

Nitrox: Online Addition of Nitrogen and Oxygen for Enhanced Analytical Performance

Introduction

Enhancing the analytical performance of ICP-MS instruments is more than ever the key to efficient and reliable routine analysis and resultoriented leading-edge research applications. A thoroughly investigated way is the addition of gases to the argon plasma to reduce interferences and system contamination and to enhance ionization for improved sensitivity, lower backgrounds and as a result better detection limits. Gases in question are for example N₂, He, O₂, methane, ethane and ammonia. Helium as a stable non-ionizing gas is used for gaseous dilution. Ethane greatly reduces a wide range of polyatomic interferences when added to the nebulizer gas. Methane and nitrogen are known to promote ionization of elements with high 1st ionization potentials and are not fully ionized within an argon plasma. The addition of oxygen helps eliminate excess carbon from depositing on the interface cone when aspirating organic solvents.

Your Benefits

- Easy to operate
- Fully automated through Analytik Jenas ASpect MS software

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- Improves detection limits through increased sensitivity and reduced interferences
- Eliminates carbon deposition when analyzing organic solvents
- Reduces sample preparation time

The Nitrox is a fully automated, mass flow controlled accessory that allows for the online addition of N₂ and O₂ gases to either the auxiliary or sheath plasma gases. Controlled by the Analytik Jena ASpect MS ICP-MS software package, the Nitrox settings are automatically stored as part of the analytical method following optimization. The Nitrox is provided in the standard scope of supply for the PlasmaQuant MS[®] Elite and is also fully compatible with the PlasmaQuant[®] MS.



Tech Note PlasmaQuant[®] MS Series: Nitrox Gas Accessory

Nitrogen addition

Nitrogen is a commonly used gas for improving ICP-MS performance by increasing ionization within the plasma, attenuating polyatomic interferences and reducing matrix effects. Particularly for key environmental elements like As and Se that suffer from polyatomic interference and are themselves reported to be only 30-40% ionized in an argon plasma due to their high ionization potentials.

Table 1: Common Polyatomic Interferences for the main Se and As isotopes and their respective 1st ionization potentials. Elements with their 1st IP<8eV are essentially 100 % ionized.

Analyte	1 st IP	Common Polyatomic Interferences
⁷⁸ Se	9.8eV	⁴⁰ Ar ³⁸ Ar, ³⁸ Ar ⁴⁰ Ca
⁸⁰ Se	9.8eV	⁴⁰ Ar ₂ , ³² S ¹⁶ O ₃
⁷⁵ As	9.8eV	⁴⁰ Ar ³⁵ Cl, ³⁶ Ar ³⁸ Ar ¹ H, ³⁸ Ar ³⁷ Cl, ³⁶ Ar ³⁹ K, ⁴³ Ca ¹⁶ O ₂

Increased Sensitivity

With the Nitrox gas accessory, nitrogen can be added via the auxiliary gas line into the plasma. Adding a small flow of nitrogen significantly improves the overall sensitivity for a range of elements including arsenic and selenium. The degree of signal enhancement depends on the metal oxide bond energy and first ionization potential of the analyte, however increases in sensitivity of 3-4 fold have been observed as shown in Figure 1.

As the flow of nitrogen is increased into the argon stream of the auxiliary gas line, the physical attributes of the plasma change somewhat from a typical argon plasma. There is a significant increase in electron density due to a greater degree of ionization and the higher axial temperatures further aid the reduction of oxide and other matrix-based polyatomic interferences. For example, the ⁴⁰Ar³⁵Cl polyatomic interference on ⁷⁵As is reduced by the hotter plasma temperatures while sensitivity of As is increased. Similarly for Se, the dilution effect of the added nitrogen reduces the amount of argon dimer entering the ICP-MS provide substantial improvement in detection limits. Figure 2 shows an optimum nitrogen flow of 40 mL/min provides maximum signal enhancement for As and Se.



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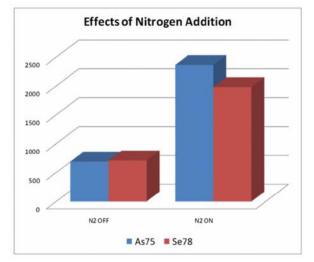


Figure 1: With Nitrogen injection an improvement of 3-4 times in sensitivity of 75 As and 78 Se can be achieved on the PlasmaQuant[®] MS ICP-MS using the Nitrox gas accessory. The above graph represents a 1ppb aqueous solution of As and Se assayed using iCRC-H₂.

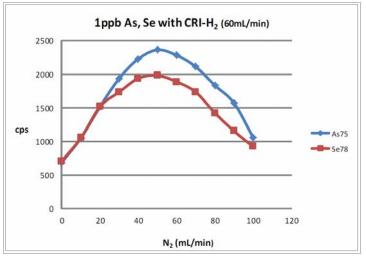


Figure 2: Optimized sensitivity of 75 As and 78 Se in a 1ppb solution on the PlasmaQuant® MS ICP-MS using the Nitrox gas accessory. Sensitivities were optimum at a N₂ flow rate of around 50 mL/min.

Reduced Matrix Interferences

A major advantage of the Nitrox gas accessory is that it significantly reduces 'oxide interferences' by more than an order of magnitude. Although less than 1% ionized in the argon plasma, oxygen is a major component of all aqueous and many organic solvents and its presence in the plasma results in extremely high backgrounds at masses 16, 18, and 32. Oxygen also readily combines with metal ions in the plasma to form polyatomic metal-oxide interferences (MO⁺). A standardized measure of the effectiveness of reducing matrix based interferences is the CeO⁺/Ce⁺ ratio. Cerium has a very strong affinity for oxygen and performance specifications of < 2% are typically reported as being acceptable for typical analyses. The assumption being the formation of new interferences with other metal oxides will be considerably less than CeO. The formation of other common matrix-based interferences such as metal chlorides will be less still given the weaker bond strength.

The addition of nitrogen to the argon plasma increases the axial temperature of the plasma, helping to break up oxide and other matrix-related interferences more efficiently. It also promotes the scavenging of oxygen by nitrogen through the formation of N-O which effectively removes a significant portion of free oxygen from the plasma for further interference reduction.



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Oxygen addition

The Nitrox gas accessory also allows for the direct analysis of organic solvents by ICP-MS through the online addition of oxygen. Reducing sample preparation times considerably by avoiding time consuming digestions traditionally used to reduce organic solvents to an aqueous state. Less sample handling also means less potential for contamination.

Improved Plasma Stability

Carbon is abundantly present in organic solvents and quickly deposits on the tips of the interface cones, either partially or completely blocking both the sampler and skimmer cones if left unchecked. Adding a small flow of oxygen into the auxiliary gas stream, at approximately 100-200 mL/min depending on the solvent, is an effective way of oxidizing and volatilizing the carbon present in the plasma. This subsequently prevents 'sooting' of the cone interface and aperture blockages.

The combination of a highly efficient, virtual center-grounded RF system, a peltier-cooled spraychamber operating at sub-zero temperatures for reduced solvent loading of the plasma, a choice of common organic or volatile organic sample introduction kits and the Nitrox gas accessory providing oxygen addition, almost any organic sample or solvent can be routinely analyzed on the Analytik Jena PlasmaQuant[®] MS.

Ordering information

The PlasmaQuant[®] MS can be upgraded with the Nitrox gas accessory. The PlasmaQuant[®] MS Elite is by default equipped with the Nitrox. Application-specific, organic and volatile organic sample introduction kits are also available. The organics kit is ideal for samples and solvents regularly analyzed in the bio-fuel and oil industries, like alcohol and kerosene-based solvents. The volatile organics kit is suited to more volatile samples and solvents like gasoline and naphtha.

Further information

For further updates, applications and other literature, please visit the Analytik Jena website at www.analytik-jena.com.

 $Reference: TechNote_ICP_MS_Nitrox_en.docx$

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