

Analysis of Highly Mineralized Aqueous Solutions by ICP-AES, a Non-dilution Method with Multi-wavelength Calibration for Major, Minor and Trace Elements

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■ Introduction

Environmental Inductively Coupled Plasma (ICP) methods, such as EPA 200.7 or SW846 Method 6010, expect that samples will be fairly dilute without an overabundance of dissolved constituents (less than 2000 ppm Total Dissolved Solids). Laboratories running mine-impacted waters, such as acid rock drainage from exposed copper tailings, or mineral digests of a “waste” sample (that is actually ore) may run Method 200.7 or 6010 as written. They do this to remain in compliance, but in doing so may get incorrect results. Often analysts will dilute samples as an effort to overcome spectral and physical interferences. Unfortunately, the dilution could render low trace metal analysis useless. This paper examines the use of features commonly available on modern ICP instruments that readily overcome many of these interferences.

ICP is widely used to measure water, waste and mineral digest samples. EPA method 200.7 and 6010 specify ICP making it required for the Clean Water Act (CWA) and/or Resource Conservation and Recovery Act (RCRA) compliance monitoring. Modern simultaneous ICPs have the advantage that if a sample “can be put into solution and aspirated into the plasma” you can measure almost every element on the periodic table. These modern ICPs, such as the Shimadzu ICPE-9800 shown in Figure 1, are capable of measuring over 70 elements and up to 110,000 emission lines. Because of the availability of numerous lines per element and the very nature of ICP, they are capable of measuring trace, minor, and major elements. ICP has a wide linear range compared to other elemental analysis techniques.



Figure 1: Shimadzu ICPE-9800 Series ICP-AES

During analysis of geochemical samples, the concentration of dissolved elements may be very high. Therefore, analysis of the major components by the traditional EPA Method 200.7 or 6010 may involve dilution of off-scale peaks to bring them within the calibration range of the instrument. Dilution may also be made simply to minimize the total salt content that can result in extinguishing the torch, clogging the nebulizer, or high carryover. The dilution makes the analysis more difficult because different elements require different dilutions, greatly increasing the number of runs and overall analysis time. However, modern simultaneous ICP-AES systems have multiple analytical lines for a single element, resulting in differences in sensitivity according to the analytical line.

For this work, we created an analysis method that uses low-sensitivity analytical lines for the high-concentration major components and high-sensitivity analytical lines for the low-concentration trace components. This eliminates the need for multiple dilutions to get major elements on-scale.

Description of the ICP Instrument

We used simultaneous Inductively Coupled Plasma Atomic Emission Spectrometer as the measuring instrument. Figure 2 shows the configuration of the Echelle spectrometer used in the Shimadzu ICPE-9800. One advantage is the ability to analyze multiple elements at the same time. The ICPE-9800 adopts a charge-coupled device detector (CCD) that can acquire information at all the wavelengths to analyze multiple components from a single measurement.

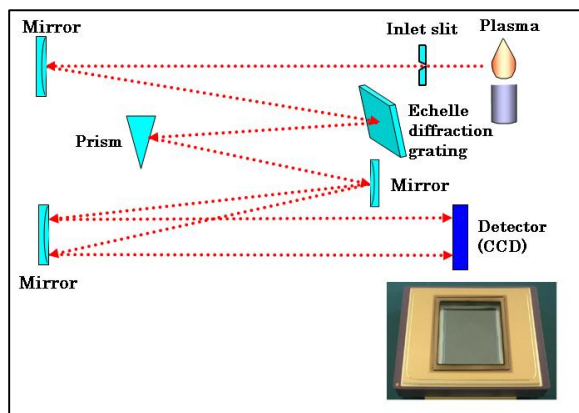


Figure 2: Echelle spectrometer used in the Shimadzu ICPE-9800

Data re-analysis of saved measurement results enables you to add elements later or change/add wavelengths after sample analysis. In addition, this instrument permits both radial and axial observations. For these analyses, we used radial observation for the high-concentration components and highly sensitive axial observation for the trace components.

The vertical torch orientation reduces carryover because droplets readily fall out by gravity. Previous sample washes from the spray chamber quickly. The less the carryover, the faster the cycle times and the more confidence you have in trace results from the next sample.

The CCD detector enables you to add elements and wavelengths even after the measurement. Since you can add wavelengths after the measurement, it is not necessary to determine the optimal wavelength in advance. This allows you to choose the correct, most interference free wavelength per individual sample analysis.

In addition, if when reviewing the data you notice an element present that was not in your analysis method, it is possible to obtain the quantitative data for the required element after the measurement.

■ Experimental

Standards were prepared to an upper concentration limit of 5000 mg/L for each element. EPA 200.7 suggests a maximum of 2000 mg/L total dissolved solids (TDS).

We created calibration curves for the high-concentration region with and without internal standard correction applied. Calibration curves from 0 mg/L to 5000 mg/L using low-sensitivity wavelengths permitted measurements of the four major component elements up to 5000 mg/L, with no signal overflow. However, the calibration without internal standard correction are slightly curved for some elements in the high-concentration region from 2000 to 5000 mg/L. Using yttrium internal standard correction improved the correlation coefficients and the linearity of the calibration curves (Figure 3).

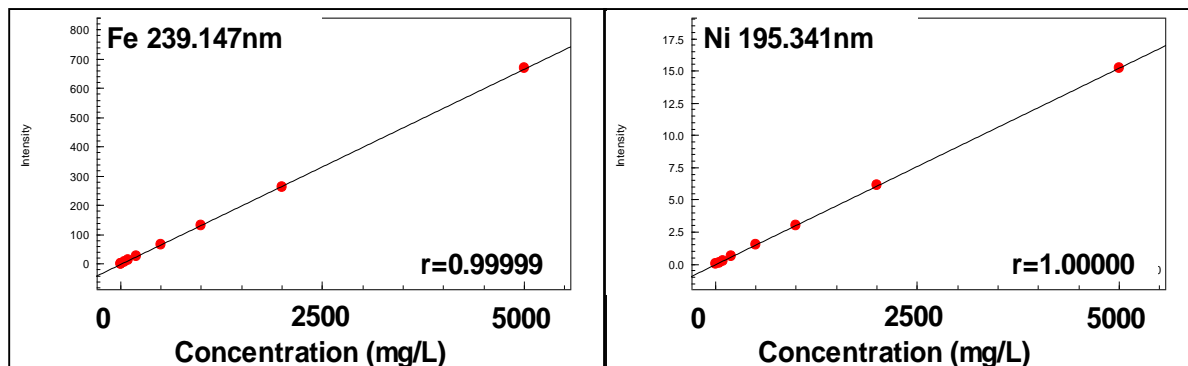


Figure 3: Calibration curves for Fe and Ni using low sensitivity lines and internal standard correction

With no internal standard correction, the calibration curve loses linearity in the region of several-thousand milligrams per liter. The high concentration interferes with plasma ionization. Consequently, for an uncorrected calibration curve, calibration curve linearity is lost in the high-concentration region. For accurate quantitation of major elements in high TDS samples, we recommend internal standard correction.

Matrix matching improves the linearity of the calibration curves

Making the total element concentration in each calibration curve standard the same as the element concentration of the high-concentration sample achieves constant ionization interference in all concentration regions (matrix matching). This improves the calibration curve linearity. We prepared the calibration curve standards shown in Table 1 and investigated the linearity of the calibration curves using the total correction method.

Table 1: Preparation of Calibration Standards for the Total Correction Method

	STD1	STD2	STD3	STD4	STD5	STD6	STD7
Fe	0	100	200	500	1000	2000	5000
Na	5000	4900	4800	4500	4000	3000	-
HCl (mol/L)	0.36	0.36	0.36	0.36	0.36	0.36	0.36
HNO ₃ (mol/L)	0.42	0.42	0.42	0.42	0.42	0.42	0.42

We prepared standards and calibrated using the concentrations shown for each element calibrated. We added sodium to match the same total element concentration from sample to sample.

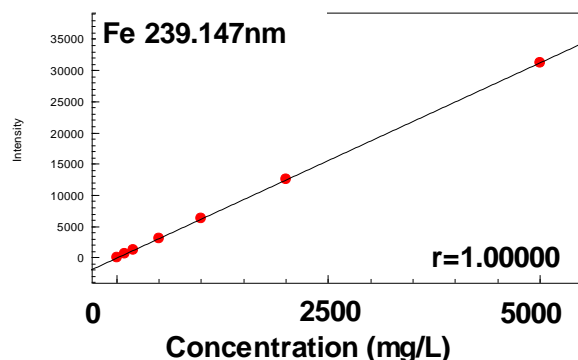


Figure 4: Calibration for iron using the total correction method

All the calibration curves for the major elements (iron, copper nickel and cobalt) had a correlation coefficient of 1.000.

Analysis of high-concentration elements

We digested 0.500 grams of ore samples 1, 2, and 3 in a mixture of hydrochloric and nitric acid. The insoluble residue of samples 2 and 3 was filtered and each sample was brought up with reagent water for a final volume of 50 milliliters. Prior to analysis, we mixed 5 milliliters of sample with 5 milliliters of 20 mg/L Yttrium standard for a final concentration of 10 mg/L Yttrium.

Table 3: Standard for evaluation of the internal standard correction

	STD1	STD2	STD3	STD4	STD5
Fe	0	500	1000	2000	5000
Cu, Ni, Co	0	200	500	1000	-
Y	10	10	10	10	10
Na	5000	3900	2500	-	-
HCl (mol/L)	0.36	0.36	0.36	0.36	0.36
HNO ₃ (mol/L)	0.42	0.42	0.42	0.42	0.42

Table 4: Standard for evaluation of the total correction method and combination of the internal standard correction and total correction method

	STD1	STD2	STD3	STD4	STD5
Fe	0	500	1000	2000	5000
Cu, Ni, Co	0	200	500	1000	-
Y	10	10	10	10	10
HCl (mol/L)	0.36	0.36	0.36	0.36	0.36
HNO ₃ (mol/L)	0.42	0.42	0.42	0.42	0.42

We prepared standards as shown in Table 3 to evaluate the internal standard correction method. We used standards prepared according to Table 4 to evaluate a combination of the total correction method and internal standard correction method.

To evaluate accuracy, we compared measurements on digested ore samples using the internal standard method to a 100-x dilution. See Figure 5 for sample results. Recoveries ranged from 97 to 100 %. The total correction method (matrix matching) yielded dilution test values from 97 to 107 %. The TDS concentration in Samples 2 and 3 is about 3500 mg/L each, which differs from the 5000 mg/L total element concentration in the prepared calibration curve standards. Therefore, we assume the measured values are higher due to the differences in the ionization interference. The combination of the internal standard method and total correction method compared to the dilution test values ranged from 99 to 101 %. The results indicate that you will get the best results by the combination of the internal standard method and total correction method.

Sample	Element	Analysis Result from Dilution Testing (wt%)	Analysis Result by Direct Analysis					
			Internal Standard Method		Total Correction Method		Internal Standard Method and Total Correction Method	
			In solid (wt%)	Dilution test value (%)	In solid (wt%)	Dilution test value (%)	In solid (wt%)	Dilution test value (%)
Sample 1	Fe	74.3	73.4	99	76.4	103	74.8	101
	Ni	13.0	12.6	97	13.0	100	12.8	99
	Cu	3.57	3.56	100	3.52	99	3.52	99
	Co	1.56	1.51	97	1.52	97	1.57	101
Sample 2	Fe	27.4	27.0	99	29.0	106	27.0	99
	Cu	9.40	9.36	100	10.0	107	9.32	99
Sample 3	Fe	25.1	24.4	97	26.6	106	24.8	99
	Cu	11.3	10.9	97	12.0	106	11.1	99

Figure 5: Results for major and minor elements

Analysis of trace elements

The previous examples were all major and minor elements. Now, let us look at the trace elements. We prepared calibration curves for internal standard correction and calibration curves spiked with sodium so that the sum total of the element concentrations in each calibration curve standard was the same. We used the latter standards for the total correction method and a combination of the total correction method and internal standard correction method. Trace elements were measured using high sensitivity wavelengths and axial view. Using separate wavelengths and views or each element permits measurement across the range from major components to trace components.

In addition, the software automatically switches to the appropriate wavelength from among the registered wavelengths, according to the concentration of the measured element.

Figures 6, 7 and 8 show the analysis results for trace elements. Each Figure shows the results for the internal standard correction method, the total correction method, and a combination of the internal standard correction method and total correction method. The figure also shows the corresponding validation test results ("True values").

For Sample 1 we obtained recoveries of 95 to 107 % for the internal standard correction method; 94 to 106 % for the total correction method; and 96 to 106 % for the combination of the internal standard correction method and total correction method.

Sample	Element	Analysis Result by Validation Test (wt%)	Analysis Result by Direct Analysis					
			Internal Standard Method		Total Correction Method		Internal Standard Method and Total Correction Method	
			In solid (wt%)	Validation Test Value (%)	In solid (wt%)	Validation Test Value (%)	In solid (wt%)	Validation Test Value (%)
Sample 1	As	0.016	0.016	100	0.015	94	0.015	96
	Cr	0.017	0.016	95	0.016	95	0.017	98
	Mg	0.033	0.032	95	0.033	99	0.033	99
	Mn	0.0020	0.0021	105	0.002	101	0.0020	101
	Pb	0.012	0.013	107	0.012	99	0.013	102
	Pd	0.025	0.026	105	0.026	106	0.026	106
	Pt	0.039	0.039	99	0.038	98	0.040	102

Figure 6: Trace metal analysis for sample 1

For sample 2, we obtained recoveries of 84 to 98 % for the internal standard correction method; 97 to 109 % for the total correction method; and 92 to 102 % for the combination of the internal standard correction method and total correction method.

Sample	Element	Analysis Result by Validation Test (wt%)	Analysis Result by Direct Analysis					
			Internal Standard Method		Total Correction Method		Internal Standard Method and Total Correction Method	
			In solid (wt%)	Validation Test Value (%)	In solid (wt%)	Validation Test Value (%)	In solid (wt%)	Validation Test Value (%)
Sample 2	As	0.0027	0.0027	98	0.0030	109	0.0025	92
	Au	0.016	0.016	98	0.016	97	0.015	92
	Co	0.010	0.011	97	0.012	108	0.011	102
	Cr	0.0093	0.0090	96	0.010	107	0.0094	101
	Mg	0.10	0.096	93	0.11	106	0.10	99
	Mn	0.0050	0.0048	96	0.0052	105	0.0048	97
	Ni	0.058	0.052	90	0.059	102	0.055	96
	Pb	0.0049	0.0042	84	0.0050	102	0.0047	96

Figure 7: Trace metal analysis for sample 2

For Sample 3 we obtained recoveries of 91 to 108 % for the internal standard correction method; 94 to 107 % for the total correction method; and 91 to 100 % for the combination of the internal standard correction method and total correction method.

Sample	Element	Analysis Result by Validation Test (wt%)	Analysis Result by Direct Analysis					
			Internal Standard Method		Total Correction Method		Internal Standard Method and Total Correction Method	
			In solid (wt%)	Validation Test Value (%)	In solid (wt%)	Validation Test Value (%)	In solid (wt%)	Validation Test Value (%)
Sample 3	As	0.057	0.057	99	0.054	94	0.052	91
	Co	0.0123	0.012	98	0.013	106	0.012	100
	Cr	0.013	0.013	94	0.014	105	0.013	98
	Mg	0.27	0.25	94	0.29	107	0.27	100
	Mn	0.013	0.012	94	0.014	102	0.013	97
	Ni	0.042	0.038	91	0.042	101	0.040	95
	Pb	0.093	0.10	108	0.099	106	0.093	99

Figure 8: Trace metal analysis for Sample 3

For all samples, we obtained recoveries between 91 and 106% for the trace components by the combination of the internal standard method and total correction method. The measured concentration can differ significantly for elements such as nickel and cobalt. In this case, the ability to use the high concentration measurement wavelength and the low-concentration measurement wavelength and automatically select the appropriate wavelength for the measured concentration was able to improve the accuracy.

Conclusion

Using a combination of the internal standard correction method and total correction method (matrix matching) permitted measurements of the major components and trace components in highly mineralized solutions (mineral samples) on the same sample solutions with a low dilution factor.

For the major components, comparison with the values measured at a high dilution factor resulted in dilution test values close to 100 %. We also obtained acceptable results for trace components, even in the high TDS matrix with abundant spectral interferences.



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