

## Tech Note

# Design Criteria for ICP Spectrometry Using Advanced Optical and CCD Technology

**The authors describe an ICP detection technology that combines photon-current conversion and a solid-state multichannel detector. The unit's ability to conduct fast simultaneous classification of multiple analytes is demonstrated.**

**Jean Michel Mermet, Agnès Cosnier, Yves Danthez, Cendrine Dubuisson, Emmanuel Fretel, Olivier Rogerieux, and Sébastien Vélasquez**

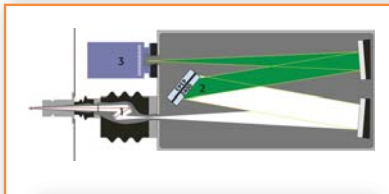
**H**istorically, inductively coupled plasma (ICP) emission spectrometers clearly have been defined as offering either sequential or simultaneous analysis. For decades, both systems have been based upon the use of photomultiplier tubes (PMTs). This type of detector presents some major advantages such as a large wavelength range, including the UV region down to 120 nm, and a high amplifier gain. However, compared to a photographic plate, the major drawback of a PMT is that it is used in a single-channel detector. Atomic emission spectrometry (AES) implies the emission of the spectrum of each element, which means that the use of a single-channel detector leads to a drastic waste of information, even when these detectors are set up in a polychromator. There is a need then for a detector that associates photon-current conversion and the richness of information of a photographic plate: this can be obtained by using a solid state multichannel detector. With the advent of solid state detectors, in particular detectors based upon charge transfer device (CTD) technology, this sequential-simultaneous classification has become less obvious as the defining criteria have shifted from the optical design to that of the type of detector used.

In the 1990s, introduction of CTD-based systems, first using a 2-D detector with an echelle grating associated to a cross dispersion, then an assembly of linear detectors along the Rowland circle of a Paschen-Runge optical mount, led to two groups of ICP systems, sequential PMT-based instruments and simultaneous CTD-based instruments. Sequential systems are considered to offer a full spectrum of information and excellent performance for resolution, as the limitation of chip and pixel size is not a factor, and they provide full flexibility for both line selection and optimization of the operating parameters, but are considered slow for laborato-

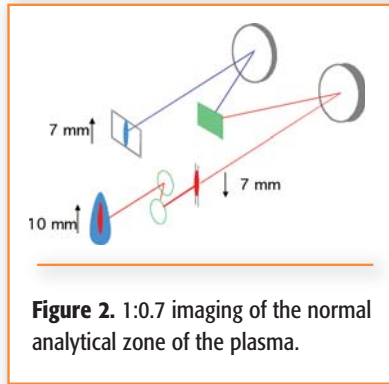
ries requiring high sample throughput. However, this sequential-simultaneous classification became more complex with the introduction of a CTD detector on a sequential dispersive system. Instead of scanning step by step the line profile and its vicinity, this information was obtained in a single shot, and the system moved then to another wavelength. The narrow bandpass obtained with the single-channel PMT detector was replaced by a larger window allowed by the multichannel CTD detector.

Today, we see the need for an instrument to handle users' increasing demand for analytical performance while still maintaining high speed, and in view of that, to select the most recent technology, particularly in the field of detection. A possible way of improving speed and reliability of the analytical results is to increase the number of analytical lines per element. One approach is to use sequential windows, but to open them beyond a single line and its vicinity, so as to obtain a large spectral window providing an abundance of spectral line and background information.

For this system to meet the analytical requirements demanded today it must provide constant resolution across the large window, so-called wavelength analytical view (WAV), while offering a large dynamic range and the same intensity response across the window, so as to allow true simultaneous determination of several lines with different intensities. Keeping in mind our requirements and considering the solid state detector and optical designs available today, we see that to obtain a large spectral window of several nanometers, with constant resolution, we must remove any optical aberrations and optimize the light gathering optics for photon collection while still maintaining excellent resolution and a large slit height. If we consider the dynamic range and constant intensity across the system, we see the need for a



**Figure 1.** Optical design. Features: 1 = achromatic entrance imager, 2 = dual holographic gratings, and 3 = advanced CCD detection system.



**Figure 2.** 1:0.7 imaging of the normal analytical zone of the plasma.

solid state detector that offers good antiblooming protection and an excellent dynamic range. If we meet the first two of our requirements, we must then perfectly match the solid state detector to the viewing mode and the optical pixel size, number and format, and advanced CCD technology.

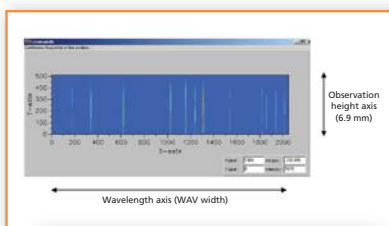
### High Performance Optics

A new optical design featuring a 0.64-m Czerny-Turner optical system (Figure 1) fulfills the requirements mentioned above. This design integrates an achromatic entrance imager 1:0.7 entrance optic for optimized imaging from the entrance slit onto the solid state detector of the best analytical zone of the plasma. The achromatic entrance imager optimizes photon collection from the entire 10-mm normal analytical zone of the plasma, optical aberrations, resolution, stray light and the 7 mm entrance slit height of the Czerny-Turner optical system. The achromatic entrance imager uses two mirrors for focusing: one concave and one plane (Figure 1). The concave mirror inherently is free of chromatic aberrations across the spectrum, rather than at one

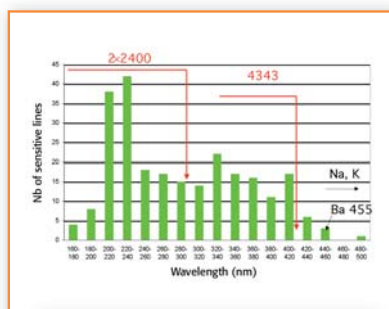
wavelength, and the plane mirror directs the light into the optical system. The entrance slit is imaged through the spectrometer onto the focal plane (Figure 2). The advanced CCD detector then is located at the super flat field position of the Czerny-Turner spectrometer, allowing an excellent constant resolution and a constant intensity within a WAV. The flat field is at least 25 mm wide. This entrance optic associated with large Czerny-Turner optical components featuring 80 mm x 110 mm dual gratings, provides the highest optical luminosity from the far UV to the near infrared.

### Chip Format and Pixel Size

The selection of pixel size is a balance between basic performance parameters. Smaller pixels will give increased resolution, assuming that resolution is not limited elsewhere in the system. Typically as the pixel size decreases, well ca-

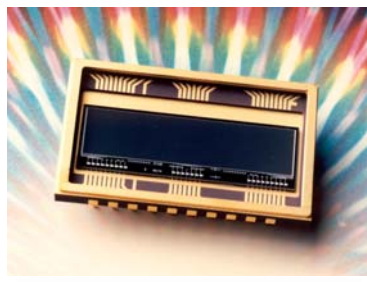


**Figure 3.** 2-D display of a spectrum on the 2048 x 512 pixels CCD.



**Figure 4.** Histogram based on the four most sensitive lines of elements (20-nm class) showing the benefit of a cut-off at 431 nm, instead of at 300 nm when using a 2400 lines/mm grating in the second order.

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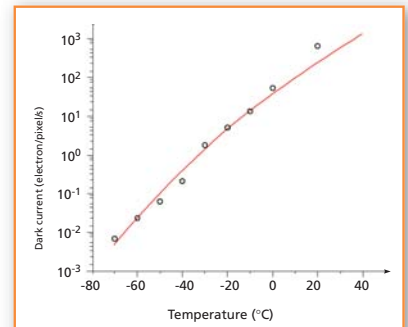
**Figure 5.** Advanced CCD Technology is provided in 2048 x 512 pixel format with blooming protection provided through individual pixel column protection and readout registers.

capacity (the amount of charge that can be stored in a pixel) and the overall dynamic range decrease. A pixel size of  $13.5\ \mu\text{m} \times 13.5\ \mu\text{m}$  is an excellent compromise. Because of a flat field of at least 25 mm wide, a CCD with rows of 2048 pixels wide was selected. Similarly, a column of 512 pixels takes advantage of the 7-mm-high image (Figure 3). The

CCD then is rectangular and of the megapixel type.

The use of this optical design with two first-order only holographic gratings back-to-back produces a spectrum that eliminates order hopping from overlapping orders, such as those produced by echelle grating spectrometers. It results also in a constant intensity across the WAV. The use of a 4343 lines/mm grating provides wavelength coverage up to 431 nm — the most useful range (Figure 4) — and the highest resolution, while a 2400 lines/mm grating will have a wavelength coverage up to 800 nm, thus allowing the determination of the alkali elements with mid-resolution.

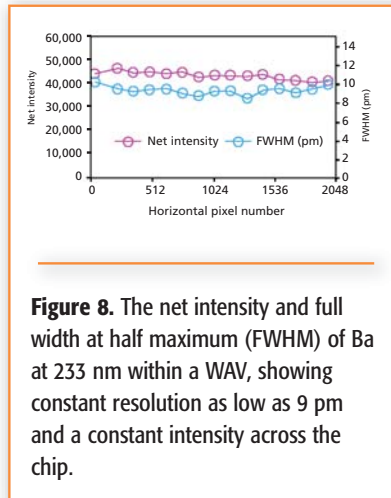
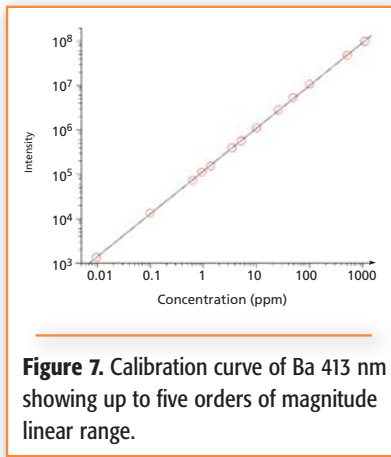
An optical design such as this provides several nanometer-wide spectral windows. The width is given by the reciprocal linear dispersion (RLD) of the grating multiplied by the detector pixel size and the number of pixels. Aberration free, holographic gratings combined with a 2048-pixel-wide CCD detector result in two sizes of the WAVs: up to 8 and 16 nm.



**Figure 6.** STE cooling as low as  $-70\ ^\circ\text{C}$  associated with AIMO reduces dark current to a value lower than 0.01 electron/pixel/s.

### Advanced CCD Technology

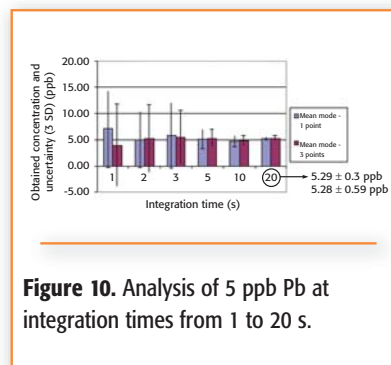
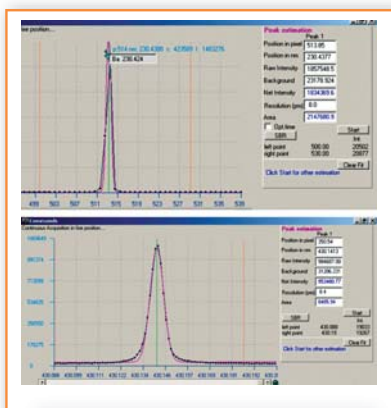
A patented CCD detector (Figure 5) is available which offers back illumination (BI), high performance advanced inverted mode operation (AIMO), resulting in an optimization for UV and visible spectroscopy, with high quantum efficiency, very low noise levels and

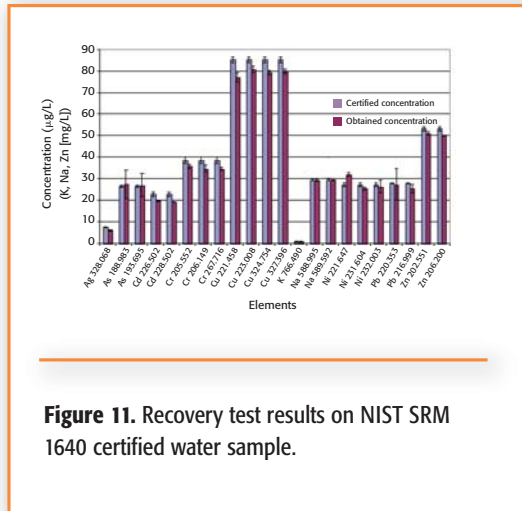


high linear range. Back illumination technology, in combination with an extremely low noise amplifier, make the device well suited to the most demanding spectroscopy applications. With a relatively constant response and an average quantum efficiency (QE) of 60% between 165 nm and 800 nm, this detector is ideal for elemental analysis by ICP-optical emission spectrometry (OES). The detector operates in AIMO, also known as multipinned phase (MPP), and offers a 100 times reduction in dark current with a minimum reduction in full well capacity, increasing dynamic range. An alternative to front side illumination, where incident UV photons are trapped in the electrode gate structure and the insulating layer, is backside illumination — the process for illumination from the re-

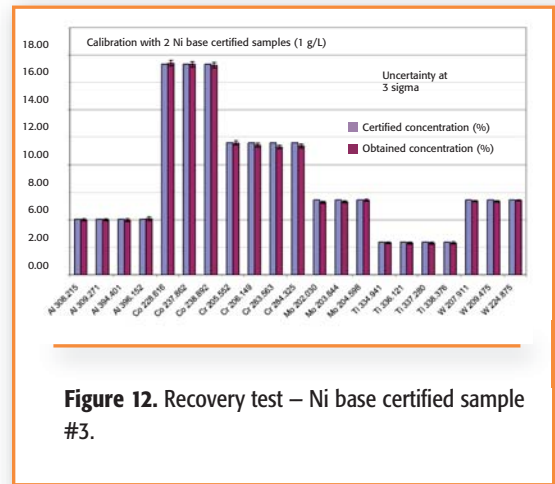
verse side. Back thinning occurs with the elimination of the substrate to allow the photons to reach the epitaxy silicon layer directly. This back thinning process usually is achieved with chemical etching, together with surface passivation and an optional UV antireflection coating. Back-thinned devices have much higher quantum efficiency than standard (front illuminated) devices. At UV wavelengths, back-thinning is expected to provide the highest quantum efficiency of any technology available today. AIMO is an improved inverted mode device structure to achieve peak signal levels higher than available with the basic IMO device, featuring additional implants to allow integration with all clock phases at zero and the whole surface inverted, thereby achieving very low levels of dark current signal. AIMO provides a decreased dark current signal without affecting the full well capacity.

In addition, the possible binning of the entire 512 pixels allows the on-chip





**Figure 11.** Recovery test results on NIST SRM 1640 certified water sample.

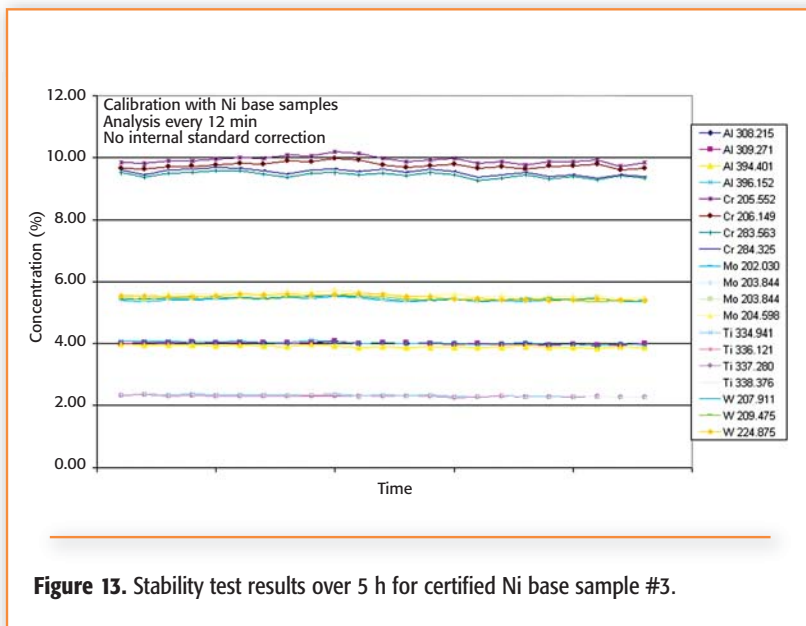


**Figure 12.** Recovery test – Ni base certified sample #3.

summation of the pixel charges for increased signal without the penalty of increasing readout noise. With air forced Super Thermo Electric (STE) using multistage Peltier cooling at  $-70\text{ }^{\circ}\text{C}$  ( $\pm 0.1\text{ }^{\circ}\text{C}$ ), the detector dark current is reduced to a negligible value less than 0.01 electron/pixel/second

(Figure 6). Associated with a very low readout noise of 3 electrons rms and full chip binning capability, this detector allows very good detection limits performance with radial viewing. The CCD contains antiblooming drains to allow low-level signal detection which can be adjacent to much stronger sig-

nals. The readout speed is as fast as 1 MHz. The full chip binning capability allows for fully automatic control to decrease the readout time to insignificant values. As a result, the ICP spectrometer can take full benefit of the maximum available dynamic range within a 16-bit data acquisition elec-



**Figure 13.** Stability test results over 5 h for certified Ni base sample #3.

tronic along with a linear range of more than five orders of magnitude (Figure 7). It then is possible to determine simultaneously multiple elements at multiple wavelengths and background within a WAV, the so-called SimShot function.

### Performance Data

The measure of any ICP spectrometer today can be determined by the quality

of analytical data it provides. This can be measured easily using figures of merit such as resolution, detection limits, speed of analysis, and so forth.

Resolution measurements confirm that the resolution is constant over a WAV (Figure 8) and over the wavelength range up to 431 nm for the 4343 lines/mm grating (Figure 9). It should be noted that the intensity response also is constant within a

**Table I. Typical detection limits at 3 sigma.**

Element	Wavelength (nm)	Detection Limit (µg/L)
Al	167.020	0.7
As	189.042	5
As	193.695	5
B	208.959	1.5
Cd	228.802	0.3
Co	228.616	0.4
Cr	267.716	0.4
Cu	324.754	0.4
Fe	259.940	0.4
Li	670.784	0.05
Mg	279.553	0.02
Mn	257.610	0.06
Mo	202.030	0.6
Ni	221.647	0.5
P	178.229	9
Pb	220.353	2.5
Sb	206.833	4
Se	196.026	4
Zn	213.856	0.3

WAV, which confirms the benefit of the optical design.

One of the main criteria of the system design was to provide excellent limits of detection while maintaining the benefits of a radial plasma view. The limits shown in Table I support this design. Such a total plasma view extends the analysis of trace elements to a variety of matrices such as organics and high dissolved solids.

The capability of the system to work at low level of concentrations is illustrated in Figure 10, where results are shown for a Pb concentration of 5 µg/L. Experimental concentrations along with the measurement uncertainty (3 standard deviations) are given as a function of the integration time. For an integration time of 20 s, the uncertainty is in the range 0.3–0.6 µg/L, depending on the measurement mode.

Additional requirements for environmental analysis demands that ICP spectrometers provide fast analysis. Results on NIST SRM 1640 (Figure 11) show

excellent recovery in less than 4 min (3 min, 40 s) for 34 elements at 57 wavelengths.

Additional flexibility of a system featuring high spectral resolution and the speed of CCD detection can offer advanced performance features for difficult matrices in metallurgy applications such as Ni base alloys. Figures 12 and 13 show excellent agreement with the CRM Ni base sample (#3) and good stability over 5 h without any use of internal standard or interelement correction. The use of multiple lines per element for analysis provides consistency in the results.

### Conclusion

The use of advanced CCD technology with low readout and dark current noise provides a high dynamic range and allows the simultaneous determination of a large number of line and background intensities across a several nanometer-wide spectral window. Additionally, the resolution and intensity

response is constant within the WAV and across the spectrum. The combination of new CCD technology with optimized optical design leads to excellent limits of detection and minimizes non-spectral matrix effects because of the radial viewing mode (total plasma view). This system allows fast multiline analysis, as well as advanced features such as automatic optimization of the signal-to-background ratio, fast temperature diagnostics and internal standardization. ■

**Jean Michel Mermert** is with Laboratoire des Sciences Analytiques, Université Claude Bernard-Lyon (France). E-mail: jeanmichel.mermert@wanadoo.fr.

**Agnès Cosnier, Yves Danthez, Cendrine Dubuisson, Emmanuel Fretel, Olivier Rogerieux, and Sébastien Vélasquez** are with HORIBA Jobin Yvon, and based in Longjumeau, France. E-mail: agnes.cosnier@jobinyvon.fr.