

EPA Compliant and Interference Free Monitoring of Agricultural Waste by ICP-MS

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1 Introduction

American agriculture is noted worldwide for its high productivity, quality, and efficiency in delivering goods to the consumer. The activities from working farms and ranches can significantly affect water quality by introducing heavy metals into agricultural waste runoff or discharge streams. The proper management of these waste streams should encompass a comprehensive testing protocol to ensure compliance with U.S. EPA Resource Conservation and Recovery Act (RCRA). In addition to testing the outgoing waste streams, incoming water can also be tested to ensure optimal produce quality. The most utilized testing protocol for RCRA compliance is U.S. EPA "SW-846 Test Method 6020B: Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)". The advantages of ICP-MS for trace metal determination in waste streams are its sensitivity towards detecting low concentrations, wide linear dynamic range, and rugged sample introduction system. Despite these advantages, certain sample types have historically plagued the sample introduction system, and interferences that can form within the plasma itself have impeded the ultra low-level detection of certain elements. Fortunately, innovative advances in ICP-MS technology have allowed avenues to overcome these difficult matrices and interferences.

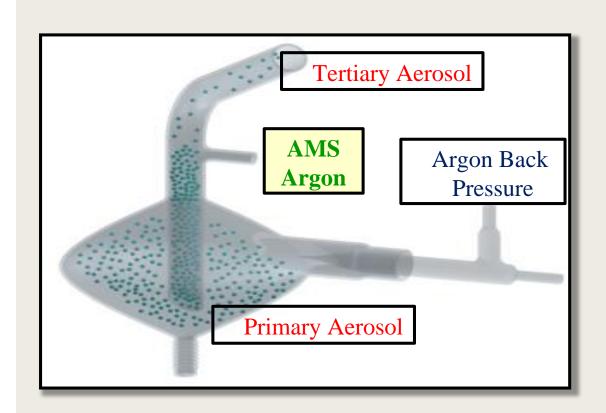
Unique Innovations of the NexION ICP-MS



Can reduce interferences utilizing helium gas (He) in kinetic energy discrimination mode (KED).

<u>Universal Cell</u>

 Can utilize other reaction gases to eliminate interferences.



AMS - All Matrix Solution

- Reduced matrix effects.
- Enhanced sample desolvation.
- Less cone deposition.

Pergo Argon Humidifier

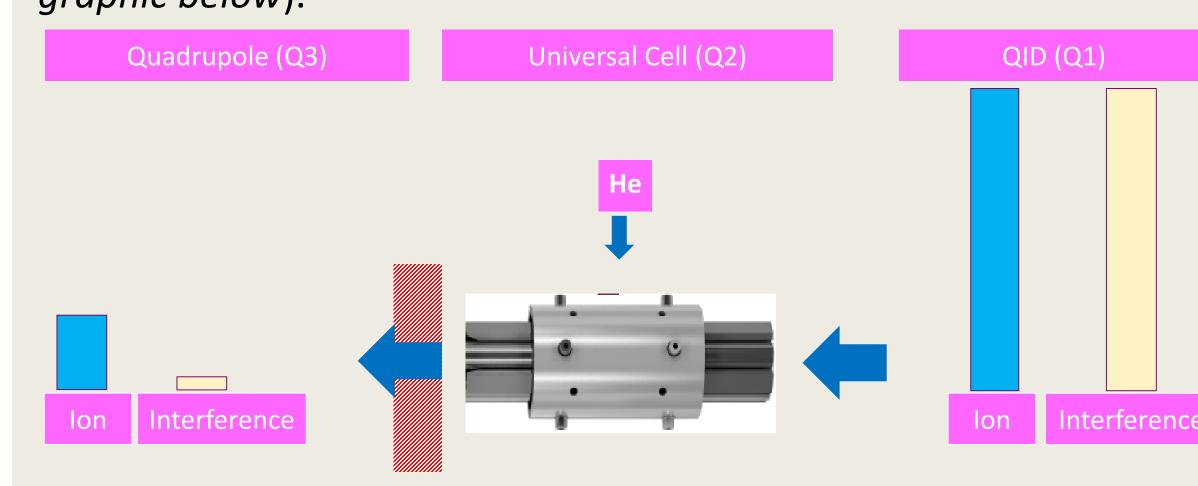


- Humidifies the argon gas feeding the nebulizer.
- Reduces sample deposition at the nebulizer tip.
- Allows for the analysis of higher total dissolved solids samples.

Experimental Conditions – PerkinElmer's NexION1000

Parameter	Description/Value
Sample Delivery Rate	350 μL/min
Nebulizer	MEINHARD plus Glass Type C
Spray Chamber	Glass cyclonic (Baffled), 2°C
Injector	2.0 mm i.d.
Nebulizer Flow	Optimized <2% Oxides
RF power	1600W
Cones	Ni (Samples, Skimmer); Aluminum (Hyper-skimmer)
Replicate Reads	3
Aerosol Dilution	2.5x
Analysis Mode	Collision Mode (KED)

All samples analyzed in KED mode to reduce interferences. Most interferences are large polyatomic ions formed within the plasma. The Universal Cell is pressurized with inert He gas. Both the polyatomic ions and the elemental analytes are introduced into the cell at roughly the same kinetic energy. The polyatomic ions, due to their larger ionic radii, suffer more collisions than the elemental analytes. A barrier between the Universal Cell and the analyzing quadrupole preferentially reject the polyatomic interferences, allowing for a cleaner analysis of the analytes. (See graphic below).



The AMS creates a gas dilution of the aerosol at the spray chamber. One advantage of the AMS is a wider linear dynamic range by virtue of a gas dilution. Another advantage is that the aerosol is further refined and controlled before it is ionized by the plasma. This is known as a tertiary aerosol. Combining these effects allows for a better tolerance of samples with higher dissolved solids, which have traditionally plagued ICPMS.

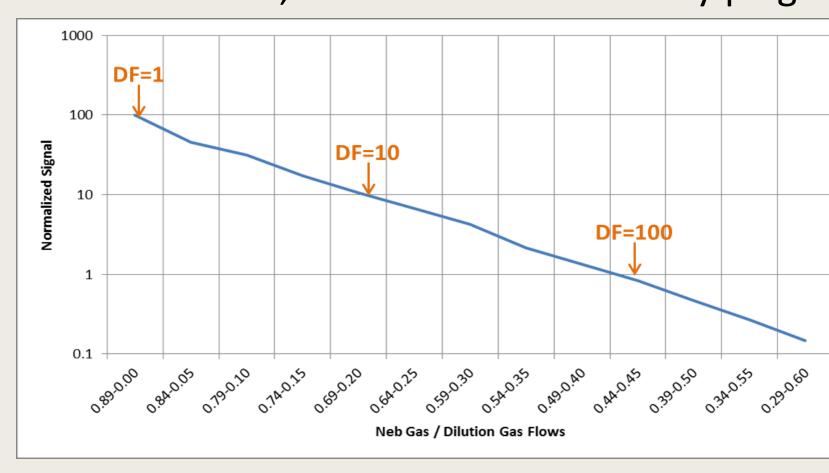
The Chart on the

left demonstrates

the linearity of

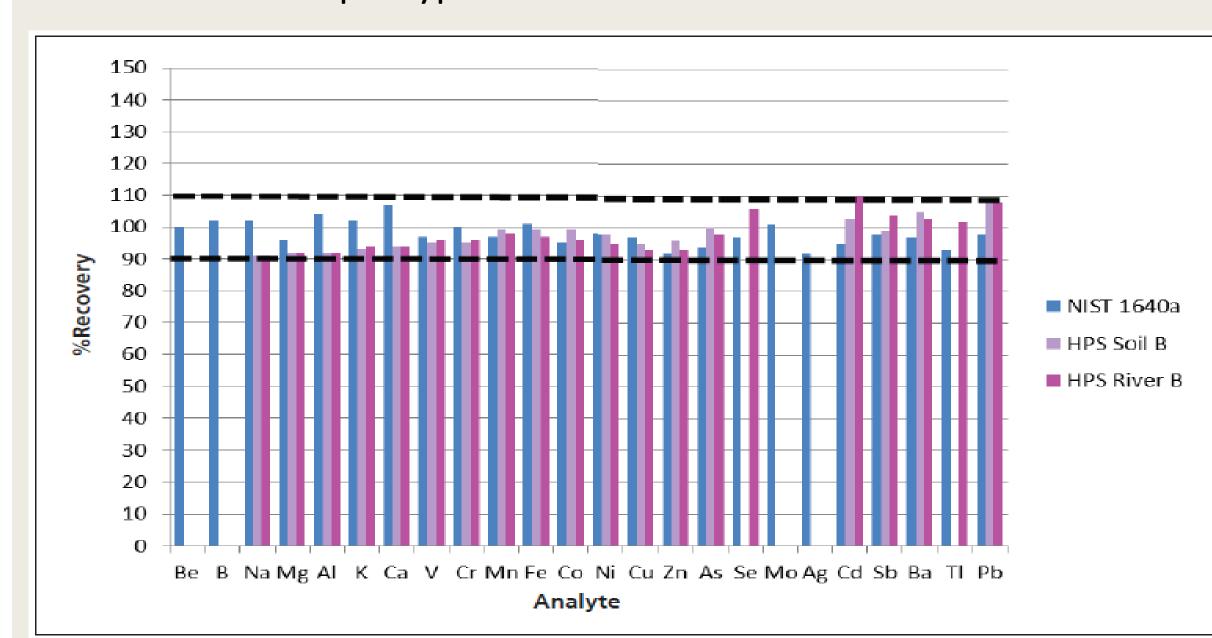
the gas dilution

performed by the

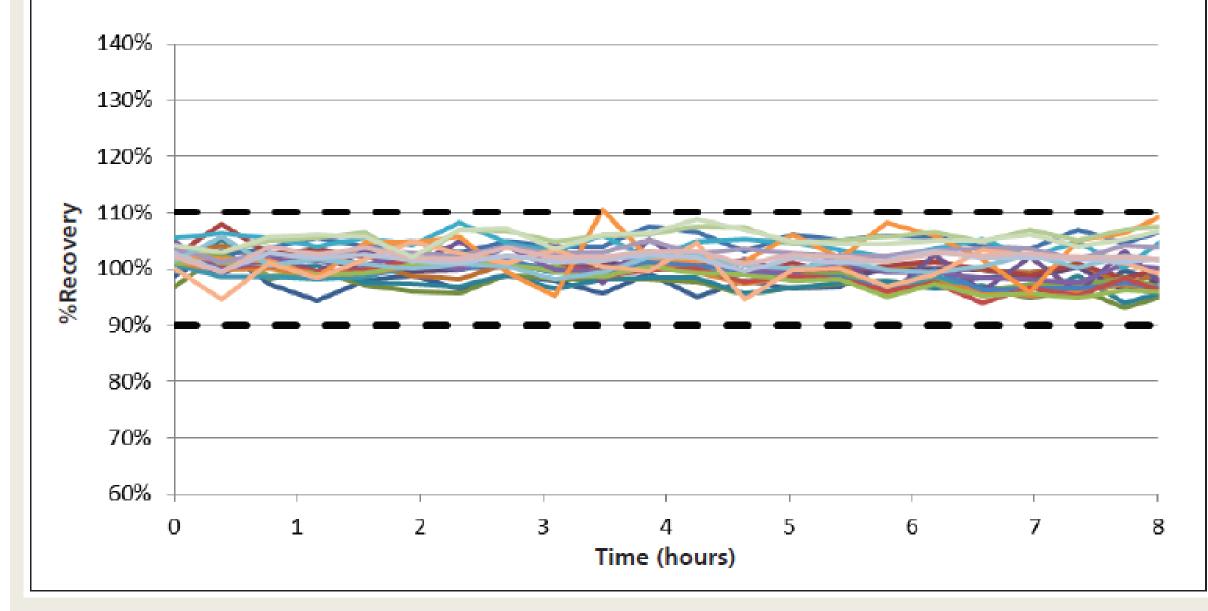


Accuracy, Performance, and Stability of NexION 1000 Following EPA 6020B

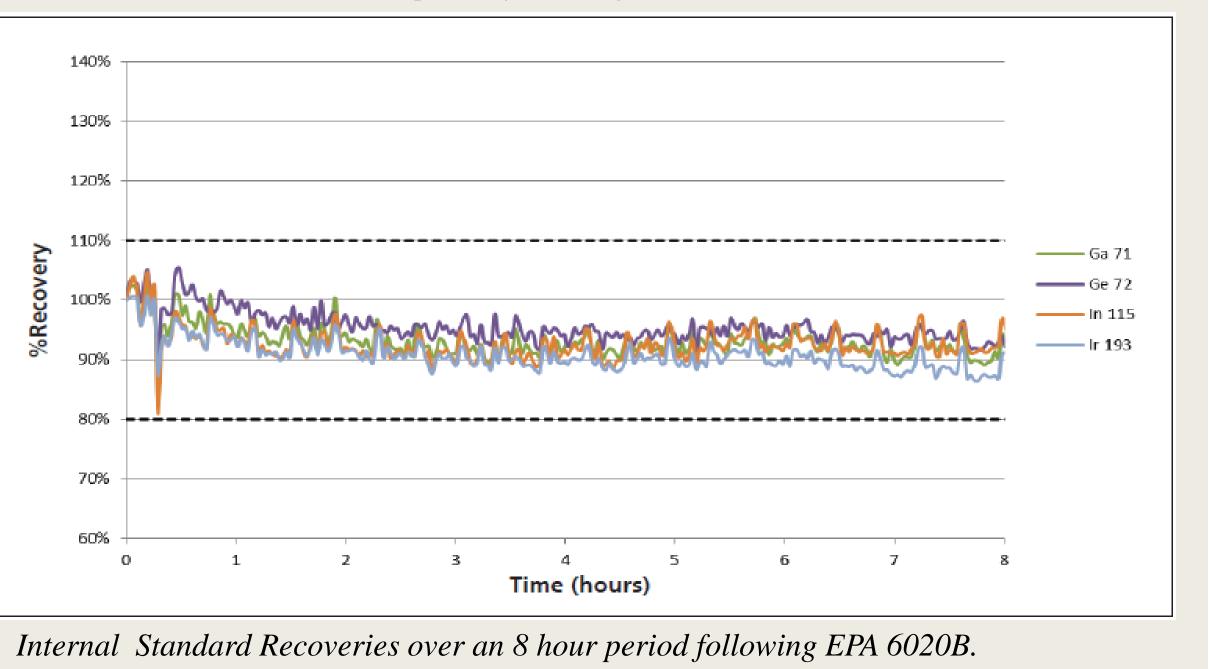
- Accuracy is benchmarked against three separate certified reference material (CRM) sample types and measured by %Recovery to the certified value.
- Performance is measured with against the %Recovery of continuing check verification samples, which are analyzed periodically after a set number of samples to test drift or deviations from the calibration curve caused by difficult samples.
- Stability is monitored by the including internal standards, which measure the analytical drift experienced by the instrument due to difficult sample types.



Recoveries of three certified reference materials (CRM's) following EPA 6020B.

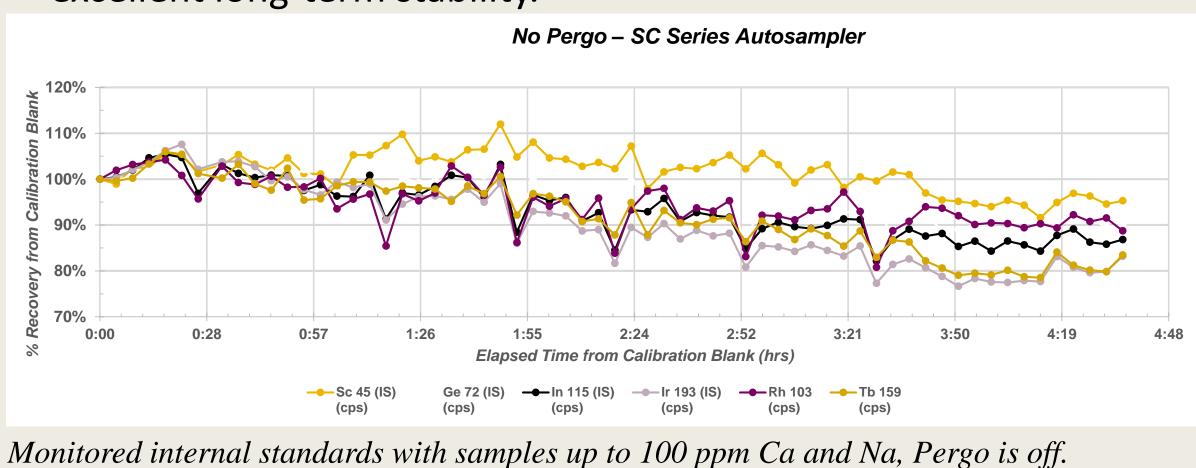


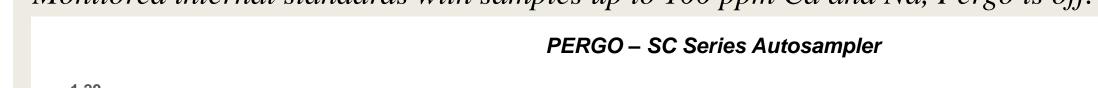
CCV Recoveries over an 8 hour period following EPA 6020B.

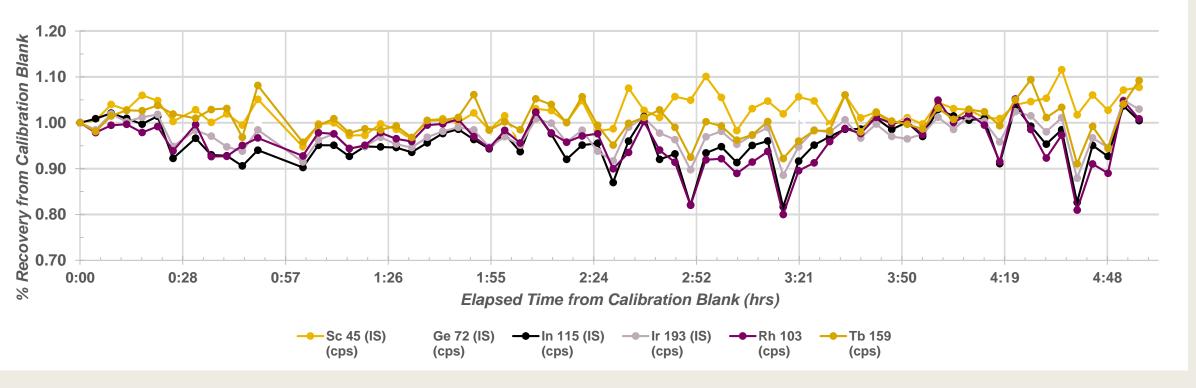


Improved Stability and Matrix Tolerance with the ESI pergo

- Samples with high concentrations of total dissolved solids (TDS)
 have traditionally plagued elemental analysis by ICP-MS.
- The pergo argon gas humidifier alleviates sample deposition by moisturizing the nebulizer tip and inhibiting deposition.
- The pergo allows for the analysis of TDS sample types with excellent long-term stability.







Monitored internal standards with samples up to 100 ppm Ca and Na, Pergo is on.

Summary

The data presented in this work demonstrates the unique advantages of modern day inductively coupled plasma – mass spectrometers (ICP-MS). Kinetic Energy Discrimination mode (KED) allows the chemist the ability to control the plasma-based interferences which have traditional impeded the low-level analysis of some elements. The all matrix solution (AMS) aides in the aerosol refinement of the sample, as well as it's de-solvation before entering the plasma. This leads too more efficient atomization of the sample within the plasma and results in enhanced analytical run stability. ESI's pergo system extends the matrix tolerance of the AMS gas dilution by inhibiting precipitant and deposition on the nebulizer tip, leading to a more stable analysis even in the presence of samples which have traditionally been tough to analyze by ICP-MS. All samples were analyzed under US EPA method 6020B compliance except for the pergo data which was measured under compliance with US EPA method 200.8. Excellent analytical recovery against Certified Reference materials was achieved, as well as long term stability and accuracy studies with continuing quality control samples throughout the run.