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Thermo Scientific iCAP PRO Series ICP-OES: Unique CID detector technology

Authors: Sebastian Weyermann and Sebastian Geisler, Thermo Fisher Scientific, Germany

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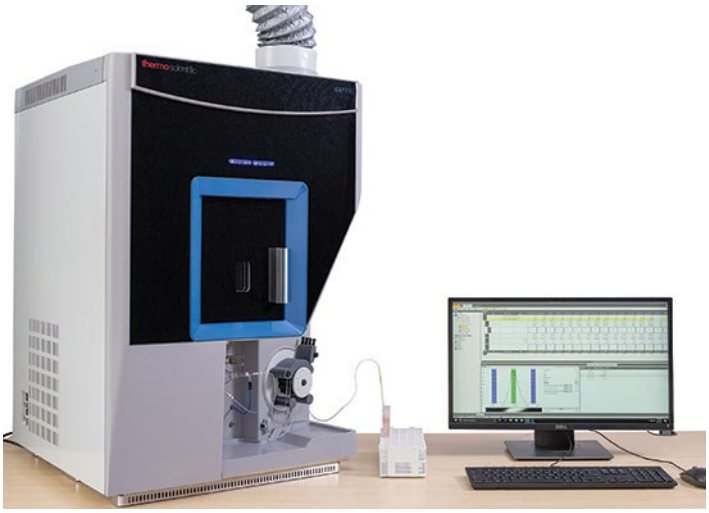

Introduction

Simultaneous inductively coupled plasma – optical emission spectrometers (ICP-OES) use polychromators to resolve complex light emissions from the test sample into a two-dimensional spectrum. This spectrum is projected onto the surface of a solid-state charge transfer device (CTD) detector to allow for wavelength identification and quantification of the elements present in the sample. The combination of a polychromator and CTD has become the industry standard for ICP-OES.

The sub-categories of CTD used in ICP-OES are charge injection devices (CID) and charge coupled devices (CCD). Both types of device have similarities in that when the light reaches the surface of the detector, photons liberate electrons in the detector substrate that 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. However, there are also fundamental differences in the way the pixels are read. 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, ensuring 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. In a CCD this can be scaled so that pixels may be processed either by rows or by segments. However, the process charge in the pixels is destroyed, resulting in non-optimal signal-to-noise ratios being obtained. In addition, other significant benefits are gained by using CID for use in atomic emission spectroscopy compared to other CTDs. For this reason, a Thermo Scientific™ CID821 detector is used in the Thermo Scientific™ iCAP™ PRO Series ICP-OES.

CID detectors offer a number of benefits:

- Immunity from blooming allows the measurement of weak analyte emission signals adjacent to intense emission signals.
- Full, continuous wavelength coverage provides flexibility to choose the ideal wavelength for the analysis of a particular analyte.
- Fullframe imaging ability to capture the entire ICP-OES spectrum (167–852 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 analysis accuracy.
- Simultaneous inter-element correction (IEC) ensures the reliability of the correction being applied.

CID design and operation

Non-destructive readout (NDRO)

CIDs are made up of a light-sensitive surface sub-divided into several thousand pixels that 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 1, 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 1, step B and C). The generated charge may be cleared by “injecting” it into the underlying substrate (Figure 1, step D). The pixel is now ready to make another measurement.

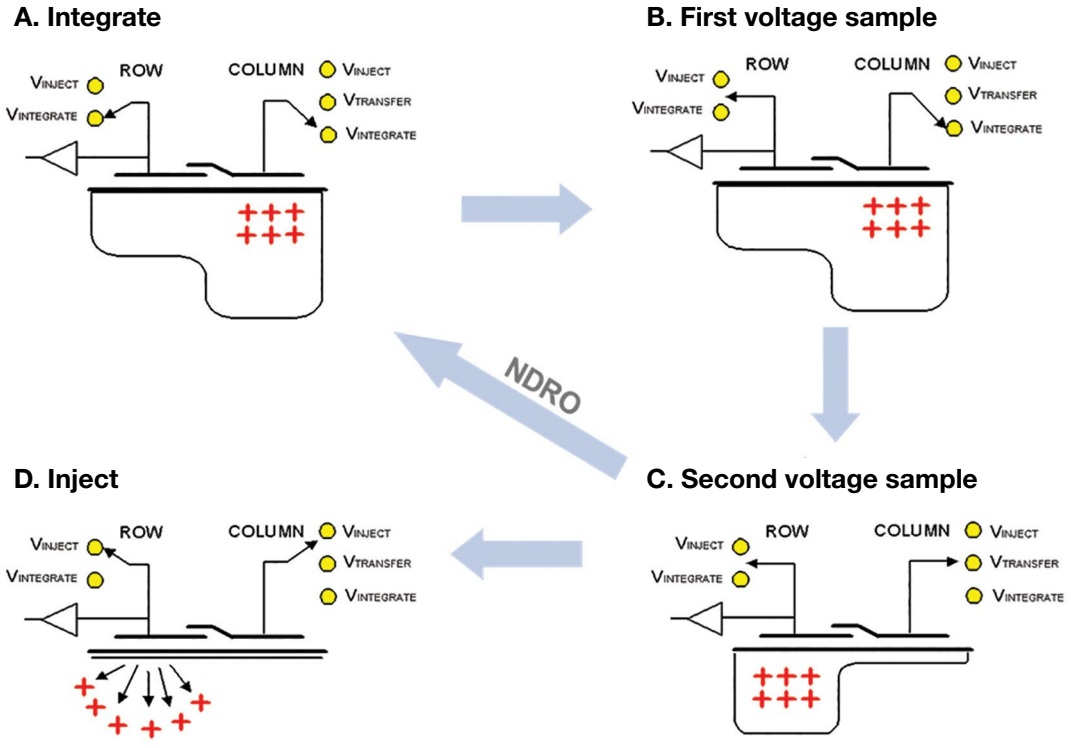

Figure 1. Basic operation of the CID pixel. The signal is integrated (A) and accumulated photon generated charge is measured as voltage difference between two photogates (B and C). Generated charge is then “injected” into the underlying substrate (D). For weak charges steps B and C are repeated and integration continues accumulating more charge (process known as non-destructive readout (NDRO).

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 and is 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 wavelengths, 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 an 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 they 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 Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (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 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.

Simultaneous corrections of background and internal standardization

The continuous wavelength coverage of the CID 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. 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.

The new CID821 detector for the iCAP PRO Series ICP-OES

In addition to the benefits already outlined, the latest CID821 detector from Thermo Fisher Scientific has several specific advantages that enhance its performance:

- Large active surface area to enable the complete spectrum capture
- Optimized pixel size for accurate spectrum modeling to minimize interferences
- Advanced high-speed signal processing combined with a wide dynamic range to allow all light intensities to be measured simultaneously.

Large active surface area

The CID821 detector has a much larger active surface area when compared to previous generations of CID detectors used in ICP-OES. This allows the entire spectrum between 167 and 852 nm to be measured using the intelligent Full Range (iFR) mode of the iCAP PRO Series ICP-OES. By capturing the entire spectrum in this way, the analysis time is minimized as multiple exposures of the detector for different regions (ultraviolet and visible) are no longer required. In addition, internal standardization is simplified as different internal standards are no longer required for the different measurement regions. A single acquisition is used on iCAP PRO radial instruments and two acquisitions on Duo (axial and radial) instruments. This reduction in the number of measurements can significantly reduce analysis times by up to 40%.

Optimized pixel size

Optimization of the pixel size on the active surface of the CID821 detector ensures a balance between the amount of charge a pixel can hold to provide accurate and reproducible results and providing sufficient data points to model the spectrum emitted by the sample. The CID821 of the iCAP PRO Series ICP-OES has pixels of 12 × 12 µm; this ensures that these two criteria are met. The Qtegra ISDS Software interprets the data from the detector to calculate the analytical result. By utilizing the optimized pixel size of the CID821 the Qtegra ISDS Software allows the user to select any point on the spectrum as background and central integration regions to ensure effective interference removal.

High speed electronics

By using the latest advances in the design of the CID821, the readout speed of the detector has been significantly increased, compared to previous generations of CID detectors. This increase in speed removes the need to carry out a pre-exposure of the detector and the need for additional post exposure of the detector for high concentrations. These two features ensure the shortest possible readout time of the detector for faster sample measurement resulting in higher sample throughput.

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Summary

There are notable differences between CID and CCD detectors, with the CID offering clear advantages in performance, many of which are derived from the ability to address pixels with non-destructive readouts. These differences include:

- Achievement of the optimum signal-to-noise ratio for excellent detection limits
- The ability to measure both high and low concentration elements that emit light in the same region of the spectrum without saturation, resulting in better accuracy and fewer reruns of samples
- Anti-blooming capability to prevent false positives
- Measurement of the whole spectrum using a Fullframe exposure to allow for examination of non-method elements and easy sample screening

Additionally, the latest CID821 used as the detector in the iCAP PRO Series ICP-OES offers benefits over previous generations of CID detectors:

- Large active surface area to enable complete spectrum capture, allowing for higher throughput
- Optimized pixel size to facilitate accurate spectrum modeling, minimizing interferences
- Advanced high-speed signal processing combined with a wide dynamic range to allow all light intensities to be measured simultaneously, shortening the analysis time and allowing for higher sample throughput

These features of the CID821 detector greatly improve the flexibility and performance of the instrument and make the iCAP PRO Series ICP-OES the ideal ICP-OES for routine and research laboratories.

Find out more at **thermofisher.com/ICP-OES**

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