



The Thermo Scientific iCAP 7000 Plus Series ICP-OES unique charge injection device (CID) detector

Keywords

Charge injection device (CID),
Charge transfer devices (CTD),
Non-destructive readout

Introduction

Solid-state, Charge Transfer Devices (CTDs) have become the detectors of choice for Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), virtually replacing the traditionally used photomultiplier tubes. These types of detectors can be grouped into two main types: Charge Injection Devices (CIDs) and Charge Coupled Devices (CCDs), depending on the structure of the detector and way the signals are processed.

CIDs and CCDs are both composed of doped silicon wafers, containing a two dimensional array of light sensitive elements called pixels. When polychromatic light passes from the plasma through the optical spectrometer it is separated into constituent wavelengths and then focused onto the detector. When the light reaches the surface of the detector photons liberate electrons in the detector substrate which are then trapped in the pixel sites; each pixel is capable of storing a number of electrons. The signal is then digitized and the counts displayed via the user interface. The fundamental difference between the two devices is the way in which the pixels are addressed. CIDs allow for individual, random access, pixel-by-pixel integration by having readout electrodes located at each pixel site. The process can be carried out non-destructively allowing the optimum signal-to-noise ratio for each integration, enabling intense and weak light emissions to be recorded simultaneously. Conversely a CCD transfers the charge sequentially from each pixel site to a buffer and then to an output register. Pixels may be processed either by rows or by segments, in the process or reading a CCD the charge in the pixel is destroyed.

CID detectors were originally developed by Hubert Burke and Gerald Michon of General Electric in 1973. Cameras using this technology were widely used in machine vision applications during the 1970s and 1980s. From 1990, CIDs were adapted for applications where extreme radiation tolerance and high dynamic range scientific imaging were required (Suraj Rhaskaran and co-authors: Performance Based CID Imaging – Past, Present and Future).

This ability to measure intense and weak images simultaneously with excellent resolution made the transition into photonics and spectrometric techniques an obvious choice. CIDs offer significant benefits for use in atomic spectroscopy compared to other CTDs and are used as the detector in the Thermo Scientific™ iCAP™ 7000 Plus Series ICP-OES.

CID Technologies, Inc. (CIDTec) is wholly owned by Thermo Fisher Scientific and has continued to develop CID technology (Figure 1). Significant improvements have been made to increase speed and sensitivity, whilst reducing the electronic noise of the detectors. These innovations have enhanced the performance of the CID, for example, random pixel addressability, non-destructive readout (NDRO), and excellent anti-blooming capability. These properties are advantageous for use with ICP-OES instruments as explained below and demonstrated in the iCAP 7000 Plus Series ICP-OES and Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

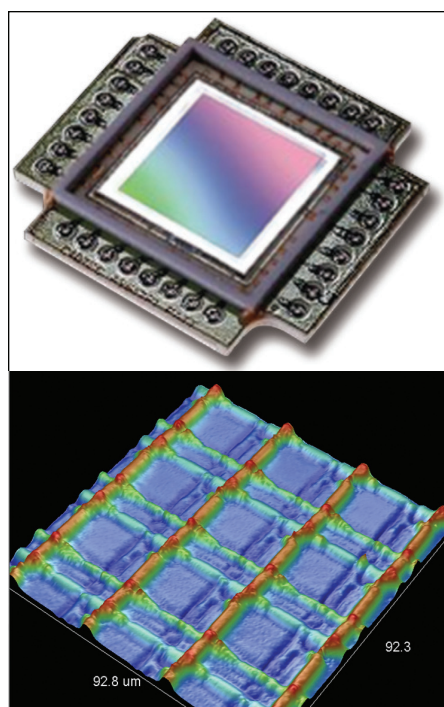


Figure 1. 3-Dimensional display of the CID surface.

Main characteristics of the CID detectors:

- Immunity from blooming allows the measurement of weak analyte emission signals adjacent to intense emission signals.
- Continuous wavelength coverage provides flexibility to choose the ideal wavelength for a method (automated by the Qtegra ISDS Software Element Finder plug-in).
- Fullframe Imaging ability to capture the entire ICP-OES spectrum (166-847 nm) permits retrospective analysis, batch analysis and contamination identification of samples.
- Non-destructive readout improves the signal-to-noise ratio of weak analyte wavelengths and ensures precision of results.
- Simultaneous background correction compensates for any flicker noise of the plasma and improves precision.
- Simultaneous internal standardization enhances the accuracy of the dynamic drift correction technique.
- Simultaneous Inter-Element Correction (IEC) ensures the reliability of the correction being applied.

CID design and operation – non-destructive readout

CIDs are made up of a light sensitive surface sub-divided into several thousand pixels which are individually addressable by column and row electrodes, allowing collection and readout of signals. The measurement sequence is carried out in the following way:

After the user sets an integration time using the instrument software, light from the plasma passes through the spectrometer and falls onto the CID detector, and integration of the signal begins. During the integration phase, the photon-generated charge is collected under the column photogate (Figure 2, step A). The accumulated charge is determined by measuring the voltage difference originated by transferring the charge between the two photogates (column and row – Figure 2, step B and C). The generated charge may be cleared by “injecting” it into the underlying substrate (Figure 2, step D). The pixel is now ready to make another measurement.

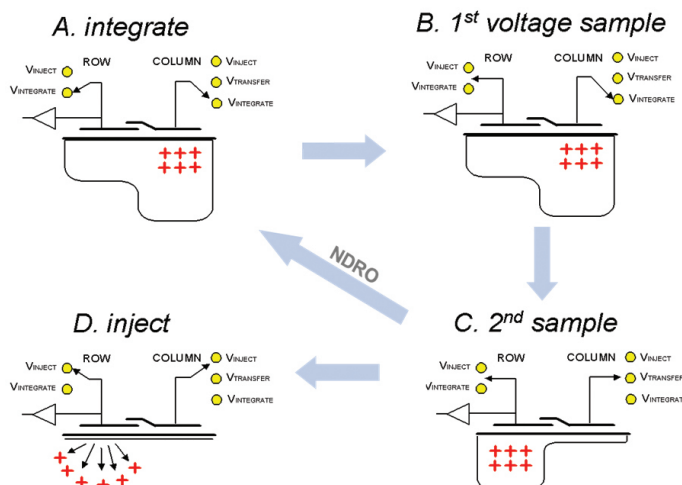


Figure 2. Basic operation of the CID pixel.

If it is determined that only a small charge is present, the integration (steps B and C) can be allowed to continue. This is termed a non-destructive readout (NDRO), in this instance the integration continues accumulating more charge.

Immunity from blooming

Blooming is the transfer of charge from a pixel that has exceeded full well-capacity (i.e. it has become saturated, full of charge) into adjacent pixels. It is a phenomenon often encountered with CCD imagers. An example is in digital cameras, where images taken with the sun in the background often obscure objects in the foreground. This is because the CCD has to be exposed for a certain length of time before the charge is collected, read and digitized (unlike CID where the charge on individual pixels can be read out at any time). If blooming occurs when analyzing samples by ICP-OES it will have a negative impact on the data by overestimating low intensity wavelengths. Blooming can be overcome by setting integration times for CCDs in particular ways. If the integration is set to measure the intense wavelengths, the weak ones are lost. Conversely, if the integration is set for the weak wavelength, some strong wavelengths can saturate and affect the signal in the surrounding pixels. This blooming effect can be minimized with the use of segmented CCD detectors (SCD), or by adding anti-blooming drains around the pixels. They both use the same technique of isolating active pixels.

The SCD has been designed with individual collection of small subarrays (over 200), corresponding to the most important ICP-OES spectral wavelengths. There are obvious downfalls to this approach when dealing with applications that necessitate the use of secondary and tertiary wavelengths to overcome spectral interferences, and indeed the determination of rare elements that may not even be available on a segmented detector.

Anti-blooming drains or gates occupy a significant amount of pixel space on the CCD, which reduces the full well capacity, and sensitivity of the chip. The anti-blooming gates surround active pixels and do not allow charge to collect in them, so have the same effect as the SCD of isolating the active pixel sites. Even with segmented chips and anti-blooming drains the CCD must still integrate its regions of interest as a complete unit. Hence it is possible for a strong matrix wavelength to saturate and affect the signal of a weak analyte if they are in the same segment of the chip. Although blooming across larger wavelength regions is avoided, saturation can still take place within sub-array pixel sites compromising the sample measurement.

Continuous wavelength coverage

The CID allows the analyst access to the full ICP-OES spectrum, the current wavelength library in the Qtegra ISDS Software contains over 55,000 wavelengths allowing for the use of secondary and tertiary wavelengths to overcome interferences and also quantification of some rare elements.

Fullframe imaging

This continuous detector coverage allows for true unknown analysis through Fullframe Imaging, which captures all of the data from the CID, regardless of the method elements specified. This Fullframe is then stored, and can be used for retrospective analysis, batch analysis or contamination identification of samples. The features of Fullframe allow the analyst to subtract Fullframes from each other, which is particularly useful for matrix stripping and contamination identification allowing for more accurate results (Figure 3).

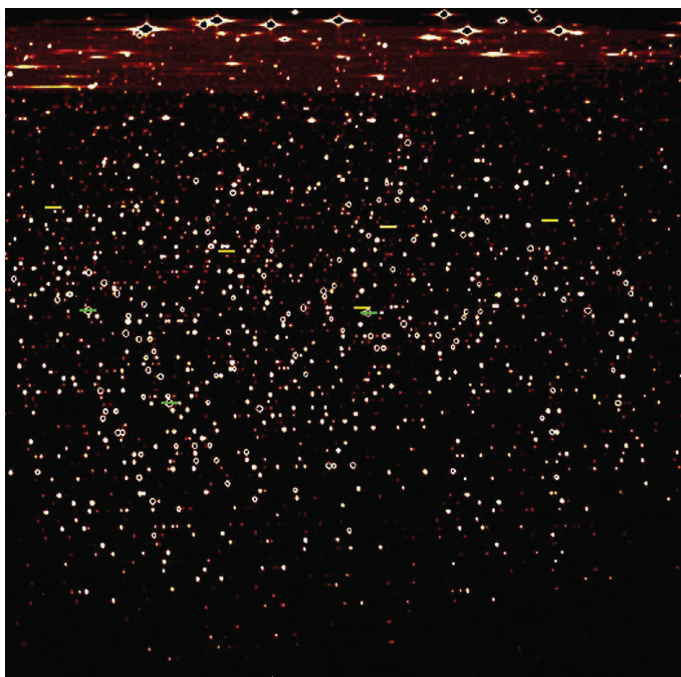


Figure 3. Fullframe showing subtraction for contamination identification.

Fullframe analysis can be performed either in a user specified mode, where the analyst sets the integration time, or in Intelliframe Imaging mode where the CID will intelligently integrate the signals.

Simultaneous corrections of background, internal standardization

Another feature of a continuous wavelength CID is that it allows for the capture and readout of the analyte peak and any correction to the data, i.e. background or internal standard correction to be collected simultaneously. This is extremely important to ensure the precision and accuracy of a method. The sample introduction system of any ICP-OES is the least well controlled part of the instrument in terms of stability and is responsible for a large contribution to any variation in emission intensity, this is true for all ICP-OES instruments. It is then critical to take all measurements associated with a sample simultaneously. When measurements are taken simultaneously, they become time-correlated, the background correction accounts for flicker noise in the plasma and most of the noise is factored out.

This is not possible when corrections are applied sequentially, and as a consequence, the precision degrades. Consider internal standards and their use as dynamic drift correction for a method. If the internal standard measurement is taken at a different time to the element it is referenced to, all manner of changes could have occurred in the plasma in the time between measurements, eliminating the effectiveness of any correction, thus leading to inaccurate results.

Conclusion

It is important to understand the differences between CID and CCD detectors discussed in this technical note. The CID detector offers significant performance advantages particularly when measuring samples with difficult matrices. The ability to carry out non-destructive readout allows the optimum signal-to-noise ratio for both very low and very high signals giving low detection limits and wide dynamic range. Random-access pixel addressing coupled with the very high readout speed allows signals from trace elements to be measured adjacent to high concentrations of matrix elements without risk of saturation, while the inherent anti-blooming characteristics of the CID prevent spill-over of charge into neighboring pixels. The continuous pixel structure of the detector allows access to the entire spectrum giving the ability to capture a Fullframe image of a sample. These images greatly simplify method development by allowing matrix subtraction, identification of unknown elements and selection of multiple wavelengths to extend dynamic range. The images can also be stored to allow retrospective analysis of elements that were not measured at the original time of analysis. These features greatly improve the flexibility of the instrument and make the CID detector of the Thermo Scientific iCAP 7000 Plus Series ICP-OES the only choice for laboratories with demanding applications.

Find out more at thermofisher.com/ICP-OES

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