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Analysis of Plating Bath Solutions with the Avio 220 Max ICP-OES using Attenuation Mode

Introduction

The analysis of plating baths presents several challenges: the presence of particulates, the need to monitor different element groups

during a typical analysis day, and the need to accurately measure high concentrations.

Typically, flame atomic absorption (FAA) and inductively coupled plasma optical emission spectroscopy (ICP-OES) are used to analyze plating bath samples. However, ICP-OES has two advantages over FAA: multi-element analysis capability and a wider linear range. Since it is common to monitor different element groups in different plating baths during a typical analysis day, ICP-OES can more easily accommodate this requirement than FAA. With ICP-OES, calibrations can be established for all monitored elements at the beginning of the analysis, and results for various element groups can be acquired as needed. With FAA, a separate lamp is required for each element, meaning that lamps would have to be changed throughout the day. In addition, since FAA is a single-element technique, each sample must be measured multiple times, once for each analyte.

Furthermore, the wider linear range of ICP-OES is critical due to high concentrations of plating elements which need to be monitored to determine when to regenerate the bath. While this analysis may seem simple since the analytes are present at high levels, these concentrations can result in non-linear responses or saturate the detector. Although software can fit non-linear curves, operating in this manner is not recommended as small changes in signal result in large changes in concentration, amplifying any errors. Therefore, it is desirable to operate within the linear range of the instrument.

Sample dilution is the obvious way to reduce analyte sensitivity, but as higher dilution factors are used, more error can be introduced, both from the physical dilution and from the possibility of introducing contamination through the diluent. Furthermore, minor elements become more difficult or impossible to detect.

Another option for measuring high concentrations is to use less sensitive analyte wavelengths, aside from the more commonly used and characterized lines. While this decreases sensitivity, it also raises the possibility of new, unknown interferences. Therefore, any wavelength changes will have to be validated, which can be a time-consuming process.

The easiest way to extend the dynamic range is to use Attenuation mode, unique to the hybrid simultaneous spectrometer technology used in the Avio® 220 Max ICP-OES.¹ Attenuation mode involves physically attenuating the emission from the plasma, thereby decreasing its intensity without the need for dilution or selecting alternate wavelengths. Attenuation mode is assigned to specific, user-defined wavelengths so that the sensitivity of other analytes is not affected. In this way, Attenuation mode augments the functionality of the auto-integration feature of Avio 220 Max system, which minimizes the exposure time at high concentrations to avoid detector saturation.

This work discusses the analysis of plating baths using the Avio 220 Max hybrid simultaneous ICP-OES, taking advantage of the combination of auto-integration and Attenuation mode.

Experimental

Samples

Three plating bath solutions were analyzed as received for several different elements which varied by sample, as shown in Table 1. Quantitative measurements were made against external calibration curves with a linear-through-zero fit using the calibration standards in Table 2. Yttrium (Y) was added via a mixing Tee to all calibration standards and samples as an internal standard.

Table 1: Plating bath sample composition.

Sample	Elements
1	B, Ni, Tl
2	Cr, S
3	Pd, Sn

Table 2: Calibration standards.

Element	Standard 1 (mg/L)	Standard 2 (mg/L)	Standard 3 (mg/L)	Standard 4 (mg/L)
B, Tl	1	10	100	---
Sn, Cr, Ni, Pd	1	10	100	300
S	10	100	1000	---

Instrumental Conditions

All analyses were performed on an Avio 220 Max hybrid simultaneous ICP-OES using the conditions in Table 3 for the elements, wavelengths, and Attenuation mode in Table 4. Since plating baths often have visible sludge accumulate in the plating tank, particulates may end up in the analytical sample. The best way to minimize the impact of particles on an analysis is with a nebulizer which is highly resistant to blockages. Therefore, a cross-flow nebulizer and a Ryton Scott double-pass spray chamber were chosen due to their ability to handle difficult samples. The cross-flow nebulizer is highly resistant to clogging, making it ideal for plating bath samples which may contain particles. In addition, the GemTip cross-flow nebulizer/Ryton Scott spray chamber combination reduces sample loading to the plasma which both minimizes sample-induced matrix effects and extends the linear calibration range.

Because of the outstanding sensitivity of the Avio 220 Max system, all analyses were performed with a radial plasma view, which further minimizes matrix effects. Several elements were measured in Attenuation mode to minimize the need for dilutions.

Table 3: Avio 220 Max ICP-OES instrumental conditions.

Component /Parameter	Description / Value
Nebulizer	GemTip cross-flow
Spray Chamber	Ryton Scott double-pass
Sample Uptake Rate	1 mL/min
Injector	Alumina, 2 mm id
RF Power	1500 W
Plasma Flow	8 L/min
Auxiliary Flow	0.2 L/min
Nebulizer Flow	0.7 L/min
Torch Position	-3
Auto Integration Range	0.2 – 1 sec

Table 4: Analytes, wavelengths and Attenuation mode.

Element	Wavelength (nm)	Attenuation Mode
B	249.677	N
Cr	267.716	Y
Ni	231.604	Y
Pd	340.458	N
S	181.975	N
Sn	189.927	Y
Tl	190.801	N
Y (Internal Std)	371.029	Y, N

In addition, auto-integration was used with a read time range of 0.2 - 1 sec. The benefit of auto-integration is that the Avio 220 Max evaluates the signal intensity and adjusts the integration time within the user-defined range to determine the most appropriate integration parameters for the best compromise between sensitivity and precision. In this way, the linear range of the Avio 220 Max is extended since more intense signals will be acquired with shorter integration times, thereby decreasing the time the detector reads the signal. This has the added benefit of increasing precision since more readings are acquired at shorter integration times within the defined read-time range.

The Avio 220 Max ICP-OES provides a high degree of flexibility for analyses, allowing users to freely choose optimum conditions for each wavelength in terms of viewing mode, viewing height and auto-integration settings. Subsequently, results for the various element groups are acquired as needed. With analytical times on the order of 20 seconds per sample and the fast startup time of Avio 220 Max ICP-OES (10 min from cold start/power off), this approach allows maximum flexibility and cost savings for individual labs.

Results and Discussion

An initial evaluation of Attenuation mode's effectiveness can be obtained by examining the calibration curves of the plating elements. A typical curve is shown in Figure 1 for chromium (Cr).

Although the correlation coefficient is greater than 0.9999, this alone is not a true evaluation of the quality of the curve, as the high standards (100, 300 ppm) can artificially skew the curve, making the low-end standards (1, 10 ppm) inconsequential.² Instead, the residual error of the calibration standards is a better means of determining the validity of the curve. With residual errors of less than 7% and 4% on the 1 and 10 ppm standards, respectively, the accuracy of the calibration is validated.

For all analytes, all regressions are better than 0.9999. Residual errors on all standards are less than 10% for all substrate elements, further validating the calibrations. Syngistix™ software allows the user to view residual errors, the correlation coefficient, and more within the Edit Calibration window for improved ease of use.

With the calibration established, each sample was analyzed, with the results appearing in Table 5.

Table 5: Plating bath results on the Avio 220 Max ICP-OES.

Plating Bath	Analyte	Concentration (ppm)
Nickel	Ni	1.46*10 ⁴
	B	5.06*10 ²
	Tl	5.08*10 ²
Chromium	Cr	1.40*10 ⁵
	S	1.87*10 ³
Tin	Sn	2.55*10 ⁵
	Pd	4.49*10 ³

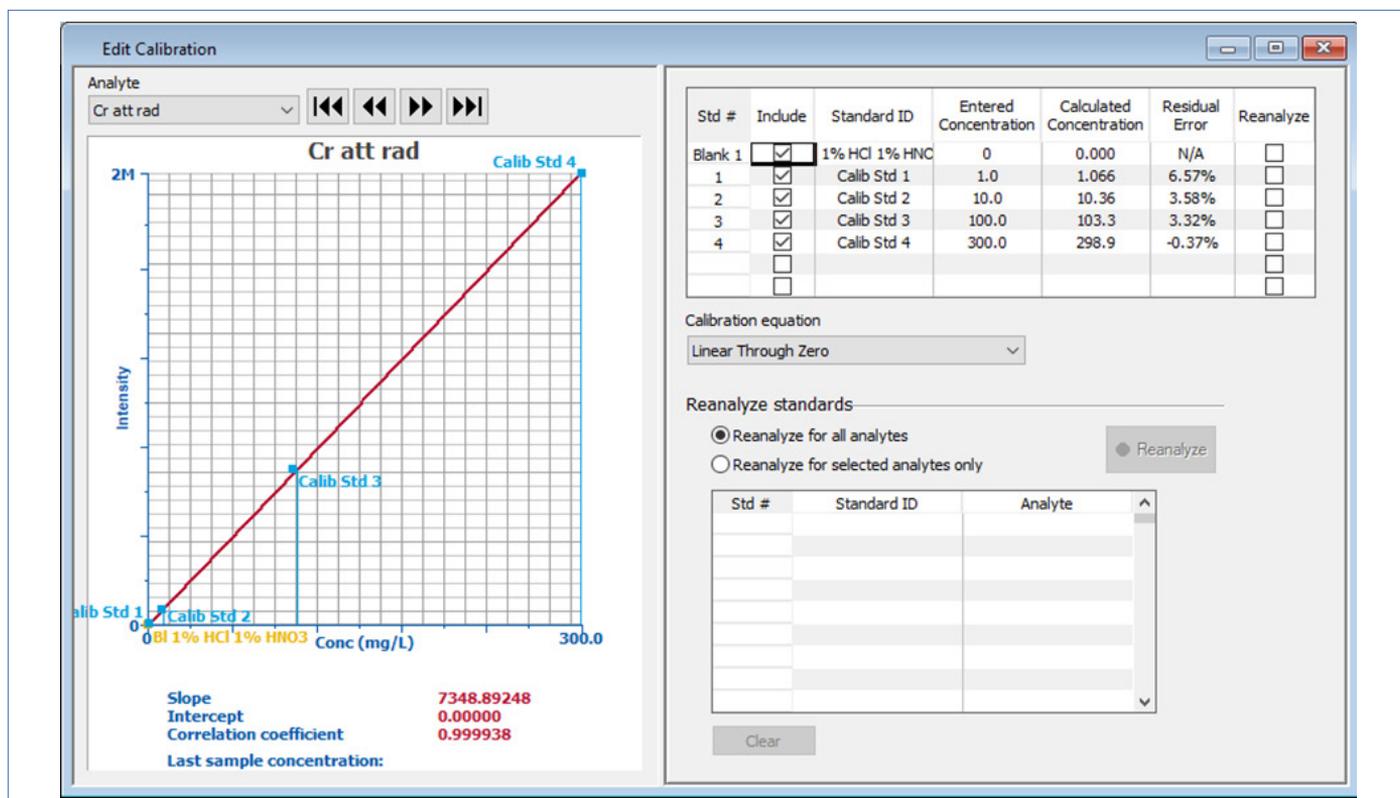


Figure 1. Calibration curve for chromium acquired in Attenuation mode.

The benefit of Attenuation mode can be seen by comparing the Cr results in the chromium plating bath acquired in both Attenuation and standard modes at different dilutions, as shown in Table 6. Without Attenuation mode, the Cr signal saturates at the 100x dilution, but is easily measured in Attenuation mode. For this solution, a minimum dilution of 100x has been selected on account of the very high analyte concentration in double-digit percent range. It has previously been shown that Attenuation mode may allow linear calibrations for analyte concentrations up to 5000 ppm (= 0.5%).¹ Comparing the results in Attenuation mode at the different dilutions, the relative standard deviation between the measurements is 2.4%. These results demonstrate that Attenuation mode allows measurements with less dilution, thereby avoiding potential issues with introduction of contamination and changing the sample matrix. Furthermore, minor or trace element concentrations can be determined at the same time, eliminating any need to analyze a sample multiple times at different dilutions.

The stability of the methodology was evaluated by monitoring and comparing the internal standard signals in both standard and Attenuation modes over an analytical run of mixed plating

bath samples. As shown in Figure 2, internal standard recoveries are automatically plotted in Syngistix software's Data Viewer as each sample is analyzed, allowing for a quick evaluation of the stability of an analysis. The attenuated Y signal closely tracks the unattenuated Y signal, demonstrating that the two internal standard signals behave in the same way, reflecting matrix load changes or changes in nebulization which affect both measurements equally. As a result, relative standard deviations for all internal standard measurements were very similar, with 4.1% and 4.3% for standard and Attenuation modes, respectively. All internal standard signals recover within 12%, demonstrating the stability and robustness of the plasma.

Table 6: Comparison of Attenuation and Standard modes for chromium in a chromium plating bath.

Dilution	Radial View (mg/L)	Attenuated Radial View (mg/L)
100x	Saturated	1.34*10 ⁵
1000x	1.37*10 ⁵	1.40*10 ⁵
10000x	1.32*10 ⁵	1.36*10 ⁵
%RSD	2.3%	2.4%

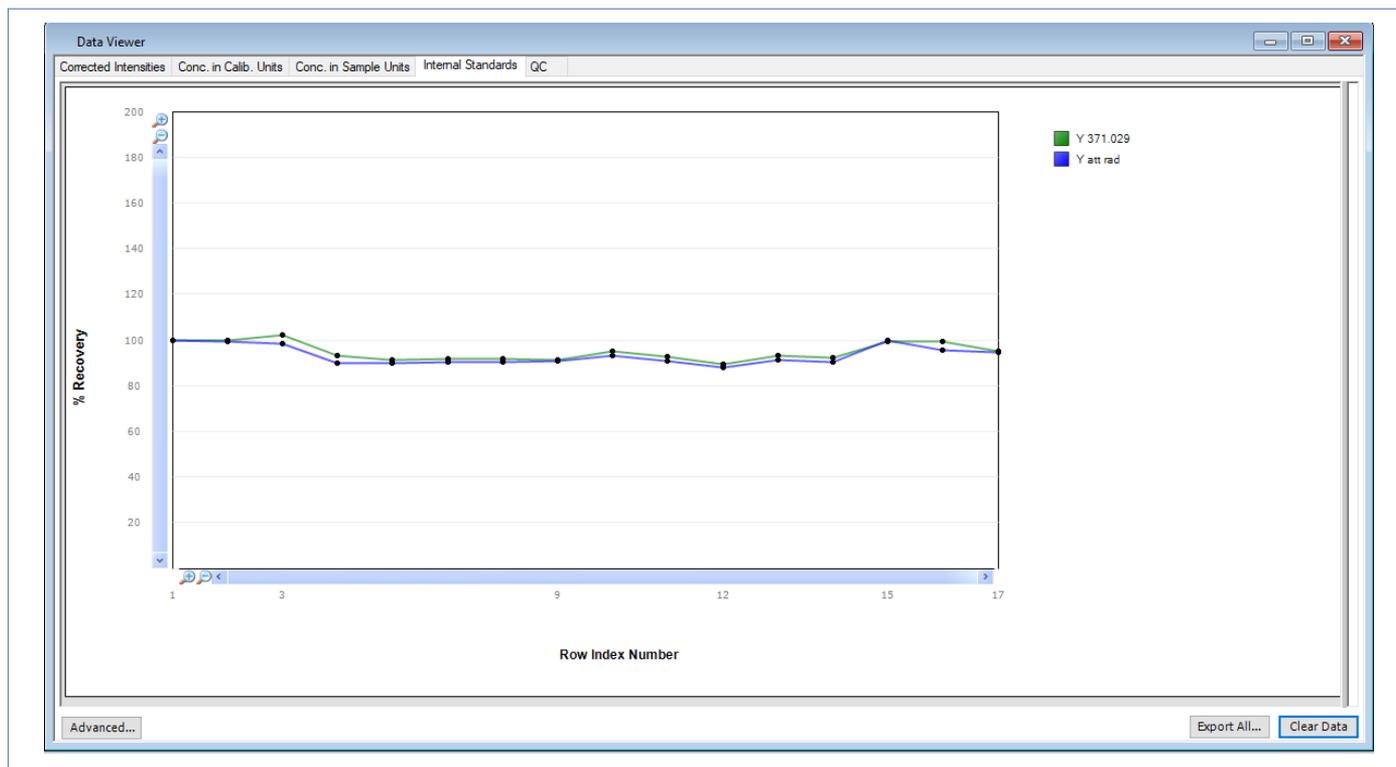


Figure 2. Internal standard recovery in standard and Attenuation modes over an analysis of plating bath samples.

Another measure of the stability was the recovery of check standards at the end of the analytical run. Figure 3 shows that both check standards recover within 10% of their true values, further demonstrating the stability and ruggedness of the methodology.

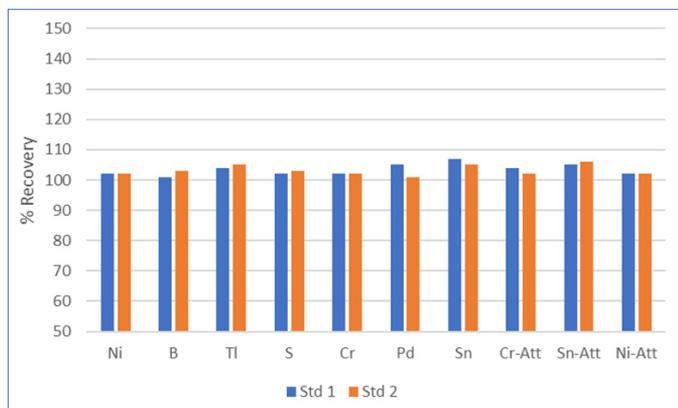


Figure 3. Recovery of check standards at the end of an analysis of plating bath samples. Standard 1 = 10 ppm (S 100 ppm); Standard 2 = 100 ppm (S 1000 ppm).

Consumables Used

Component	Part Number
Orange/Blue (0.25 mm id) Flared PVC Peristaltic Pump Tubing (internal standard)	N0773112
Gray/Gray (1.30 mm id) Santoprene Peristaltic Pump Tubing (drain)	N0777444
Internal Standard On-Line Mixing Tee Kit	N0774068
GemTip Cross-Flow Nebulizer	N0780546
Ryton Scott Double-Pass Spray Chamber	N0790384
Boron Pure Standard, 1000 ppm	N9303760 (125 mL) N9300106 (500 mL)
Chromium Pure Standard, 1000 ppm	N9300173 (125 mL) N9300112 (500 mL)
Nickel Pure Standard, 1000 ppm	N9300177 (125 mL) N9300136 (500 mL)
Palladium Pure Standard, 1000 ppm	N9303789 (125 mL) N9300138 (500 mL)
Sulfur Pure Standard, 1000 ppm	N9303796 (125 mL) N9300154 (500 mL)
Tin Pure Standard, 1000 ppm	N9303801 (125 mL) N9300161 (500 mL)
Thallium Pure Standard, 1000 ppm	N9300170 (125 mL) N9300158 (500 mL)
Yttrium Pure Standard, 1000 ppm	N9303810 (125 mL) N9300167 (500 mL)
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)

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Conclusion

This work has demonstrated the ability of the Avio 220 Max hybrid simultaneous ICP-OES to perform accurate, stable analyses of plating bath solutions. With the combination of the auto-integration and Attenuation mode capabilities of the Avio 220 Max, high analyte concentrations can be easily and accurately measured, as the linear range of the instrument is greatly extended, minimizing the need for dilution, which reduces contamination and gains efficiency by allowing the analysis of major, minor or trace elements in the same sample without the need for multiple dilutions. This benefit is available without a time penalty as the measurement mode is freely selectable for each wavelength in the method, allowing for highly efficient analysis methods.

References

1. "Attenuation Mode on the Avio 220 Max ICP-OES", Technical Note, PerkinElmer, 2021.
2. "Sensitivity, Background, Noise, and Calibration in Atomic Spectroscopy: Effects on Accuracy and Detection Limits", White Paper, PerkinElmer, 2018.