CCD and CID solid-state detectors

Technical overview

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 for routine analysis 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. Once in use, additional PMT detectors were necessary to access additional analyte wavelengths. Solid-state detection systems in 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.

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. In one case, as many as 32 detectors are used 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.

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 impact 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 increase risk of condensation must also be considered. Excessively low temperatures beyond –40 °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. Consequently, a more effective and 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.

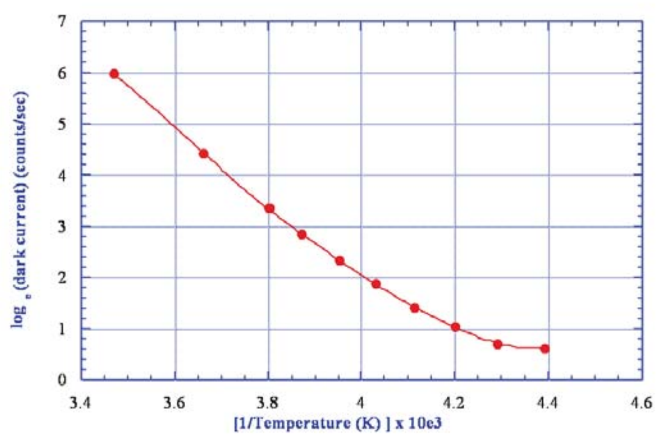

Figure 1. Association between detector temperature and dark current performance of the Agilent VistaChip II CCD detector. Operating at –35 °C (4.2 on the X-axis), the dark current performance is approximately 10 electrons per second per pixel (1 on Y-axis). In comparison, a CID is cooled to –45 °C to 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 ~160 nm. The silicon dioxide layer used to insulate the detector's photosensitive pixels can absorb analyte emissions in the range 160–200 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 less common. 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 advantages

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 pixels becomes too great, increasing analysis times and the risk of pixel saturation.

Agilent 720/725 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 720 Series utilizes a custom-designed and proprietary CCD detector (Figure 2). Know 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 includes 70,000 photosensitive pixels that are located across 70 linear arrays (or rows) and positioned to exactly match the image produced by the echelle optics. No pixel is wasted in covering the full wavelength range from 167 to 785 nm. 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.

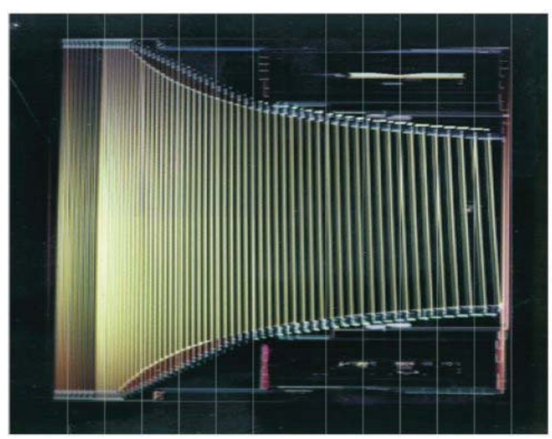

Figure 2. Custom-designed and proprietary CCD detector. With unique I-MAP and AIT, speed and versatility is unmatched, and full wavelength coverage is provided from 167–785 nm.

Agilent CCDs are hermetically-sealed in an atmosphere of inert gas, protecting them from moisture, hydrocarbons and particulates and requires no additional gas purging, startup delay or maintenance. The VistaChip II is mounted on a triple-stage Peltier device for accurate cooling down to –35 °C.

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.

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

The 1 MHz processing speed of the VistaChip II is the fastest of any charge transfer device detector used in ICP-OES. 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 the anti-blooming drain.

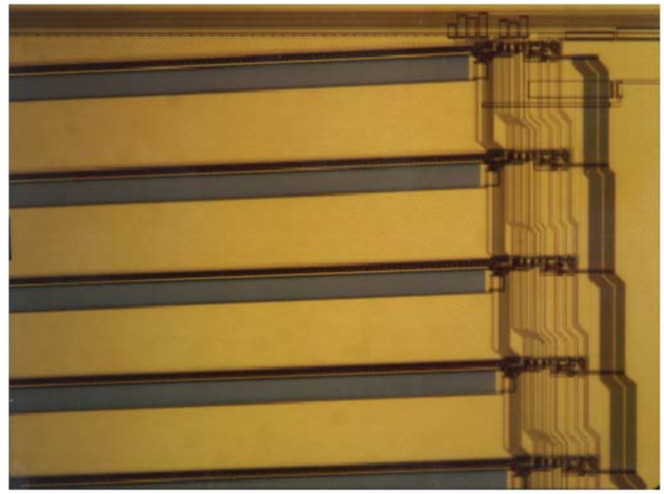

Figure 3a. Zoomed image showing five linear arrays containing photosensitive pixels and associated readout circuitry on the Agilent VistaChip II.

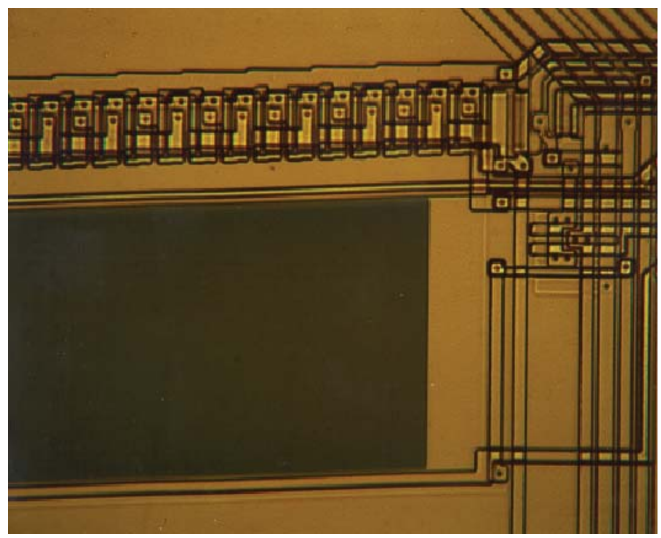

Figure 3b. Zooming even closer shows the control circuitry above each pixel that provide Adaptive Integration capability. The anti-blooming circuitry (drain) located below each pixel array is also visible.

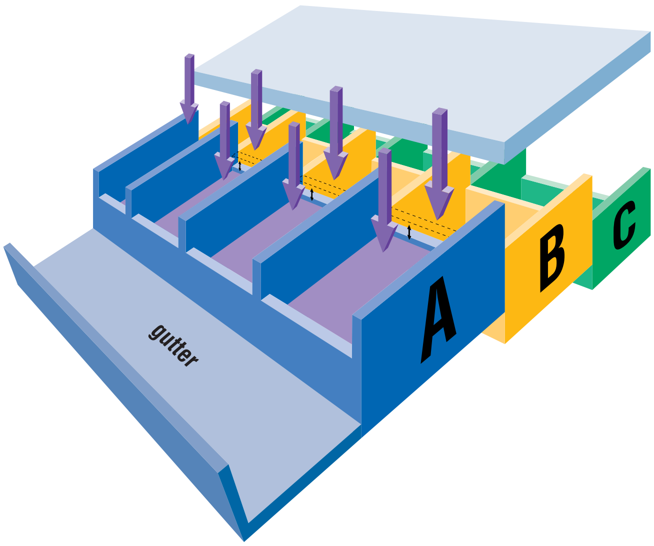

Figure 4. Schematic of a single DLA on the VistaChip II CCD illustrating the potential barriers between pixels and the anti-blooming drain.

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 720/725 Series is the only ICP-OES to offer true simultaneous measurement of up to 73 elements from parts-per-billion to percent levels. The 720/725 offers superior precision and productivity, delivering industry-leading sample throughput and the lowest gas consumption per sample.

www.agilent.com/chem

Published August 1, 2012
Publication number: 5991-0881EN

Agilent Technologies