

The Evolution of Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

Part I: The 1970s

Since its commercial inception in 1974, ICP-OES has seen significant technological advancements over its 39-year lifespan. In this four-part series, we will summarize the evolution of ICP-OES technology and show how it has come to be applied to an ever-growing amount of sample types and elements of interest, as it has matured. Each series will cover the significant milestones that have occurred in ICP-OES through the past four decades. Because the ICP-OES specialization is very much a language of its own, useful terminology will appear in **bold** and will be defined in an upcoming downloadable glossary of ICP-OES Terms and Definitions.

What is ICP-OES?

Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) is a multielement technique used to measure the concentration of various elements in a variety of sample matrices. Also known as **Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)**, the technique is capable of measuring a majority of elements in the Periodic Table and is currently one of the most widely used methods for elemental analysis today.

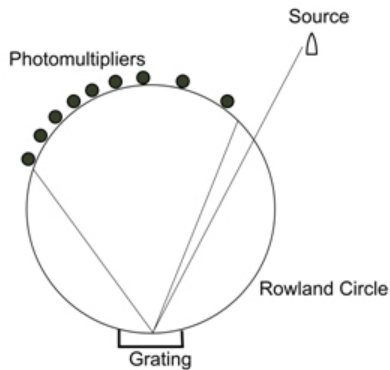
ICP-OES uses extremely high temperature argon plasma to excite atoms to the point where they emit their characteristic **wavelengths** of light (**emission lines**). The intensity of the emitted light (**emission intensity**) is directly proportional to the concentration of the elements in the sample. By measuring the emitted light by known and varying concentrations of an element (by performing a “**calibration**”), the concentration of an unknown sample can be determined by comparison.

Historical Overview

There is little question that ICP-OES has emerged as the dominant technique for trace multielement analysis. From 1983 to 2013, approximately 48,000 ICP-OES systems have been installed.¹ These instruments are used to perform analysis of a broad range of sample types in numerous industries including: agricultural, environmental, geochemical, metallurgical, petrochemical and wear metal, as well as many others.

1970s – The Early Years

The first commercial ICP-OES instruments were introduced in 1974. These ICP forerunners were based on the **Paschen-Rünge** optical design, which included permanently mounted **diffraction grating**, and fixed **entrance** and **exit slits** (generally referred to as **fixed optics**). These instruments produced a simple linear spectrum that fell along the focal curve of the instrument. A schematic of this design and its associated spectrum is shown below:



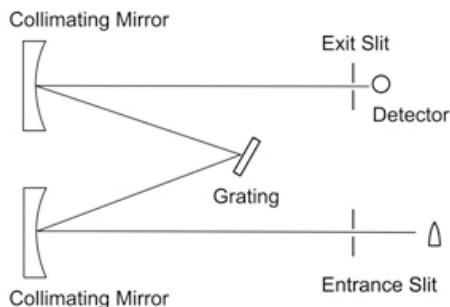
These early ICP instruments were modified versions of arc/spark emission spectrometers (used in the metallurgical industry) in which the arc emission was substituted with inductively coupled plasma. Despite their exceptional speed (with typical **integration times** of only one to three seconds), they tended to lack the spectral **resolution** provided by modern ICP instruments and were subsequently prone to **interelement interferences** from the emission line rich ICP source.

Because these instruments were designed around a fixed entrance/exit slit architecture and used **PhotoMultiplier Tubes (PMT)** for light detection, they lacked the wavelength versatility required to measure elements other than those incorporated into the instrument when it was built. Because ICP's origins are based in the metallurgical industry, this limitation was not initially an issue as Metal analysis laboratories tend to focus exclusively on a small number of sample matrices and elements of interest (e.g. aluminum alloys, iron alloys, etc.). But as the use of ICP-OES has expanded, many laboratories have had an increasing desire to analyze diverse sample types and more elements of interest.

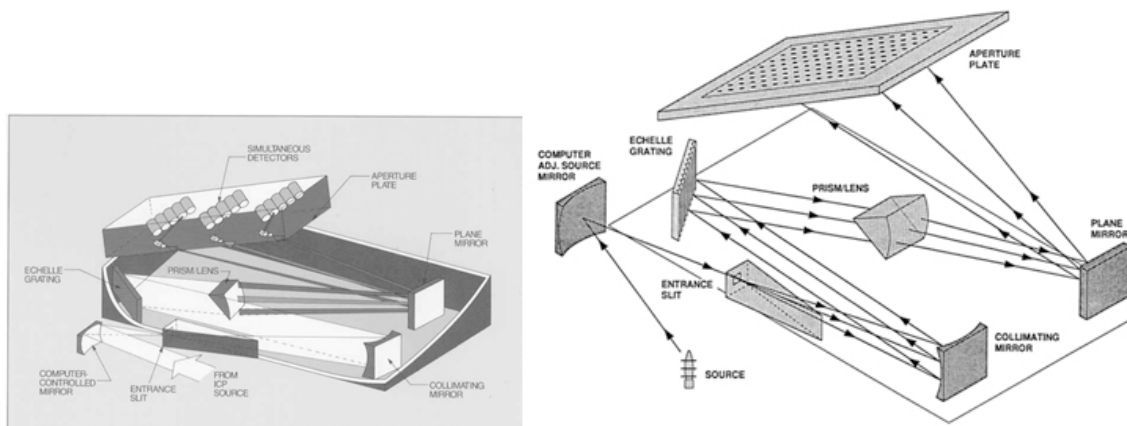
Part II: 1980s – It Was All About Versatility

In part II of the series, we jump into the 1980s, and the next era in innovation.

The wavelength restrictions associated with the Paschen-Rünge optical design led to the development of **sequential spectrometers** in the early 1980s. Most of these instruments relied on the principle of scanning a dispersive optic (typically a ruled or holographic diffraction grating) to select the specific wavelength of light corresponding to the **element of interest**. These instruments were extremely versatile, possessing the ability to access nearly any wavelength in the electromagnetic spectrum from 160 - 900 nm. Their downside lay in their ability to access only one wavelength at a time (thus named **sequential**), resulting in slow analysis times. On an instrument of this type, a typical analysis could take several minutes to cover the 10 to 20 elements of interest. A schematic diagram of a typical scanning sequential spectrometer is shown in the schematic below:



Additional improvements in wavelength versatility were achieved in the early 1980s with the development of the **echelle optical system** introduced by Teledyne Leeman Labs. These instruments relied on a **high dispersion echelle grating** in combination with a second dispersive optic (usually a prism) to produce a 2-dimensional spectrum or **Echellogram**. One of the hallmarks of echelle spectrometers is that they produce very high resolution spectra from relatively small optical systems; typical only 0.3 to 0.8 meters in length. Teledyne Leeman Lab's early echelle spectrometers were capable of accessing more than one wavelength at one once (**simultaneous**), as well as sequential or even a combination of both, using a single optical system. The result was an instrument with both high speed and versatility in one compact benchtop configuration. The graphics below depict a typical 2-Dimensional Simultaneous Echelle Spectrometer and a Sequential Echelle Spectrometer.



At the same time as Leeman Lab's development and introduction of the echelle optic system, other manufacturers began offering combination units incorporating both Paschen-Rünge simultaneous spectrometers and scanning sequential spectrometers in one large instrument. Both of these approaches (Echelle or combination Paschen-Rünge/Sequential Spectrometer) gave the user the capability of high **throughput** for routine samples and the versatility to quantify nonroutine samples when trace element demands changed.

And so the world of ICP-OES analysis was beginning to broaden, capable of analyzing a variety of sample matrices and elements of interest.

[Part III: 1990s – The Dawn of Dual View Plasmas and Array Detectors](#)

With the 1970s known as the birth of ICP-OES and the 1980s as the era of versatility, the decade of the 1990s was the dawn of some major breakthroughs in ICP optical spectrometry. These breakthroughs centered on the Plasma orientation and solid state Detectors, which initiated hopes of simultaneous detection of the entire ICP spectrum.

Plasma Torch Orientation

On early ICP-OES instruments, the **plasma torch** was mounted in the vertical (or radial) orientation and the plasma was viewed from the side. During the early 1990s, researchers began to investigate the possibility of turning the plasma on its side and viewing it “end on” (axial position).

By looking at the wavelength emission “through” the central channel of the plasma, emission intensity increased significantly resulting in a 5-10 fold improvement in **detection limits** for most elements. The downside to the increased intensity was a tendency to certain interferences requiring knowledge of the sample matrix to get the desired result. This led to the development of dual-view systems where both **radial viewing** and **axial viewing** were incorporated into one instrument. In this case, the historically difficult elements (e.g. As, Se, Tl, Sb and Pb), which were not prone to interferences, could be viewed axially, yielding higher sensitivity, while all other elements prone to interferences could be viewed radially.

Solid State Detectors

At the same time that Plasma orientation was evolving, solid-state, charge transfer device (CTD) **detectors** (a.k.a. **Array detectors**, **CCDs**, **CIDs**) were replacing photomultiplier tubes (PMT). Prior to solid-state detectors, virtually all ICP – OES instruments used photomultiplier tubes (PMT) to convert photons of light into electrical energy. Although PMTs are extremely effective light detectors, they have a few fundamental limitations that have inspired manufacturers and users of ICP-OES products to seek alternatives. These limitations include the following:

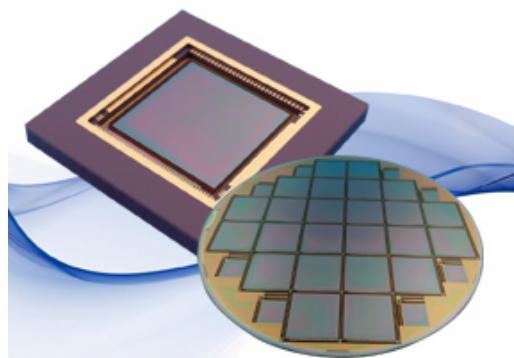
- PMT can only be used to measure one wavelength of light at time in ICP-OES. Simultaneous instruments require one PMT for each analyte wavelength. Considering that there are tens of thousands of emission lines in the ICP spectrum, it is impossible to build a PMT – based simultaneous instrument that will provide simultaneous detection of the entire ICP spectrum.
- The physical size, and electronic characteristics of a PMT limit how close they can be placed together; and to a large extent, how close two analyte wavelengths can be configured.
- PMTs are cost prohibitive. The single PMT in most sequential ICPs can cost anywhere from \$100 - \$500. Because a single PMT is required for each emission line, a 40 element simultaneous ICP can contain a fortune in PMTs alone, and take well over a month to build and align.

Despite these limitations, anyone who has ever seen the unparalleled analysis speed of a PMT-based ICP simultaneous ICP, or compared the speed of PMT-based sequential to that of an array detector-based sequential, will find their appeal difficult to refute.

Promises and Challenges

As stated earlier solid – state detectors held the promise of the ability to choose any set of simultaneous wavelengths at any time. This promise took nearly another decade to be delivered. For manufacturers, these detectors presented both significant opportunities and significant challenges. The opportunity was the allure of being able to produce a simultaneous ICP without all of the labor and material costs associated with PMT-based instruments. The challenge was in figuring out how to compress the ICP spectrum down onto the size of the solid – state detectors that were available at the time (only about 6 mm by 6 mm) without destroying one of the most important aspects of any ICP – OES, optical resolution. The small size of the early array detectors resulted in very significant limitations to both the resolution and the wavelength coverage of those array detector-based instruments.

The largest detector available in today’s instruments is, at a minimum, 16 times the size of the early arrays allowing the user to capture the full ICP spectrum in a single integration. Challenges aside, when the first commercially-available CTD-based instruments were introduced it began a market revolution that would result in a near complete transition from PMT-based simultaneous ICPs to array detector-based simultaneous ICPs. Aside from the difference in initial cost, the dilemma about whether to purchase a



simultaneous or a sequential ICP suddenly disappeared. In theory, every wavelength in the UV and visible portions of the spectrum could now be accessed.... all at the same time. Slowly but surely the vast majority of the ICP-OES marketplace changed.

In the final post of our Evolution of ICP series, we move into the 21st century, and modern ICP-OES, including advancements in measuring halogen elements by ICP, time resolved analysis for interfaces for LC and **laser ablation** for solid sampling.

Part IV – 2000 to Present

The instruments being marketed today have reached a level of sophistication that would not have seemed possible 40 years ago. Though the fundamental principles of the technique have not changed, the technology has seen significant advancements, especially in the design of the ICP source, optical spectrometer and detection systems. Simultaneously, milestones in real-time elemental coverage, sample throughput and ease-of-use, continue to make it easier to reach new pinnacles in productivity and data quality.

In the 1990s, labs faced the dilemma of purchasing a simultaneous or a sequential spectrometer. With the introduction of charge-transfer device detectors, that disappeared, as every wavelength in the UV and visible portions of the electromagnetic spectrum were now accessible at the same time. This changed the entire ICP-OES, and by the early 2000s, nearly all the ICP-OES manufacturers were using solid state detector technology.

In the last decade, further advancements have occurred, including the ability to measure the halogen elements by ICP allowing the analysis of chlorine and bromine at low concentrations. New instruments also included time resolved analysis for interferences for LC, using TRA as a detector for chromatography. Advancements in sample introduction include cooled spray chambers and switching valves to increase sample throughput.

Laser ablation

Among the most recent advancements is the evolution of lasers as part of the vaporization process. While the use of laser beams as a solid sampling device for atomic spectroscopy were first investigated in the early 1960's, it was another 25 years before the trace element user community explored coupling laser ablation with ICP-MS. Previously solid samples were processed through an acid dissolution procedure. Today, laser ablation is considered a truly routine sample introduction device for ICP-MS and has proved to be an invaluable tool for carrying out trace element studies on a wide variety of solid materials. In particular, the ability to analyze small spots or inclusions on the surface of rocks and minerals was a huge benefit for the geological community. More recently, laser ablation has been fine tuned and optimized as a bulk sampling tool for ICP-OES.

Choosing the Right Instrument Manufacturer

There are a number of different ICP-OES designs on the market today, and many share similar components (Nebulizer, spray chamber, plasma torch). Where they differ significantly is the design of the optical components and detection systems.

With more than 30 years of supplying ICP Spectrometers, Leeman Labs understands that there is not a single ICP-OES instrument that is ideal for all applications. Leeman Labs' family of ICP Spectrometers is available in radial, axial or dual view configurations with simultaneous array detector systems or high speed PMTs. The evolution of ICP-OES continues, which makes selecting the right instrument manufacturer even more important.



Teledyne Leeman Labs ICP Spectrometers are considered a workhorse in the industry. For more information on these ICP-OES Spectrometers, visit our [website](#) or contact us for more information.

References

1. Thomas, Robert. *Practical Guide to ICP-MS: A Tutorial for Beginners*; CRC Press, Taylor & Francis Group: Boca Raton, 2013; p xxi.