

Simplifying Your ICP-OES Analyses While Optimizing Productivity and Precision

Combining capabilities for high-throughput and high-precision ICP analysis in a single system can increase laboratories' flexibility and efficiency across a wide range of applications.

Because it is well suited for the inorganic analysis of environmental samples, specialty metals and alloys, food products and other complex sample types, inductively coupled plasma-optical emission spectroscopy (ICP-OES) has become a cornerstone in commercial testing and industrial quality control (QC) laboratories. Today's ICP laboratories are expected to provide faster turnaround, higher accuracy and precision, and lower detection limits than ever before on an ever-expanding array of challenging samples. Their success in this competitive market depends on meeting clients' needs while continually looking for new operational efficiencies that boost their bottom line.

This article describes innovative technological and workflow enhancements designed to meet these challenges. The performance of a novel simultaneous ICP system configured for high-throughput and high-precision ICP analyses of complex samples is demonstrated for key applications in the environmental, advanced materials, and metals industries.

THE CHALLENGES

In recent years, the need for rapid, accurate analysis of large numbers of highly complex samples per day has begun to push the limits of conventional ICP systems. Laboratory managers need strategies and tools to increase productivity and ensure accuracy while maintaining a profitable business—and those



Erica Cahoon
Portfolio Director, ICP-OES
PerkinElmer Inc.
Shelton, CT, USA



Ken Neubauer
Principal Applications Scientist
PerkinElmer Inc.
Shelton, CT, USA

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We demonstrate the performance of a novel fully simultaneous ICP-OES system (Avio® 560 Max, PerkinElmer Inc., Shelton, CT, USA) capable of both high-throughput and high-precision ICP analysis across a broad range of applications.

strategies can vary greatly from customer to customer and from application to application.

Many testing labs are constantly racing against the clock, trying to run as many samples per day as their people and systems can handle so they can complete as many customer orders as possible. Profitably maintaining this high level of productivity and throughput requires instrument systems that deliver long-term stability with minimal maintenance and downtime.

High precision and accuracy levels are also critical to customer satisfaction and profitability, and therefore should not be compromised to increase throughput. Acceptable accuracy levels are application-dependent, but many customers are now demanding results with relative standard deviations (RSDs) of < 0.2%. By contrast, RSDs in traditional ICP analysis typically range from 0.5% to up to approximately 3% or higher. It can be challenging to achieve precision on the lower end of that range, and many applications

do not require it. However, labs competing for clients with samples such as catalysts, lithium-ion battery components, precious metals, and recyclable materials need to offer highly precise determinations. High-throughput labs, such as those analyzing waters, soils, foods, pharmaceuticals and lubricants, are looking for fast sample-to-sample analysis to handle their daily workload. Clearly, different ICP applications demand different types of hardware and software capabilities.

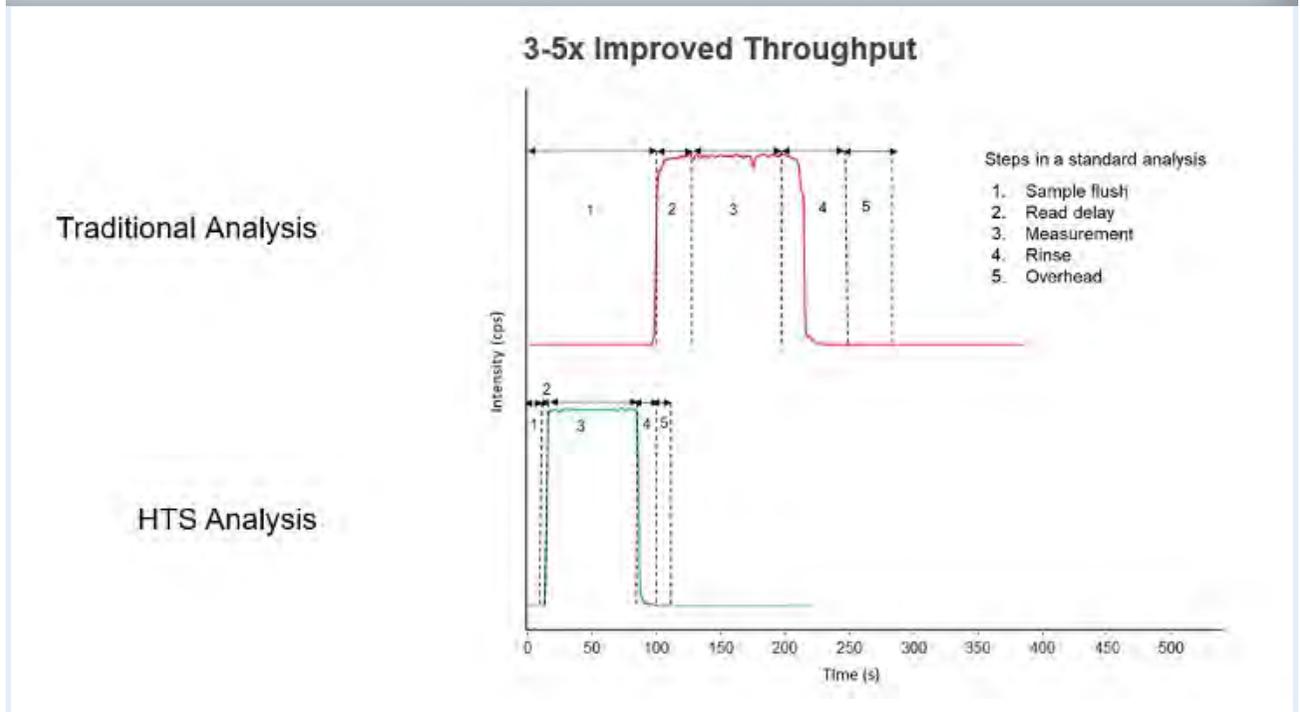
SOLUTIONS

In the following, we demonstrate the performance of a novel fully simultaneous ICP-OES system (Avio® 560 Max, PerkinElmer Inc., Shelton, CT, USA) capable of both high-throughput and high-precision ICP analysis across a broad range of applications. The instrument is distinguished by a built-in high-throughput system (HTS), precise control over key factors affecting analytical precision, and advanced ICP software (Syngistix™, PerkinElmer Inc., Shelton, CT, USA) that automates all steps in the analytical process.

HIGH THROUGHPUT

FIGURE 1 contrasts the Avio 560 Max's HTS, a valve-and-loop, high-throughput system which minimizes the time required for the sample to reach the nebulizer and washout time after analysis by using a vacuum to both rapidly fill and wash the sample loop, with a conventional ICP setup in key areas of instrument performance. The figure illustrates the time required for a standard instrument to work through the primary steps in a typical analysis: sample flush, read delay, measurement, rinse, and overhead. Throughput data from

Figure 1: Avio 560 Max ICP-OES with built-in HTS for 3–5x faster sample-to-sample times.



the HTS analysis is provided in the lower plot in [FIGURE 1](#), showing significant acceleration of the sample flush, read delay, and rinse cycles. The measurement step itself remains consistent between the two methods to avoid jeopardizing analytical performance.

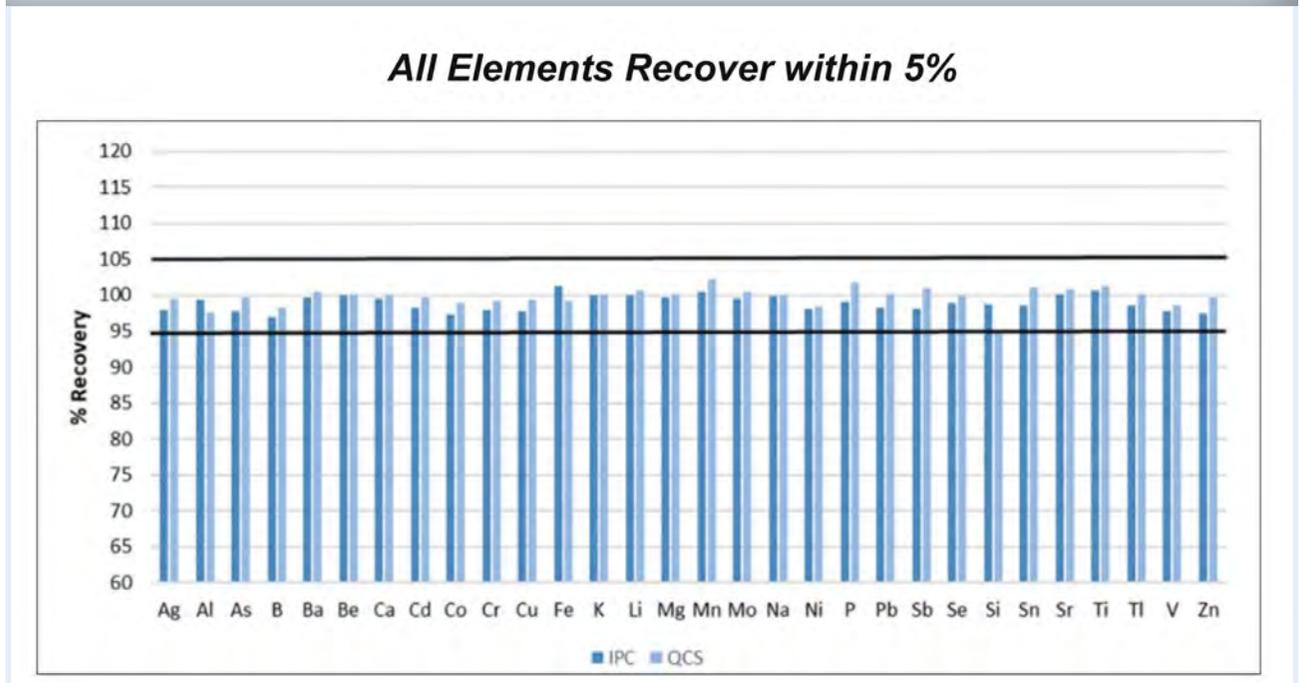
HIGH-THROUGHPUT ANALYSIS OF WASTEWATER

United States Environmental Protection Agency (EPA) Method 200.7 regulates the determination of metals and trace elements in waters by ICP-OES. Any company that discharges water into the environment must monitor its metal content by this method, which is also mandatory at all stages of the wastewater treatment process.

With few exceptions, these companies rely on outside labs to run these samples, creating an

enormous volume of time-sensitive work for commercial testing services. By automating the process as much as possible, they are better able to keep up with this increasing demand and thereby increase their profitability.

There are a few considerations when implementing Method 200.7 on a high-throughput ICP system. The first consideration is the integration time used for the analysis. In this test, we used auto integration with a read time range of 0.5–5 s. Both the instrument and the software automatically determine the best read time to obtain the best quality data in the shortest amount of time. For lower concentrations or low signals, the system will deliver read times on the order of 5 s but will select shorter read times of approximately 0.5 s for high-intensity or high-concentration analytes.

Figure 2: High-throughput analysis of water - Results: initial quality control.

Another key factor is the length of time required to pass the sample through the plasma and to wash out the system before moving on to the next sample. For faster throughput, the Avio 560 Max ICP-OES was used, due to its built-in HTS. This process enables an analysis to start in only 12 s from the time the autosampler probe goes into the sample. After the analysis is complete, it takes only 3 s to wash out the sample and move on to the next sample. Under these conditions, the system can generally achieve sample-to-sample times of approximately 60 s.

Initial quality control. Method 200.7 states that two initial quality control samples must be measured directly after the calibration curve is established – the instrument performance check (IPC) and the quality control sample (QCS). Both samples must be prepared at the same concentration, which is typically about

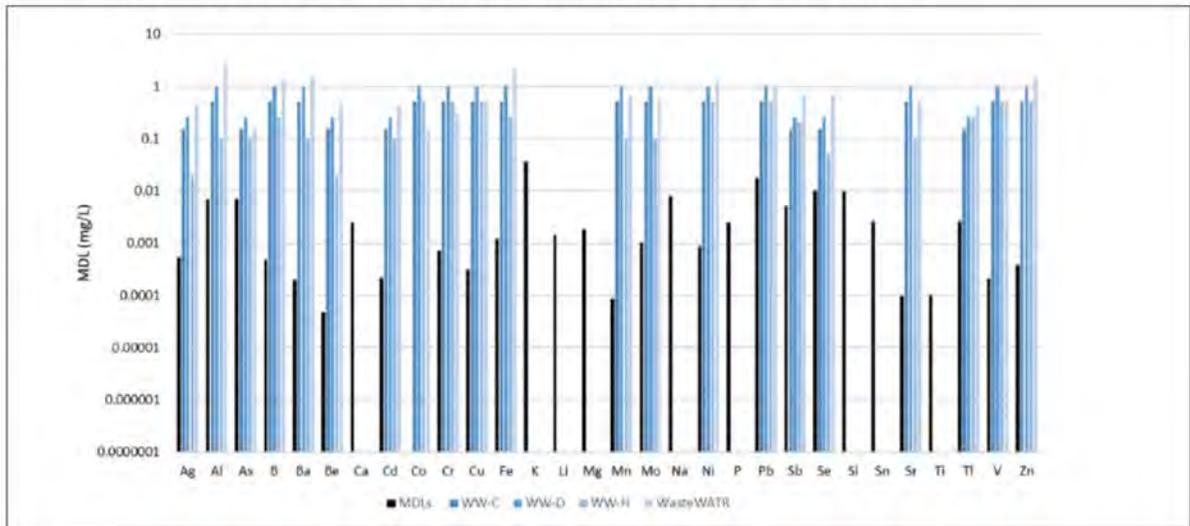
halfway up the calibration curve. Both must recover within 5% of their nominal values.

Both the IPC and QCS are made from different stock standards. The IPC is made from the same stock solutions as the calibration standards, which helps ensure the integrity of the calibration. However, the QCS is made from second-source standards, providing further confirmation of the accuracy of the stock standard used to obtain our calibration curve. **FIGURE 2** shows the results from a typical initial quality control run. Both the IPC (dark blue bars) and QCS (light blue bars) fall well within the $\pm 5\%$ recovery range, as marked by the horizontal black bars.

Method detection limits. Method 200.7 also requires the establishment of method detection limits. Although it does not specify what the detection limits must be, Method 200.7 requires detection limits be determined to characterize

Figure 3: High-throughput analysis of water - Results: method detection limits.

- 3.14 * Standard deviation of 7 measurements of a blank spiked at 2-3 times the instrument detection limit



MDLs much lower than reference materials

the instrument. To meet this requirement, the instrument detection limits (IDLs) are established first, and then a calibration blank is spiked with each analyte at concentrations of two-to-three times the IDL. The spiked blank is run seven times and the standard deviation of these measurements is multiplied by 3.14 to determine the method detection limit. Method detection limits for this application are presented in [FIGURE 3](#), where the black bars show the method detection limits for a typical run and the blue bars show analyte concentrations in four of the wastewater reference materials we used for our analysis.

Accuracy and stability. Accuracy was determined by analyzing four different wastewater reference materials, as shown in [FIGURE 4](#). All reference materials recover within a $\pm 10\%$ accuracy range. It is worthwhile to note that, although we used

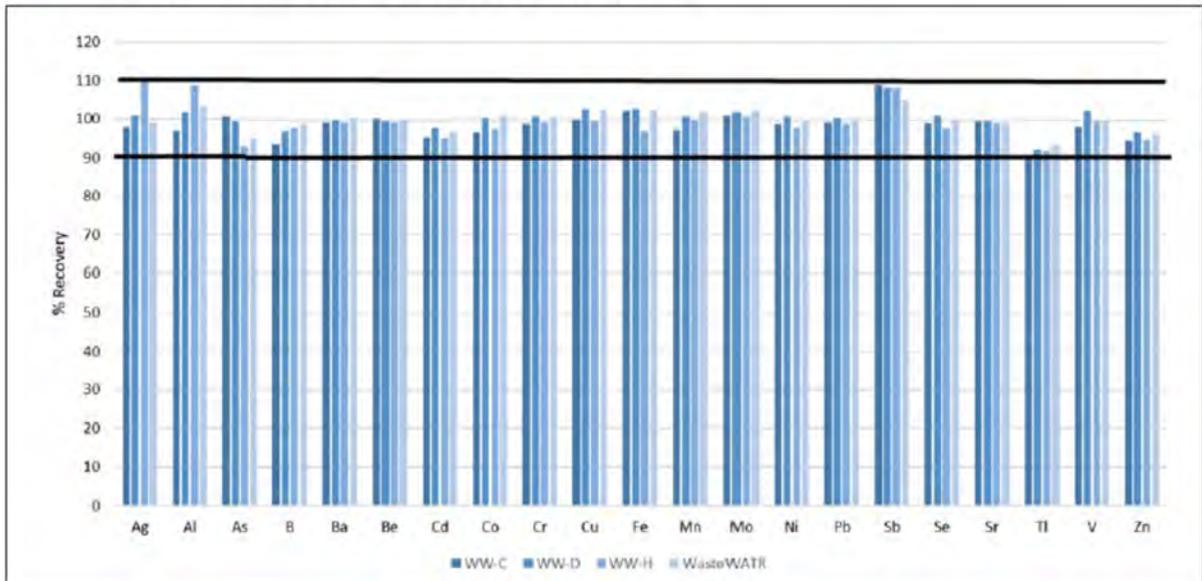
clean reference materials in these tests, we subjected them to the sample preparation procedures specified in Method 200.7 to simulate real-world laboratory conditions more closely.

Method 200.7 requires the IPC standard to be run every 10 samples during analysis, with recoveries within 10% (only the first IPC must recover within 5%). To demonstrate the stability of the Avio 560 Max HTS, we conducted a four-hour analysis of wastewater samples. [FIGURE 5](#) shows recovery of all elements within 10% throughout the analysis during the initial performance check.

In summary, we have shown that the Avio 560 Max's HTS system allows analysts to meet or exceed the regulatory requirements for accuracy, stability, and detection limits for challenging environmental applications.

Figure 4: High-throughput analysis of water - Results: analysis of certified reference materials.

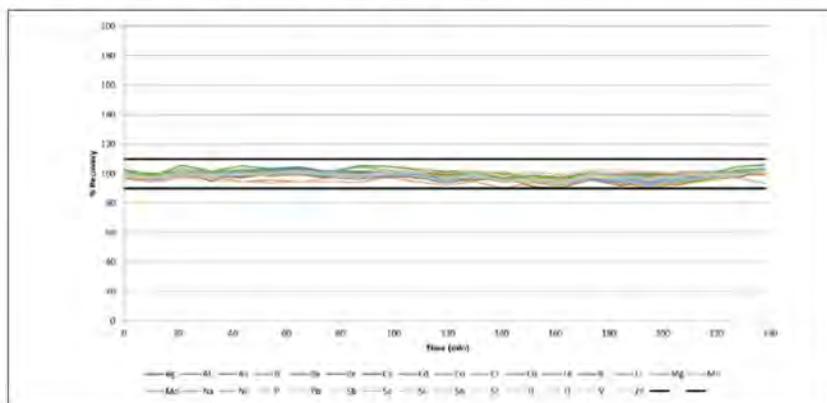
- Run wastewater reference materials



***Recoveries within 10% for all elements
in 4 different reference materials***

Figure 5: High-throughput analysis of water - Stability: IPC recovery over a 4-hour analytical run.

- Run IPC every 10 samples during a 4-hour wastewater analysis
 - Recoveries must be within 10% of true values



All recoveries within 10% over 4 hours

HIGH PRECISION

Factors influencing precision. Measurement precision in ICP is influenced by several factors, including, but not limited to, counting statistics (also known as shot noise), flicker noise, and the internal standard. Counting statistics are caused by detector emission, and conventional wisdom suggests that simply increasing the number of counts that reach the detector will overcome its effects. Although this is often the case, there are limits. Too many counts per second can slightly degrade RSDs, in which case users should consider switching the orientation of their plasma or using a different spray chamber to normalize the analytical signal. Flicker noise is multiplicative noise in the analytical signal that has a noise magnitude proportional to the magnitude of the signal. Flicker noise originates from the plasma source and largely results from the production and transport of sample aerosol droplets during the sample introduction process. Several instrumental components contribute to flicker noise, including the peristaltic pump, nebulizer, spray chamber, plasma torch, and sample injector.

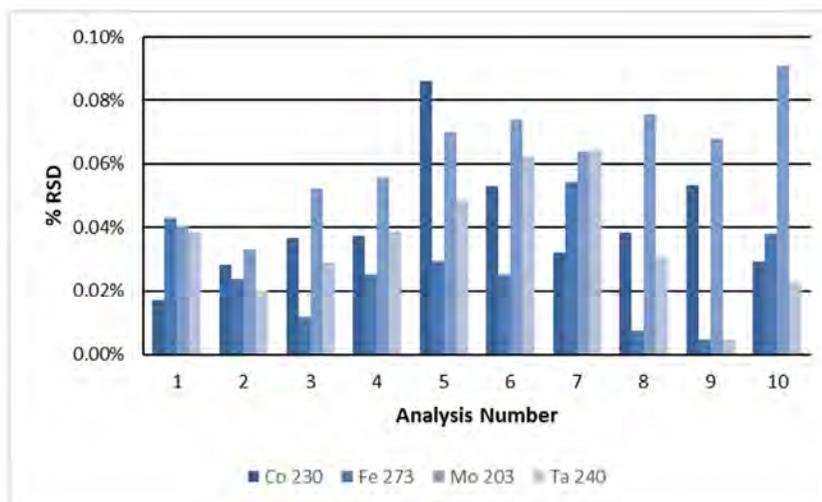
The internal standard plays a critical role in optimizing instrument performance – especially when working at the highest levels of precision. True high-precision ICP-OES (HP-ICP-OES), only available on PerkinElmer's Avio 550/560 Max, requires fully simultaneous technology capable of measuring the internal standard at the same time and under the exact same conditions as the analyte, a capability standard ICP-OES systems lack. Even very slight time differences between measurement of the internal standard and analyte will not

account for noise differences. By measuring both at exactly the same time, any variation that affects the analyte also affects the internal standard in the same way. This technology is key to achieving precision of 0.1% RSD or less, even for challenging samples, such as simulated complex metal alloys, as shown in [FIGURE 6](#). To demonstrate the system's capabilities for both high-throughput and high-precision analysis, the following section describes its performance in three demanding applications that are increasingly common in the real world.

HP-ICP-OES FOR MAJOR ELEMENTS

HP-ICP-OES provides advantages for a variety of applications that require the exact determination of composition/concentration levels for major/matrix components. This level of precision is especially useful for recovering valuable rare earth metals in electronics recycling, as well as in determining the composition of catalysts, nutrient levels in fertilizers, and the ratios of major components in alloys.

To illustrate how HP-ICP-OES performs in these types of analyses, we applied the technique to a sample of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (commonly known as NMC), an advanced material used in the manufacture of cathode components found in lithium-ion batteries. The performance of these increasingly popular components relies heavily on the ratio of nickel to manganese to cobalt. Manufacturers must precisely establish and maintain specific ratios to ensure consistent product quality. To meet these needs, an ICP method must be capable of measuring the components with high precision when

Figure 6: Precision on alloy analysis with HP-ICP-OES on the Avio 560 Max.

Alloy
All RSDs < 0.1%

determining their molar ratios. It is essential to achieve RSDs less than or equal to 0.1% repeatedly over time.

The NMC material requires special sample preparation, beginning with digestion in a hot block. A volume of 0.1 g of NMC is placed in a digestion tube with 2 mL of concentrated hydrochloric acid, and then heated in the hot block at 120 °C for 30 min. Once cooled to room temperature, the sample is diluted to 50 mL with deionized water. To prevent unwanted shot noise, as mentioned above, the sample is then diluted 5x for analysis.

The raw data from our analysis of the same sample digested three different times is presented in [FIGURE 7](#). The first box highlighted in orange shows concentrations in solution ranging approximately from 15 ppm to 65 ppm. The center orange box presents those

concentrations as weight percentages, where lithium is 7.7 wt% and nickel is more than 30 wt%. The third highlighted column indicates RSDs for nickel, cobalt, manganese, and lithium all below 0.12%, achieving our goal of 0.1% or less. Finally, to demonstrate short-term stability, we selected one sample and measured it 10 times over 20 min, achieving exceptional stability, with the RSDs of the 10 measurements being less than 0.5% for all analytes.

HP-ICP-OES ANALYSIS OF ALLOYS

The exact composition of alloys is critical to maintaining their unique properties. Analytical methods must deliver repeatable results at high levels of accuracy and precision. To demonstrate the high-precision capabilities of the Avio 560 Max ICP-OES system, a customer-provided test was performed: measure cobalt, iron, molybdenum, and tantalum at concentrations ranging from 150 to 300 ppm

Figure 7: HP-ICP-OES analysis of NMC - Results: raw data.

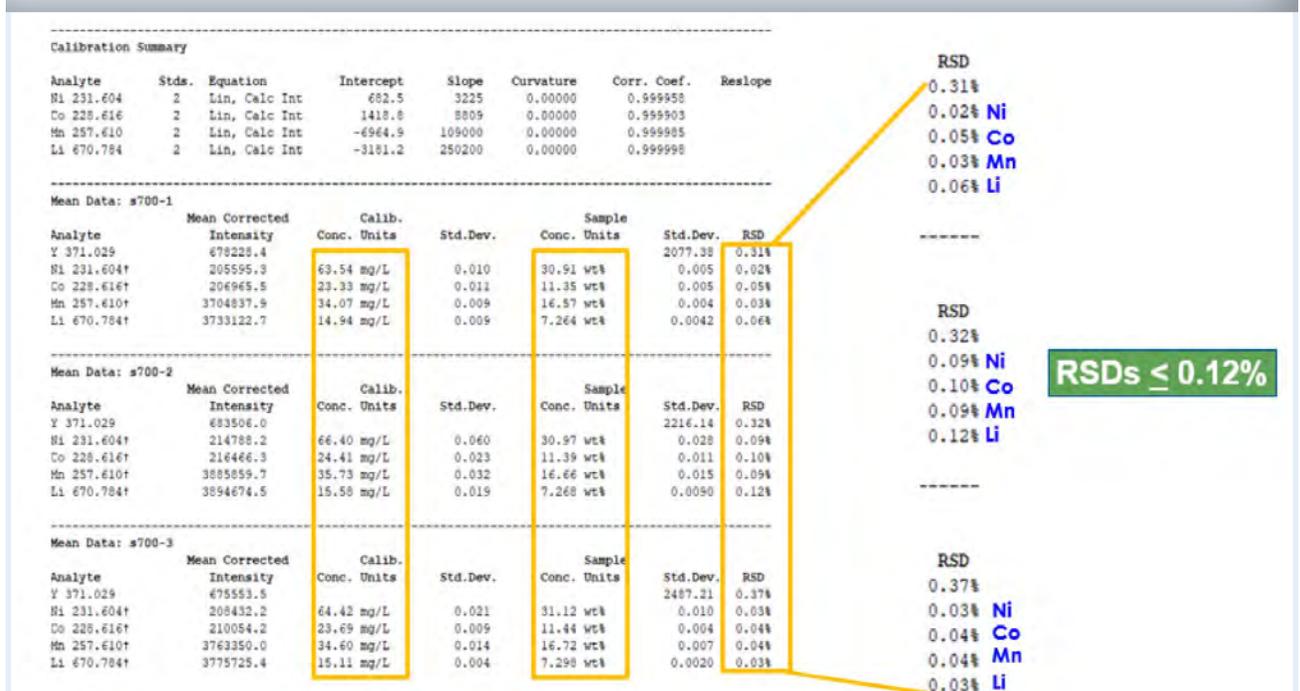
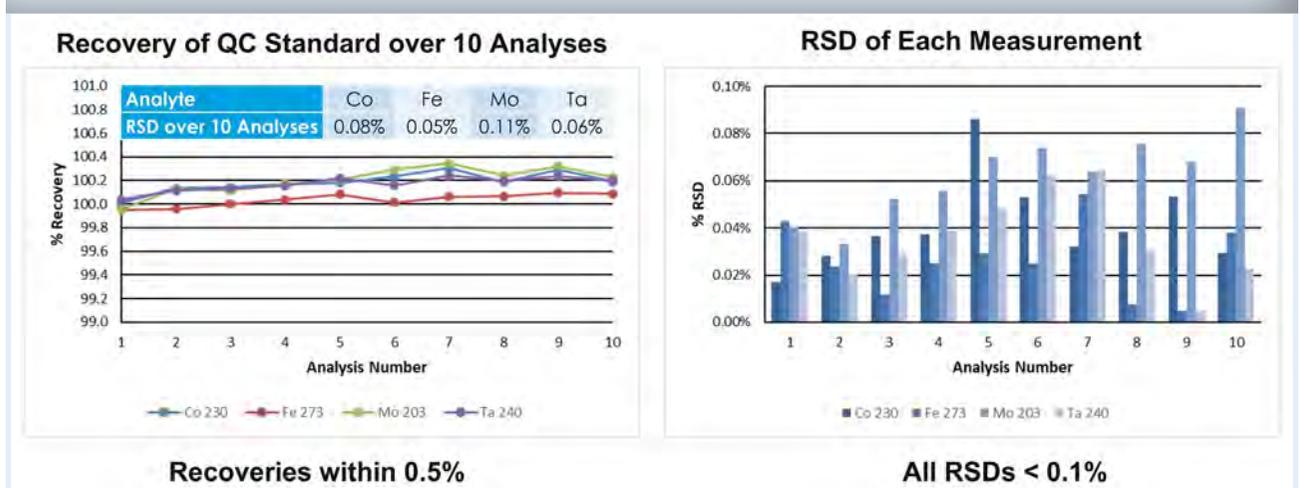


Figure 8: HP-ICP-OES applied to alloy composition.



in solution, which represent the concentrations in an alloy after the sample preparation. The client further specified that recoveries must be within 2% for cobalt, iron, and molybdenum, and within 1.4% for tantalum. The goal of this test was for nine out of 10 measurements to fall within the defined range, with all 10 analyses

achieving deviation of 0.5% or less. To increase accuracy, we performed a linear bracketing calibration, in which calibration standards are prepared to come very close to the expected concentration. This method prevents the influence of low-level standards or x-axis intercept on the calibration curve, thereby

providing the most accurate results in HP-ICP-OES. The results from the analyses are shown in **FIGURE 8**. The graph on the left plots percent recoveries for each element over 10 analyses, with recoveries ranging from about 99.9% to 100.4% and RSDs over 10 analyses ranging from 0.11% down to 0.05%. The chart on the right shows that the RSDs of each analyte from each of the 10 individual analyses are all less than 0.1%.

CONCLUSION

In summary, both high throughput and high precision are important for different ICP-OES application areas. Labs faced with high sample loads require high throughput. However, there are also applications where the concentration of major elements is critical, and accurate, precise results are a must. Technologies that provide the flexibility to meet both requirements, such as those on PerkinElmer's Avio 560 Max fully simultaneous ICP-OES, can help laboratories increase their productivity, meet customers' demands for speed and accuracy, and thereby increase their profitability.



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