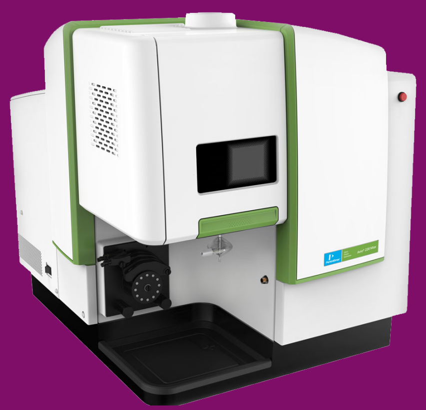
TECHNICAL NOTE

ICP-Optical Emission Spectroscopy



Attenuation Mode on the Avio 220 Max ICP-OES for Simplified Analysis of High Concentration Elements

Introduction

In ICP-OES analyses, it is common to measure elements present at high concentrations, such as minerals, matrix elements in alloys, and plating bath solutions, to name just a few examples. However, when concentrations are too high, the response becomes non-linear, as shown in Figure 1. This can produce inaccurate results.

In order to overcome this limitation, sensitivity must be decreased through one of several commonly-employed methods: viewing the plasma radially instead of axially, transferring less sample to the plasma (via sample dilution, changing plasma and/or sample introduction conditions), and/or selecting less-sensitive wavelengths. While all of these are valid solutions, none are ideal.

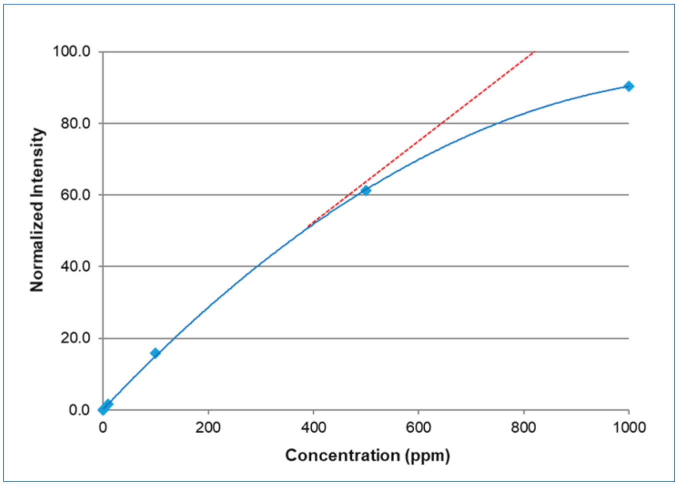


Figure 1: Representation of a non-linear response in ICP-OES at high concentrations without the benefits of Attenuation mode.

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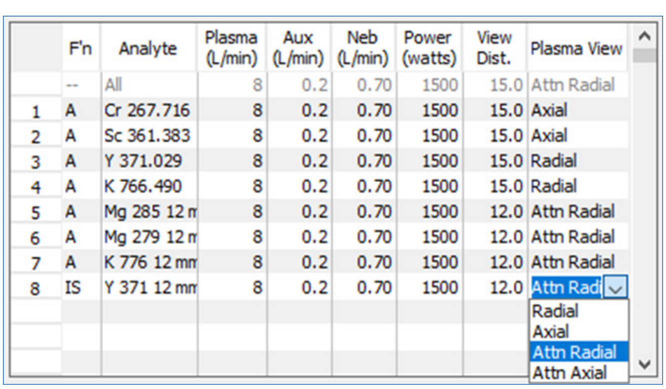
Measuring analytes in radial mode is a common method of reducing analyte sensitivity and has the added benefit of reducing matrix effects. However, for samples with very high analyte concentrations, radial mode may also result in non-linear signals.

If less sample is introduced to the plasma or the plasma conditions are changed to decrease signal intensity, the ability to measure low-concentration analytes at the same time as the high-concentration analytes is lost. To attain accurate results for both low- and high-level analytes, the sample will have to be measured twice. Preparing the sample twice costs double the time and effort in the lab and is also prone to human error.

Choosing a less sensitive wavelength is also a common approach to dealing with high concentrations. However, if a new wavelength is selected, it must be characterized and validated before being incorporated into a production method, which can be a time-consuming process. It may also be difficult to find an alternate wavelength that ideally addresses the sample concentration and is interference-free.

Attenuation Mode on the Avio 220 Max ICP-OES: Analysis of High Concentration Elements Made Easy

In addition to the more common methodologies mentioned above, the Avio® 220 Max ICP-OES also offers a unique approach to address challenges associated with high-concentration elements: Attenuation mode. Only available on the Avio 220 Max, Attenuation mode involves moving an attenuation screen into the light path before the light enters the spectrometer, which reduces signal by 90%. The Avio 220 Max is a unique hybrid simultaneous instrument that can attenuate the signal by wavelength with just a simple selection in the method, as shown in Figure 2. This ability allows both high- and low-concentration analytes to be measured in the same sample analysis in the same method, with no extra dilution step.



	F'n	Analyte	Plasma (L/min)	Aux (L/min)	Neb (L/min)	Power (watts)	View Dist.	Plasma View
	--	All	8	0.2	0.70	1500	15.0	Attn Radial
1	A	Cr 267.716	8	0.2	0.70	1500	15.0	Axial
2	A	Sc 361.383	8	0.2	0.70	1500	15.0	Axial
3	A	Y 371.029	8	0.2	0.70	1500	15.0	Radial
4	A	K 766.490	8	0.2	0.70	1500	15.0	Radial
5	A	Mg 285 12 n	8	0.2	0.70	1500	12.0	Attn Radial
6	A	Mg 279 12 n	8	0.2	0.70	1500	12.0	Attn Radial
7	A	K 776 12 mn	8	0.2	0.70	1500	12.0	Attn Radial
8	IS	Y 371 12 mn	8	0.2	0.70	1500	12.0	Attn Radi

Figure 2: An example analysis method for a magnesium-rich mineral digest. The main matrix element (Mg) is measured in Attenuation mode (easily selected from a drop-down menu), while the Cr impurity is analyzed in axial view, without attenuation. For potassium (K) the linear range is extended by monitoring both radial and attenuated radial signals in the same analysis. Note that the optimum viewing distance (in mm) is freely selectable for each line.

The Effectiveness of Attenuation Mode

In conventional analysis, detector saturation at high concentrations may limit the working range. However, on the Avio 220 Max ICP-OES, detector saturation at high concentrations is minimized by the automatic setting of appropriate read times through the auto-integration function in Syngistix™ for ICP software. With the additional benefit of Attenuation mode, very high working ranges can be achieved. The analysis of a chromium (Cr) plating bath serves as an example of the benefit of Attenuation mode. In plating baths, it is important to monitor the concentration of the plating element to determine when the bath needs to be regenerated. Because the Cr content is so high, a dilution of at least 1000x is required to prevent saturation of the Cr 267.716 nm signal, the preferred Cr wavelength (Table 1). However, with Attenuation mode, the solution only needs to be diluted 100x to attain the correct concentration. Smaller dilutions are preferred as they are less prone to error and limit the possibility of introducing contaminants, allowing impurities to be measured at lower concentrations.

To determine the accuracy of Attenuation mode, the Cr plating bath was diluted 100x, 1000x, and 10000x and analyzed in both regular and Attenuation modes. The Cr concentration measured at the various dilutions agree with each other, validating the results.

Dilution	Cr 267.716 No Attenuation (mg/L)	Cr 267.716 Attenuation (mg/L)	Cr Attenuation Multiplied by Dilution Factor (mg/L)
100	Saturated	1,328	132,800
1,000	136	140	140,000
10,000	13.2	13.7	137,000

Table 1: Determination of Cr in a Cr plating bath solution.

Another example demonstrating the benefits of Attenuation mode involves the measurement of magnesium and potassium at very high concentrations. In the following, the performance of Attenuation mode is examined for the two primary Mg lines. The data were obtained using yttrium as an internal standard and without any further additives, such as ionization buffers.

Table 2 shows the preferred wavelengths for Mg, as listed in the Syngistix for ICP software wavelength table. Mg 285.213 nm is the most sensitive Mg line, which is useful when measuring low Mg concentrations. When measuring higher Mg concentrations, Mg 279.077 nm is the preferred line. However, the linear range of either line can be extended with Attenuation mode.

	Wavelength (nm)	State	Pref	Intensity (W)
Mg	285.213	I	1	17500
Mg	279.077	II	2	830

Table 2: Analytes, wavelengths, states and sensitivities listed in preference order (data taken from Syngistix wavelength table).

Figure 3 shows the calibration curve for Mg at the preferred line of 285.213 nm, acquired in Attenuation mode with a radial plasma view. Despite the high sensitivity of this line (Table 2), a linear calibration (r=0.999966) is obtained up to 500 ppm (Figure 3).

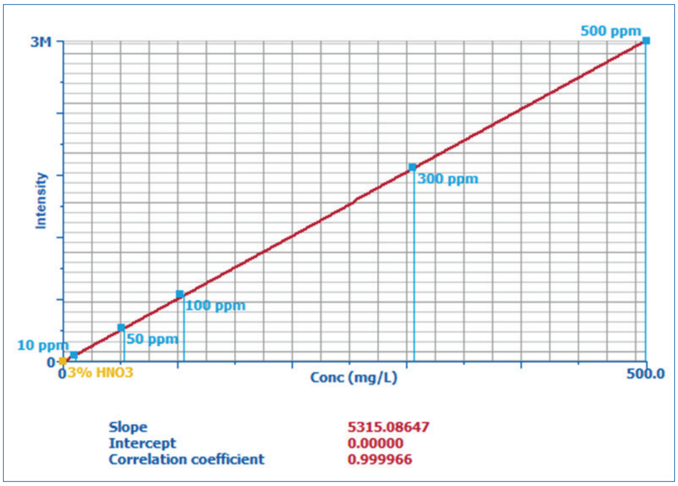


Figure 3: Calibration curve for Mg at 285.213 nm acquired in attenuated radial mode.

When higher concentrations of Mg need to be measured, switching to a less-sensitive wavelength (279.081 nm) allows a linear calibration to be attained up to 5000 ppm with a regression of 0.999958 using Attenuation mode, as shown in Figure 4. However, as discussed previously,[1] the regression of the calibration curve can be artificially enhanced by the presence of high concentration standards that dominate the curve. In order to further examine the linearity of the response over the entire range from 10 to 5000 ppm, the calibration readback values are presented in Table 3, which show that all standards recover within 10% of their nominal value, indicating that the calibration is accurate and demonstrating linearity of the response over the entire range.

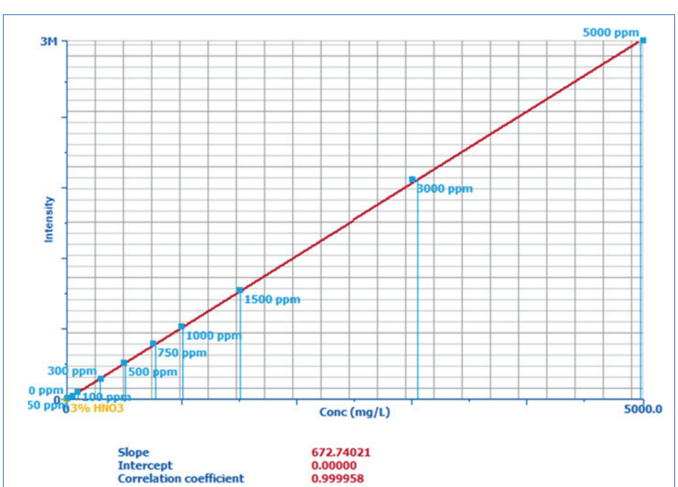


Figure 4: Calibration curve for Mg 279.081 nm, demonstrating linearity to 5000 ppm using Attenuation mode.

Calibration Standard	Entered Conc. (ppm)	Calculated Conc. (ppm)	Residual (%)
Blank	0	0	0
10 ppm	10	9.69	-3.1
50 ppm	50	48.1	-3.8
100 ppm	100	96.0	-4.0
300 ppm	300	302	0.7
500 ppm	500	503	0.1
750 ppm	750	765	2.0
1000 ppm	1000	1031	3.1
1500 ppm	1500	1547	3.1
3000 ppm	3000	3191	6.4
5000 ppm	5000	4863	-2.7

Table 3: Calculated concentrations and residuals for Mg calibration standards from 10-5000 ppm for Mg 279.081 nm.

With Attenuation mode, the primary wavelength for K (766.490 nm) has a linear calibration up to 3000 mg/L, as shown in Figure 5. Therefore, it is possible to measure K- and Mg-rich solutions directly without dilution at concentration levels of thousands of ppm.

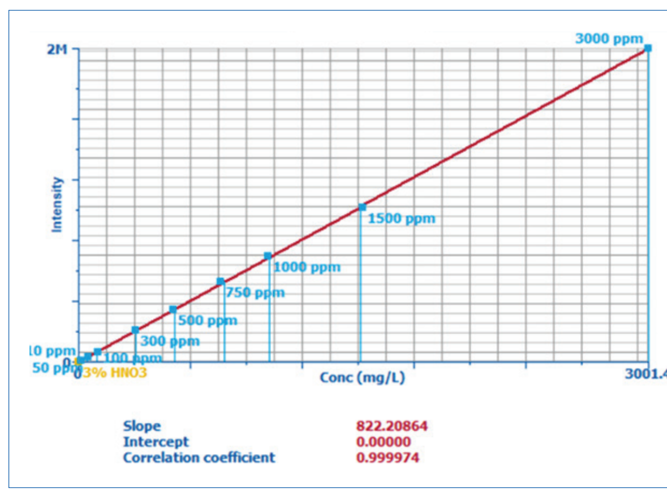


Figure 5: Calibration curve for K 766.490 nm, demonstrating linearity to 3000 ppm using Attenuation mode.

Summary

The Avio 220 Max hybrid simultaneous ICP-OES incorporates Attenuation mode, a unique mode to selectively reduce analyte signal, allowing higher concentrations to be measured, thereby extending the dynamic range of ICP-OES without affecting the ability to measure analytes present at lower concentrations. The benefits of Attenuation mode to the user include simplified methodology, minimal sample dilution, and the ability to measure higher concentrations without having to use and characterize alternate wavelengths.

Reference

1. "Sensitivity, Background, Noise, and Calibration in Atomic Spectroscopy: Effects on Accuracy and Detection Limits", PerkinElmer white paper, 2018.

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