Technical Overview

Innovative Freeform Optical Design Improves ICP-OES Speed and Analytical Performance

Agilent 5800 ICP-OES and Agilent 5900 ICP-OES

Introduction

The innovative optical design of the Agilent 5800 and 5900 ICP-OES has transformed each instrument's analytical performance, size, warm-up and purge times. These improvements are due to the customized design and novel location of freeform optics into the polychromator of the fully simultaneous ICP-OES instruments. The US patented freeform optic-design has led to direct improvements in both detection limits and resolution of the 5800 and 5900, even when using 99.99% purity bottled argon as a purge gas. The optical layout is compact, so the instrument is quick to purge, reducing the wait time before samples can be measured.

What are the advantages of freeform optics?

Reduction in size of instrument footprint

The freeform optical surface is the key to unlocking previously unattainable optical size reduction, as well as improving performance. The polychromator optical system has reduced in volume by 50% compared to previous designs, enabling the footprint of the 5800 and 5900 to be reduced significantly. As one of the smallest ICP-OES available, the 5800 and 5900 ICP-OES save valuable bench space in the laboratory.

Enhanced analytical performance

The freeform optic, synchronous dual view pre-optics (5900), and Vista Chip III detector of the 5800 and 5900 enable both true simultaneous measurements and full wavelength coverage from 167 to 785 nm. This unique design is key to the unmatched multi-elemental analysis speed and performance of the 5800 and 5900 ICP-OES. The new hardware configuration has led to improvements in detection limits by 40% on average, as well as improved optical resolution. Also, significant improvements have been made to reduce instrument warm-up time and purge time, due to the reduced internal volume and thermal mass of the optics.

Polychromator design

Polychromators have the distinct advantage of measuring all wavelengths at the same time. A polychromator therefore differs from a monochromator that can typically measure only one analyte wavelength of interest per measurement, requiring multiple sequential measurements to capture all analyte wavelengths of interest. Most modern simultaneous ICP-OES instruments use an echelle polychromator to separate and focus analyte emissions from the plasma onto a detector for elemental analysis. The optical emissions generated in the plasma are directed through the pre-optics to an entrance slit (or sometimes, directed through multiple entrance slits, sequentially). The entrance slit defines the physical size of the emission from the plasma entering the polychromator. The emission is channeled by mirrors, dispersed by a prism and diffraction grating, and finally onto the surface of the detector. This process produces a two-dimensional (2D) emission image, where pixel positioning on the detector corresponds to a specific emission wavelength that is characteristic of an element present in the analyte solution.

Freeform optical component

Uniquely, the echelle polychromator used in the 5800 and 5900 ICP-OES produces a single echelle image of the entire spectrum. The image is focused onto a single detector using a freeform collimating mirror, grating, prism, and focus mirror ensuring sharp focusing and high light intensity.

There is no need for multiple detectors or multiple entrance slit optics to achieve high resolution and fully simultaneous wavelength coverage, which ensures superior analytical speed. Instruments that use multiple detectors or multiple entrance slit optics often require separate sequential measurements to be taken to cover the whole spectrum, increasing analysis times and reducing sample throughput.

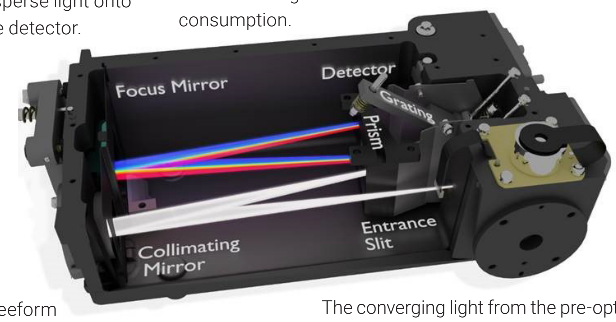

Figure 1. Computer aided design schematic of the echelle polychromator with freeform collimating mirror used in the Agilent 5800 and 5900 ICP-OES. The system has no moving parts and is temperature-controlled to provide excellent long-term stability.

Improving resolution and peak shape

The optical resolution of an ICP-OES is characterized by the physical attributes of the optical system and is defined as the full-width at half maximum (FWHM). The use of high diffraction orders that are characteristic of the Agilent echelle optical design is coupled with a freeform collimating mirror. This combination of components leads to improved resolution and sensitivity in the 5800 and 5900 ICP-OES.

The use of a freeform collimating mirror in the Agilent polychromator design provides better resolution compared to designs that use parabolic and/or toroidal optical components. The freeform collimating mirror improves light-focus by reducing the spread of the light in both directions (tighter in width and height). Reduced spread is especially useful for wavelengths that are focused away from the center of the detector. Table 1 shows typical resolution performance of the 5800 and 5900 ICP-OES for representative emission lines.

Table 1. Typical resolution performance of the Agilent 5800 and 5900 ICP-OES (based on FWHM).

Element and Wavelength (nm)	Typical Resolution of 5800 and 5900 (pm)
As 188.980	< 6.5
Mo 202.032	< 7
Zn 213.857	< 7.5
Pb 220.353	< 7.5
Cr 267.716	< 9.5
Cu 327.395	< 13
Ba 614.171	< 32

The tighter focus of light achieved by replacing the standard shaped mirrors with freeform optics also improves peak shape. The excellent optical resolution of the 5800 and 5900 ICP-OES is demonstrated by the doublet peak of thallium (Tl) 190.794 and Tl 190.807 nm shown in Figure 2. Both peaks are symmetrically shaped and easily resolved.

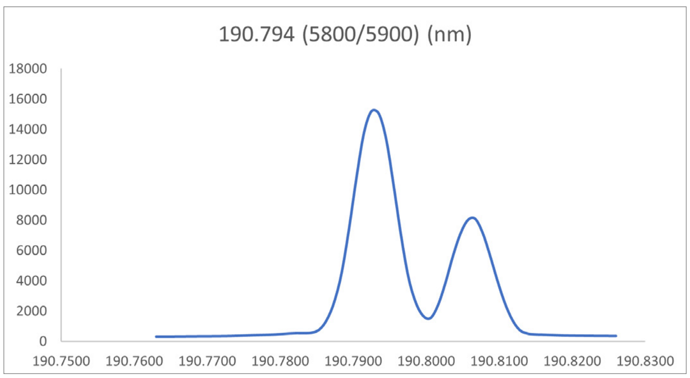

Figure 2. Clear resolution of the Tl 190.794 and 190.807 nm doublet peak using an Agilent 5800 or 5900 ICP-OES.

What are freeform optics?

Traditional ICP-OES optical system designs use simple spherical, toroidal, or parabolic mirrored surface shapes to collect and focus the light emitted from the plasma. Since these surfaces are fundamental in functional form, they are simple to design and manufacture. But these surfaces have some limitations in collecting and transmitting the emitted plasma light and transforming it into separate analytical element wavelength emissions across the wavelength range simultaneously.

In these traditional systems, typically only one wavelength will traverse the optical system to be correctly focused onto the 2D detector array or arrays. All other wavelengths will have slightly compromised optical paths resulting in various degrees of defocus, known as optical aberrations. Aberrations lead to lower signal-to-noise (poorer detection limits) and wider peaks (poor resolution). Optical designs in ICP-OES typically use a number of components in an attempt to minimize the performance degradation. However, optical systems built with simple symmetrical components do not have the flexibility to correct for multiple types of aberrations simultaneously across the whole spectrum.

The innovative, highly customized asymmetric and aspheric surface of the Agilent freeform collimating mirror corrects for all types of optical aberrations across the entire wavelength range, including both the visible and ultraviolet wavelengths, simultaneously. The high degree freeform surface corrects spherical aberrations, coma, and astigmatism, which typically occur on wavelengths as they deviate from the center of the detector. Agilent engineers have pioneered both the design of the freeform collimating mirror surface and precise manufacturing by replication (Figure 3) for use inside the 5800 and 5900 polychromator.

How do freeform optics reduce focal length but increase resolution and detection limits?

Traditional ICP-OES systems require a long focal length of 400 mm or more to effectively separate wavelengths and achieve adequate resolution. The unique freeform collimating mirror in the 5800 and 5900 ICP-OES optics makes it possible to reduce the optical focal length to just 253 mm, while improving resolution and sensitivity across the detector. The surface of the freeform mirror is not a symmetric parabolic surface. It is a novel shape, designed to improve the focus of light onto the detector, as shown in Figure 3. The flexibility of the freeform surface allows for any optical distortions to be greatly reduced by a mirrored optical surface profile. The surface profile is customized to match the ideal mirror shape needed by any wavelength that is defocused from its correct optical axis.

The freeform mirror provides sharper focus and higher light intensity at the detector than standard spherical shaped mirrors. The higher light intensity leads to a higher signal-to-noise ratio on the detector pixels, improving detection limits by 40% on average compared to traditional optical systems.

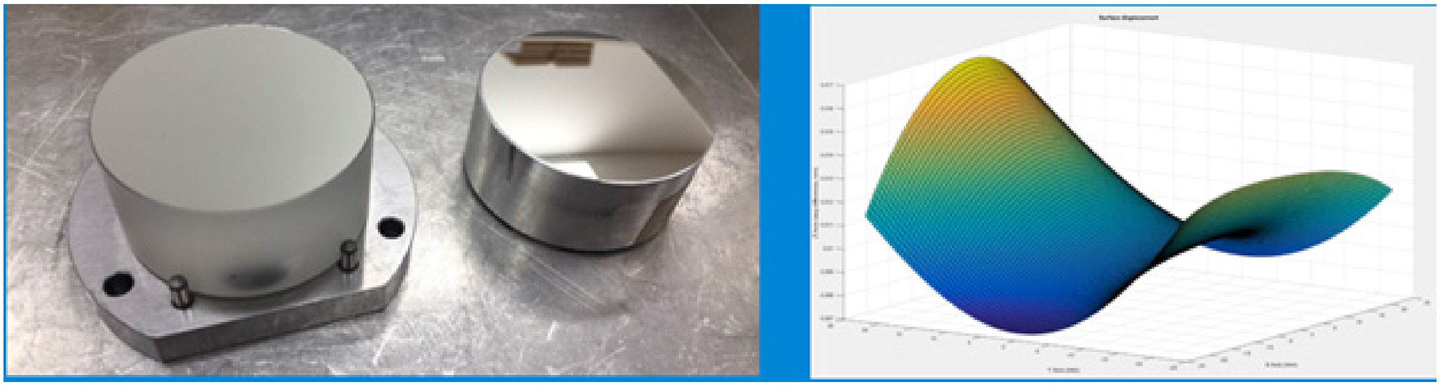

Figure 3. Left: Mirrors used for the replication process. Right: Deviation of the freeform surface from a perfect spherical surface. The freeform surface has a unique shape that has been optimized to provide a sharper focus and higher light intensity on the detector, producing higher sensitivity. The freeform "saddle" surface shape deviation is in the order of microns.

Vista Chip III detector

The Vista Chip III detector (Figure 4) was designed to work with the new freeform polychromator hardware and advanced IntelliQuant software within Agilent ICP Expert (*1–3*). The detector is a charge-coupled device (CCD). To continuously cover a wavelength range from 167 to 785 nm, the CCD is made up of approximately 70,000 light sensitive pixels spread across 70 diagonal linear arrays (DLAs). The layout of the pixels on the detector has been designed to match the unique echelle pattern produced by the 5800 and 5900 polychromator. It uses image-mapping technology (I-MAP) to exactly match the echelle image, allowing it to fit onto a small, perfectly shaped, 2D detector.

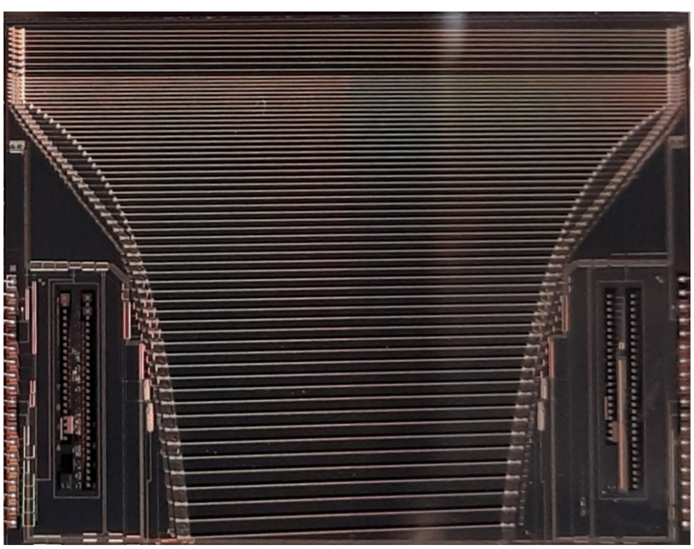

Figure 4. Vista Chip III detector with I-MAP and Adaptive Integration Technology for higher speed, full-wavelength coverage from 167 to 785 nm.

The position and length of each DLA on the detector is aligned to match the free spectral range of each diffraction order produced by the echelle optics (Figure 5). The detector is Peltier cooled to –40 °C to minimize dark current and readout noise.

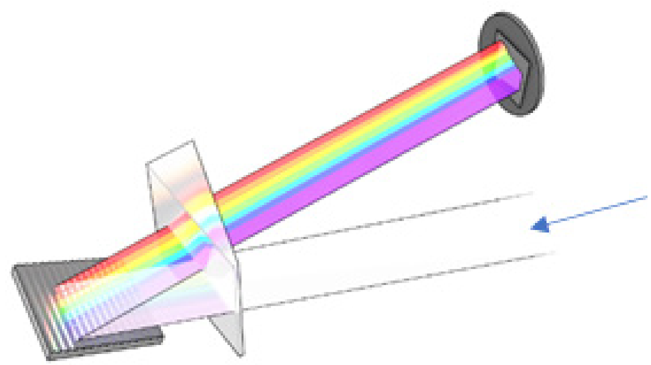

Figure 5. Schematic of how the light from the collimating mirror passes through the prism onto the grating, and back through the prism towards the focus mirror (not shown). The focus mirror then concentrates the dispersed light onto the detector surface. The grating separates light containing all wavelengths into a spectrum of separate wavelengths, spreading them into overlapping DLA orders. The prism then separates the wavelength ranges into a second dimension, so that the entire wavelength range can fit onto a small, square, 2D detector.

Fast signal readout

With a 1 MHz pixel processing speed and pixel location efficiency, the Vista Chip III CCD sets the benchmark for ICP-OES detector speed. Duplex circuitry enables pixels to be read out from both sides of the detector, ensuring a readout speed significantly faster than competitive systems. With the 5800 and 5900 ICP-OES, the entire spectrum from 167 to 785 nm can be measured in less than half a second. Figure 6a shows a close-up of five DLAs on the Vista Chip III CCD. Figure 6b shows the micro-electronic circuitry used to control the photosensitive pixels.

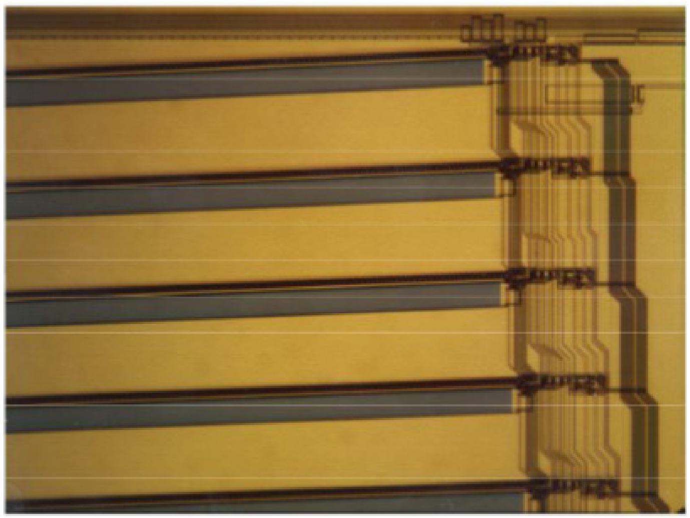

Figure 6a. Individual DLAs on one side of the Vista Chip CCD with associated readout circuitry.

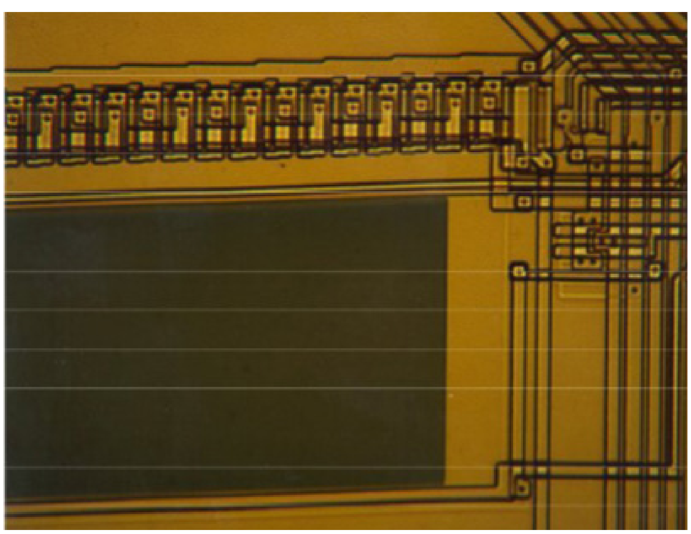

Figure 6b. A single DLA at higher magnification. The dark region is the photosensitive area. The antiblooming drain can be seen running continuously along the bottom of the photosensitive area and the readout control circuitry for each pixel along the top.

Adaptive Integration Technology

Adaptive Integration Technology (AIT) is an intelligent algorithm that prevents overrange signals by automatically adjusting the integration time for each emission line depending on the incoming signal intensity (Figure 7). Some competitor systems group wavelengths that need similar integration times together. Each group of wavelengths is then measured one after the other (sequentially), which leads to longer analysis times. AIT automatically sets the optimum integration time for each wavelength, allowing all element concentrations to be determined with a single, truly simultaneous measurement, regardless of the analyte concentration or the sensitivity of the chosen emission line. By increasing the efficiency of signal processing, AIT optimizes the sample analysis times of the 5800 and 5900 ICP-OES.

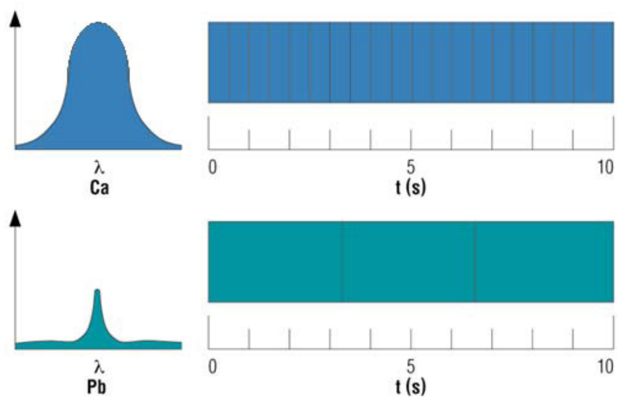

Figure 7. Using a 10 s replicate read time, AIT averages many short readings for high-intensity signals and fewer, longer readings for low intensity signals, simultaneously providing the optimum signal-to-noise ratio.

Antiblooming on every pixel

Emissions are collected on light sensitive pixels (A) across the CCD detector surface, where they are converted to an electronic signal, transferred and held at register B before being read-out at register C (Figure 8). 'Blooming' is an undesirable property of a solid-state detector. It occurs when intense illumination of one part of the detector can interfere with the measurement of nearby pixels. Unlike segmented CCD detectors, the Vista Chip III CCD features antiblooming protection on every pixel. If pixels are saturated by a very intense signal, the excess signal overflows into the antiblooming gutter, rather than neighboring pixels. Antiblooming protection ensures that trace elements can be accurately measured in the presence of high concentrations of other elements.

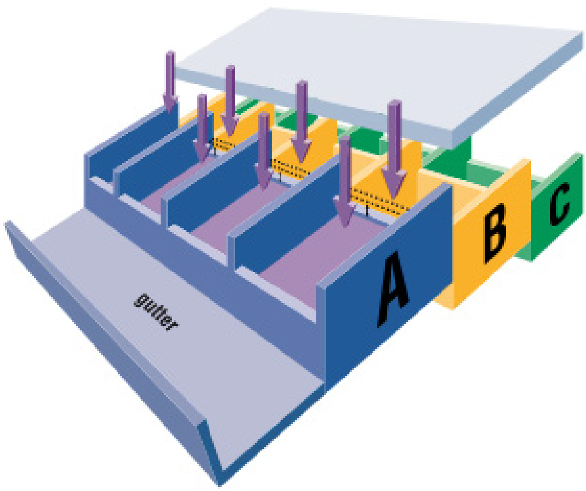

Figure 8. Schematic of a single DLA on the Vista Chip III CCD illustrating the potential barriers between pixels and the antiblooming gutter.

Conclusion

The Agilent 5800 and 5900 ICP-OES use the most innovatively designed freeform optics in the polychromator and a specially designed Vista Chip III detector that have lowered detection limits and improved optical resolution. Advantages of the asymmetric and aspheric surface of the Agilent freeform collimating mirror include:

- Correction for all types of optical aberrations across the entire wavelength range, including both the visible and ultraviolet wavelengths, simultaneously.
- Correction for spherical aberrations, coma, and astigmatism, which typically occur on wavelengths as they deviate from the center of the detector.
- Sharp focusing and high light intensity at the detector leading to an excellent signal-to-noise ratio and an improvement in detection limits by 40% on average compared to traditional optical systems.

The advanced polychromator design has also led to a reduction in the optics volume by 50%, meaning less time spent purging and a significant reduction in the footprint of both instruments. The synchronous dual view pre-optics (of the 5900) and Vista Chip III CCD detector enable true simultaneous measurements and full wavelength coverage from 167 to 785 nm within less than half a second.

The overall hardware design of the 5800 and 5900 is key to their unmatched multi-elemental analysis speed and performance, including fast, insightful full screening analysis of samples using IntelliQuant software.

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