

Semi-Quantitative Environmental Analysis using the XSERIES 2 ICP-MS

Key Words

- Data Analysis
- Environmental
- PlasmaLab Software
- Semi-Quantitative Analysis
- XSERIES 2 ICP-MS

Abstract

ICP-MS can be used to generate semi-quantitative data for analytes that are not present in calibration solutions. This note describes how semi-quantitative analysis is performed on the Thermo Scientific XSERIES 2 ICP-MS and highlights some unique features of PlasmaLab software for facilitating the use of this powerful analysis mode. Example data for reference materials is provided.

How it Works

In plasma mass spectrometry we can take advantage of the fact that the ionization and transmission efficiencies of analytes are relatively predictable. All things being equal, we would get the same number of integrated counts for 1 mole of chromium as for 1 mole of rhodium since it is the number of ions striking the detector that causes the counts to be registered. However, when working in mass concentrations rather than molar, there are a number of factors that we need to consider when converting the integrated ion intensity to an analyte concentration.

1. The number of ions present must be considered.

For chromium, a 1 g/L solution would contain 0.019 moles (1 g / 52.01 g/mole), whereas a 1 g/L rhodium solution would contain 0.010 moles (1 g / 102.91 g/mole)*.

2. The abundance of the isotope used for analysis must be considered.

Because we normally measure a single isotope of an element in mass spectrometry, the number of atoms of analyte present depends upon the abundance of that isotope. For example, in nature, chromium-52 is 83.8 % abundant, while rhodium-103 is 100 % abundant.

3. The efficiency of transforming analytes in solution into ions in the plasma must next be considered.

Each element has a characteristic first ionization potential, e.g. for chromium, 6.77 eV, and for rhodium 7.46 eV. The higher the ionization potential, the more difficult it is to completely ionize a unit quantity of the element, thus the less efficient is the production of ions. Once we have generated ions, the sampling and transmission efficiency of the mass spectrometer must be considered. The actual transmission efficiency of an analyte depends upon its mass-to-charge ratio. Most ICP mass spectrometers tend to transmit mid-mass isotopes with greatest efficiency. Low mass isotopes tend to be transmitted with the lowest efficiency due to scattering effects.

Variations in isotopic abundance can easily be corrected since we know the average percentage abundance of each isotope in nature. Variations in ionization efficiency can be corrected by the use of a Relative Sensitivity Factor (RSF). The response of the instrument versus mass can then be mapped by plotting abundance and RSF corrected sensitivity for a handful of analytes spanning the mass range. This plot is known as the 'response curve' of the instrument.

Once the response curve has been established, the sensitivity of any analyte may be extrapolated from the curve and the instrument software may calculate the semi-quantitative concentrations.

PlasmaLab Software Flexibility

There are several methods of acquiring semi-quantitative data within PlasmaLab software:

1) Fast, simple semi-quantitative analysis

A method template is used within PlasmaLab software, which allows a response curve to be simply, rapidly and conveniently generated from ten analytes present in the standard Thermo Scientific instrument tuning solution (stock concentrate supplied with the instrument). Semi-quantitative concentrations can then be obtained (in less than 3 minutes per sample) for around 70 analytes using peak-jumping data acquisition. When this method is used with internal standards, the curve may be stored and used to generate extremely rapid semi-quantitative data for samples, without the need for establishing a new calibrated response curve.

*Relative atomic masses of chromium and rhodium are 52.01 g/mole and 102.91 g/mole, respectively.

2) Semi-quantitative measurement of un-calibrated elements

Analytes not present in calibration solutions can be measured semi-quantitatively within any routine method. The semi-quantitative analytes are measured using a peak jumping acquisition in the same run as the fully quantitative analytes since their responses are integrated against a response curve generated from the sensitivities of the fully-quantitatively calibrated analytes. This mode can also be used with standard addition calibrations to take advantage of matrix-matching. The final report contains both the quantitative and semi-quantitative data, with a clear indication of which method was used.

3) Semi-quantitative measurement of analytes that were not selected

PlasmaLab uniquely allows the use of a ‘Survey Run’ acquisition prior to the main run analysis of any sample. This consists of a rapid (13 second) full (or partial) mass spectrum capture. This provides qualitative data and allows the mass spectrum for each sample to be viewed and fingerprinted. This can give information about whether analytes are present or absent and the occurrence or absence of interferences. Furthermore, the count rates in the scan may be integrated against a response curve generated from the fully-quantitative calibrations, providing calculated semi-quantitative concentrations for any isotope scanned. This invaluable information can be accessed at any time. This is particularly useful for providing further analytical information without further work after a sample has initially been analyzed and is therefore extremely useful for analytical service laboratories. How often have customers and other end-use users of data come back to you to request information on analytes that have not been analyzed? Often, the sample will have been disposed of and cannot be reanalyzed for further elements. This unique tool eliminates this problem, allowing you to get at the information you need.

Example Data

1) Fast, simple semi-quantitative analysis

The semi-quantitative method template was used to acquire semi-quantitative data for 71 analytes in two certified reference materials, NIST 1640 and NIST 1643e. A blank and a the standard Thermo Scientific tune solution (analytes ⁷Li, ⁹Be, ⁵⁹Co, ⁶⁰Ni, ¹¹⁵In, ¹³⁷Ba, ¹⁴⁰Ce, ²⁰⁸Pb, ²⁰⁹Bi, and ²³⁸U) diluted to 10 ppb were used to generate the response curve, which is shown below in Figure 1. Data was acquired on an XSERIES 2 fitted with the Xt interface.

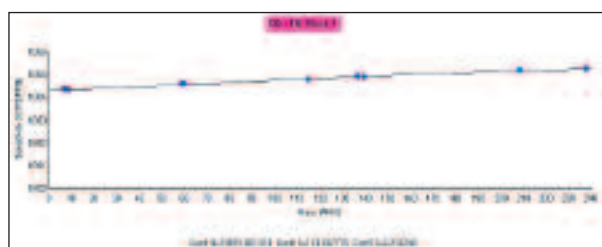


Figure 1: Semi-quantitative response curve generated from 10 elements in the tune solution using the supplied SQ method template.

| ANALYTE | UNIT | RESULT | SD | CERTIFIED | REC % |
|-------------------|------|--------|-------|-----------|-------|
| ⁷ Li | ppb | 51.64 | 0.354 | 50.7 | 102 |
| ⁹ Be | ppb | 36.81 | 0.2 | 34.94 | 105 |
| ¹¹ B | ppb | 308.2 | 5.535 | 301.1 | 102 |
| ¹³ C | ppm | 8.499 | 0.186 | | |
| ²³ Na | ppb | 30810 | 37.98 | 29350 | 105 |
| ²⁴ Mg | ppb | 6480 | 43.86 | 5819 | 111 |
| ²⁷ Al | ppb | 57.33 | 0.664 | 52 | 110 |
| ²⁸ Si | ppm | 4.456 | 0.059 | 4.73 | 94 |
| ³¹ P | ppm | 0.012 | 0.001 | | |
| ³⁴ S | ppm | 7.537 | 0.031 | | |
| ³⁷ Cl | ppm | 19.9 | 1.29 | | |
| ³⁹ K | ppb | 1109 | 11.35 | 994 | 112 |
| ⁴⁴ Ca | ppb | 6683 | 100.9 | 7045 | 95 |
| ⁴⁵ Sc | ppb | 0.993 | 0.025 | | |
| ⁴⁷ Ti | ppb | 1.026 | 0.016 | | |
| ⁵¹ V | ppb | 14.69 | 0.141 | 12.99 | 113 |
| ⁵² Cr | ppb | 43.83 | 0.47 | 38.6 | 114 |
| ⁵⁵ Mn | ppb | 140.8 | 1.377 | 121.5 | 116 |
| ⁵⁶ Fe | ppb | 49.76 | 0.665 | 34.3 | 145 |
| ⁵⁸ Co | ppb | 21.06 | 0.23 | 20.28 | 104 |
| ⁶⁰ Ni | ppb | 27.96 | 0.308 | 27.4 | 102 |
| ⁶⁶ Cu | ppb | 91.55 | 0.601 | 85.2 | 107 |
| ⁶⁶ Zn | ppb | 53.21 | 0.51 | 53.2 | 100 |
| ⁷¹ Ga | ppb | 0.015 | 0.002 | | |
| ⁷² Ge | ppb | 0.058 | 0.004 | | |
| ⁷⁵ As | ppb | 29.03 | 0.136 | 26.67 | 109 |
| ⁷⁸ Se | ppb | 21.65 | 0.505 | 21.96 | 99 |
| ⁸² Se | ppb | 23.78 | 0.378 | 21.96 | 108 |
| ⁸⁵ Rb | ppb | 2.092 | 0.015 | 2 | 105 |
| ⁸⁸ Sr | ppb | 149.2 | 1.565 | 124.2 | 120 |
| ⁸⁹ Y | ppb | 0.181 | 0.002 | | |
| ⁹⁰ Zr | ppb | 0.149 | 0.001 | | |
| ⁹³ Nb | ppb | 0.003 | 0.001 | | |
| ⁹⁵ Mo | ppb | 45.92 | 0.472 | 46.75 | 98 |
| ¹⁰¹ Ru | ppb | 0.001 | 0 | | |
| ¹⁰³ Rh | ppb | 0.005 | 0.001 | | |
| ¹⁰⁵ Pd | ppb | 0.038 | 0.003 | | |
| ¹⁰⁷ Ag | ppb | 9.092 | 0.075 | 7.62 | 119 |
| ¹¹¹ Cd | ppb | 23.4 | 0.115 | 22.79 | 103 |
| ¹¹⁵ In | ppb | 0.008 | 0.001 | | |
| ¹¹⁸ Sn | ppb | 2.213 | 0.013 | | |
| ¹²¹ Sb | ppb | 14.91 | 0.065 | 13.79 | 108 |
| ¹²⁵ Te | ppb | 0.012 | 0.001 | | |
| ¹³³ Cs | ppb | 0.137 | 0.001 | | |
| ¹³⁷ Ba | ppb | 170.6 | 1.052 | 148 | 115 |
| ¹³⁹ La | ppb | 0.311 | 0.002 | | |
| ¹⁴⁰ Ce | ppb | 0.377 | 0.003 | | |
| ¹⁴¹ Pr | ppb | 0.095 | 0.001 | | |
| ¹⁴⁶ Nd | ppb | 0.411 | 0.007 | | |
| ¹⁴⁷ Sm | ppb | 0.07 | 0.003 | | |
| ¹⁵³ Eu | ppb | 0.024 | 0.001 | | |

continues opposite

| ANALYTE | UNIT | RESULT | SD | CERTIFIED | REC % |
|-------------------|------|--------|-------|-----------|-------|
| ¹⁵⁷ Gd | ppb | 0.057 | 0.002 | | |
| ¹⁵⁹ Tb | ppb | 0.007 | 0 | | |
| ¹⁶³ Dy | ppb | 0.033 | 0.001 | | |
| ¹⁶⁵ Ho | ppb | 0.006 | 0 | | |
| ¹⁶⁶ Er | ppb | 0.016 | 0.001 | | |
| ¹⁶⁹ Tm | ppb | 0.002 | 0 | | |
| ¹⁷² Yb | ppb | 0.012 | 0 | | |
| ¹⁷⁵ Lu | ppb | 0.002 | 0 | | |
| ¹⁷⁸ Hf | ppb | 0.005 | 0 | | |
| ¹⁸¹ Ta | ppb | 0.001 | 0 | | |
| ¹⁸² W | ppb | 0.035 | 0.002 | | |
| ¹⁸⁵ Re | ppb | 0.003 | 0 | | |
| ¹⁸⁹ Os | ppb | 0.015 | 0.001 | | |
| ¹⁹³ Ir | ppb | 0.001 | 0 | | |
| ¹⁹⁵ Pt | ppb | 0.001 | 0 | | |
| ¹⁹⁷ Au | ppb | 0.003 | 0.001 | | |
| ²⁰² Hg | ppb | 9.393 | 0.813 | | |
| ²⁰⁵ Tl | ppb | 0.02 | 0.004 | <0.1 | |
| ²⁰⁸ Pb | ppb | 29.37 | 0.037 | 27.89 | 105 |
| ²⁰⁹ Bi | ppb | 0.031 | 0.012 | | |
| ²³² Th | ppb | 0.022 | 0.001 | | |
| ²³⁸ U | ppb | 0.679 | 0.002 | | |

Table 1: Results for NIST 1640

| ANALYTE | UNIT | RESULT | SD | CERTIFIED | REC % |
|------------------|------|--------|-------|-----------|-------|
| ⁷ Li | ppb | 20.4 | 0.088 | 17.4 | 117 |
| ⁹ Be | ppb | 13.18 | 0.134 | 13.98 | 94 |
| ¹¹ B | ppb | 169.5 | 1.872 | 157.9 | 107 |
| ¹³ C | ppm | 25 | 0.077 | | |
| ²³ Na | ppb | 24360 | 235.6 | 20740 | 117 |
| ²⁴ Mg | ppb | 9510 | 113.8 | 8037 | 118 |
| ²⁷ Al | ppb | 176.3 | 1.463 | 141.8 | 124 |
| ²⁸ Si | ppm | 0.466 | 0.034 | | |
| ³¹ P | ppm | 0.049 | 0.002 | | |
| ³⁴ S | ppm | 1.884 | 1.076 | | |
| ³⁷ Cl | ppm | 50.62 | 2.383 | | |
| ³⁹ K | ppb | 2596 | 32.38 | 2034 | 128 |
| ⁴⁴ Ca | ppb | 31440 | 396.4 | 32300 | 97 |
| ⁴⁵ Sc | ppb | 0.154 | 0.003 | | |
| ⁴⁷ Ti | ppb | 0.424 | 0.038 | | |
| ⁵¹ V | ppb | 47.61 | 0.474 | 37.86 | 126 |
| ⁵² Cr | ppb | 24.7 | 0.258 | 20.4 | 121 |
| ⁵⁵ Mn | ppb | 47.59 | 0.764 | 38.97 | 122 |
| ⁵⁶ Fe | ppb | 135.3 | 3.361 | 98.1 | 138 |
| ⁵⁹ Co | ppb | 30.2 | 1.08 | 27.06 | 112 |
| ⁶⁰ Ni | ppb | 65.53 | 0.91 | 62.41 | 105 |
| ⁶⁵ Cu | ppb | 24.15 | 0.537 | 22.76 | 106 |
| ⁶⁶ Zn | ppb | 61.29 | 0.794 | 78.5 | 78 |
| ⁷¹ Ga | ppb | 0.004 | 0.001 | | |

continues opposite

| ANALYTE | UNIT | RESULT | SD | CERTIFIED | REC % |
|-------------------|------|--------|-------|-----------|-------|
| ⁷² Ge | ppb | 0.028 | 0.002 | | |
| ⁷⁵ As | ppb | 51.27 | 0.923 | 60.45 | 85 |
| ⁷⁸ Se | ppb | 7.489 | 0.063 | 11.97 | 63 |
| ⁸² Se | ppb | 8.332 | 0.052 | 11.97 | 70 |
| ⁸⁵ Rb | ppb | 16.16 | 0.101 | 14.14 | 114 |
| ⁸⁸ Sr | ppb | 417.5 | 3.772 | 323.1 | 129 |
| ⁸⁹ Y | ppb | 0.005 | 0.001 | | |
| ⁹⁰ Zr | ppb | 0.052 | 0.005 | | |
| ⁹³ Nb | ppb | 0.007 | 0.001 | | |
| ⁹⁵ Mo | ppb | 132.9 | 1.802 | 121.4 | 109 |
| ¹⁰¹ Ru | ppb | 0.001 | 0 | | |
| ¹⁰³ Rh | ppb | 0.029 | 0.018 | | |
| ¹⁰⁵ Pd | ppb | 0.099 | 0.004 | | |
| ¹⁰⁷ Ag | ppb | 1.212 | 0.027 | 1.062 | 114 |
| ¹¹¹ Cd | ppb | 6.099 | 0.068 | 6.568 | 93 |
| ¹¹⁵ In | ppb | 0.002 | 0 | | |
| ¹¹⁸ Sn | ppb | 0.043 | 0.008 | | |
| ¹²¹ Sb | ppb | 59.12 | 0.588 | | |
| ¹²⁵ Te | ppb | 0.657 | 0.012 | 1.09 | 60 |
| ¹³² Cs | ppb | 0.001 | 0 | | |
| ¹³⁷ Ba | ppb | 665.4 | 8.752 | 544.2 | 122 |
| ¹³⁹ La | ppb | 0.017 | 0 | | |
| ¹⁴⁰ Ce | ppb | 0.016 | 0.001 | | |
| ¹⁴¹ Pr | ppb | 0.002 | 0 | | |
| ¹⁴⁶ Nd | ppb | 0.009 | 0.001 | | |
| ¹⁴⁷ Sm | ppb | 0.003 | 0 | | |
| ¹⁵³ Eu | ppb | 0.065 | 0 | | |
| ¹⁵⁷ Gd | ppb | 0.005 | 0.001 | | |
| ¹⁵⁹ Tb | ppb | 0 | 0 | | |
| ¹⁶³ Dy | ppb | 0.001 | 0 | | |
| ¹⁶⁵ Ho | ppb | 0 | 0 | | |
| ¹⁶⁶ Er | ppb | 0.012 | 0.001 | | |
| ¹⁶⁹ Tm | ppb | 0 | 0 | | |
| ¹⁷² Yb | ppb | 0.002 | 0 | | |
| ¹⁷⁵ Lu | ppb | 0.001 | 0 | | |
| ¹⁷⁸ Hf | ppb | 0.006 | 0 | | |
| ¹⁸¹ Ta | ppb | 0.01 | 0.003 | | |
| ¹⁸² W | ppb | 0.083 | 0.012 | | |
| ¹⁸⁵ Re | ppb | 110.5 | 0.506 | | |
| ¹⁸⁹ Os | ppb | 0.019 | 0.002 | | |
| ¹⁹³ Ir | ppb | 0.002 | 0.001 | | |
| ¹⁹⁵ Pt | ppb | 0.003 | 0.001 | | |
| ¹⁹⁷ Au | ppb | 0.006 | 0 | | |
| ²⁰² Hg | ppb | 2.051 | 0.044 | | |
| ²⁰⁵ Tl | ppb | 8.428 | 0.022 | 7.445 | 113 |
| ²⁰⁸ Pb | ppb | 21.55 | 0.121 | 19.63 | 110 |
| ²⁰⁹ Bi | ppb | 14.66 | 0.088 | 14.09 | 104 |
| ²³² Th | ppb | 0.001 | 0 | | |
| ²³⁸ U | ppb | 0.002 | 0 | | |

Table 2: Results for NIST 1643e

2) Semi-quantitative measurement of un-calibrated elements

In this example, a US EPA method 200.8 analysis was performed. Data was required for additional elements that were not present in the calibrations solutions for method 200.8. The method template was amended to allow peak jumping measurement of those analytes and they were measured semi-quantitatively, using the response curve generated from the fully quantitative calibrations.

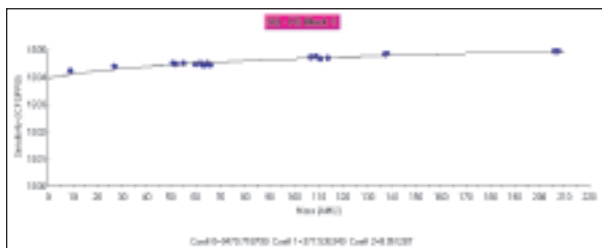


Figure 2: Semi-quantitative response curve generated from 19 isotopes in a method based on US EPA method 200.8.

| ANALYTE | UNIT | RESULT | CERTIFIED | REC % |
|------------------|------|--------|-----------|-------|
| ¹¹ B | ppb | 280 | 301.1 | 93 |
| ²³ Na | ppm | 29.2 | 29.35 | 99 |
| ²⁴ Mg | ppm | 6.064 | 5.819 | 104 |
| ³⁹ K | ppm | 1.114 | 0.994 | 112 |
| ⁴⁴ Ca | ppm | 6.42 | 7.045 | 91 |
| ⁵⁶ Fe | ppb | 29.27 | 34.3 | 85 |

Table 3: Results for un-calibrated elements in NIST 1640 from 200.8 Calibration Response Curve

3) Semi-quantitative measurement of analytes that were not selected

In this example, the same result file as in 2) above was used. A request for data for strontium was received after the analysis was complete and the samples had been disposed of. Since strontium is not included in method 200.8 and was not initially requested for peak jumping measurement, the data would not normally be available. Because of the XSERIES 2's unique survey run capability, data has been collected at all scanned masses and the intensity for strontium is automatically integrated against the response curve generated from the fully quantitative calibrations without additional input required from the user (see Figure 2). Figure 3 shows the mass spectrum for the sample generated from the survey run. The semi-quantitative result for strontium from the survey run was 117.2 ppb, compared with the known value of 124.2 ppb. This is a recovery of 94.4 %.

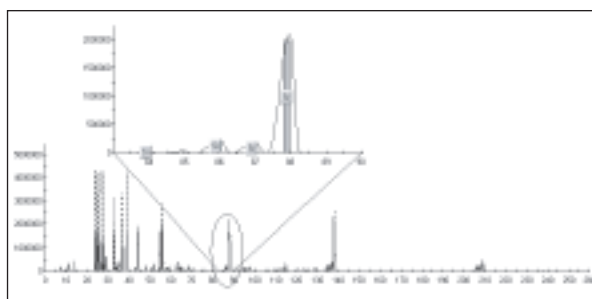


Figure 3: Mass spectrum for NIST 1640, including zoomed region showing fingerprinted strontium isotopes.

Conclusion

The results for the certified analytes in the analyses of reference materials show good agreement with the known values when measured semi-quantitatively. Most recoveries are in the range 70-130 %.

Semi-quantitative analysis is a powerful tool in ICP-MS and the XSERIES 2 PlasmaLab software makes performing this type of analysis simple, rapid and flexible.

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