

# Determination of silicon in diesel and biodiesel by Microwave Plasma-Atomic Emission Spectrometry

## Application note

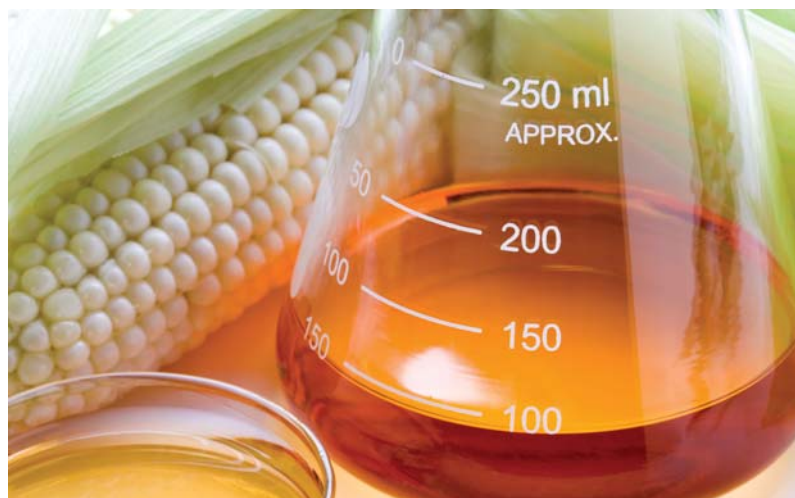
Energy and fuels

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### Introduction

The presence of metals and metalloids in petrochemical products can influence the performance of engines, and contribute to shortening the lifetime of the machinery. In addition, some elements act as catalyst poison, contributing to increases in the amount of toxic gases and particulate matter emitted by vehicles. Silicon compounds such as siloxanes, for example, are added to diesel as anti-foaming agents. During combustion, these compounds decompose to form silicon oxide, which can form a coating layer on the catalyst element of the exhaust system and significantly increase air pollution [1]. Thus, regulation in this field of analysis is increasingly common and recent legislation in Brazil has established the maximum concentration of Si plus Al in diesel as  $80 \text{ mg kg}^{-1}$  [2].



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This application note describes the determination of Si in diesel and biodiesel samples using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). This instrument produces a robust and stable plasma using magnetically-coupled microwave energy. A nitrogen gas generator feeds the microwave plasma and no additional gas source is required to run the instrument, which significantly reduces operating costs.

Different sample preparation procedures were evaluated and the instrument robustness was demonstrated by analyzing samples diluted in 90% ethanol. In this case, adequate recoveries were achieved even by applying a simple non-matrix-matched external calibration method with aqueous standard solutions.

## Experimental

### Instrumentation

The Agilent 4100 MP-AES was used in all determinations. The sample introduction system was composed of solvent-resistant tubing, a double-pass cyclonic chamber and the inert OneNeb nebulizer. This nebulizer provides a more homogeneous aerosol, with smaller and narrow-distributed particles, which increases nebulization efficiency and improves sensitivity [3].

An external gas control module (EGCM) was used to inject air into the plasma and prevent carbon deposition on the torch and the optical components. This device also contributes to plasma stability and background emission reduction in organic sample analyses.

The Agilent MP Expert software allows automatic background correction (Auto), improving precision and accuracy. The Auto background correction consists of recording, storing and automatically subtracting a background spectrum from each standard and sample solution analyzed. The MP Expert software also performs the optimization of nebulizer pressure and viewing position for each wavelength used. In this work, a standard reference solution used to obtain the analytical calibration curve was also used to very quickly and easily optimize such parameters. The instrumental operating conditions and settings to determine Si are presented in Tables 1 and 2.

**Table 1.** Agilent 4100 MP-AES operating conditions for Si determination in diesel and biodiesel samples

Instrument parameter	Operating condition
Nebulizer	Inert OneNeb
Spray chamber	Cyclonic double-pass
Read time (s)	10
Number of replicates	3
Stabilization time (s)	15
Background correction	Auto

**Table 2.** Silicon viewing positions, nebulizer pressures and External Gas Control module (EGCM) settings

Sample medium	Wavelength (nm)	Nebulizer pressure (kPa)	EGCM
Micro-emulsion	251.611	100	Medium
	288.158	120	Medium
Aqueous	251.611	120	Medium
	288.158	160	Medium

A closed-vessel microwave oven (Ethos 1600, Milestone, Sorisole, Italy) equipped with 45 mL PFA vessels was employed for the digestion of diesel and biodiesel samples.

### Reagents and standard solutions

Nitric acid (Merck, Darmstadt, Germany) previously purified by a sub-boiling distillation system (Milestone), and hydrogen peroxide 30% m/m (Synth, São Paulo, SP, Brazil) were employed to digest the samples. Polyoxylene(10)octylphenil ether (Triton X-100, Acros Organics, Geel, Belgium), n-propanol and light mineral oil (Tedia, Rio de Janeiro, RJ, Brazil), without any additional purification, were used for the preparation of micro-emulsions. A 1000 mg/L Si stock solution (Tec-Lab, Hexis, São Paulo, SP, Brazil) was adequately diluted to prepare aqueous and micro-emulsion standard reference solutions and to carry out spiking studies in digested samples and micro-emulsions. Analytical grade ethanol (J. T. Baker, Hexis, São Paulo, SP, Brazil) was used for direct sample dilution. A Si 1000 mg/L stock solution in organic medium (Conostan, Quimlab, Jacareí, SP, Brazil) was used in spike studies of ethanol-diluted diesel and biodiesel samples. External calibration with aqueous standard reference solutions in HNO<sub>3</sub> 1% v/v was performed for Si determination in both the digested samples and those simply diluted in 90% v/v ethanol.

### Samples and sample preparation

Biodiesel samples were provided by the Center of Characterization and Development of Materials (CCDM, Federal University of São Carlos, São Carlos, SP, Brazil). Diesel fuel samples containing 5% v/v of biodiesel (B5), in accordance to the Brazilian legislation [4], were obtained in local gas stations of São Carlos, SP, Brazil.

Three sample preparation procedures were evaluated: microwave-assisted digestion, micro-emulsion preparation in n-propanol, and dilution in ethanol. The sample digestions were performed by using 50% v/v HNO<sub>3</sub> (7 mol/L) and 3.0 mL of H<sub>2</sub>O<sub>2</sub> 30% m/m. Table 3 presents the heating program employed.

**Table 3.** Heating program for the microwave-assisted acid digestion of diesel and biodiesel samples

Step	Applied power (W)	Time (min)	Temperature (°C)
1	250	2	80
2	0	3	80
3	550	4	120
4	650	5	200
5	750	5	200

Micro-emulsions were prepared by adding 0.5 mL of Triton X-100 and 0.5 mL of a 20% v/v HNO<sub>3</sub> aqueous solution to 1.0 mL of diesel or biodiesel. The volume was then made up to 10 mL with n-propanol and the mixture was homogenized for 2 min with a vortex mixer [5]. During the preparation of the micro-emulsion standard reference solutions, the sample was replaced by 0.2 mL of mineral oil, which simulates the sample matrix viscosity. The direct dilution of samples in ethanol was carried out by adding 9 mL of the solvent to 1 mL of sample.

## Results and discussion

### Instrumental limits of detection in different media

Limits of detection (LOD) and quantification (LOQ) for both 1% v/v HNO<sub>3</sub> and micro-emulsion media were calculated by using the background equivalent concentrations (BEC) and the signal-to-background ratios (SBR) obtained with a Si 1.0 mg/L standard reference solution and 10 consecutive blank measurements in each case. The LOD and LOQ values are presented in Table 4.

**Table 4.** Figures of merit for silicon determination by MP-AES.

a = Linear dynamic range starting at the limit of detection.

b = Repeatability presented as the relative standard deviation for a 2 mg/L Si solution (n = 10).

	HNO <sub>3</sub> 1% v/v			Micro-emulsion		
	LOD (µg/L)	LDR <sup>a</sup> (Decades)	RSD <sup>b</sup> (%)	LOD (µg/L)	LDR <sup>a</sup> (Decades)	RSD <sup>b</sup> (%)
Si (251.611 nm)	20	2.3	1.6	5	2.6	1.6
Si (288.158 nm)	240	0.9	1.3	5	2.5	0.4

Considering the legislation for Si [2], all three procedures developed presented adequate sensitivity for application in quality control. It is important to note that the plasma produced by the 4100 MP-AES is stable and it was not extinguished even by introducing high concentrations of n-propanol or ethanol. Moreover, no carbon deposition was observed either on the torch or on the pre-optic window after several hours of operation.

### Accuracy

The accuracy of all three procedures was evaluated using spike studies with both sample matrices. For the digested samples and the micro-emulsions, volumes of 3.0 or 1.0 mg/L of Si in aqueous medium were respectively added either after the digestion or directly to the samples during the micro-emulsion preparation. Two different spike concentrations were evaluated for the ethanol dilution procedure: 0.5 and 1.0 mg/L of Si in organic medium. Results are shown in Table 5 and all recoveries were between 80 and 102%.

The combination of a homogeneous nebulization obtained through using the OneNeb nebulizer, the efficient background reduction from the EGCM and the reliable background correction provided by the Auto feature of the software were all fundamental to obtaining precise and accurate results for the analyses of such high carbon matrices.

**Table 5.** Spike experiments for Si determination in diesel and biodiesel after sample digestion, dilution in 90% v/v ethanol or micro-emulsion preparation. Concentrations reported in mg/L.

a = Spike solution in aqueous medium.      b = Spike solution in organic medium.

Sample	Si emission line (nm)	Digestion <sup>a</sup>		Ethanol <sup>b</sup>		Micro-emulsion <sup>a</sup>	
		Added	Recovered	Added	Recovered	Added	Recovered
Biodiesel	251.611	3.0	3.05 ± 0.07	0.5	0.45 ± 0.03	1.0	0.89 ± 0.05
				1.0	0.99 ± 0.09		
	288.158	3.0	3.05 ± 0.01	0.5	0.40 ± 0.04	1.0	0.89 ± 0.06
				1.0	1.02 ± 0.17		
Diesel	251.611	3.0	3.09 ± 0.10	0.5	0.47 ± 0.01	1.0	0.96 ± 0.03
				1.0	0.91 ± 0.01		
	288.158	3.0	3.07 ± 0.15	0.5	0.46 ± 0.01	1.0	0.96 ± 0.04
				1.0	0.95 ± 0.01		

## Conclusions

Silicon determination is not an easy task, especially for fuel matrices, which present high viscosity and a high carbon load. In this work, accurate Si determinations were successfully carried out simply by diluting the samples in ethanol and using external calibration with aqueous solutions. The sample preparation procedures evaluated are environmentally friendly since less toxic solvents are used. In addition, high sample throughput can easily be achieved in routine, unattended automated analyses. No carbon deposit or reduction of performance was observed while introducing high carbon loads to the Agilent 4100 MP-AES without the use of a cooled spray chamber. Two important advantages of this instrument are its low running costs and laboratory safety, as no expensive or flammable gases are required. Considering cost, performance and multielement capabilities, the Agilent 4100 MP-AES is a suitable and efficient alternative to flame AA for this application and presents better performance for critical elements such as the one investigated here. The simple dilution in ethanol and external calibration with aqueous solutions is recommended for the determination of Si in diesel and biodiesel samples considering its simplicity and sample throughput.

## References

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