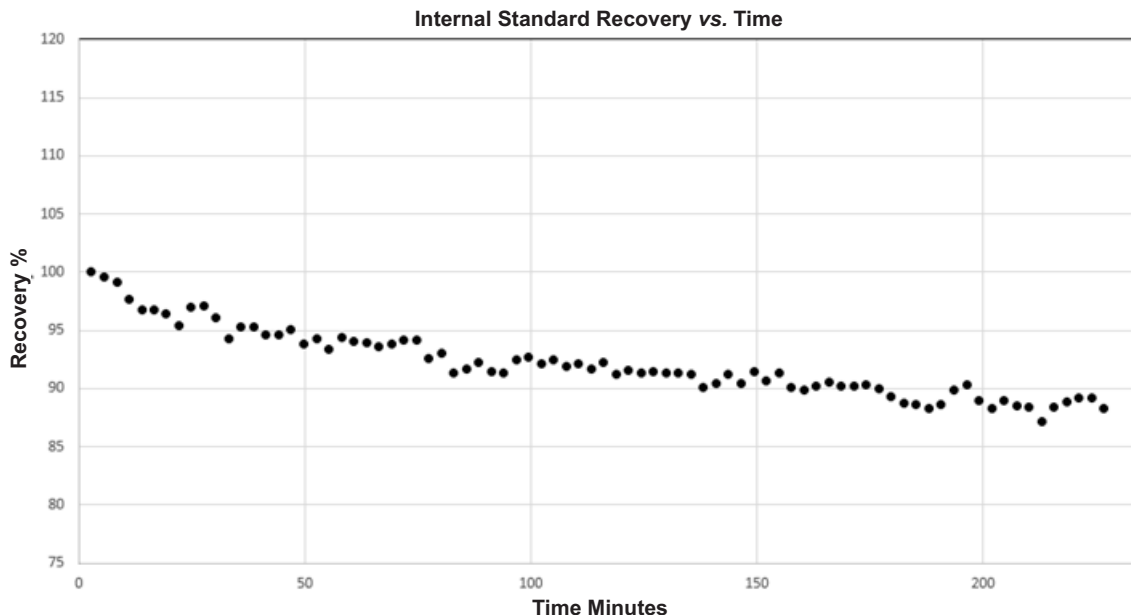


Figure 1. Internal Standard Recovery vs. Time.

ences. Later generations of ICP-MS began using Collision Reaction Cells (CRC), which also used Kinetic Energy Discrimination (KED). This method of correction vastly reduced the overall interference profile with almost no need for correction equations.

The laboratory’s new iCAP-RQ takes advantage of technologies that further improves upon Interference Reduction (Figure 2). The iCAP-RQ uses a 90° deflection

before the CRC. This achieves a reduction in photons and neutrals entering the CRC. When deflection is optimal, it provides removal of unwanted material. These materials would contaminate the sensors over time and significantly reduce performance or require additional maintenance, especially when located in the high vacuum region of the analyzer. Thermo Fisher’s new collision cell design, employing curved flatpole rods, was developed for the iCAP-RQ. The design provides high transmission to the cell

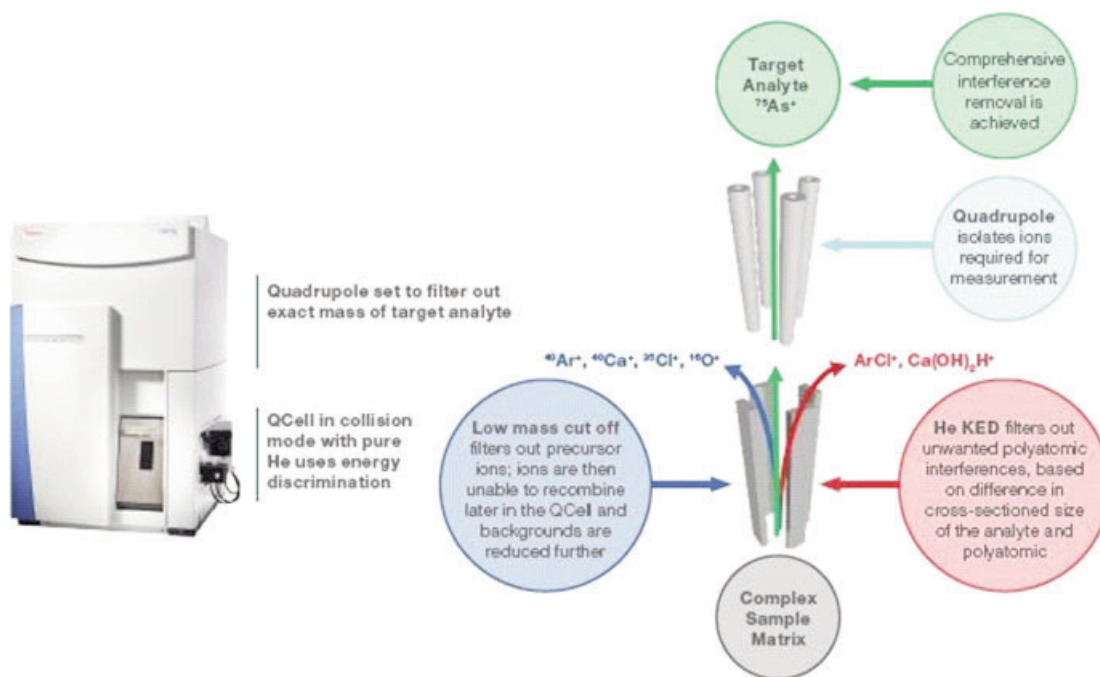


Figure 2. Interference Reduction iCAP-RQ.

entrance with a low mass cut-off in the middle of the cell. This unique design delivers high sensitivity and robustness, as well as sufficiently high, low mass cut-off to ensure elimination of any reaction products (Kutscher, 2019).

6) *Either maintain or reduce operational costs.* The two largest going-forward expenses for ICP-MS operations are argon gas consumption and service costs. For argon gas, the longer the instrument takes to perform its measurements, the greater the argon consumption and cost. The iCAP-RQ has a number of design features that reduce measurement time. Sample loading and rinsing in traditional ICP-MS systems use a peristaltic pump. To reduce the sample loading and rinse times, the pump is run at a high speed to reduce uptake and rinsing times. While this works, it still requires a significant amount of time to ready the instrument for measurement.

The iCAP-RQ is equipped with an Elemental Scientific Incorporated SC-4DX Fast auto sampler, coupled to a SampleSense sample introduction valve. The auto sampler uses a vacuum pump to load a sample loop, rather than a peristaltic pump, and the SampleSense uses an optical sensor technology to detect when the sample loop is fully loaded and then triggers the instrument to measure. These two improvements to the sample uptake and rinsing functions saves a significant amount of overall analysis time per sample. The iCAP-RQ is also about ten times more sensitive than the old X-Series II. With the improvement in overall sensitivity, the mass counting times can be reduced, effectively reducing the overall measurement time. The improved efficiency of these functions has the ability to reduce argon consumption by fifty percent.

Service costs for ICP-MS instrumentation are very expensive. If service is required on an “as need” basis, the cost per visit from a mainland-based service provider has to include flights, accommodations, per diems, labour and parts. These are costs beyond the control of the laboratory.

To avoid unexpected service costs, the laboratory has always had in place an annual fixed-cost service contract.

These contracts, while costly, provide a fixed budgetary commitment, and also include contractual terms that cover all costs with a fixed service response time. These terms help avoid long down times that cause interruptions to the laboratory’s work flow. With periodic maintenance incorporated into the service contract, the instrumentation is serviced on a regular basis, which helps GSNL avoid major analytical interruptions. With the purchase of the iCAP-RQ, the laboratory received a one-year full warranty and two additional years of full service contracts. These are savings of tens of thousands of dollars over the next three years.

## CONCLUSION

With the EOGS becoming effective on March 31, 2020, for the geochemical laboratory’s ICP-MS, the replacement process was undertaken. After going through the procurement process, a Thermo Fisher Scientific iCAP-RQ ICP-MS was selected. This ICP-MS provides the best fit for the geochemical services required, both in specifications and cost. Once the instrument was installed, an evaluation was performed, and expectations were met or exceeded.

Going forward, the selection of the iCAP-RQ as a replacement ICP-MS will function to provide ICP-MS analytical services for the next decade and beyond.

## REFERENCES

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