



The Use of Spectral Subtractions and Broad Wavelength Coverage to find “New” Wavelengths for ICP-OES

INTRODUCTION

Since the introduction of ICP-OES in the 1970s most instruments have offered a wavelength range which approximates 165 to 777 nm. Once the transition from photomultiplier tube to array detector occurred, wavelength coverage tended to be reduced by either limiting the user to discrete spectral segments where (in the manufacturer's opinion) the most useful emission lines existed or where the manufacturer chose to eliminate large regions of the spectrum that were deemed unnecessary. In most cases this was necessary for reasons of cost (i.e., the smaller the area covered by detector elements, the less expensive the instrument is to build) and/or physical size limitations of historically available array detectors. The Prodigy High Dispersion ICP does not suffer from these limitations. The system is shown in Figure 1.

Prodigy's large format programmable array detector (L-PAD) and long focal length optical design make it the only commercially available ICP to offer continuous wavelength coverage between 165 – 1100 nm. Prodigy does this while providing very high spectral resolution in the critical 175 to 350 nm region. Prodigy's long focal length optical system combined with L-PAD are shown in Figures 2 and Figures 3.

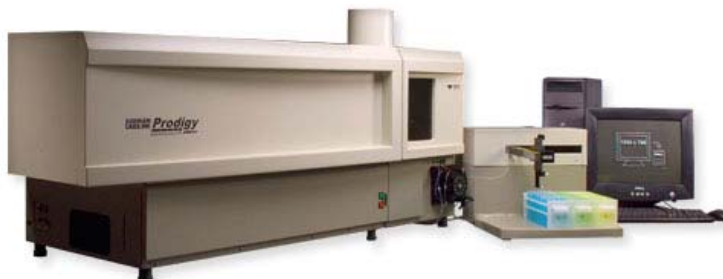


Figure 1. Prodigy High Dispersion ICP

There are distinct advantages to such large wavelength coverage. Two examples are illustrated in this paper. First, access to a new cesium emission line at 894.347 nm is shown to yield a detection limit over 600 times lower than the previously thought to be “primary emission line” at 455 nm. Second, access to an Iodine line that is free from Phosphorus and Chromium interferences that affect the 178.251 and 206.163 nm lines is demonstrated.

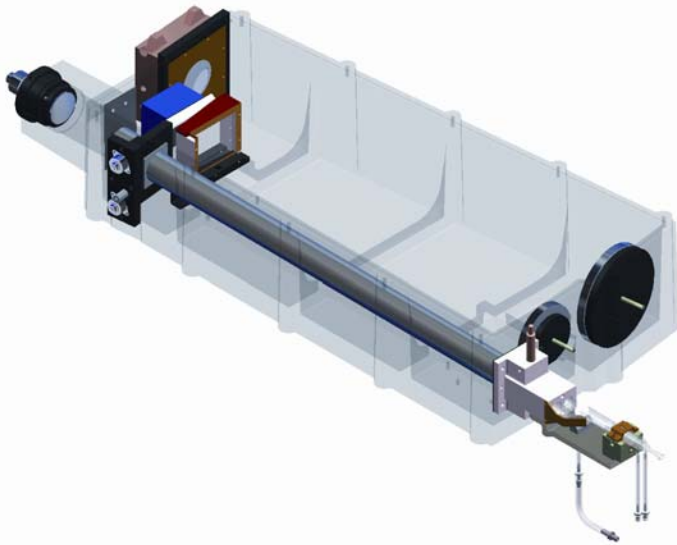


Figure 2. Prodigy's long focal length optical system is nearly twice the size of competing designs. This provides the user with superior wavelength coverage, resolution and stray light performance

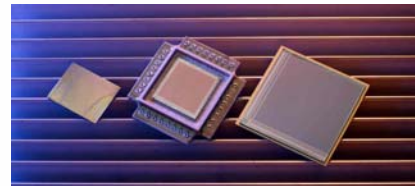


Figure 3. Prodigy's L-PAD detector (on the right) on the same scale as two other competing designs. Note: the L-PAD provides over 4 times the active area of the competing designs.

Features of Prodigy's Design include:

- Image Stabilized ICP Source**..... exceptional stability and fast warm-up
- Computer-Controlled Source Mirrors**..... optimizes ICP viewing positions. Also selects Axial, Radial or DV modes of operation
- Operator Selectable Input Slits**..... provides application-selectable resolution to match analytical requirements (optional)
- Dual Pass Prism and High Incidence Optics**..... for exceptional resolution and light throughput
- Long Focal Length Optical System**..... for superior dispersion and resolution
- Temperature Controlled Optical System**..... for superior long-term stability
- Ultra Low Outgas Optical System**..... for superior low UV performance and low purge gas flows
- Modular Design**..... for simplicity and serviceability

EXPERIMENTAL

The first step in searching other options for “new” wavelengths is to acquire two full spectra from 165 to 1100 nm; one while nebulizing a standard containing the element(s) of interest and one while nebulizing a high purity blank. A spectral subtraction of the blank from the standard is then performed using Prodigy’s Spectroscopy Tools. These spectra are shown in Figures 4 through Figures 6 for an experiment involving cesium. The blue rectangles shown in each spectrum are the regions of the detector (pixels) that would be used during fully quantitative analysis.

DISCUSSION – FOR CESIUM

The spectra in Figures 4 and 6 show the very intense 894.347 nm emission line. Although the spectrum in Figure 4 also shows a Cs emission line at 852.12 nm, that line has an argon interferent which will cause it to be less analytically reliable than the 894.34 nm line.

It is important to note that the 894 nm line found in this work is outside the wavelength range of virtually all other PMT and array detector based ICP-OES systems.

The comparative 3 sigma detection limits for the classic 455.528 line and the new 894.347 nm line are shown in Table 1. This work has resulted in a new analytical line with a 600 fold improvement in detection limit over the previously used line at 455 nm.

Wavelength, nm	Axial detection limit in ppm
455.528	1.2
894.347	0.002

Table 1. 3 Sigma Detection Limits for Cs

IODINE EXPERIMENT

The Spectra in Figures 7 through Figure 9 show a number of Iodine lines of varying sensitivity. The often used iodine lines at 178.251 and 206.163 suffer from serious interferences in matrices containing phosphorous and chromium, thereby making accurate quantitation difficult. In addition, since Iodine is not frequently determined by ICP-OES, most line libraries used suffer from a lack of available Iodine lines.

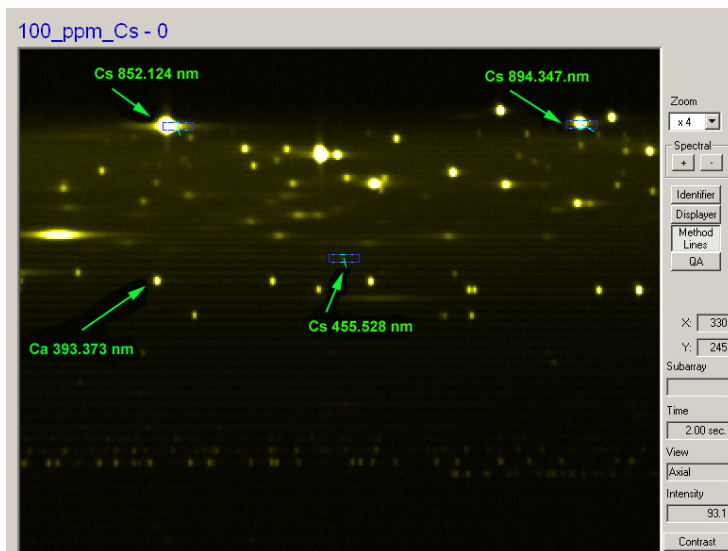


Figure 5. Spectrum of 5% HNO₃

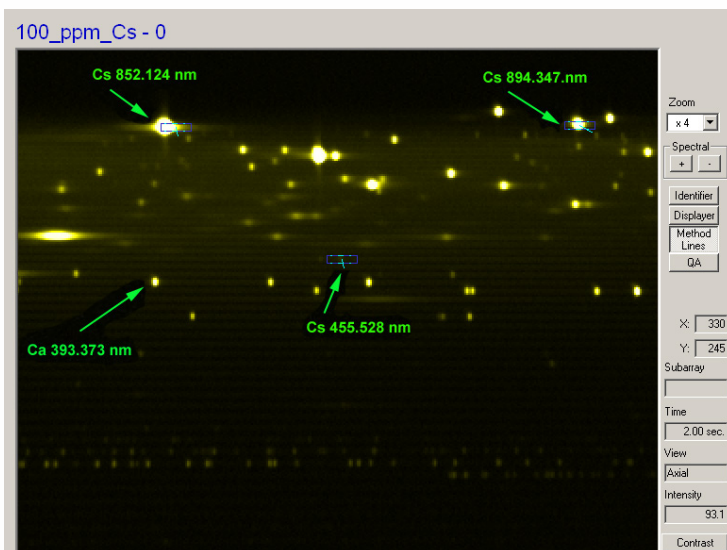


Figure 6. Spectral Subtraction of 5% HNO₃ from 100 ppm Cs

Using the spectral subtraction capability combined with the Prodigy's broad and continuous wavelength coverage, it was possible to find the 183.038 nm emission line that was sufficiently sensitive and free from spectral interference to successfully perform the required analysis.

CONCLUSION

Prodigy's large format programmable array detector and long focal length optical system make it the only commercially available ICP to offer full wavelength coverage between 165 to 1100 nm and with high spectral resolution. The Prodigy data system is capable of performing the necessary spectral additions, spectral subtractions and elemental fingerprint overlays often needed to solve today's analytical challenges.

Spectral addition/subtraction capabilities combined with elemental fingerprinting tools are broadening QC and Forensic applications which ICP-OES is being used to address. Two areas of high visibility at the moment are product quality testing and counterfeit drug manufacturing. There are numerous other applications in homeland security, health and human safety and patent infringement areas where these techniques are poised to assist today's analyst.

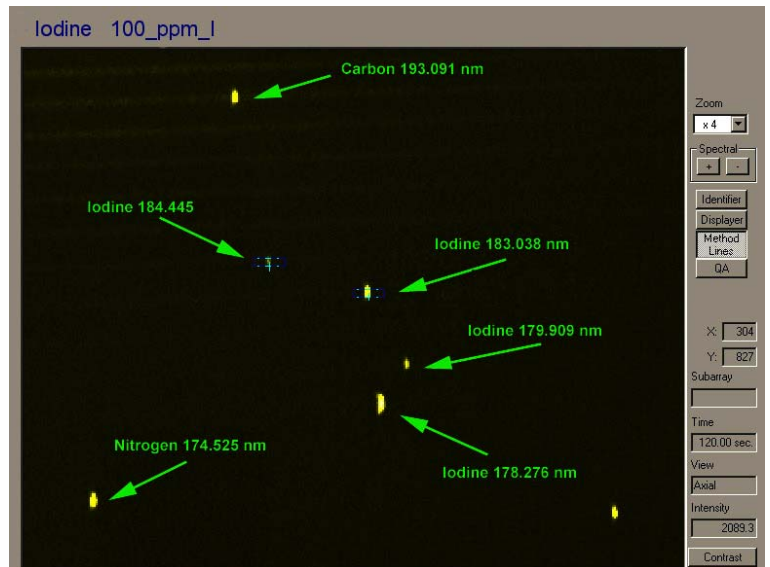


Figure 7. Spectrum of 100 ppm Iodine.

To discuss how Teledyne Leeman Labs can help you solve your elemental analysis challenges, contact us at 1-800-634-9942 or visit us at www.LeemanLabs.com.

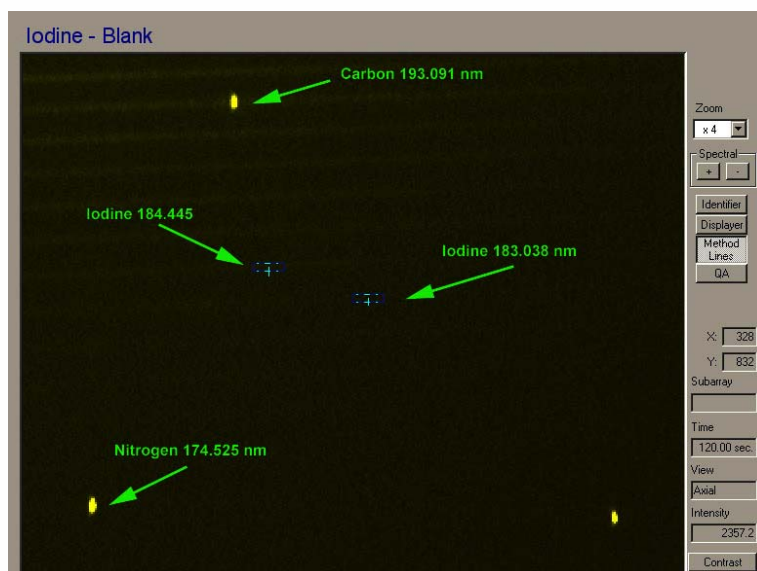


Figure 8. 5% HNO₃ Blank.

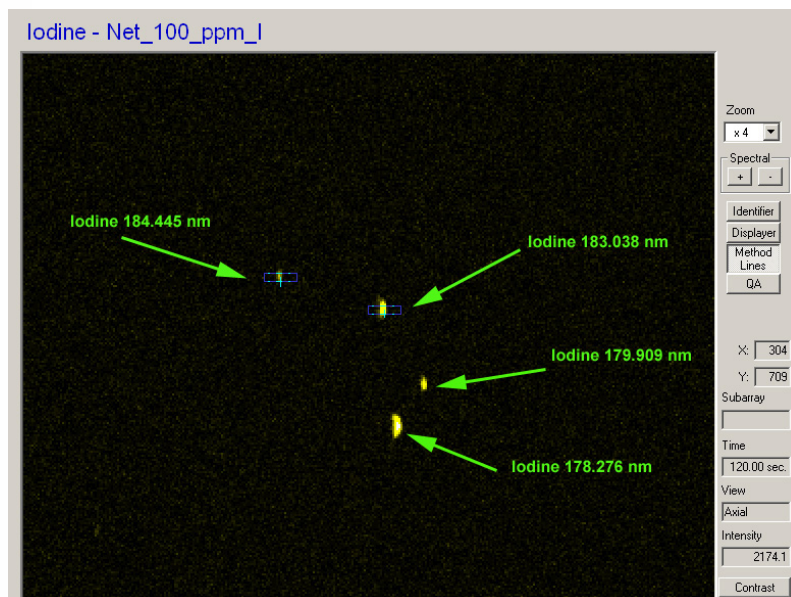


Figure 9. Spectral Subtraction HNO₃ Blank from 100 ppm Iodine.