iCAP MX Series ICP-MS: Extending analytical capabilities with linear dynamic range and analyte specific scan control

Keywords
ICP-MS, linear dynamic range, detection system, cross calibration, method dynamic range, multi element analyses

Introduction

ICP-MS is a technique with high sensitivity and specificity that is typically used in applications where the lowest detection limits are required. “Real world” samples contain a very wide range of concentrations across all analytes of interest, normally classified between major elements (predominantly alkaline and alkaline earth elements) and trace level contaminants (for example, arsenic, cadmium, mercury and lead). While the concentration range within each of the groups usually does not exceed 4–5 orders of magnitude, the overall concentration range to be covered in a single reading may well reach or exceed 10 orders of magnitude. Beyond the instrument’s ability to handle samples with elevated amounts of matrix, the linear dynamic range (LDR) is a key contributor to its ability to decipher complex samples.

The Thermo Scientific™ iCAP™ MX Series ICP-MS Detector utilizes a powerful detection system to provide the analyst with a high LDR and extended lifetime. According to IUPAC[1], the term *dynamic range* of an analyzer refers to the ratio between the maximum and minimum usable indication (detection limit), in which the response is directly proportional to the concentration of an analyte.

This technical note details the range of techniques available with the Thermo Scientific™ iCAP™ MSX ICP-MS and the Thermo Scientific™ iCAP™ MTX ICP-MS that allow laboratories to confidently achieve ng·L^{-1} detection limits for trace elements while optimizing sensitivity for specific matrix analytes, present at concentrations of several hundred or even thousand mg·L^{-1} during a single analysis of a sample.

Detection techniques

ICP-MS instruments normally use electron multipliers as detection systems, where different signal ranges are measured using specific gain factors. The signals are calibrated between both regimes by means of a cross calibration, so that the user always sees a calibrated signal independently from the detector regime used for analysis.

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The iCAP MX Series ICP-MS offers three different settings for the detection system, which differ in the average cross calibration factor and the maximum count rate that can be recorded. The standard setting extends the lifetime of the ion multiplier and provides a maximum count rate of typically 3 x 10^9 cps, which is more than sufficient for many applications. The detector can also be operated to analyze even higher signals, exceeding 1 x 10^{10} cps. However, signals recorded with high count rates may be biased by other effects, such as changing ionization in the plasma or transportation through the mass spectrometer.

Analysts can further leverage isotope selection or user adjustable resolution settings per analyte to further increase the accessible concentration range for different analytes in a sample, using the intuitive and guided process of method creation within Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

All data shown in the following was measured using the iCAP MSX ICP-MS instrument. However, the described findings and adjustments can also be transferred to the iCAP MTX ICP-MS.

Linear dynamic range

To demonstrate the linearity of the detector, ^{175}Lu was chosen as the analyte since it is quasi-monoisotopic (^{175}Lu has a natural abundance of 97.4%) and can be measured with negligible blank levels. The linear measurement range of the detection system can be applied to any isotopes measured in the count rate range of 0.1 cps to over 10^{10} cps (equivalent to over 11 orders of linear dynamic range) (Figure 1). For this test, the high sensitivity mode was used, in combination with kinetic energy discrimination using pure helium as collision gas (S-Off-KED).

In between the lowest and the highest point in the calibration curve (1 pg·L^{-1} and 35 mg·L^{-1}, respectively), the full linear dynamic range of the detection system was used, with a resulting correlation coefficient of 0.9995. Note: no internal standard was used during this measurement.

The sensitivity and very low detector background count rate of the iCAP MX Series ICP-MS instruments means that they are capable of ultra trace element analysis at ng·L^{-1} levels and below. The wide LDR means that the most sensitive elements (i.e., lanthanide elements with 1st ionization potentials below 6 eV) can be calibrated with linear response from concentrations of only a few ng·L^{-1} up to concentrations in the mg·L^{-1} range, whereas the calibrated range for less sensitive elements can be extended to even higher levels. For all elements, it is possible to extend the calibrated range up to several thousand ppm by means of selecting an alternative and less abundant isotope or attenuating signals through choosing alternative resolution settings on the analyzing quadrupole.

Method dynamic range

As mentioned above, the concentration range spanning across all analytes of interest may significantly exceed the linearity requirements for each individual analyte of a panel. Typically, within an analytical method, different sets of calibration standards are used to cover the expected range of concentrations for trace impurities, but also the major components of a sample. For each of the two categories, in which the full dynamic range can be leveraged, the calibrated range is usually limited.

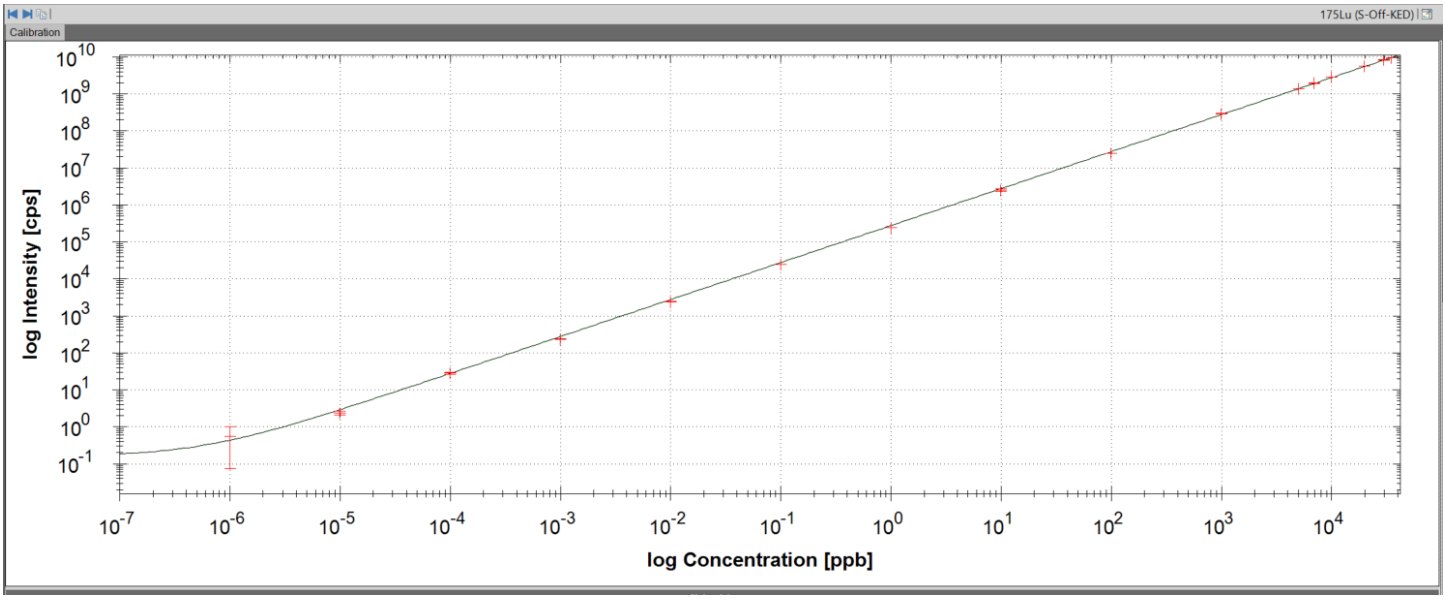

Figure 1. Calibration curve for ^{175}Lu between 1 pg·L^{-1} and 35 mg·L^{-1}. The detection system of the iCAP MSX ICP-MS used for this test recorded the signal intensity of the blank as <0.2 cps, whereas the highest point of the calibration curve may exceed 10^{10} cps.

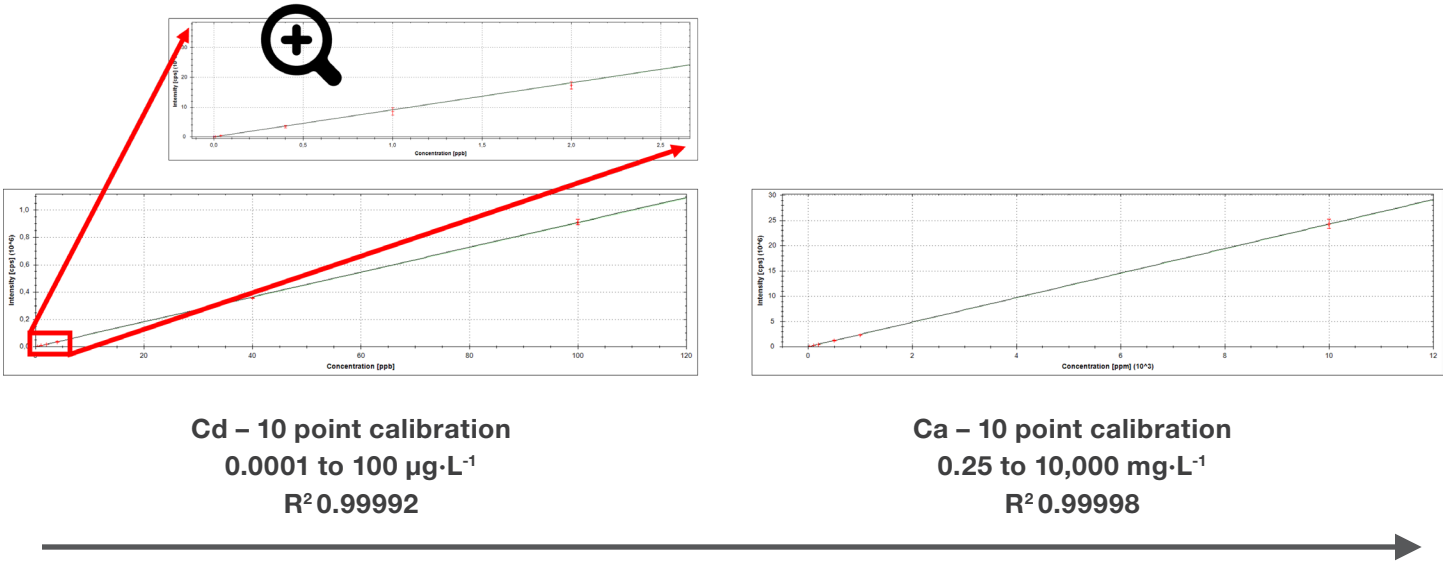

Figure 2. Calibration curves as typically run in an ICP-MS method. Cd is calibrated between 0.0001 to 100 µg·L^{-1}, whereas Ca is calibrated between 0.25 and 10,000 mg·L^{-1}. Both calibration curves show excellent linearity, with a total concentration range of 11 orders of magnitude covered.

However, the difference between the lowest and the highest calibrated concentration can be described as the dynamic range of a method. To investigate the analytical range of the system, calibration curves covering a concentration range between 0.1 µg·L^{-1} and 10,000 mg·L^{-1} were acquired for selected analytes. Cadmium was chosen as a representative element for analytes typically determined at very low levels, whereas calcium represented typical matrix elements, analytes with concentrations in the high mg·L^{-1} or even % range. For both elements, a series of 10 calibration standards were prepared covering at least five orders of magnitude in concentration (Cd: 0.1 ng·L^{-1} to 100 µg·L^{-1}, Ca 0.25 mg·L^{-1} to 10,0000 mg·L^{-1}). To mimic conditions typically used in applied testing laboratories, the measurements were performed using the matrix mode, the most recommended interface configuration for measurement of a wide range of samples. Kinetic energy discrimination (KED) using pure helium as collision gas was applied to eliminate potential interferences. As the measurement of analyte concentrations of several hundred mg·L^{-1} is only needed for samples comprising a significant amount of total dissolved solids, argon gas dilution (AGD) was applied in the measurements of calcium.

The resulting calibration curves, measured using optimized conditions for each element, showed excellent correlation coefficients of 0.9999, while recorded signal intensities again covered the full dynamic range of the detector. For both analytes, the selected internal standards were found to be well within 90%–110% of the intensity measured in the acid blank.

Analyte specific scan control

Alternative isotopes of multi-isotopic elements may be used for quantitation to extend the dynamic range. Since the relative abundance of each isotope of a naturally occurring element is unique, choosing a low abundance isotope will enable calibration of a higher concentration range. Qtegra ISDS Software allows the use of more than one isotope per element, such that the dynamic range may be further extended, for example, by a factor of 6 if using both ^{60}Ni (26.1%) and ^{62}Ni (3.9%). On-the-Fly Resolution switching for selected analytes allows data to be collected in the most sensitive Normal Resolution mode or alternatively using High Resolution mode (average peak width of 0.35 amu for ^{115}In). The reduction of peak width to attenuate signals from analytes present in elevated concentrations extends the LDR to higher concentrations (Figure 3).

Alternatively, this setting also allows mathematical correction for doubly charged ion interferences on single quadrupole ICP-MS instruments, like the iCAP MSX ICP-MS. However, analysis must be accomplished with sufficient mass resolution (at least better than 0.5 amu) to resolve a specific non-interfered (doubly charged) isotope of the interfering element from potential overlaps with other analytes. For the correction of ^{150}Nd^{++}, interfering with ^{75}As^{+}, *m/z* 72.5 (corresponding to ^{145}Nd^{++}) is monitored. However, it is crucial to fully separate its signal from potential overlaps with ^{72,73}Ge (a common internal standard), as otherwise overcorrection would occur.

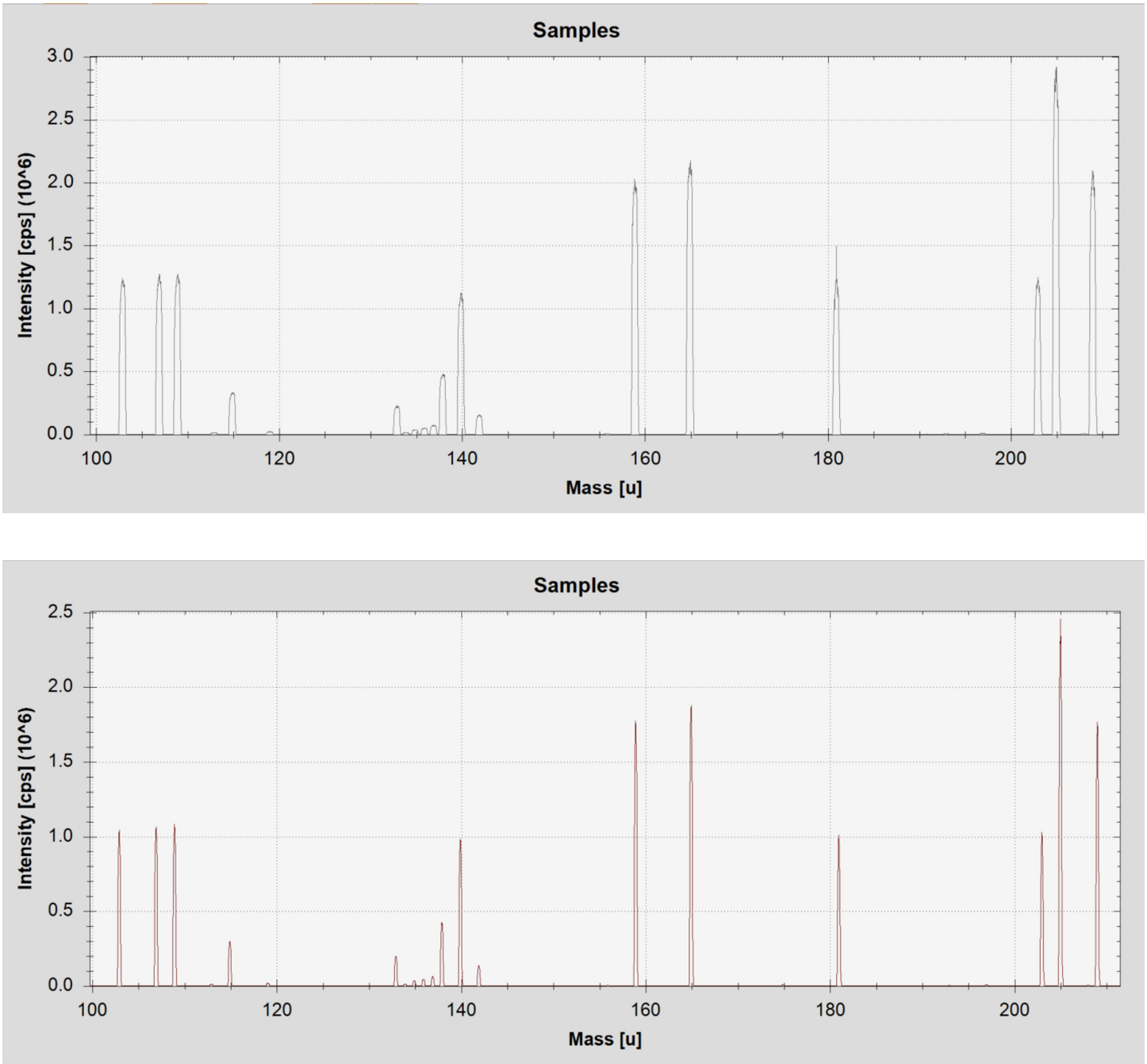

Figure 3. Mass spectra acquired on an iCAP MSX ICP-MS for a multi-element solution in the mass range 150 to 210 amu in (A) normal resolution and (B) high resolution.

All iCAP MX Series ICP-MS instruments can achieve the required resolution. This is demonstrated in Figure 4, showing a survey scan spectrum. The analyzed solution contained germanium, arsenic, selenium, and a mixture of different lanthanides. Please note that signals appearing at half mass (i.e., 72.5 u) are baseline resolved from all other signals. The accuracy of the iCAP MX Series ICP-MS mass calibration allows single point data acquisition at the peak maximum to optimize counting statistics and results in highly efficient data acquisition in both resolutions.

Required correction equations (based on natural isotopic abundances) can be easily set up in a LabBook or template in Qtegra ISDS Software.[2]

A triple quadrupole-based ICP-MS system, like the iCAP MTX ICP-MS, would resolve such interference by using reactive gases (i.e., O_2). In this case, $^{75}As^{+}$ reacts with O_2 to form $^{91}[^{75}As^{16}O]^{+}$, while the interferences ($^{150}Sm^{++}$ and/or $^{150}Nd^{++}$) do not react and are eliminated in the third quadrupole.

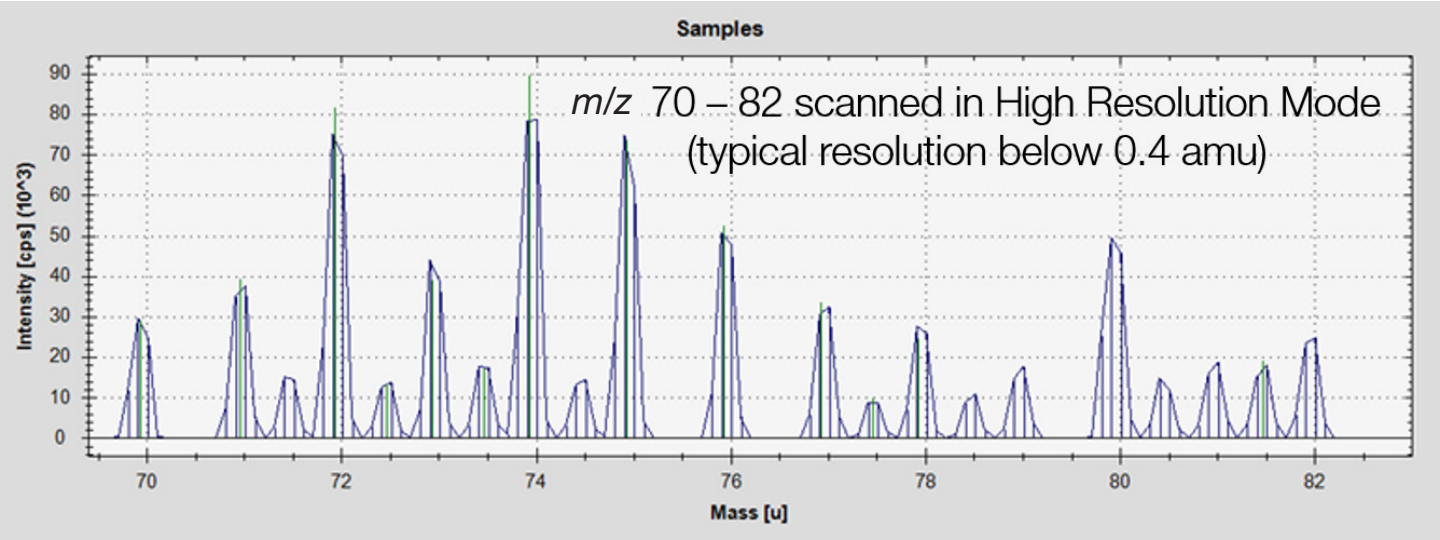

Figure 4. Survey scan spectrum between *m/z* 70–82 acquired using high resolution.

Conclusion

The iCAP MX Series ICP-MS instruments combine innovative hardware with intuitive workflows in software to provide laboratories with powerful options to address all challenges that different samples may have to offer. All options available to analysts are seamlessly brought together to provide the user with the ideal system for quantifying all the elements in many types of samples using a single data acquisition method under optimum conditions for each element.

- Both instruments allow for up to 11 orders linear dynamic range for one-shot analysis if needed, but in general use a setting to extend detector lifetime for typical applications such as in applied testing.
- Very low background counts allow for excellent detection limits, combined with powerful options to remove interferences, both of polyatomic as well as isobaric nature.
- Solutions to enable the analysis of samples containing high amounts of matrix elements, even the ability to accurately quantify them at %-levels.
- Wide choice of isotope specific data acquisition modes for optimum data acquisition.

The unique combination of innovative hardware and intuitive software makes the iCAP MX Series ICP-MS extremely versatile and able to meet the most challenging applications in trace elemental analysis.

References

1. IUPAC Compendium of Chemical Terminology.
2. Thermo Fisher Scientific Smart Note 214.

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