

ICP - Mass Spectrometry

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Advantages of a Novel Plasma Generator for the NexION 1100/2200/5000 ICP-MS Systems

Inductively Coupled Plasma as an Ionization Source for Mass Spectrometry

Since its first commercial introduction in 1983 by PerkinElmer-SCIEX, inductively coupled plasma mass spectrometry (ICP-MS) has become the fastest growing trace-element detection technique covering a diverse range of applications. Hurdles in successfully coupling an ICP source to a mass spectrometer were initially overcome with design breakthroughs such as a center-tapped ground coil to minimize plasma potential and eliminate secondary discharge between the plasma and the grounded MS interface. Further evolution of plasma RF generators led to a unique free-running design where impedance changes in the plasma were matched instantaneously through small changes in the frequency with no moving parts. In addition, plasma potential was kept at minimum by electronically balancing the plasma with respect to the ground potential.

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Plasma Generation

Inductively coupled plasma is a region of hot, partially ionized gas formed within the outer tube of an assembly of three concentric quartz tubes, known as the torch. Figure 1 (Page 2) shows a schematic diagram of an ICP torch assembly in operation. Argon gas flows through each of the three tubes at different flow rates for plasma generation, cooling and protecting the quartz surfaces from the high-temperature plasma, and finally for introducing the sample aerosol into the central channel of the plasma.

The torch is surrounded at the top end by an induction coil (also known as the load coil) connected to a radio-frequency (RF) generator. The induction coil is traditionally made of a coiled copper tube and is gas- or liquid-cooled by the flow of the coolant through the coil. A high-voltage Tesla discharge produces electrons and argon ions in the downstream gas flowing through the region encircled by the load coil. The interaction of the electromagnetic field with ions and electrons causes them to accelerate. However, given their significantly lighter mass, electrons gain much higher velocities compared to positive ions and hence play a dominant role in collision processes that occur in the plasma. Electrons collide with argon atoms, and upon sufficient energy transfer, ionization of more argon atoms occurs with the release of additional electrons that would subsequently take part in the collision processes. The plasma is sustained shortly after ignition when the rate of electron release from atoms matches the rate at which they recombine with ions. The latter process involves release of energy in the form of photons that produces the plasma continuum emission superimposed by argon line spectra.

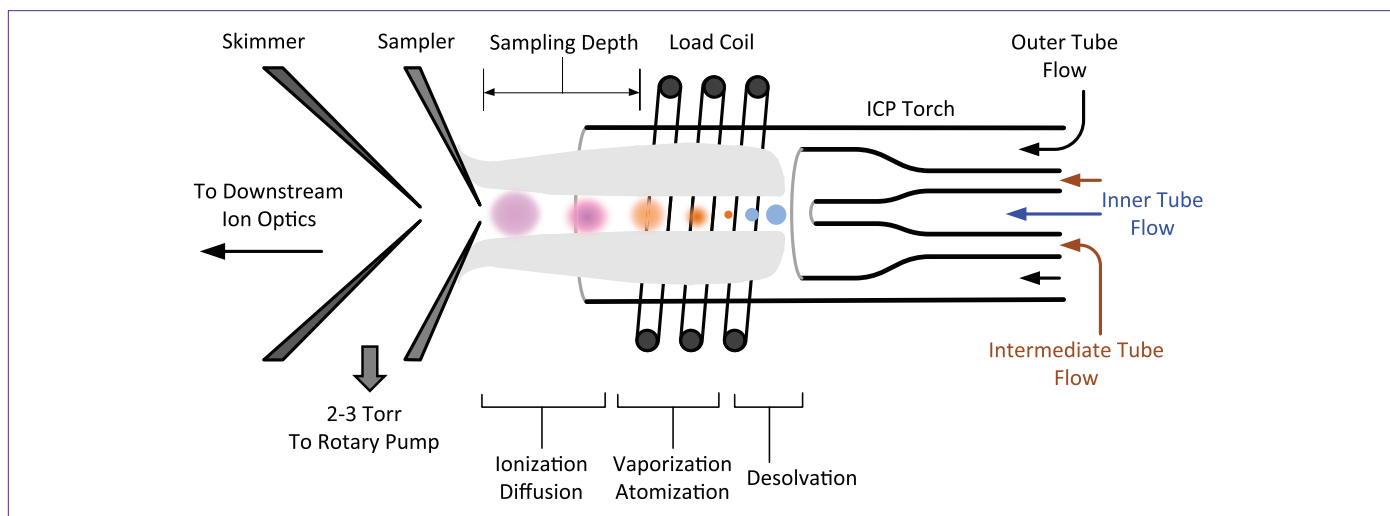


Figure 1. Schematic diagram of an Ar ICP source against a typical MS interface showing processes occurring to convert a droplet of sample aerosol into ions in the plasma.

Most of the energy from the RF field couples to the outer regions of the plasma akin to a “donut” shape where temperatures can reach 10,000 K, whereas the central channel region is typically at around 5000 to 7000 K, depending on the plasma operating conditions. Figure 2 shows simulated temperature fields in argon ICP demonstrating a thermal inhomogeneity within the plasma volume. Therefore, an ICP cannot be assumed to be in thermodynamic equilibrium due to the inherently different nature of collisional processes that occur including ionization, recombination, and excitation. However, a partial local thermodynamic equilibrium (LTE) can be safely assumed to characterize the ICP based on ionization temperature (T_{ion}), gas kinetic temperature (T_{gas}), electron temperature (T_e), excitation temperature (T_{exc}), and rotational temperature (T_{rot}).

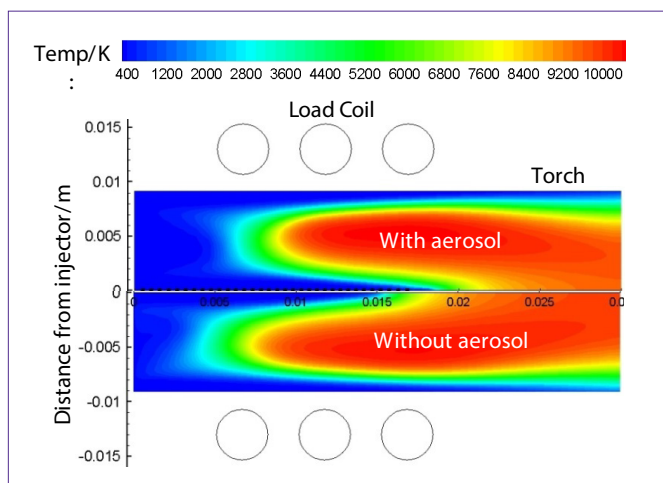


Figure 2. Simulated gas kinetic temperature fields in an argon ICP torch with (top half) and without (bottom half) aerosol introduction. The simulation model is based on a two-dimensional, time-dependent ICP model assuming optically thin RF plasma at local thermodynamic equilibrium (LTE).

Figure 1 also depicts the processes that would lead to the generation of an ion cloud in the plasma for each droplet. Droplets in the sample aerosol undergo a sequence of desolvation, vaporization, atomization, and ionization during their residence time in the plasma. One could consider the regions of the plasma dominated by such processes as distinct, but in practice, the sample aerosol does not consist of monodisperse droplets and contains a distribution of droplet sizes. Hence, it is believed that these regions overlap to some extent. In addition to the above-mentioned processes, the diffusion of the sample vapor and the resulting ion cloud in the plasma can significantly affect the intensity of the signal. The signal is typically at its maximum around the point in plasma where vaporization and ionization processes are nearly complete but diffusion is yet to become dominant. In addition to droplet size, the duration of such processes in the plasma is, to a large degree, dependent on the operating conditions such as plasma sampling depth, plasma power, nebulizer gas flow rate, and the inner tube diameter.

Important Properties of an Ideal RF Generator for ICP-MS

The main function of any RF generator is to deliver a well-defined and stable alternating current to the load coil to ignite and sustain the plasma reliably. For maximum transfer efficiency of RF power to the plasma, the impedance of the source (i.e., the generator) and the load (i.e., the plasma source) need to match as part of a single electrical circuit. This is typically termed as resonance or impedance match condition. The impedance (Z) of the circuit depends on frequency of operation and has both a real (resistive) and imaginary (reactive) component to define the phase relationship which in Cartesian terms can be defined as:

$$Z = R + jX$$

where j is the imaginary term ($\sqrt{-1}$) and R and X are resistance (Ω) and reactance (Ω) defining the real and imaginary components of impedance, respectively.

The impedance of the plasma is a dynamic variable that can change rapidly in response to changing plasma operating conditions, such as RF power, gas flow rates, gas type, sample/vapor load, sample type, frequency of operation, and sampling depth. The ability of the generator circuitry to rapidly detect and react to changes in load impedance is crucial to minimize the reflected power and maintain robust plasma conditions. ***This feature sets apart design approaches based on instantaneous matching of impedance by slight changes in the frequency of operation from those relying on relatively slow and failure-prone moving parts such as servo-driven capacitors in their impedance matching networks.***

Another important aspect of RF generators is the way the generator drives the load coil. If the output RF drive is single-ended and one end of the load coil is always connected to the ground, the generator is said to be an unbalanced RF drive source. Plasmas produced by such circuitry exhibit relatively high plasma potential, which would lead to a secondary discharge between the plasma and the grounded sampler cone of the mass spectrometer. Mechanical approaches to minimize the plasma potential include those using interlaced load coils (essentially two intertwined load coils with opposite grounding polarity) or moving, electrostatic shields to act as a grounded shield between the load coil and the plasma.

If the generator is designed to drive the load coil with two identical RF outputs but 180° out of phase, the generator is categorized as a balanced RF source. This approach was first developed and patented by PerkinElmer-SCIEX under the trade name PlasmaLok™. The phase relationship between the two opposing waveform outputs creates a virtual ground at the electrical center of the load coil. Plasma potential with such design is kept at minimum regardless of the plasma operating conditions (e.g., inner tube flow rate, plasma power, matrix composition) and hence does not play a significant role in defining the kinetic energy of the plasma species. Consequently, independent optimization of plasma operating conditions and ion optics is facilitated.

Other properties, such as power transfer efficiency, size, simplicity, cooling strategy, ruggedness, consumables, maintenance, and the ability to rapidly switch between high and low RF power extremes, also play an important role in the design of an RF generator.

Latest Solid-State Transistor Technology Meeting Innovative Circuits

The latest ICP-MS RF generator by PerkinElmer, designed for the NexION® 1100/2200/5000 ICP mass spectrometers, takes advantage of the newest circuit design techniques as well as state-of-the-art components to deliver a plasma source with uncompromised performance, robustness and long-term reliability.

Over the past two decades, demand for faster, smaller and more efficient semiconductor electronics has enabled continuous improvements in developing more compact electronic circuitry that require less power and incorporate more functionality. Power electronics also benefited from the latest semiconductor advancements to achieve higher power density, efficiency,

and excellent thermal stability. The design team at PerkinElmer selected the latest generation of laterally diffused metal oxide semiconductor (LDMOS) transistor technology to empower the RF generator in the NexION 1100/2200/5000 ICP-MS systems with superior advantages at the semiconductor level.

The high power density advantage enables the RF generator to reach 1.6 kW of power with minimal number of power transistors, thus eliminating the efficiency penalty of a power-combining circuit to sum the power from numerous lower-power transistors. It also minimizes the gain, efficiency, current, and thermal mismatch that typically exist among numerous transistor devices.

The higher output rating of the advanced transistors also translates to better long-term reliability, because of the increased margin for back-off operation, as the available power exceeds the actual delivered power. For example, to generate 800 W RF power, a power transistor rated at 1.2 kW will have a longer lifetime compared to that rated for 800 W, which always operates at its maximum limit.

Although the latest transistor technologies offer many advantages, the use of such transistors cannot guarantee a high performance solid-state plasma generator on their own. While making strides in higher speed, efficiency and density, the evolution of silicon transistors is offset by lower device breakdown limits due to device shrinkage and optimization. For example, the gate of traditional power transistors can often withstand ± 40V, but the latest transistors suffer gate breakdown at around -7V. The older transistors are also more immune to fast voltage transients that are beyond the transistor frequency response, due to the gain roll off at the harmonic frequencies.

The lower breakdown voltages of the latest transistors do not pose a serious problem in typical low-power consumer electronics. However, a much lower breakdown tolerance in modern transistors could become problematic in ICP-MS RF generators unless design features are in place to overcome the drawback. An inductively coupled plasma load, unlike a typical electronic load such as a broadcast antenna, is relatively unstable and has a wide impedance range. Prior to plasma ignition, the plasma coil is a pure reactive load with most of the RF power reflected back to the transistors. After plasma ignition, the plasma coil abruptly changes to become a real load absorber for RF power. The RF impedance of the plasma is also affected by the sample solution. All these operations present rapid changes to the RF impedance, reflected power, and voltage transients. A few RF cycles of uncontrolled voltage spikes and current surges are sufficient to cause a power transistor to break down. As a result, most ICP-MS manufacturers prefer to use older power transistor technology despite risks such as obsolescence as well as less flexible designs and sub-optimal power transfer efficiency. To realize the many advantages offered by the latest transistors, PerkinElmer scientists designed and tested advanced and novel circuit techniques to eliminate the risk of lower breakdown voltage. The result is an RF generator capable of uncompromised reliability, speed, efficiency, and plasma robustness.

Direct-Feedback Oscillator Design

Plasma RF generator designs are typically divided into two approaches: the driven design and the oscillator design. In the driven design, the plasma load coil is directly driven by an amplified, fixed-frequency RF signal source. Since the plasma impedance is dependent on the sample loading into the plasma, the impedance matching network must be constantly monitored and adjusted over time. In some systems, the matching network consists of one or more mechanically tunable (motor-driven) variable capacitors. Driven-mode plasma generators typically have good amplitude stability with lower phase noise while the plasma conditions are unchanged. However, the response time of such systems is relatively slow when the plasma impedance undergoes a sudden change due to, for instance, sample changeover, a rapid transient sample load, or introduction of different types of gas into the plasma.

The primary advantage of an oscillator-based plasma generator is the faster response time for impedance matching when the plasma is loaded with different samples. In a typical oscillator design, the plasma is driven by a variable-frequency oscillator, such as a voltage-controlled oscillator (VCO). The oscillation frequency is adjusted by a controlled voltage to achieve optimal impedance matching. The phase mismatch of the impedance network is used as the feedback signal to adjust the frequency for optimal impedance matching. Since the frequency adjustment is achieved by electronics, the response time is virtually instantaneous compared to the driven-mode plasma generators with mechanical adjustment. However, the phase mismatch signal is usually an analog signal at a lower frequency compared to the RF frequency. Therefore, the speed of frequency adjustment is limited by the response time of the VCO, plus the total time constant of all low-pass filters in the circuitry.

Unlike a typical VCO-type oscillator design, the output matching network of the NexION 1100/2200/5000 RF generator is an integral part of the oscillation core. The direct sampling of the plasma load coil output as a feedback signal enables impedance matching within a few RF cycles, which translates into a few microseconds. Consequently, this enables a much faster response compared to a typical VCO-type oscillator where plasma matching duration takes in the order of a second. This becomes crucial, especially for optimal power transfer, to stabilize the plasma during plasma ignition and during the analysis of difficult samples where plasma impedance changes abruptly and the plasma would otherwise extinguish if the impedance is not matched fast enough.

The oscillator is also designed to have a differential oscillation core based on a balanced design approach, so that the RF output drives the plasma load coil differentially to minimize the plasma potential. In addition, the output power generated by a pair of high-power transistors drives the plasma load coil with a low-loss impedance matching network, without the need for power-combining a series of transistors. The impedance matching network is also designed with robust components that have rated breakdown limits far exceeding the required operating conditions.

Most plasma generators operate at nominal frequencies of either 27 or 40 MHz. There has been much debate surrounding the effect of RF generator frequency on analytical performance characteristics of ICP-MS. However, many studies in the past disregarded the effect of secondary discharge, MS interface, and ion sampling processes when comparing the two frequencies. In addition, an important determining factor for the choice of plasma frequency, which is the effect of balanced vs. unbalanced generator, was often not considered. Techniques such as electrostatic shields for unbalanced systems become much less effective as the frequency of operation increases, which explains their limited use only at 27 MHz. During the development of the NexION ICP-MS systems, extensive simulations and in-lab studies were performed to determine the optimum operating frequency based on analytical performance and plasma fundamentals. Using a balanced RF generator, lower frequencies typically produce plasmas with slightly higher gas kinetic temperatures due to slightly thicker skin depth; however, at higher frequencies, the coupling efficiency improves, which leads to better robustness and plasma stability as well as improved tolerance to complex matrices, organic solvents, and mixed-gas plasmas. Based on the results of the studies, the NexION RF generator is targeted to operate at around 34 MHz, which is roughly the mid-point between 27 MHz and 40 MHz for a more well-rounded performance between these two frequencies.

A Trouble-Free, Fire-and-Forget Experience

The NexION plasma generator offers the user a trouble-free, "fire-and-forget" experience. It is designed to ignite the plasma with close to 100% success rate. For instance, a number of NexION instruments underwent accelerated ignition tests: the plasma was ignited 4000 times on each instrument and shut off during a back-to-back test. Success rates ranged from 99.97% (1:4000) to 100% (no failures).

Long-term Reliability

Long-term reliability of the plasma generator is an important part of a trouble-free user experience. The RF generator board is water-cooled to prolong the service lifetime. In addition, an ensemble of advanced electronics is provisioned, as part of the RF circuitry, to protect the power transistors, facilitating long-term reliability. The RF generator circuitry on the NexION 1100/2200/5000 systems also utilizes both wideband and narrowband circuit techniques to safeguard the transistors from fast transients and voltage breakdowns.

Power and current mismatches between power transistors are undesirable effects for any plasma RF generator. The problem manifests when one of the transistors is driven harder and running hotter than the other transistor, which negatively impacts the transistor reliability. Such problems typically originate from mismatches in device gain, output load, or input drive strength that would lead to uneven power loading of the transistors. Since the mismatch has numerous causes, the problem cannot be addressed by one circuit alone. Therefore,

through a rigorous design and test approach, our design team ensured that the currents of the two power transistors in the NexION RF plasma generator are controlled and balanced to be virtually equal to one another. This is the hallmark of a symmetrical, well-balanced differential RF plasma generator; an advantage not only to reduce the plasma potential, but also to increase the MTBF (mean time between failures) of the plasma generator.

The NexION plasma generator is equipped with a dedicated 32-bit microcontroller (MCU) with built-in firmware. The MCU implements a digital control loop to monitor and supervise the plasma operating conditions. It ensures that the transistors are running at the optimal operating voltage and current to maximize the margin against voltage breakdown and current meltdown simultaneously. A novel feature is that the MCU can monitor the health condition of the power transistors in real-time during normal operation. In the event that the MCU detects that the transistors are on the verge of breakdown or at the onset of failure, the MCU will take the appropriate action and shut down the plasma generator automatically to prevent any component damage. This feature helps prolong the power transistors' service lifetime. The MCU also provides a suite of diagnostic information during operation and shares the information with the user through the Syngistix™ for ICP-MS software.

LumiCoil - An Innovative Plasma Load Coil

NexION 1100/2200/5000 ICP-MS systems also utilize a patented plasma load coil, called LumiCoil™, designed by the Research and Technology group at PerkinElmer specifically for the novel solid-state RF generator. Traditionally, plasma load coils are made from copper tubes and require active liquid or gas cooling to minimize oxidation and degradation of the coil over time. In addition to oxidation, copper load coils are susceptible to chemical attack especially when corrosive samples are used. The formation of the oxide layer on the copper surface not only leads to further overheating of the coil causing more oxide buildup, but also changes the characteristics of the coil as an RF inductor leading to inefficient power transfer to the plasma. Coil degradation can also cause long-term signal drift and significant reduction in sensitivity especially for high IP elements. Severe oxidation to the point of flaking can also cause arcing between adjacent turns of the coil. Consequently, copper induction coils are generally considered consumable parts that need to be replaced periodically, depending on the operating conditions of the instrument.

A Self-cooling Load Coil: LumiCoil

The LumiCoil RF coil is designed to greatly increase the operating lifetime, plasma stability, and the MTBF of the plasma generator by eliminating load coil oxidation and corrosion. The highlight of LumiCoil is an array of fins distributed along the coil. Unlike traditional load coils, this innovative coil design does not require active cooling. Instead, the fins significantly increase the surface area of the coil so that air ventilation around the coil is sufficient

to keep the coil at the proper service temperature. Servicing and cleaning the LumiCoil RF coil, if required, is also easier since there are no leak-prone liquid or gas lines.

Optimal Power Coupling with LumiCoil

Increasing the load coil surface area as a solid piece to facilitate cooling and with no regards to the RF current direction would degrade the plasma power density. The reason is that the RF power is magnetically coupled from the load coil to the argon plasma. An oversized coil winding surface encourages stray RF current to flow through the added metal surfaces. This lowers the mutual inductance and complicates the magnetic flux linkage between the load coil and the plasma generated in the torch.

Therefore, in the LumiCoil design, the position of each fin is calculated and designed with a narrow width to suppress concentric RF current flowing radially between the fins (shown in red color in Figure 5). The unique design of the fins in LumiCoil forces the RF drive current to only flow through the well-defined windings of the coil (shown in blue color in Figure 5) and in close proximity to the torch. This way, the magnetic flux linkage is maximized for inductive coupling of the RF power to the torch.



Figure 3. Copper load coil used in most ICP sources.



Figure 4. LumiCoil: a patented technology exclusive to the NexION 1100/2200/5000 ICP-MS systems.

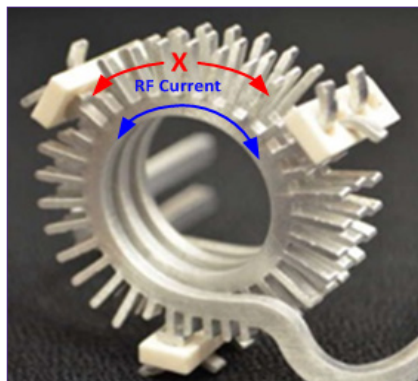


Figure 5. Optimal RF current flow to maximize the magnetic flux linkage.

Extended Operating Lifetime

LumiCoil technology uses a special alloy of solid aluminum core for the windings, which forms a layer of aluminum oxide on its surface. The oxide layer is highly resistant to chemical attack, and it effectively eliminates the heat-induced oxidation process of the material to protect the coil. Consequently, compared to the copper load coil, the LumiCoil has a much longer operating lifetime. Testing on multiple units with various sample types has demonstrated that the LumiCoil shows no sign of degradation even after a year of continuous operation, compared to a regular copper load coil, which lasted only three months under the same test conditions. Hence, LumiCoil technology enables the user to focus more on sample analysis and less on the maintenance of the load coil (i.e., less down time, higher productivity). This not only increases the overall sample throughput of the instrument but also reduces the number of replacement parts in the system and thus reduces the operating cost of the instrument.

The LumiCoil is also designed to achieve superior mechanical rigidity compared to a traditional plasma load coil. Rigid ceramic spacers maintain the correct distance between the coil windings and protect the coil from deformation. In addition, the heat and mechanical stress is distributed evenly along the coil.

With the advantages of extended lifetime, optimal inductive coupling, and using air instead of expensive liquid or gas cooling, LumiCoil technology complements the state-of-the-art RF generator to offer a trouble-free plasma operation.

Long-term Stability and Matrix Tolerance

In addition to improved sensitivity, the NexION 1100/2200/5000 ICP-MS systems are also designed to achieve long-term stability and matrix tolerance partly due to the design of the RF generator to produce a robust plasma with excellent matrix-matching capabilities. This is evident from tests performed for applications dealing with complex matrices with high total dissolved solids, such as EPA method 6020B. Figure 6 shows a plot of internal standard stability for method 6020B over 11 hours of continuous operation. Certified Reference Materials Soil Solution A and Soil Solution B (High Purity Standards™, Charleston, South Carolina, USA) at 1 g L^{-1} were used over the course of experiments in combination with Interference Check Solution-A (ICS-A) and QC checks (i.e., CCB, and CCV) every 10 soil samples. The results show excellent stability of internal standards over the course of experiments, which included the analysis of 280 soil samples in addition to blank and QC checks. The stability plot also shows a minimum amount of signal suppression between the blank, QC checks, and soil samples.

Robust Plasma for Challenging Samples

The plasma generator used in the NexION 1100/2200/5000 systems is designed to handle challenging samples with improved robustness. Figure 7 shows examples of a variety of sample matrices (aqueous and organic) that are used at the standard uptake rate (i.e., $300 \mu\text{L min}^{-1}$) using a room-temperature spray chamber and no special adjustment on the nebulizer gas or auxiliary gas flow rates.

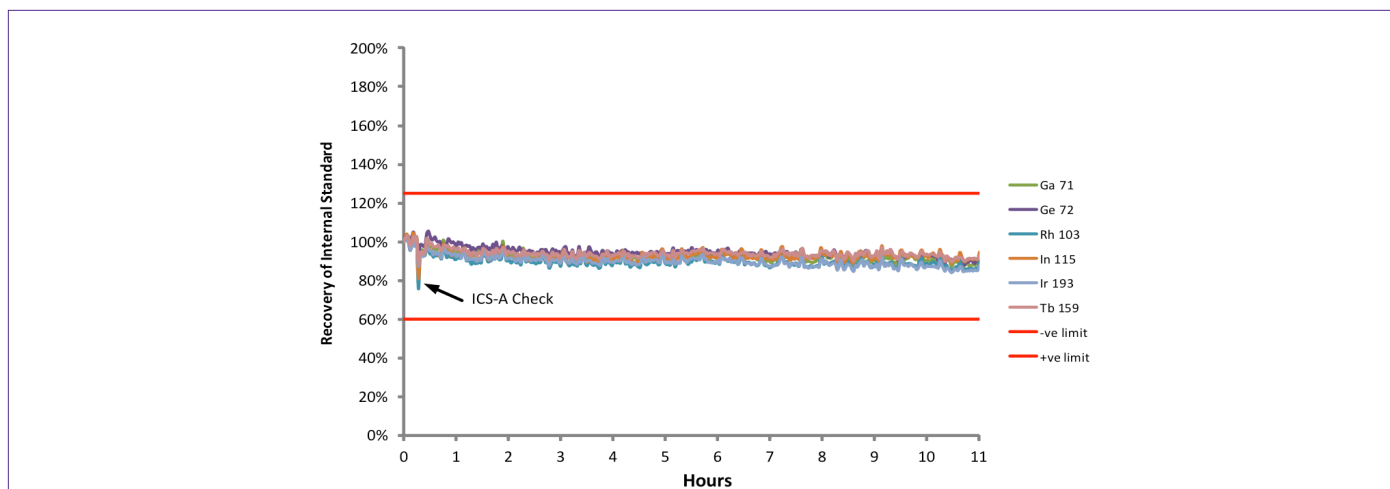


Figure 6. Internal standard recovery obtained as part of method 6020B analysis of 280 soil samples for 11 hours using the NexION 2200 ICP-MS. Blank and CCV checks were also performed every 10 samples and are included in the plot.

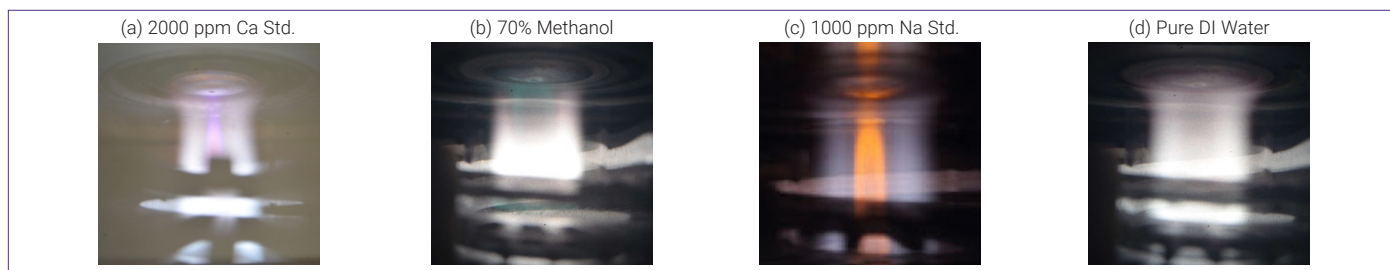


Figure 7. Examples of a variety of sample matrices used with NexION 2200 under normal conditions.

Robust Plasma for Mixed Gases

There are a number of growing applications that require the addition of gases, other than argon, to the plasma source. Mixing gases such as O₂ and He with argon is more common especially when analyzing organic samples or when an ICP-MS is coupled to a laser ablation (LA) system. Mixed gas plasmas with other noble, diatomic, or polyatomic gases are typically used for reducing spectroscopic and non-spectroscopic interferences, or for improving the ionization of some elements. The fast matching capability of the RF generator available on the NexION 1100/2200/5000 ICP-MS instruments and its inherent robustness makes the systems especially suited and easy to use with mixed gases. The speed of impedance matching through small shifts in frequency makes the NexION systems tolerant even to sudden introduction of mixing gases. To demonstrate the ruggedness of the plasma source with the NexION 2200, Figure 8 shows a stable plasma in operation with the sample introduction completely removed and with the injector tube exposed to open air.

Figure 9 shows the plasma operating with 70 mL min⁻¹ of methane (CH₄). The plasma continues to remain stable and operate uninterrupted even when the methane gas flow is abruptly switched on and off.

Fast Plasma Power Switching

Operating ICP-MS under cold plasma conditions has been effective for many applications, including those related to the analysis of chemicals for semiconductor processes, to improve the background equivalent concentration (BEC) of a number of elements that suffer from spectral overlaps by argon-based polyatomic interferences. Multi-mode methods in the NexION 1100/2200/5000 ICP-MS systems can now take advantage of a combination of hot and cold plasma conditions combined with cell-based modes, such as Reaction and Collision. The NexION plasma generator enables fast power switching between cold and hot plasma conditions to increase the throughput of such multi-mode methods. Figure 10 shows four consecutive power transitions of a NexION 2200 system between 500 and 1600 W, while measuring cobalt at 59 amu. The results show that the actual switching time between the two power levels is practically negligible and the Co signal stabilizes in less than 30 seconds for each power level. The time required for signal stabilization is mostly dominated by thermal effects and the time required to reach thermal equilibrium after each power change.



Figure 8. NexION 2200 ICP-MS with stable plasma operating with its back open to air.

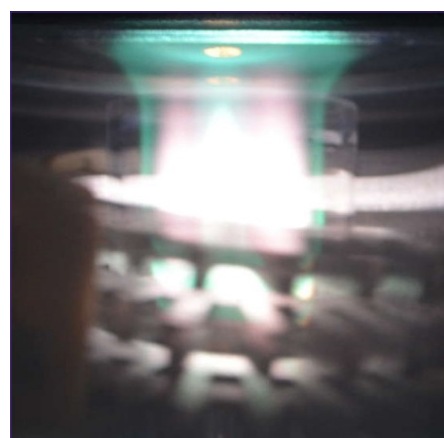


Figure 9. Stable Ar/CH₄ plasma with NexION 2200 ICP-MS.

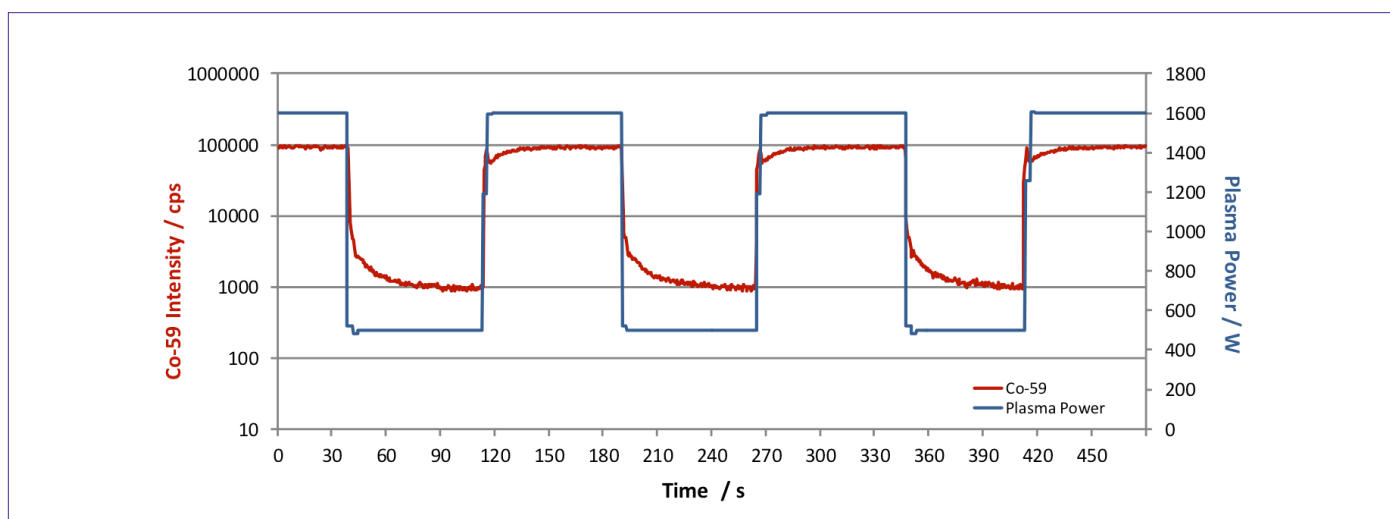


Figure 10. The output power and Co signal response of NexION 2200 under power transitions between 500 and 1600 W.

Conclusion

The novel and patented plasma generator and LumiCoil technology available on the NexION 1100/2200/5000 ICP-MS systems were specifically designed to enhance analytical performance as well as reliability and lower operating cost. The balanced and free-running RF generator design focuses on many attributes such as robustness, high efficiency, wide power range, fast power switching, and instantaneous impedance matching without the need for any mechanical matching network or cascade of transistors. In addition, on-board firmware intelligence and long-life components make the NexION RF generator essentially a maintenance-free system. This, combined with the novel design of the self-cooling LumiCoil, provides a reliable plasma source for a wide range of demanding applications including environmental, geological, biological, and semiconductor with a variety of sample types and plasma conditions.