Accurate Determination of Si in Petrochemical Solvents by ICPMS with microFAST S4 and PerkinElmer NexION

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Features:

• Fully automated, syringe-driven autocalibration and autodilution
• Direct analysis of undiluted organic solvents
• Automatic addition of internal standard
• Accurate Si results, regardless of species
• Syringe loading of samples
Abstract
The microFAST accurately determines low ppb concentrations of Si and other metals in undiluted, organic solvents by ICPMS. A dedicated syringe loads a sample or standard onto an injection valve where it is autodiluted or analyzed directly. A low flow rate carrier then injects the diluted sample and internal standard into a heated spray chamber for introduction to the ICPMS. The combination of a low flow rate and heated spray chamber ensures that Si is accurately determined at low ppb levels (detection limit = 2.4 ppb, n=6, 3.4σ), regardless of the volatility of the Si species or solvent type.

Introduction
Rapid multi-element capabilities and superb detection limits often make ICPMS the technique of choice for trace elemental determination. However, determination of Si by ICPMS is hindered by very high background, mostly from the presence of polyatomic interferences, such as CO and N₂. In organic solvents, Si determination is further complicated by the increased abundance of carbon-based interferences from the solvent. In order to measure Si at low ppb levels, all of these polyatomic interferences must be dramatically reduced while maintaining adequate sensitivity for Si.

Together, the microFAST S4 and NexION accomplish the necessary reduction in polyatomic interferences required for this analysis. First, the microFAST S4 introduces sample at very precise, low flow rates, limiting the total amount of carbon that enters the plasma and reducing carbon-based polyatomic interferences. Next, plasma conditions are optimized to minimize the Si background while maximizing sensitivity for Si and other elements. Lastly, the DRC is optimized with simultaneous introduction of both NH₃ and H₂ which efficiently removes carbon-based interferences and stabilizes the Si background for excellent long-term results, regardless of solvent.

Traditional analysis of organic solvents by ICPMS is done by diluting samples in o-xylene and introducing the sample into a chilled spray chamber at flow rates between 100-300 µL/min. This approach produces inaccurate results for elements present in organometallic species that differ from those in the calibration standards. For example, with traditional sample flow rates and spray chamber temperatures, the different transport efficiencies of volatile organometallic Si species cause inaccurate results and long washout times. In addition, small changes in solvent composition may cause Si background shifts.

The low flow rate sample introduction and heated chamber of the microFAST S4 eliminate these common problems with Si determination in organic solvents. The heated chamber drives nearly 100% of Si into the plasma regardless of the volatility of any Si species. The low sample flow rate maintains plasma stability despite nearly 100% of the sample and solvent reaching the plasma. In addition, shifts in Si background due to changes in solvent composition and carryover from volatile species are eliminated. This “total consumption” sample introduction system ensures accurate results for Si regardless of species or solvent.
**Experimental Conditions**

- microFAST S4 sample introduction system
- PC\textsuperscript{3x} heated Peltier cyclonic chamber, 60 °C
- Zero waste, drainless spray chamber
- 1.8 mm sapphire injector
- 20 µL/min sample flow rate
- 10 µL/min internal standard flow rate
- Wash time 35 s
- NexION 300D ICPMS
- Oxygen addition (20% O\textsubscript{2}/80% Ar) at 0.36 L/min to prevent carbon buildup on the cones
- DRC mode, reaction gas, 0.4 mL/min NH\textsubscript{3} and 2 mL/min H\textsubscript{2}

![PC\textsuperscript{3x} heated Peltier cyclonic chamber](image)

**Figure 1.** microFAST S4 system schematic

**DRC Conditions**

DRC mode with either NH\textsubscript{3} or H\textsubscript{2} gas significantly reduces the Si background. However, with only one of these gases, there are enough remaining polyatomic interferences that the Si background is still too high for good long-term results. However, simultaneously adding both NH\textsubscript{3} and H\textsubscript{2} to the chamber reduces the background substantially, improves long-term stability, and allows accurate Si determination in a wide variety of solvents.
Figure 2. With only H\textsubscript{2} as a DRC gas (upper figure), excess carbon forms various polyatomic interferences, as shown by the incorrect isotopic abundance measured for Mg isotopes. With both NH\textsubscript{3} and H\textsubscript{2} as DRC gases (lower figure), the carbon background is negligible, and the natural Mg isotopic abundance shows effective polyatomic interference removal.
Autocalibration of Si in o-Xylene

Figure 3. microFAST S4 autocalibration from a single 250 ppb Si standard in o-xylene. 10 ppb to 250 ppb. Sample flow rate 20 µL/min, internal standard flow rate 10 µL/min.

Accurate Si Determination

Figure 4. Five different silanes and siloxanes prepared at 10 ppm Si and diluted to 1 ppm were determined with the microFAST S4. The microFAST S4 provides accurate and precise results regardless of species. 10 ppb to 250 ppb. Sample flow rate 20 µL/min, internal standard flow rate 10 µL/min.
**Figure 5.** Washout for five Si compounds from 1000 ppb (10 ppm solution autodiluted by 10x) is shown for two different sample introduction settings on the microFAST S4. The traditional sample introduction setting is most similar to established analytical methods for organic solvent analysis. Washout with a low flow rate and heated chamber is much better than that for traditional sample introduction. Traditional sample introduction: 100 µL/min, spray chamber at -2°C. microFAST S4 sample introduction: 20 µL/min, spray chamber at 60 °C.

**Figure 6.** The blank readback against an o-xylene calibration blank is shown for three solvents: o-xylene, kerosene, and hexanes. DRC mode with only H₂ shows a large variation in blank level for different solvents. DRC mode with NH₃ and H₂ improves blank reproducibility dramatically. Some of the variation in the blank may be due to real differences in Si concentrations, but the much larger variations in H₂-only mode indicate insufficient interference removal is the predominant cause of the background instability.
Conclusion:
The microFAST S4 achieves accurate Si determination by ICPMS at low ppb levels. The Si detection limit is 2.4 ppb (n=6, 3.4σ) in o-xylene at 20 µL/min. The combination of microFAST S4 and NexION ICPMS provides the necessary polyatomic interference removal to achieve excellent detection limits and reproducible blanks required for low ppb Si detection in undiluted organic solvents by ICPMS.

Benefits:
- Automatically calibrate from a single stock standard
- Minimize offline sample preparation and dilution
- Routine analysis of different organic solvents with the same configuration
- Excellent washout
- Low maintenance
- High sensitivity

patents pending