

# CCD and CID solid-state detectors

## Technical Overview

5110 ICP-OES



### Introduction

Many of today's ICP-OES instruments have progressed from traditional photomultiplier tube (PMT) detection systems to solid-state charge transfer devices including the charge-coupled device (CCD) and charge injection device (CID). The role of the detector has not changed in that it converts light energy (photons) from analyte emissions generated in the plasma into an electrical signal that can be quantified. These type of solid-state detectors provide many advantages over PMT detectors, including:

- Greater choice of analyte wavelengths compared to PMT-based simultaneous ICP-OES, for increased flexibility
- Simultaneous measurement, providing much faster analysis times compared to sequential scanning ICP-OES
- Smaller, more analytically stable echelle optic design that complements the two-dimensional layout of the detector



**Agilent Technologies**

Prior to the mid-1990s, PMT-based simultaneous ICP-OES provided significant gains in sample throughput over sequential systems, but were less flexible in adapting to a laboratory's changing requirements. Wavelength selection was limited and often foreknowledge of analyte wavelengths was required before purchase. Often, additional PMT detectors were necessary to access additional analyte wavelengths. Solid-state detection systems such as CCDs and CIDs overcame many of the deficiencies inherent in PMT-based simultaneous systems. These modern ICPs provided the productivity gains demanded by laboratories, with additional advantages of lower cost of ownership, greater flexibility and more powerful hardware and software features.

When early CCD detectors were developed for ICP-OES, the costs of CCD technology, and associated development costs, were high. In these early days, there were also technical limitations in the way CCD's were controlled and in particular the circuitry used for readout was, by today's standards, quite slow and cumbersome. For these reasons, some of the early CCD detectors for ICP-OES were Segmented CCD's, otherwise known as SCD's. Due to the developments costs associated with new CCD design, some of these SCD's are still used in ICP-OES systems today. Limitations in the SCD design means these detectors only cover a select portion of the wavelength range—only select 'segments'. The slow readout circuitry results in additional time overheads when more wavelengths are selected, or when wavelengths of varying intensity are measured on a single sample. This results in measurement times that are different for different samples, even using the same method.

Following the introduction of the first CCD and CID detectors for use in ICP-OES, there has been much debate over the advantages of each device. CCDs are renowned for their high sensitivity and low noise characteristics, providing low detection limits and superior signal-to-noise ratio performance. Conversely, CIDs are perceived to offer greater detector control including non-destructive readout (NDRO) whereby the accumulated signal is removed from the exposed pixel, measured and then returned to the pixel for further collection. NDRO provides an alternative means of

improving the signal-to-noise ratio performance given that CIDs typically exhibit poorer noise performance in comparison.

## Detector cooling

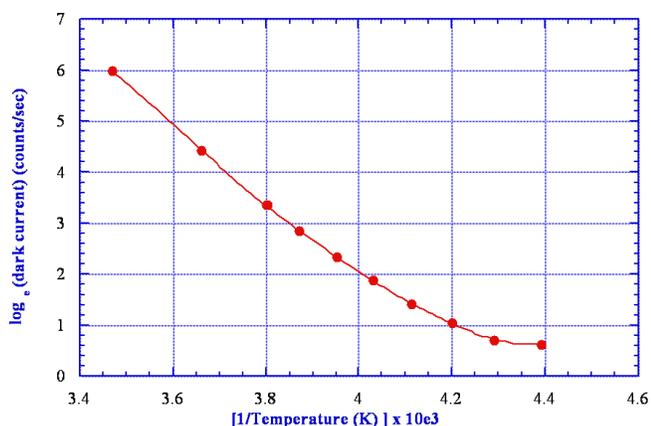
Charge transfer device detectors are often, but not always, cooled to sub-zero temperatures. This is usually done via a Peltier cooling device. CCDs and CIDs are semiconductor devices and will exhibit background signal noise, called 'dark current', when the detector is not exposed to any light source. Cooling of the detector greatly improves detection limits by lowering the dark current.

Not all simultaneous ICP-OES are able to offer detector cooling and it is often a limitation of non-echelle optical designs. One design used as many as 32 detectors to cover the necessary wavelength range, and the cost to cool each makes it an unviable option. As a consequence, detection limits are sacrificed. This is why echelle optical systems are often employed, as they complement the two-dimensional array of solid-state detectors, and typically only require a single detector to cover the necessary wavelength range.

While it is possible to capture the entire wavelength range on a single array detector, many ICP-OES systems compromise by employing multiple CCD/SCD detectors or by using multiple entrance slits onto a single CID detector (requiring sequential readings), to capture the wavelength range of interest.

The temperature to which CCDs and CIDs are cooled in modern ICPs ranges anywhere from 15 °C to -70 °C. As mentioned, detectors operating at higher temperatures will tend to exhibit higher dark current signal that negatively impacts detection limits. The relationship between dark current and temperature is non-linear and there will be a point where the benefit of lower detector temperature becomes negligible. The added cost of further cooling and the increased risk of condensation must also be considered. Excessively low temperatures beyond -45 °C lower the dew point near the detector to dangerous levels, exposing the detector to the risk of condensation forming on its surface. This can be detrimental to the operation of the detector.

In this situation, a costly gas filtering system is required to remove moisture from the argon gas stream that passes over the detector. Alternatively, detectors can be hermetically-sealed in an inert gas, eliminating the need for a detector purge gas and associated gas filtering system.



**Figure 1.** Association between detector temperature and dark current performance of the Agilent VistaChip II CCD detector. Operating at  $-40\text{ }^{\circ}\text{C}$  (4.3 on the X-axis), the dark current performance is approximately 7 electrons per second per pixel (0.7 on Y-axis). In comparison, a CID is cooled to below  $-45\text{ }^{\circ}\text{C}$  to achieve a similar dark current.

## Low UV performance

The lower wavelength range of an ICP-OES often extends into the low UV region, typically down to  $\sim 167\text{ nm}$ . The silicon dioxide layer used to insulate the detector's photosensitive pixels can absorb analyte emissions in the range 167–200 nm, reducing the sensitivity of important analyte wavelengths of aluminium, sulfur, phosphorus, arsenic and selenium. To improve quantum efficiency in the UV range, CIDs use a fluorescent surface coating. When the incoming low UV photon collides with the coating, a secondary photon of higher wavelength is emitted, allowing it to pass through the silicon dioxide layer. The fluorescent coating deteriorates over time and requires periodic replacement.

For CCD detectors used in ICP-OES, the addition of a fluorescent coating is not common. Instead, the transmission efficiency of low UV wavelengths is improved through better design that requires no ongoing maintenance cost. This includes:

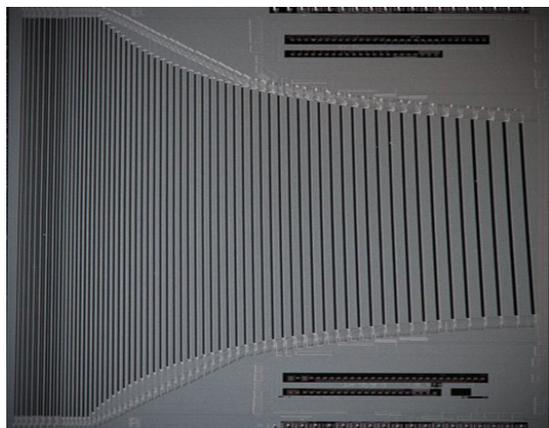
- Thinning of the outer silicon dioxide layer via chemical means
- Addition of a doping agent to the silicon dioxide compound
- Back-illumination of the CCD to increase the active area of the detector by avoiding the on-chip circuitry
- Locating the controlling circuitry off-pixel

## CID characteristics

Modern CIDs offer random access integration (RAI) and non-destructive readout (NDRO), allowing detector pixels to be interrogated at different speeds without destroying the accumulated electric charge (signal). RAI effectively allows automatic adjustment of the integration time with respect to the incoming signal intensity at an analyte wavelength (or region of interest). Upon interrogation, if sufficient signal above the background noise is collected, it is then processed for measurement. Otherwise, additional time is spent accumulating signal to improve the signal-to-noise ratio before processing. With pixel numbers greater than 260,000, only regions of interest (ROI) are typically interrogated. Otherwise, the time required to repeatedly integrate a large number of pixels becomes too great, increasing analysis times and the risk of pixel saturation. This characteristic means that adding additional wavelengths to be measured also increases readout times, hence increasing sample to sample measurement times for methods with more wavelengths.

## Agilent 5110 VistaChip II CCD

While the pixel layout of most CCD and CID detectors used in ICP-OES consists of a large area pixel array, the Agilent 5110 ICP-OES utilizes a custom-designed and proprietary CCD detector (Figure 2). Known as the VistaChip II, it combines the superior noise and sensitivity performance of a CCD with the pixel control of a CID. The VistaChip II utilizes Image Mapping Technology (I-MAP), and requires only 70,000 light sensitive pixels located on 70 diagonal linear arrays (DLA) to cover the full wavelength range from 167 to 785 nm – no pixel is wasted. Located in between each linear array are the VistaChip's high-speed controlling electronics, providing full pixel control and offering Adaptive Integration capability and Anti-Blooming protection on every pixel.



**Figure 2.** Custom-designed and proprietary CCD detector. With unique I-MAP and AIT, speed and versatility is unmatched, and full wavelength coverage is provided from 167–785 nm.

Agilent CCDs are hermetically-sealed in an atmosphere of inert gas, protecting them from moisture, hydrocarbons and particulates and requiring no additional gas purging, startup delay or maintenance. The VistaChip II is mounted on a triple-stage Peltier device for accurate cooling down to  $-40\text{ }^{\circ}\text{C}$ ,  $5\text{ }^{\circ}\text{C}$  lower than the previous VistaChip II application in the Agilent 700 Series ICP-OES, for the lowest dark current noise.

## Adaptive Integration Technology

Adaptive Integration Technology (AIT) provides real-time interrogation of pixels allowing simultaneous integration of all analyte wavelengths, irrespective of the incoming signal intensity. The integration time is simultaneously adjusted for each wavelength to achieve the optimum signal-to-noise ratio. Due to the true simultaneous nature of the VistaChip II and AIT, there is no time penalty when adding additional wavelengths to a method.

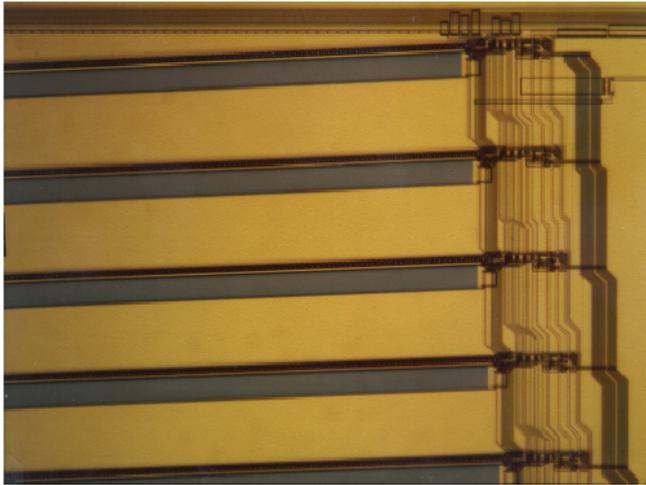
Adaptive Integration is also perfect for speciation type applications including chromatography and laser ablation, allowing transient signals to be simultaneously collected for all elements.

With 1 MHz pixel processing speed, the VistaChip II sets the benchmark in ICP-OES detector speed. Duplex circuitry enables pixels to be read from both sides of the detector (Figures 3a and 3b), ensuring a readout speed significantly faster than competitive systems. This extends the upper dynamic range of the detector compared to other CCDs and CIDs, reducing the likelihood of pixel saturation and signal over-ranging. Able to actively adapt using integration times ranging from 1 microsecond to 100 seconds, the VistaChip II provides a full 8 orders of dynamic range.

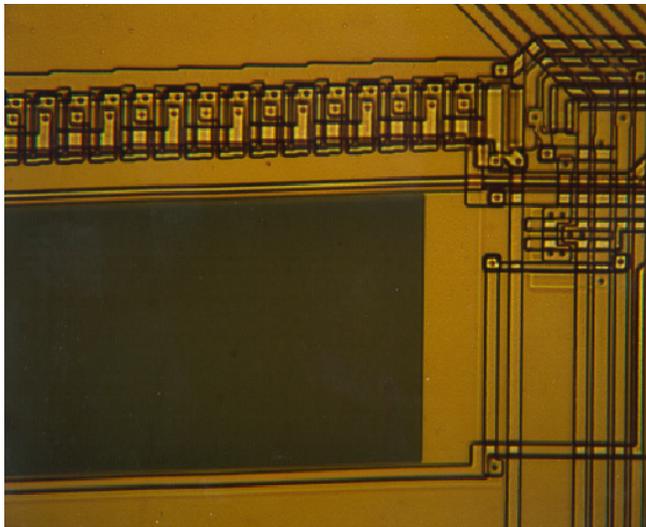
In the unlikely situation that pixels saturate from an intensely strong signal, the VistaChip II offers anti-blooming protection on every pixel, allowing weak signals to be measured in the presence of over-ranging signals.

## Anti-blooming

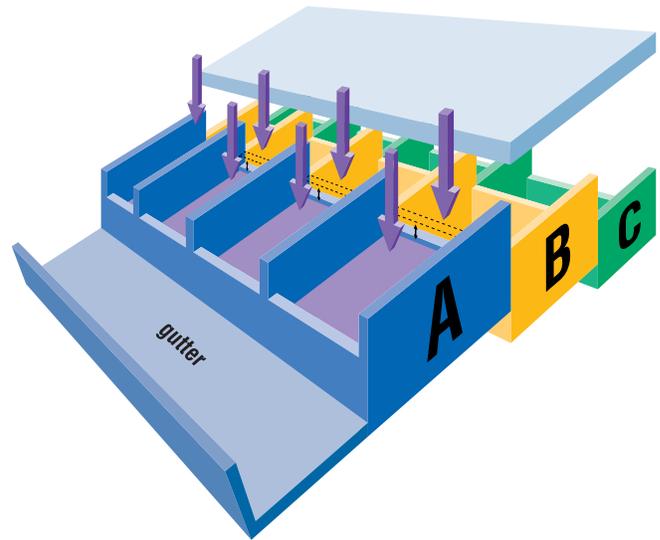
Pixel blooming occurs when the charge of over-exposed or saturated pixels spill over into neighbouring pixels or circuitry, destroying the integrity of information collected in the region. Less advanced charge transfer device detectors are more susceptible to blooming. While some CCDs offer blooming protection between pixel segments, they do not necessarily protect individual pixels within a segment. Conversely, the Agilent VistaChip II CCD provides blooming protection on all pixels, whereby excess charge is directed into an anti-blooming drain.



**Figure 3a.** Zoomed image showing five linear arrays containing photosensitive pixels and associated readout circuitry on the Agilent VistaChip II CCD detector.



**Figure 3b.** Zooming even closer shows the control circuitry above each pixel that provides Adaptive Integration capability. The anti-blooming circuitry (drain) located below each pixel array is also visible.



**Figure 4.** Schematic of a single DLA on the VistaChip II CCD illustrating the potential barriers between pixels and the anti-blooming drain.

## Summary

The Agilent VistaChip II, now in its 2nd generation, combines the superior analytical performance of a CCD with fast, Adaptive Integration performance and blooming protection often associated with CIDs, providing the 'best of both worlds'. Hermetically-sealed, the VistaChip II requires no gas purging or startup delay.

With the VistaChip II at its heart, the Agilent 5110 ICP-OES is able to measure the full wavelength range in a single exposure, without the need for multiple detectors or multiple slits. With a robust vertical torch on all configurations, including the Synchronous Vertical Dual View (SVDV), Vertical Dual View (VDV), and the dedicated Radial View (RV), the Agilent 5110 ICP-OES offers superior robustness, precision and productivity, delivering industry-leading sample throughput and the lowest gas consumption per sample.

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Published May 1, 2016

Publication number: 5991-4842EN



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