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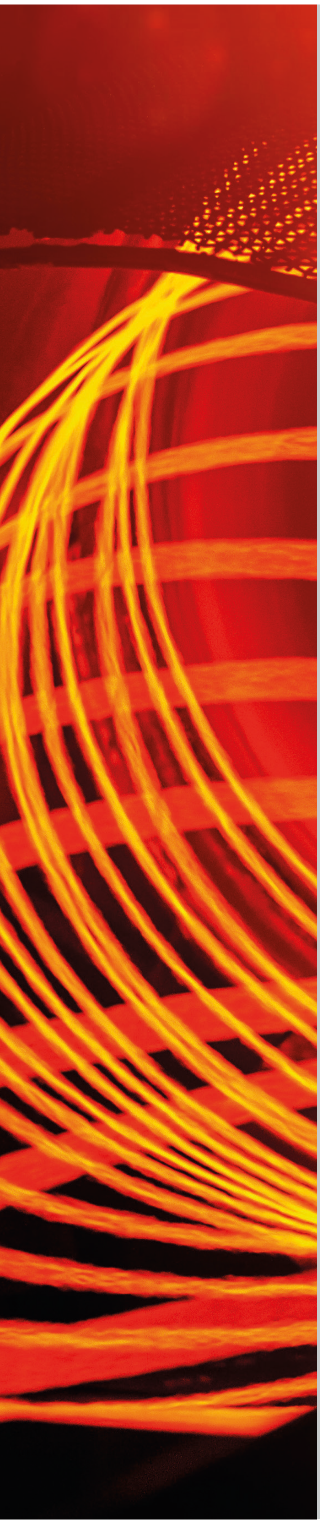
SPECTRO ANALYTICAL INSTRUMENTS



PMT vs. CMOS: The Paradigm Shift in Metal Analyzer Detector Technologies

Introduction

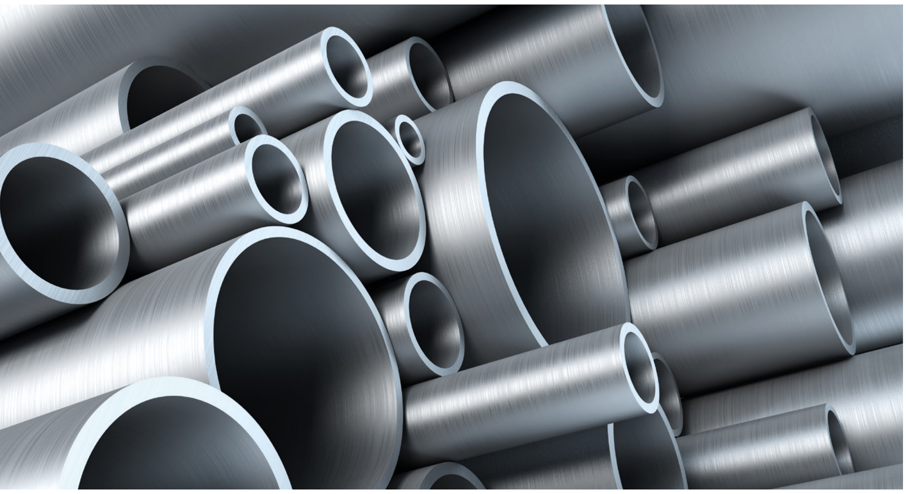
Testing metal samples can pose complex challenges. Demanding examples come from large foundries and primary producers of steel, aluminum, or copper, as well as many secondary metal processors, aerospace and automotive companies, testing laboratories, governmental and academic labs, and more. These users must identify and measure — with especially high accuracy and precision — all the elements and compounds in their incoming, in-production, and outgoing materials. Most utilize a high-end *stationary metal analyzer.*

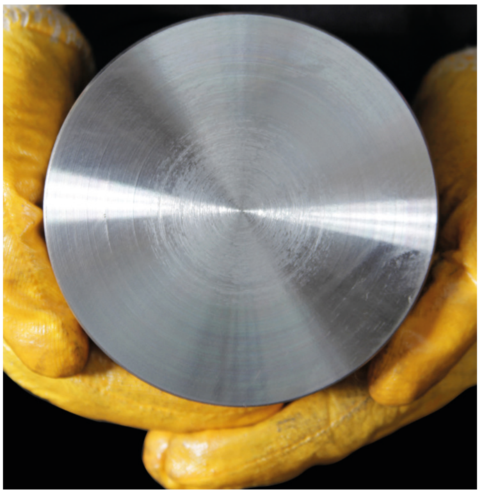
A key factor for analyzer performance: its detector technology.

Today, most users meet these challenges with instruments containing legacy PMT detectors. Though difficult to manufacture and problematic to reconfigure once installed in an analyzer, PMT technology has been the preferred choice in steel mills and comparable applications for several decades.

Now, however, specialized CMOS-based detectors have been perfected for this use. The following report demonstrates that solid-state CMOS detectors, when incorporated in an advanced stationary metal analyzer, can equal or surpass PMT detector performance and reliability in every critical metric:

- Flexibility
- Sensitivity
- Stability
- Measurement speed
- Durability
- Manufacturing & quality consistency





Background

The Principles of OES

The instruments discussed here are classed as arc *spark optical emission spectrometry* or *arc spark OES* analyzers. Analysis begins when a metal sample is placed on the *spark stand*. The stand is internally flushed with argon gas to prevent contamination by elements in the air. An electrode several millimeters from the sample discharges a high-voltage impulse, or spark, which arcs to the metal. The spark vaporizes or depletes some of the sample material, atomizing and ionizing it. This excited material emits energy, which becomes electromagnetic radiation, or light.

Specific spectral wavelengths of that light are characteristically emitted by specific elements. So each element has unique emission spectra, or analytical wavelengths. And the intensity of the light is directly proportional to the concentration level of a given element in the excited sample.

Emitted light reaches the *optical system*, and its wavelengths are separated by a diffraction grating. The light is directed onto a *detector array* and associated *readout electronics*, which provide data to allow the analyzer's software to quantify each light wavelength and intensity. Result: the user can identify and measure each element in the sample.

Note that the process involves numerous complications. The relevant wavelengths encompass the entire ultraviolet and infrared spectrum, from 120 nanometers (nm) to 780 nm. Emission profiles are complex: iron (Fe) alone possesses more than 4,000 different analytical emission lines.

Of course, each component of the OES process is important. But the part played by the detectors is especially critical.

The Trouble With Tubes

Photomultiplier tubes (PMTs) have long been the preferred detector choices for high-end spectrometers used by primary metal producers and other demanding users.

A legacy vacuum tube technology, a PMT detector consists of an evacuated glass housing enclosing several light-detection elements. Light from a sample's arc spark excitation enters the tube and strikes a thin photocathode layer, which ejects electrons. These are focused, greatly amplified, and

converted into electronic signals. A tube requires operating power of up to 1200 volts.

As analyzer components, PMTs are considered relatively robust. Their ability to enable accurate identification and measurement of the elements for which they are configured has been proven over many years. In terms of performance, they are noted for high gain, low noise, and good speed of measurement. Their excellent trace element detection capability is aided by their markedly high dynamic range.

However, PMTs also suffer from significant drawbacks.

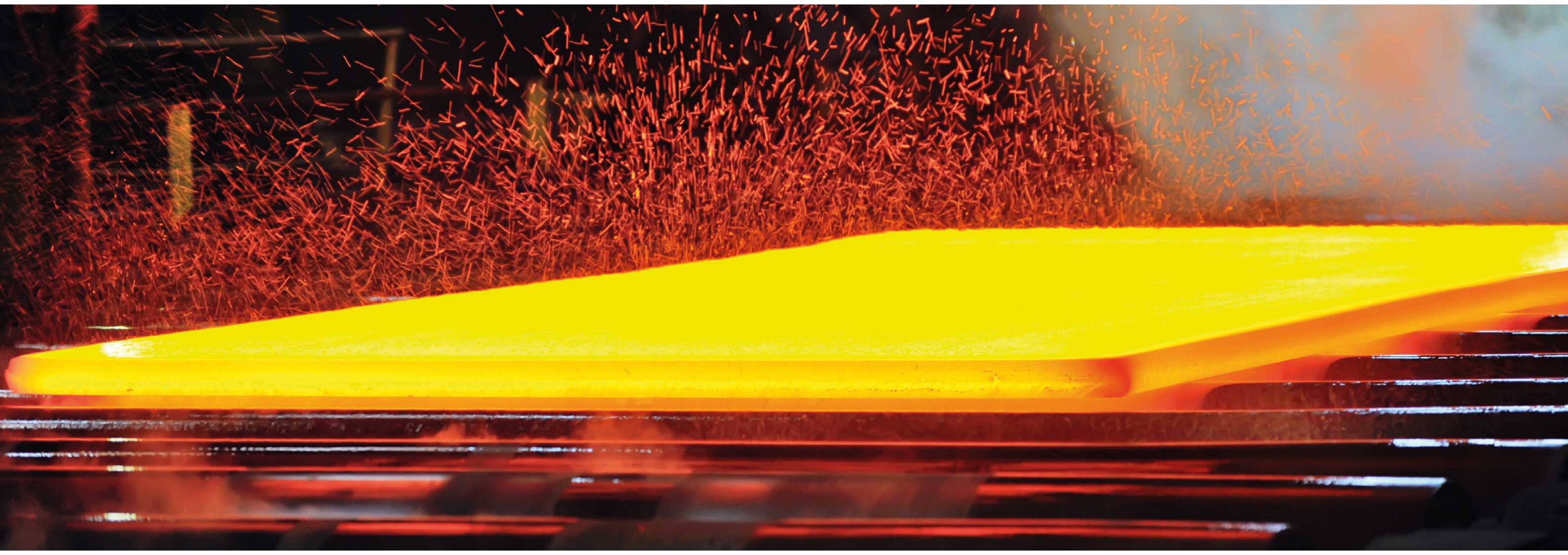
As a one-of-a-kind item, each PMT presents individual variations that must be painstakingly accommodated — impairing efforts for consistent manufacturing, quality control, and even use. PMTs are expensive. Each PMT detects a single specific element. Each PMT-based analyzer must be configured to detect only a relatively small number of elements in given matrices. Adding or subtracting another element necessitates major hardware alterations. Analytical lines from closely adjacent elements may cause interference. If a PMT detector fails, the analyzer is blind to that element's wavelength, potentially degrading performance of the entire optical system.

These and other problems indicate why PMT technology has been supplanted by solid-state solutions in a number of other spectrometer markets, from *inductively coupled plasma optical emission spectrometry* (ICP-OES) devices to mobile metal analyzers to benchtop and midrange stationary metal analyzers.

The Pros and Cons of CCDs

To overcome PMTs' disadvantages, many spectrometer manufacturers turned to detectors based on the *charge coupled device (CCD)*.

Invented in 1969, CCDs were first used in camera and imaging sensors. A CCD is basically a solid-state integrated circuit (IC) that's etched onto a silicon substrate. It contains a linear array of several thousand miniature light-sensitive elements (also known as pixels). Fundamentally, a CCD sensor captures light and converts it into an



electrical charge. The more light captured, the greater the charge.

In CCD-based spectrometers (first introduced in 1999), each pixel's signal of the intensity of light at its location is fed to the spectrometer's readout electronics for processing. Later generations of CCD detectors are commonly used in today's midrange ICP-OES spectrometers. In those instruments, CCDs are prized for their high resolution and durability, plus their consistent capability to deliver specified sensitivity and low noise levels. Example: for midsized companies, foundries, and fabricators, the world's best-selling stationary metal analyzer is probably the SPECTROMAXx spectrometer from SPECTRO Analytical Instruments. This popular seventh-generation instrument uses CCD-based detectors to great effect.

Currently available *hybrid* systems, which feature both PMT and CCD detectors, manage to combine some of the desirable characteristics of each technology.

However, for demanding tasks such as primary metal production, pure CCD-based systems have not been able to match the performance of PMT-based analyzers. This is especially true with regards to low detection limits and the identification of inclusions, enabled by technologies such as TRS and SSE (see „Achieving Sensitivity and Precision" below.)

The CMOS Solution

That's all changed with the advent of today's next-generation, linear CMOS detectors. Like CCD-based models, *complementary metal oxide semiconductor (CMOS)* detectors are solid-state devices manufactured with proven IC detector technology. So they share basic CCD advantages over PMTs, such as quality consistency and reproducibility. But years of development have gone into making CMOS a new, distinctly different detector type that's a great improvement over CCD technology.

A CMOS detector is a multichannel semiconductor device wherein parts of the readout electronics — performing tasks such as analog-to-digital conversion and noise reduction — are integrated onto the sensor die during fabrication of each integrated circuit. So these key image processing functions take place on the chip itself. Result: advantages such as greater dynamic range and higher data throughput.

Till this development, some users have believed that PMT detectors are inherently superior to solid-state detectors. The remainder of this report demonstrates that the latest CMOS detector technology — as incorporated into an advanced instrument such as the new SPECTROLAB S stationary metal analyzer — has now reversed the equation.

Maximizing Flexibility

PMT: One Detector, One Line — No Flexibility

One inherent limitation of PMT technology: every PMT unit in an analyzer requires its own exit slit (to separate a given wavelength of light emanating from the diffraction grating). One PMT must be dedicated to each emission line.

With multiple 28 mm or 13 mm diameter detectors on a crowded mounting plate, the distance between each detector is critical. Every detector and every slit must be perfectly positioned via a demanding manufacturing process to achieve correct focus on its corresponding wavelength. It not, it can take extensive remeasuring to determine that the line is off-profile.

The one detector / one line constraint also sharply limits the total number of elements that an analyzer can handle. The average PMT-based instrument is factory-configured to detect a maximum of only 80 wavelengths. This doesn't mean it can

measure 80 elements. Each element may require analysis of multiple wavelengths, based on its matrix and concentration range. For example, in a multi-matrix configuration, nickel (Ni) alone may demand seven different wavelengths for optimal analysis. With an 80-wavelength ceiling, highly configured PMT-based systems very soon run out of elements they can detect.

Additionally, two elements of interest to the user may have optimum lines that are too closely adjacent. In some cases, there's actually not enough room on the plate to accommodate precise positioning of their dedicated PMTs and slits. So for one of the elements, the makers must choose a compromise wavelength, instead of the best analytical one. This degrades performance on that element for every measurement the analyzer makes.

Finally, there's the flexibility factor — or lack thereof. In many modern mills or factories, it's not uncommon for new materials or alloys to be considered for research and development, to be encountered in an evolving supply chain, or to be added to a product line. Problem: a facility that depends on a PMT-based analyzer can't easily add or subtract even a single element of interest. Only elements specified for the instrument's initial configuration can be detected.

Trying to change an existing element selection means that production must halt while both hardware and software are modified. A quite complex calibration/profiling/recalibration process must then be endured. This may take an extended — and expensive — visit from a manufacturer's representative, or even a return to the factory. And depending on the element and specific fit/positioning constraints on the mounting plate, reconfiguration may ultimately prove impossible.

CMOS+T: Full-Spectrum Coverage for Maximum Flexibility

By contrast, CMOS detectors are not limited to one detector / one element. So in the SPECTROLAB S analyzer, via a dedicated mirror, all of the thousands of pixels on the CMOS detector are exposed to all light lines emitted from the sample. Thus, in addition to efficient single-element focus, the system can capture full coverage of every wavelength on the entire relevant analytical spectrum simultaneously, from 120 to 780 nm. This full-capture range exceeds anything possible with a PMT-based analyzer.

SPECTRO's proprietary CMOS+T technology delivers flexibility that allows the instrument maker to design the optimal optical configuration for each customer, regardless of application. For example, users may specify any combination of the 10 standard primary metal producers' matrices: iron (Fe), aluminum (Al), copper (Cu), nickel (Ni), cobalt (Co), magnesium (Mg), titanium (Ti), tin (Sn), lead (Pb), or zinc (Zn).

And a CMOS detector system doesn't suffer from the 80-wavelength limit that so seriously restricts how many elements a PMT-based instrument can handle. For example, one recent SPECTROLAB S installation configured the instrument to detect wavelengths emitted in 170 different analytical lines — measuring a total of 59 different elements.

In addition, no compromises or remeasurements are necessary for closely adjacent emission lines. The optimum line may always be analyzed for the most accurate result.

This kind of CMOS-based analyzer design also allows for full future-proof flexibility. Again, there's no limit on the total number of selectable elements. If an unknown element is encountered and/or a new element or elements enters the supply stream, the instrument maker can simply supply a new analytical method via software update. So metal producers can add coverage of newly necessary materials containing bismuth (BI), tungsten (W), manganese (Mn), or other matrices quickly and easily.

CMOS full-spectrum-coverage design empowers other powerful software capabilities. Archiving and auditing programs can provide full forensic audits of any and all reported spectra, to discover unwanted elements. In addition, solid-state detectors allow the use of programs such as SPECTRO's iCAL 2.0. This enables recalibration/profiling/standardization using only a single sample; less operator intervention; and long-term measurement stability regardless of variations in samples or ambient temperatures.

Achieving Sensitivity and Precision

Until now, in applications such as high-end metal analysis, analyzers based on PMT detectors still outperformed other spectrometers at detecting trace elements, as well as delivering precise measurement at all concentration levels. They owed much of this remaining dominance to two related analytical techniques in particular: TRS and SSE.

Time resolved spectroscopy (TRS) measures changes (such as in a sample's emission energy levels and emission direction) occurring during predefined, discrete segments within a single spark discharge. Given a PMT's high dynamic range, system software can use this data to minimize background noise plus interference effects between elements. Result: high sensitivity for improved detection limits.

Single spark evaluation (SSE) records and analyzes each of a number of sparks in succession. System software can also use this data to detect inclusions — miniature foreign bodies found in a mass of a different material. In certain metals, even quite small inclusions can negatively impact a material's mechanical performance. The analyzer can

Table 1: LoDs for iron-based material

LoD in ppm		
Element	**PMT**	**CMOS+T**
Pb	3.5	1.9
Sb	9.3	9.2
W	5	4.5
Ag	0.4	0.1
Se	15	2.5
Ce	7.2	2.6
Bi	5.6	2.9
Zr	1.5	0.9
As	3.6	1.6
Ti	1.5	1.1
Cu	6.7	2.4
Co	1.5	1.2

Table 2: LoDs for aluminum-based material

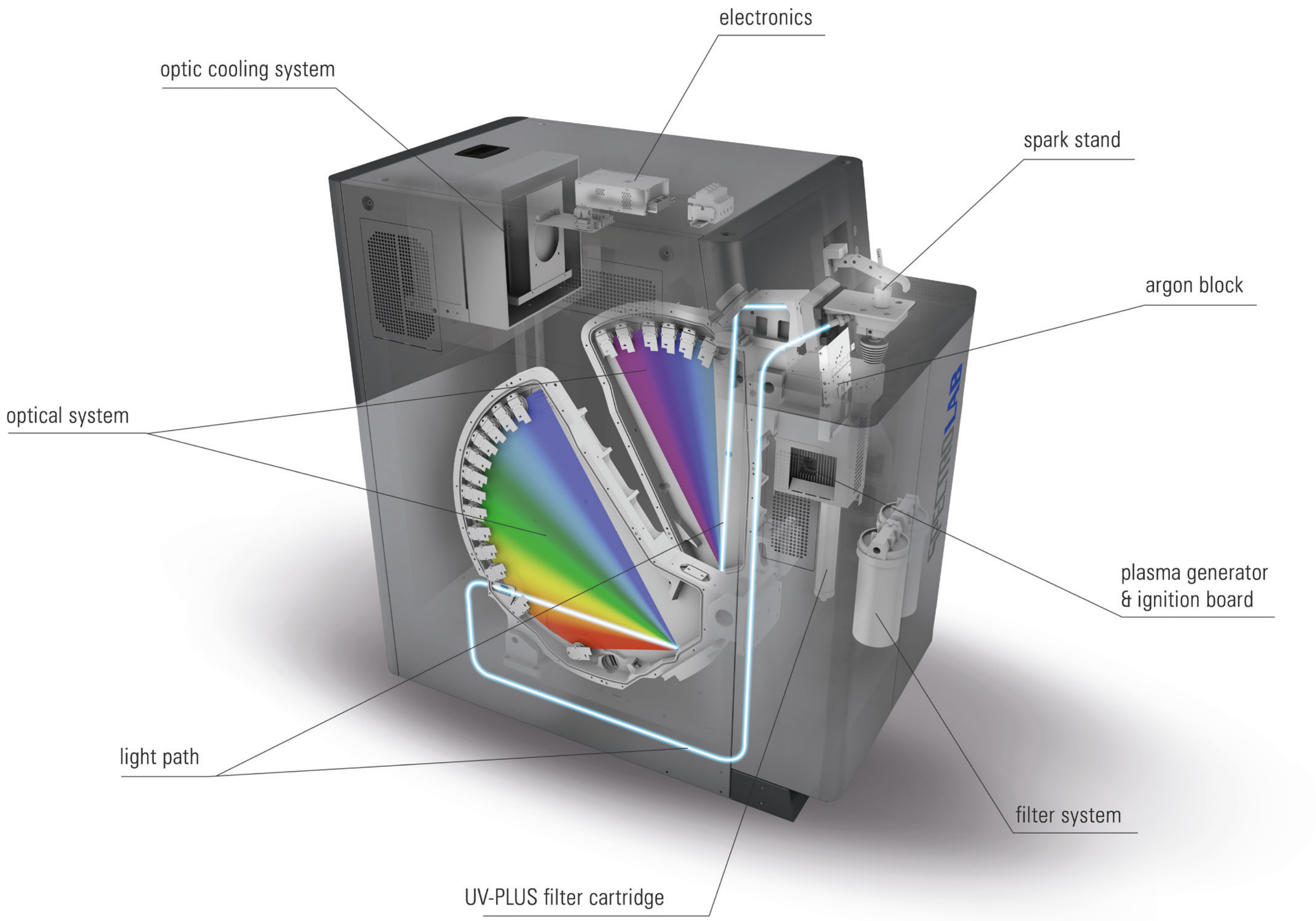
LoD in ppm		
Element	**PMT**	**CMOS+T**
Bi	1.8	1
Tl	0.6	0.5
Pb	1	0.3
Cu	8.3	1
B	0.5	0.2
Sb	2	1.5
Sr	0.05	0.05
Mo	0.3	0.2
La	0.7	0.6
Hg	0.9	0.4
Ce	4.5	1
Mn	1	0.6

alert users to inclusions in otherwise “clean” materials, such as manganese sulfide (MnS) in steel.

Unfortunately, CCD-based detectors are inherently unable to deliver the performance necessary for TRS or SSE.

However: today, an advanced CMOS-based analyzer such as SPECTROLAB S employs proprietary technology with the advantage that each detector in its lithographically printed semiconductor array is much more reproducible and consistent in terms of sensitivity and noise behavior than is possible with a one-off PMT. Even more critically, the CMOS+T system can use its full-spectrum ability to achieve a previously unprecedented feat: TRS capture of an entire relevant spectra. To this, it adds other advantages of its optical system and image processing — such as an external shutter to isolate single sparks; the ability to utilize the best combination between an analytical line and a reference line; and its own high dynamic range.

All these combine to help the spectrometer meet or exceed the detection limits, sensitivity, and precision (see accompanying tables) previously available only with PMT detection that employed TRS and SSE capabilities. So applications such as determination of steel cleanliness can enjoy unmatched precision. CMOS+T technology can handle requirements from complex single-base configurations to multi-matrix setups. And it can provide excellent results everywhere from single parts per million (ppm) trace element levels to high concentrations of expensive materials such as chrome (Cr) and nickel (Ni).



Ensuring Stability

As mentioned, PMT limitations may force manufacturers to configure less-than-ideal wavelengths for certain elements. Among other problems, this can impact measurement accuracy. If not temperature-stabilized, PMT-based analyzers can be greatly affected by even small variations in room temperature. These factors can degrade reproducibility, and readouts of the same concentration of the same element can vary unacceptably over time.

CMOS+T technology allows better stability and reproducibility of results, in both the short and long terms. Instrument designers may choose the optimum correlation between analytical and reference lines — for the most stable measurement approach possible. In addition, SPECTROLAB S adds further stability via iCAL 2.0 software, which includes online correction for measurement drift caused by temperature fluctuation or other issues.

Accelerating Speed of Measurement

As a class, OES analyzers are noted for fast measurement. Often located close to the mill or factory floor, they avoid production delays caused by waiting for results. Stationary metal analyzers equipped with PMT detectors are no exception, providing most results in seconds or a few minutes.

A CMOS-based system can do even better. The SPECTROLAB S analyzer, for example, leverages inherent CMOS speed with features such as dynamic preburn time and plasma control, to further optimize and reduce processing intervals. Measurement times can be significantly lower than with PMT-based systems. This is a real benefit in automated, high-throughput environments. For example, the system can achieve highly accurate results for materials such as low-alloy steel within less than 20 seconds.

Enjoying Industrial-Strength Durability

Most PMT detectors provide robust service lives. Nevertheless, a PMT failure may occasionally occur — rendering the analytical line for its associated element unreadable until a replacement can be installed.

New CMOS-based detectors for metal analyzers such as SPECTROLAB S are designed for even more reliable, industrial-strength service. Additionally, due to the technology's unique full-spectrum capture: if CMOS detection for one emission line should ever fail, the system can simply utilize a closely alternative line, instead of losing the capacity to measure that element entirely.

Drawing on Dependable Manufacturing Sources

The reliability and quality control performance of CMOS detectors should equal or exceed that of PMT detectors, when sourced from first-tier makers. And SPECTRO Analytical Instruments itself is one of the world's leading manufacturers of analytical devices using elemental analysis technologies such as ICP, OES, and XRF.

CONCLUSION

SPECTRO Analytical Instruments possesses years of experience designing metal analyzers using both PMT-based and CCD-based detectors. In fact, a previous model of their flagship metal analyzer SPECTROLAB offered a hybrid PMT/CCD system, designed to maximize these technologies' complementary capabilities.

The continued development and optimization of CMOS semiconductor detectors has transformed the paradigm. Today, using an all-CMOS detector array, coupled with SPECTRO's proprietary CMOS+T technology, instruments such as the new SPECTROLAB S analyzer have proven to meet or exceed every aspect of both CCD- and PMT-based performance.

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