Application Note: 30064

Thermo Scientific ELEMENT XR: Extended Dynamic Range High Resolution ICP-MS

Key Words

- ELEMENT XR
- Extended Dynamic Range
- Geological Analysis
- High Resolution ICP-MS
- Laser Ablation

Introduction

High resolution ICP-MS (HR-ICP-MS) is widely used in geochemical applications for interference-free multi-elemental determinations in complex sample matrices and for the measurement of precise isotope and elemental ratios at low concentrations, as well as a detector for laser ablation analysis. The linear dynamic detection range is of immense importance in ICP-MS because of the wide range of elements and concentrations to be analyzed in a single analysis. This is particularly critical for laser ablation analyses where, in addition to measuring ultra-trace elements, a major matrix component is often used as an internal standard to correct for the amount of material ablated from each sampling point.

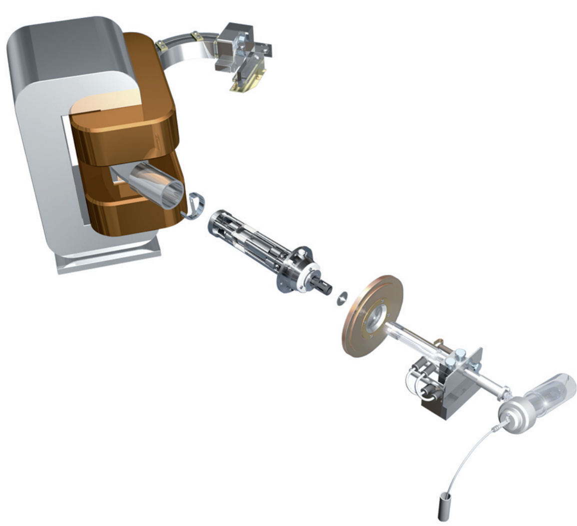

Figure 1: Thermo Scientific ELEMENT 2 schematic.

The Thermo Scientific ELEMENT 2 HR-ICP-MS employs a single high performance, discrete dynode, dual mode secondary electron multiplier (SEM) with a linear dynamic range of over nine orders of magnitude. This detection range allows the measurement of count rates from the very low 'background noise' of 0.2 cps to a maximum of ~5×10^9 cps. With the very high elemental sensitivities achievable with the ELEMENT 2 (~2,000,000 cps per ng/g of a mid mass element, e.g. ^{59}Co), this count range corresponds to a measurable concentration range of sub fg/g (ppq) to over a µg/g (ppm) in solution mode.

While this measurement range is suitable for most applications, it is still insufficient for the simultaneous quantitation of matrix elements (%), traces (ppb) and ultra-trace (ppt/ppq) in a single analysis in many sample types.

For the analysis of these samples, there are few alternatives available to the analyst:

- Dilute the sample to bring the major matrix elements into the detectable range and reanalyze.
- Use an additional analytical technique for the analysis of the major matrix elements in the same sample preparation. For example, for the analysis of nuclear, geochemical, environmental and clinical materials, the analysis of the major matrix elements is commonly performed by AAS or ICP-OES and the trace and ultra-traces by ICP-MS.
- Defocusing of the ion beam to reduce the ion flux incident on the detector.

However, neither of the first two alternatives is practical in routine analyses due to the higher cost resulting from increased sample manipulation and longer analysis times and defocusing can lead to problems in signal stability, matrix effects and reproducibility. Up until now, no single technique provides the analyst with an instrumental solution to the problem of quantification from ppq to percentage levels in all sample matrices.

Implementation of a Faraday Detector in the Thermo Scientific ELEMENT XR

For the detection of low count rates < ~ 5 M cps, the Counting mode of the SEM is used and between ~ 50 k cps to ~ 5 G cps, the Analog mode. The operating ranges of these two SEM modes allow for a large cross-over range (50 k cps – 5 M cps) where both modes are simultaneously valid; in this range a cross-calibration is automatically performed for every spectrum acquired, ensuring accurate analysis. By choosing a single detector mode, the 'Both' mode, the user allows the Element control software to choose the appropriate detector mode (either Counting or Analog) for each isotope measured.

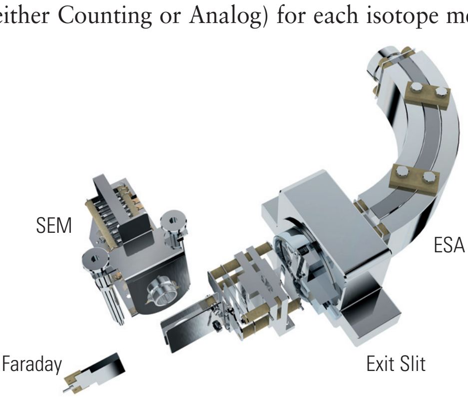

Figure 2: Implementation of the Faraday detector in the Thermo Scientific ELEMENT XR detection system.

A new detection system (Figure 2) has been implemented in the Thermo Scientific ELEMENT XR HR-ICP-MS which is based upon the proven design of the ELEMENT 2. Through the combination of a single Faraday collector with the SEM, the linear dynamic range of the ELEMENT XR can be increased by an additional three orders of magnitude, when compared to the ELEMENT 2, to over 10^{12}. With this increase in dynamic range, through measurement in Counting, Analog and Faraday detector modes, the maximum measurable concentration achievable with the ELEMENT XR is over 1000 µg/g (ppm) (Figure 3). Additionally, by moving higher concentration elements into higher resolutions, a further ~ 50-fold increase in measurable concentration can be achieved.

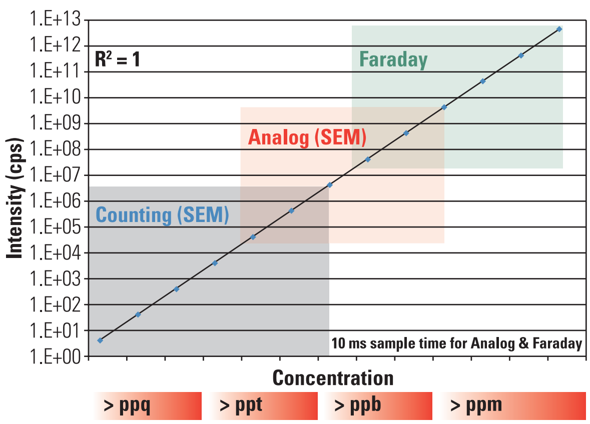

Figure 3: Detection range of the combination Faraday and SEM detector system in the Thermo Scientific ELEMENT XR. The plot shows the intensities from the measurement of single element ^{175}Lu solutions with concentrations between 2 fg/g and 2000 µg/g (10 ms sample time for Analog and Faraday).

New Thermo Scientific ELEMENT XR Detection System

Integration of Faraday detector circuit

- Sample times of down to 1 ms.
- No decay time required after the measurement of high intensities.
- Automatic switching between SEM (Analog and Counting detection modes) and Faraday with delay times < 1ms.
- Wide cross-over ranges (> 2 orders of magnitude) between different detector modes to allow for accurate, automated cross-calibration.
- Automatic cross-calibration between Faraday and Analog signals.
- Dynamic range: 5 x 10^7 cps – > 1 x 10^{12} cps (1 ms sample time).

Analog Detector Circuit

- Sample times of down to 1 ms.
- Automatic cross-calibration between Counting and Analog signals for each individual spectrum.
- Dynamic range: 5 x 10^4 cps – >1 x 10^9 cps (1 ms sample time).

Counting Detector Circuit

- Low dark noise: < 0.2 cps.
- Sample times of down to 100 µs.
- Large SEM Plateau range (~ 300 V).
- Dynamic range: 0.2 cps – 5 x 10^6 cps.

Triple Detector Mode

The Faraday detector is fully supported in the Element control software. With the introduction of the Faraday detector, a 'Triple' detector mode has been introduced that allows the Element software to choose the appropriate detector mode (Counting, Analog or Faraday) for the observed count rate. Therefore, in unknown samples this single, intelligent detector mode can be used for the analysis of all isotopes from sub ppq to percentage concentration levels.

An example of the use of this automatic choice of detector mode can be seen in these three displays in the Element software of a scan made across the ^{36}Ar peak in low resolution using the 'Triple' mode of the detector:

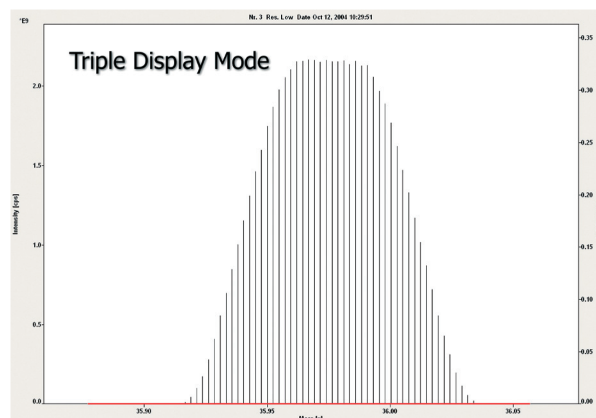

Figure 4a: Triple Display Mode of the Element Software.

- In this display, the 'Triple' display mode is used to show the ^{36}Ar peak independent of the detector mode actually used.

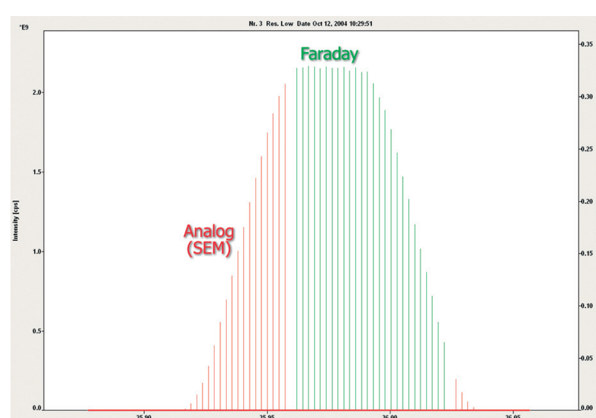

Figure 4b: Analog and Faraday display.

- Here, the ^{36}Ar peak is shown with the data from the Analog (SEM) detector in RED and for the Faraday in GREEN.

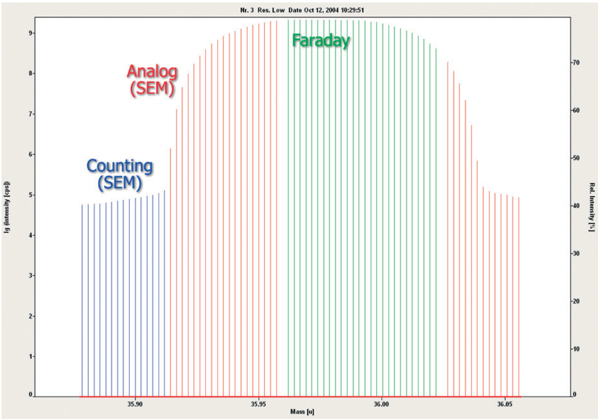

Figure 4c: Counting, Analog and Faraday display.

- Here, the ^{36}Ar is displayed with the intensity shown in a logarithmic scale in order to see the low intensities recorded by the Counting (SEM) in BLUE.

The use of the triple detector mode to measure the complete intensity range can be seen in the following scan made across ^{36}Ar, ^{38}Ar and ^{40}Ar.

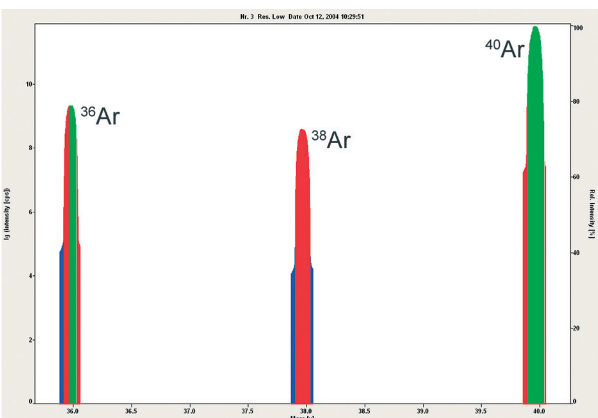

Figure 5: Spectrum across ^{36}Ar, ^{38}Ar and ^{40}Ar showing the incorporation of the Faraday detector (Triple detector mode) for the analysis of count rates > 1 x 10^9 cps (logarithmic intensity scale).

Applications

The possible applications with such a wide detection range in a single instrument include:

Geological Studies

- Determination of majors, traces and ultra-traces in survey analyses, replacing complimentary analysis techniques (e.g. AAS or ICP-OES).
- Use of the matrix element as internal standard in laser ablation analysis:
  - Na in fluid inclusions.
  - Al in melt inclusions.
  - Ca in bone / corals / otoliths etc.
  - C in diamond analyses.
- Concentration determination in minerals by laser ablation.
- Elemental ratios by laser ablation (e.g. Ca / Sr etc).

Industrial Applications

- Use of the matrix element as internal standard in laser or spark ablation analysis in the analysis of high purity metals.
- Si as internal standard for depth / spatial profiling of wafers.

Isotope Ratio Analysis

- Measurement of large ratios at high concentrations.
- Sr, Hf and Pb isotopes by laser ablation.

Example 1

The determination of the rare earth elements (REE) in fluid inclusions is of great interest as they provide important information on mineral alteration etc. and their analysis by laser ablation ICP-MS is carried out a routine basis in many laboratories. However, the choice of an internal standard in the analysis of these samples is limited to a small number of elements. Sodium, which can be found at weight percentage levels in fluid inclusions, would seem to be an ideal internal standard (as it is measurable by micro-thermometry) but in previous laser ablation ICP-MS studies its high concentration level has limited its use due to saturation of the Analog detector circuit.

With the newly increased dynamic range available on the Thermo Scientific ELEMENT XR, ^{23}Na in low resolution can be used as internal standard – still within the operating range of the Faraday detector – while other analytes (for example the REE and Th and U) at concentrations more than six orders of magnitude lower, can be detected – with maximum sensitivity – at the same time using the Counting mode of the SEM.

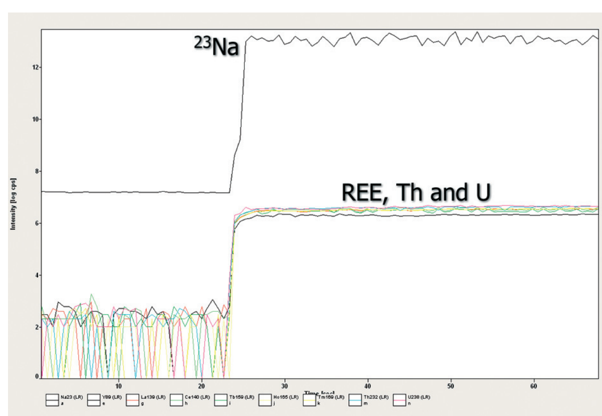

Figure 6: Laser analysis profile (20 s gas blank and 45 s sample) for a selection of elements in a fluid inclusion. ^{23}Na (at count rates > $10e^{12}$ cps in the sample) used as internal standard in the laser ablation for the analysis of the REE, Th and U in fluid inclusions.

Example 2

Multi-element analysis of iron meteorites with the Thermo Scientific ELEMENT XR. Analysis of matrix element (Fe), traces (P) and ultra-traces (Au) in a single analysis. In this example, medium resolution (MR, R = 4000) is used to remove interferences from common polyatomic interferences at ^{31}P (and to a lesser extent at ^{56}Fe), while maintaining sufficient sensitivity for the analysis of ^{197}Au.

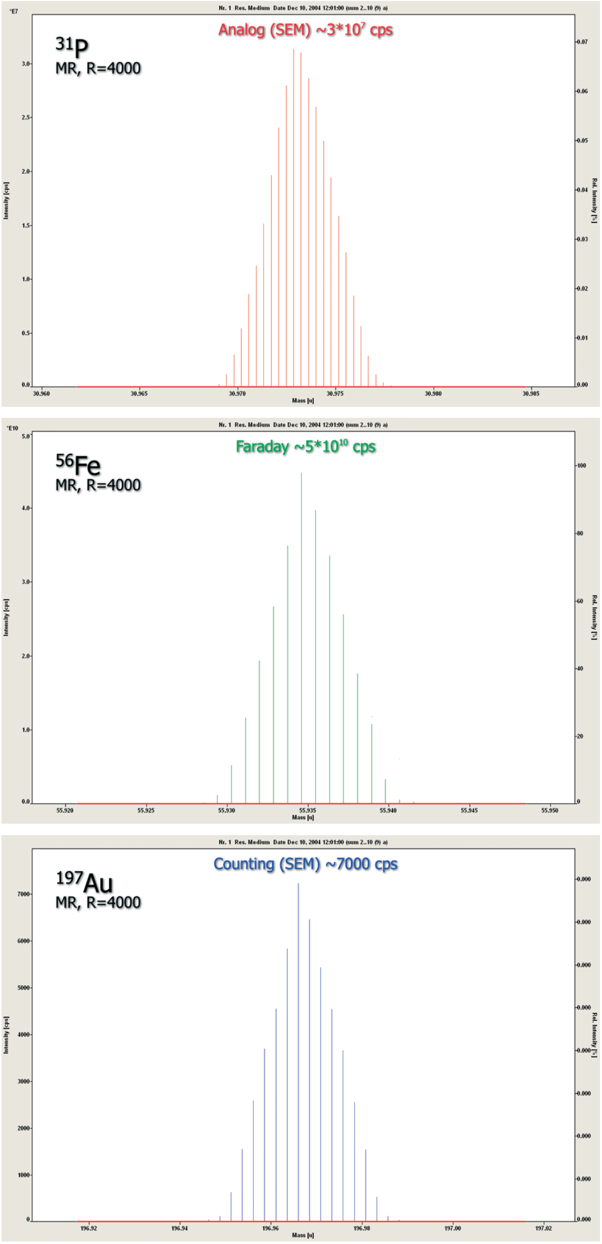

Figure 7: Spectra for ^{31}P, ^{56}Fe and ^{197}Au in an iron meteorite using Medium Resolution (MR, R = 4000) with the Thermo Scientific ELEMENT XR.

Conclusions

A unique detection system in ICP-MS, combining a dual mode SEM with a Faraday detector, has been introduced with the Thermo Scientific ELEMENT XR HR-ICP-MS. This addition significantly increases (by at least three orders of magnitude) the linear dynamic range, allowing count rates of over 10^{12} cps to be measured with the ELEMENT XR. Through a combination of intelligent hardware and software, the simultaneous measurement of elements at concentrations from < fg/g to > 1000 µg/g is now possible in a single analysis.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

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