Introduction
Magnesium alloys, once reserved for aerospace and other special applications, are now found in many common products ranging from smart phones to sporting equipment to automotive parts. These alloys are by far the lightest of readily available industrial metals, yet can be stronger than aluminum. Favorable mechanical properties make magnesium alloys easy to machine and damp vibrations, widening their appeal to manufacturers. On the other hand, magnesium has high chemical activity, making it more susceptible to corrosion if left unprotected, especially in humid environments. Coatings in the form of electroplated metals, chemical surface conversion, or spray coating of ceramics and cements are all techniques used successfully to protect magnesium alloys.

In this note, we examine a magnesium alloy plate to determine the type of anti-corrosion coating present. In the same experiment, the chemistry of the bulk magnesium alloy can also be observed. All data was collected using the ChemReveal® Desktop LIBS Analyzer. In LIBS—laser induced breakdown spectroscopy—a laser pulse, focused at the sample surface, creates a spark that atomizes a small amount of material and produces an optical emission signal characteristic of the elemental composition. Because only a small amount of material is removed from the sample with each pulse, repeated laser shots produce spectra that initially represent the surface chemistry and transition to spectra characteristic of the bulk alloy.

Results
We used a ChemReveal Desktop LIBS analyzer equipped with a 50 mJ, 1064 nm Nd:YAG laser and a proprietary, 4-channel spectrometer, covering the range from about 190—980 nm. Instrument settings were as follows:

- Laser energy: 50 mJ/pulse
- Spot size: 100 µm
- Sample shots: 1 shot/spectrum, 200 total spectra penetrating into sample
- Acquisition delay: 1 µs
- Purge Gas: Argon
Figure 1 shows a LIBS spectrum of the magnesium alloy surface following a few laser shots. Many elements are observed, including the purge gas, argon. A purge gas is an experimental option to enhance the signal intensity of some analytes, or to exclude atmospheric gases when N, O, and H need to be measured in the sample. Magnesium lines are abundant in Figure 1, but so also are many minor components. Using a time series of spectra collected at the same spot on the sample, it is possible to look at the trend in element composition as a function of depth. A moderate laser power was used in order to collect several spectra of the coating before it was totally removed. Figure 2 shows selected spectra as the experiment progressed, focusing on only two elements, calcium and aluminum. A plot of the intensity of each peak with time would indicate that calcium is found only near the surface, and therefore is part of the coating.

Figure 3 overlays the relative intensity of several elements vs. laser shot number. The laser shot number is correlated with depth into the sample. The rapid decrease in Ca, P, and Na indicates that these elements are at the surface only. One type of chemical conversion coating on magnesium is treatment with a salt of dihydrogen phosphate, allowing the phosphate group to form a layer of $\text{Mg}_3(\text{PO}_4)_2$, co-crystallized with the phosphates of the counter ions of the dihydrogen phosphate regent, $\text{M}_x(\text{PO}_4)_z$. Because the likely counter ions, Ca and Na, follow the same concentration profile, it appears both are incorporated into the coating layer when produced with this treatment.

As the experiment progresses from the surface more deeply into the material, the coating elements are removed through laser ablation, leaving only the bulk magnesium alloy. Figure 3 also shows that the intensity, and thus the concentration, of aluminum is constant with depth assuring us the aluminum is part of the bulk alloy chemistry and not part of the coating. Aluminum is commonly found in magnesium alloys at concentration up to 6%.

![Figure 1: Typical LIBS spectrum for the magnesium plate sample.](image-url)
Figure 2: LIBS spectra of the magnesium alloy in the 392 – 398 region following 1, 5 and 25 laser shots. Calcium intensity rapidly declines and the aluminum intensity increases, showing a transition from surface coating to bulk alloy.

Figure 3. LIBS Intensity of several elements recorded over 100 laser shots. Emission lines selected for each plot: Ca 396 nm, P 215 nm; Na 589; Al 394. Y-axis is relative to a reference intensity for each element.
Summary

The ChemReveal LIBS Desktop Analyzer can be a valuable tool supporting research or quality control of metals and alloys. With a proper experimental design, the technique can be extended to distinguished coatings from the bulk composition. The type of coating on a magnesium alloy was identified in this work. Extending the analysis to quantitative results for the chemistry of the bulk alloy would be very straightforward, requiring only a set of magnesium standards spanning the alloy chemistry concentrations. This work shows the importance of removing the surface layer prior to analysis for bulk properties. LIBS or spark OES spectra of an as-received surface would be affected by interferences from the surface coating. With LIBS, the coating can be removed with a series of laser cleaning shots, allowing accurate measurement of the bulk alloy chemistry without need for mechanical surface preparation.