

Background

ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) is the work-horse for routine analyses within our analytical chemistry laboratories. A new spectrometer was purchased and installed at the end of 2005 to replace an ageing model. This new instrument is the IRIS Intrepid II XDL from Thermo Electron, which was chosen after a thorough comparison of several models offered by various manufacturers.

Due to different performance characteristics, compared to the old apparatus, a complete new validation was required.

We validated the method for different sample types: reactor loop waters and Boom Clay pore waters (further referred to as Boom Clay waters). This report is confined to the latter, which constitutes a significant proportion of our routine analyses, and are samples from experiments performed within the framework of geological disposal and radio-active waste projects. Boom Clay water is derived either from piezometers installed in the HADES underground research facility or from the squeezing or leaching of clay cores. Water samples from radionuclide migration experiments within Boom Clay are also analysed.

Objectives

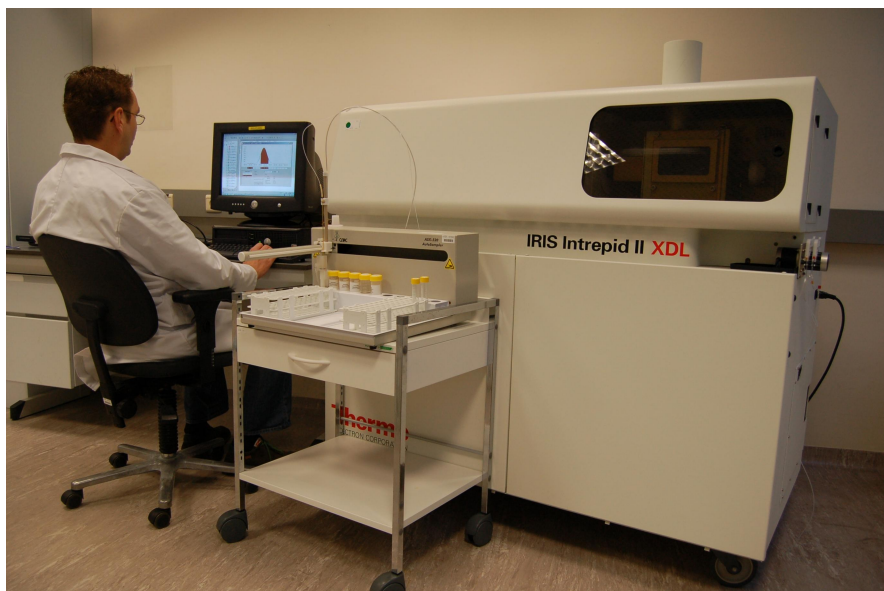
Validation is the process of demonstrating that the method is fit for the intended purpose. So in this case it means quantifying the performance parameters of the method used for analysing Boom Clay waters and verifying that the values obtained are acceptable.

The validation results must be as representative as possible for the matrix under investigation, which was achieved by using the remainders of previously analysed Boom Clay waters. The possibility to perform a specific validation for this particular matrix and the ability to measure such radionuclide containing samples are just two of the advantages of having an analytical service within SCK•CEN: external laboratories will most likely neither be able nor willing to do these.

Principal results

The elements of interest in Boom Clay water are: Al, B, Ba, Ca, Fe, K, Li, Mg, Mn, Na, Si and Sr. The performance parameters which must be investigated and/or quantified for all these elements are the following: selectivity/specificity, limit of detection, linearity, reproducibility, trueness and ruggedness.

By carefully selecting the spectral lines during method development, based on our existing expertise and literature studies, we made the method as specific as possible, i.e. free from interferences. However, because perfect specificity is not possible, further investigation of both spectral and non-spectral interferences was conducted by analysing standards of elements which can cause interference problems. From this it appeared that any remaining interferences could be satisfactorily compensated for by using inter-element correction models.



The IRIS Intrepid II XDL

Limits of detection were determined by measuring, under reproducibility conditions, method blanks and real samples. Although the latter are more representative, for the elements which are only ever present at high concentrations in real samples we had no choice but to use the values calculated from the method blanks. For these major elements, however, the limit of detection is of little relevance. The limits of detection obtained with the new instrument are, with the exception of lithium, equivalent to or better than those obtained with the previous instrument. For several elements there was even a ten-fold improvement. The limit of detection for lithium increased from 20 µg/L to 50 µg/L, which is still acceptable.

To check linearity, we measured the intensities of a blank and ten standards, spread equidistantly over the desired concentration ranges. The residual standard deviations after a linear and a quadratic regression were then compared by means of a statistical test, as described in ISO 8466-1. The regressions (either linear or quadratic) which gave the best result for any given element were incorporated into the method, after which the calibration models were tested again by analysing a large number of known standards having different concentrations against the proposed routine calibration. All measured residuals were acceptable.

Nine pools of Boom Clay waters were analysed in duplicate by two different analysts. To incorporate as much variability as possible, these analyses were performed on different days and almost completely independently of each other. As for many instrumental analytical techniques, the concentration range can be divided into two regions: one of low concentrations with constant s_R (reproducibility standard deviation, in absolute units) and one of high concentrations with constant CV_R (reproducibility coefficient of variation, in percent). In our experiments, the s_R was equal to or less than half the limit of detection for a given element and the CV_R was 5%, at maximum.

To demonstrate trueness (absence of systematic error), we spiked eleven pools of samples with different concentrations of all elements. A statistical test on the measured recoveries indicated no significant bias for any of the elements.

Measurement of two certified reference materials also gave satisfactory results.

As the reproducibility and trueness tests were carried out as if they were routine analyses, and were spread over many days, the normal instrumental variations are incorporated herein. Nevertheless, two important instrumental parameters were investigated further: the pump speed and the applied RF power. The settings we use for routine analysis seemed to be sufficiently rugged, meaning that small deviations resulted in negligible decreases or enhancements of the analytical signals.

Lastly, the validation study also allowed us to calculate the measurement uncertainty. As for the reproducibility, the measurement uncertainty can be split into one for low concentrations, having a constant value (in absolute units), and one for high concentrations where the measurement uncertainty is proportional to the concentration (constant in percent). The first is different for each element and is equal to the detection limit of the element; the latter is equal to 10% (for the 95% confidence interval) for all elements. This is very good compared to typical measurement uncertainties in other laboratories.

The correctness of these measurement uncertainties has already been demonstrated in two proficiency tests.

Future work

An extensive quality control program has been set up to monitor continuously the validation parameters. This includes the regular measurement of quality control standards, method blanks, certified reference materials, and participation in proficiency tests. We now have almost one year's experience with the instrument and the results from the validation study are still valid. However, deterioration in future performance (e.g. because of aging of the instrument) cannot be excluded. Should this situation arise, the quality control program will detect it, after which (part of) the validation will need to be repeated.

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Main reference

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