# Rapid and robust determination of silicon in gasoline using the Thermo Scientific iCAP PRO XP ICP-OES Radial system

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## Goal

This application note demonstrates a rapid detection method for the determination of silicon in gasoline using the Thermo Scientific™ iCAP™ PRO XP ICP-OES Radial system according to the Chinese Standard Method Determination of Silicon Content in Motor Gasoline GB/T 33647-2017.[1] Following a simple dilution, the gasoline samples are directly introduced into the plasma where oxygen is added to reduce potential interferences and achieve a detection limit of <20 µg·kg$^{-1}$.

Gasoline samples were diluted with isooctane and introduced into the ICP-OES system directly. An integrated additional mass flow controller was used to add oxygen to the plasma to reduce potential carbon deposits and interferences from the carbon molecular spectral band. Silicon had an excellent linear range for the set concentration range (with coefficient of determination $R^2$> 0.999) and the method detection limit was <20 µg·kg$^{-1}$. The recovery rates of the spiked samples were all between 90% and 110%. All performance specifications can meet the testing requirements specified by the National Standard Method Determination of Silicon Content in Motor Gasoline GB/T 33647-2017.[1]

## Introduction

During the petrochemical production process, contamination may occur. The unintentional incorporation of specific elements into gasoline after the refining of fuel oil is of concern as it can impact the properties of the gasoline. One element of concern is silicon, which has an adsorption effect in gasoline. Even at very low concentrations, silica powder generated during the gasification and combustion of gasoline can adhere to the surface of oxygen sensors in the car, causing the sensor to fail. Consequently, large amounts of deposits can be generated in the engine and on the catalytic converter with costly consequences. This kind of contamination can cause the catalytic system to fail in less than one tank of fuel. Therefore, accurate determination of silicon in gasoline is particularly important.

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## Experimental

### Instrument

The iCAP PRO XP ICP-OES Radial system was selected for the analysis. This model features a vertical torch that enables the analysis of complex matrices, such as organics, while achieving low detection limits. The iCAP PRO XP ICP-OES system utilizes an additional mass flow controller to add oxygen, which has two benefits. Firstly, the potential interferences from carbon-based emissions are removed, and secondly, the carbon depositions on the torch are reduced, enabling long term analysis to take place.

The iCAP PRO XP ICP-OES system was fitted with a volatile organics sample introduction system (Table 1) and a ceramic D-Torch which is made of fully inert SiAlON, a heat resistant ceramic (Figure 1). The ceramic D-torch is resistant to damage when analyzing complex matrices, such as organics, and corrosion resistant. It is especially suitable for direct injection of organic matrices, reducing the frequencies of torch maintenance and therefore greatly reducing the costs of analysis.

**Table 1. Instrument parameters**

| Parameter | Setting for iCAP PRO XP ICP-OES Radial |
|---|---|
| Pump tubing | Solvent flex orange/white |
| Drain tubing | Solvent flex white/white |
| Spray chamber | IsoMist™ cooled at -15 °C |
| Nebulizer | Concentric glass nebulizer |
| Center tube | 1.0 mm alumina injector |
| Torch | Removable ceramic D-torch |
| Peristaltic pump speed | 20 rpm |
| Nebulizer gas flow | 0.35 L·min$^{-1}$ |
| Auxiliary gas flow | 1.5 L·min$^{-1}$ |
| Coolant gas flow | 12 L·min$^{-1}$ |
| Additional gas flow | 40 mL·min$^{-1}$ oxygen |
| RF power | 1300 W |
| Radial viewing height | 10 mm |
| Exposure time | 10 s |
| eUV/iFR | iFR |

1A 1B

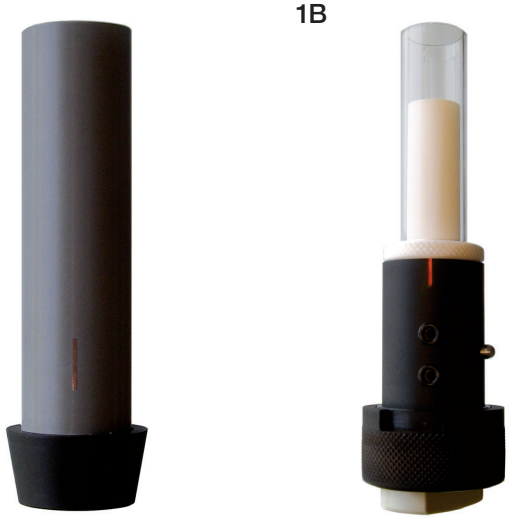


**Figure 1. (A) Ceramic outer tube of the D-Torch; (B) D-Torch with quartz outer tube to show torch geometry**

### Standards preparation and sample preparation

A blank solution was prepared by diluting blank gasoline at a ratio of 1:4 by weight. Standard solutions were prepared by diluting a single element silicon oil based standard (CONOSTAN™, silicon standard in oil, 900 mg·kg$^{-1}$) with isooctane to produce solutions containing the following concentrations—0.1, 0.2, 0.5, 1.0, and 2.0 mg·kg$^{-1}$.

Samples were prepared by accurately weighing 2.0 g of the well-mixed gasoline sample in a LDPE plastic bottle and diluting with isooctane diluent at the gasoline to diluent ratio of 1:4 (w/w).

### Method development

A LabBook was created within the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ ISDS Software. The LabBook contains all the information to complete the analysis. The wavelength for analysis was selected (Si 251.611 nm) and the parameters for analysis set (Table 1). The instrument was calibrated with the standards, the sample analyzed, and the sub array examined (Figure 2) for any potential interferences.

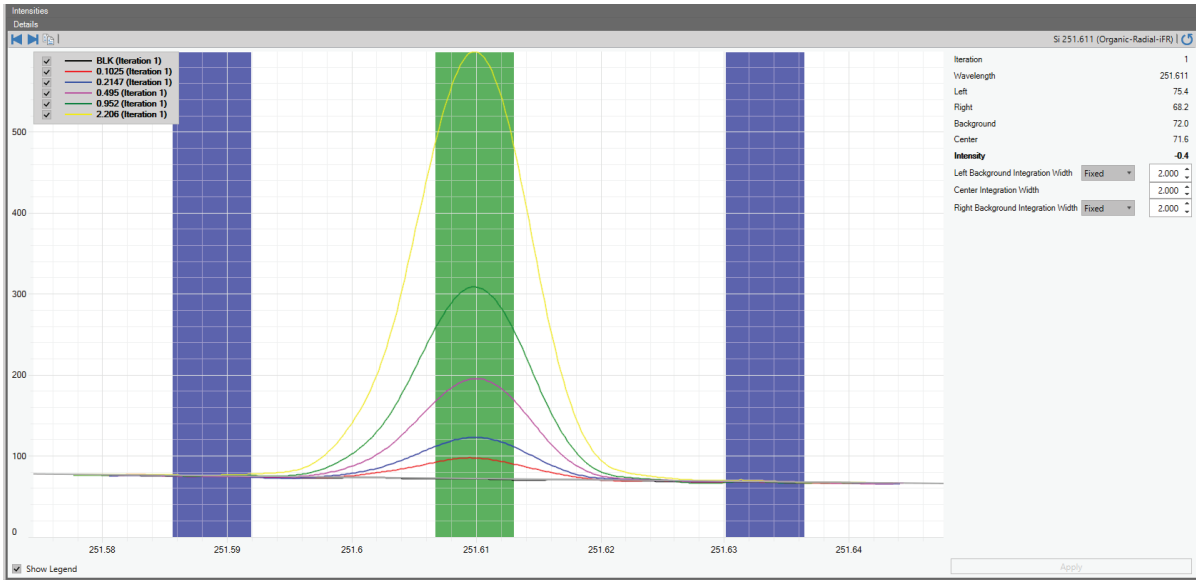
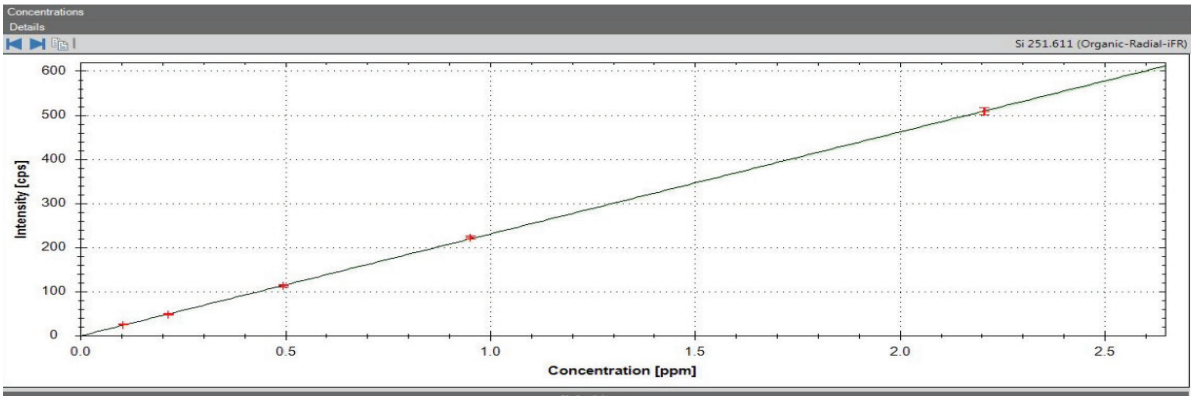



**Figure 2. Overlay of the silicon spectrum (251.611 nm) of gasoline blank and gasoline standard solution (containing silicon at 0.1, 0.2, 0.5, 1.0, and 2.0 mg·kg$^{-1}$)**




| Element | Fitting method | Slope | Correlation coefficient R² |
|---|---|---|---|
| Si 251.611 nm | Linear | 230.991 | 0.9999 |

**Figure 3. Silicon linear response assessed with gasoline standards over a calibration range of 0.1, 0.2, 0.5, 1.0, and 2.0 mg·kg$^{-1}$**

## Linearity

The linearity of silicon was assessed using the gasoline prepared standard solutions over a calibration range of 0.1, 0.2, 0.5, 1.0, and 2.0 mg·kg$^{-1}$ (Figure 3). The results of this experiment demonstrated excellent linear response with $R^2$ = 0.9999 and RSE = 4.3%.

## Sensitivity

Instrument detection limit, method detection limit, and method quantification limit of silicon in organic matrix were assessed by taking 10 consecutive measurements of a blank solution and calculating the standard deviation based on these measurements. The method detection limit (MDL) was established as three times the standard deviation multiplied by a dilution factor of 5 (2.0 g → 10 g). The limit of quantification of the method (MQL) is 10 times the standard deviation of the blank solution multiplied by a dilution factor of 5 (2.0 g → 10 g). The results are shown in Table 2.

**Table 2. Detection limit, MDL and MQL**

| Element | Instrument detection limit (mg·kg$^{-1}$) | MDL (mg·kg$^{-1}$) | MQL (mg·kg$^{-1}$) |
|---|---|---|---|
| Si 251.611 nm | 0.00403 | 0.020 | 0.067 |

### Recovery

For the recovery test, three types of gasoline samples (92#, 95#, 98#) were used for the experiments. For this, 2g of each sample were taken according to the sample preparation method described in the GB/T 33647-2017 method. To this, a known amount of silicon standard solution was added with solvent solution to a final weight of 10 g. The recovery data calculated from these samples indicates excellent accuracy (Table 3).

**Table 3. Recovery test**

| Sample | Measure result ($mg \cdot kg^{-1}$) | Spike ($mg \cdot kg^{-1}$) | Spike recovery (%) |
|---|---|---|---|
| 92# | 0.076 | 0.235 | 95.3 |
| 95# | 0.087 | 0.232 | 90.1 |
| 98# | 0.085 | 0.981 | 92.3 |

### Precision of measurements

To test the repeatability of measurements, a blank gasoline sample containing silicon at 0.230 $mg \cdot kg^{-1}$ was used and seven repeat measurements performed. The precision of measurement was excellent with %RSD < 1.5 (Table 4), demonstrating the suitability of the method.

**Table 4. Reproducibility test**

| Repeat | Si concentration ($mg \cdot kg^{-1}$) |
|---|---|
| 1 | 0.208 |
| 2 | 0.215 |
| 3 | 0.214 |
| 4 | 0.209 |
| 5 | 0.207 |
| 6 | 0.211 |
| 7 | 0.210 |
| Average results | 0.211 |
| Standard deviation | 0.003 |
| RSD % | 1.42 |

## Conclusion

- The Thermo Scientific iCAP PRO XP ICP-OES Radial system was used to establish a rapid analytical method for the determination of silicon in gasoline. Using this method, one sample can be quantitatively analyzed for its silicon content in under 1 min.
- The iCAP PRO XP ICP-OES Radial system uses a variable frequency and efficient RF generator, which can quickly match the load change of a highly volatile organic sample injection. The robust ceramic D-torch technology and the easily applied addition of oxygen ensures the plasma remains stable, whether it is injected directly with a gasoline sample or diluted with isooctane.
- The accuracy and precision of measurement were excellent with recovery values between 90 and 95% and repeatability of results with %RSD < 1.5.
- The direct injection method using isooctane dilution has a higher analysis efficiency than the digestion method or the extraction method, and it has extremely low detection limits and an ultra-high accuracy, which greatly improves the analysis efficiency.
- This analytical setup with the iCAP PRO XP ICP-OES Radial system together with the robust sample introduction system used in these experiments represent a viable option for laboratories servicing the oil and petrochemical industry and meets all the analytical requirements (such as GB/T 33647-2017) needed for routine analysis of silicon in gasoline samples.

## Reference

1. GB/T 33647-2017: Determination of silicon content in motor gasoline – inductively coupled plasma optical emission spectrometry (ICP-OES).

Find out more at **thermofisher.com/ICP-OES**

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